Techno-Economic Analysis of Monoglyceride and Diglyceride Production from Waste Cooking Oil

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การวิเคราะห์เชิงเทคนิคและเศรษฐศาสตร์ของการผลิตโมโนกลีเซอไรด์และไดกลีเซอไรด์จากน้ำมันประกอบอาหารเหลือทิ้ง

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โมโนกลีเซอไรด์ (MGs) และอนุพันธ์ของโมโนกลีเซอไรด์มีการใช้กันอย่างแพร่หลายและถือเป็นกลุ่มอิมัลซิไฟเออร์ที่สำคัญที่สุด ซึ่งอิมัลซิไฟเออร์เหล่านี้สามารถผลิตได้จากน้ำมันประกอบอาหารเหลือทิ้ง (WCO) ผ่านกระบวนการสองขั้นตอน คือ ทรานส์เอสเทอริฟิเคชัน-กลีเซอโรไลซิส หรือ กระบวนการไฮโดรไลซิส-กลีเซอโรไลซิส กระบวนการทรานส์เอสเทอริฟิเคชัน-กลีเซอโรไลซิสมีข้อดีในแง่ของอัตราการเกิดปฏิกิริยาสูงและให้ผลผลิตสูง สำหรับปฏิกิริยาไฮโดรไลซิส ไตรกลีเซอไรด์จะถูกเปลี่ยนเป็นกรดไขมันอิสระ (FFA) ซึ่งต้องใช้อุณหภูมิในการเกิดปฏิกิริยาที่สูงขึ้น แต่การใช้น้ำเป็นสารตั้งต้น จะทำให้กระบวนการแยกไม่ซับซ้อน ในการศึกษานี้จะทำการวิเคราะห์เชิงเทคนิคและเศรษฐศาสตร์ของ 4 กรณีที่แตกต่างกันของการผลิตโมโนกลีเซอไรด์ โดยใช้โปรแกรม ASPEN Plus V11 ในกรณีที่ I และ IV โมโนกลีเซอไรด์จะถูกสังเคราะห์จากน้ำมันประกอบอาหารเหลือทิ้งผ่านการทรานส์เอสเทอริฟิเคชันและไกลเซโรไลซิส ซึ่งกรณีที่ I ใช้ตัวเร่งปฏิกิริยาเอกพันธุ์ และกรณีที่ IV ใช้ตัวเร่งปฏิกิริยาวิวิธพันธุ์ และในกรณีที่ II และ III โมโนกลีเซอไรด์จะถูกสังเคราะห์จากน้ำมันประกอบอาหารเหลือทิ้งผ่านปฏิกิริยาไฮโดรไลซิสและกลีเซอรอไลซิส โดยกรณีที่ III จะมีการเติมกลีเซอรอลจะเพิ่มเพื่อให้ได้อัตราส่วนโมลของกลีเซอรอลต่อกรดไขมันอิสระ ที่ 1:1 ซึ่งเป็นการปรับปรุงกระบวนการจากกรณีที่ II ให้ดีขึ้น ผลการจำลองพบว่า กระบวนการทรานส์เอสเทอริฟิเคชัน-กลีเซอโรไลซิสจะให้การผลิตโมโนกลีเซอไรด์ที่สูงกว่ากระบวนการไฮโดรไลซิส-กลีเซอโรไลซิส ซึ่งถึงแม้ว่ากรณีที่ I จะให้ผลผลิตโมโนกลีเซอไรด์สูงสุด แต่กรณีที่ IV สามารถลดหอกลั่นหนึ่งหอในการแยกและรีไซเคิลกลีเซอรอลที่ไม่ทำปฏิกิริยา ซึ่งส่งผลให้สามารถลดการใช้พลังงานเมื่อเปรียบเทียบกับกรณีที่ I นอกจากนี้การเติมกลีเซอรอลเพิ่มในกรณีที่ III ทำให้การใช้พลังงานและผลผลิตของโมโนกลีเซอไรด์เพิ่มขึ้นด้วยเมื่อเปรียบเทียบกับกรณีที่ II ซึ่งกรณีที่ IV จะมีต้นทุนการผลิตและราคาขายของโมโนกลีเซอไรด์ที่ต่ำที่สุด ส่วนกรณีที่ I III และ IV จะมีต้นทุนการผลิตโมโนกลีเซอไรด์ต่อตันของโมโนกลีเซอไรด์ที่ผลิตได้ยังคงต่ำกว่าราคาของโมโนกลีเซอไรด์ในปัจจุบัน ซึ่งบ่งชี้ว่ากระบวนการเหล่านี้สามารถมีความคุ้มค่าเชิงเศรษฐศาสตร์ นอกจากนี้ ราคาผลิตภัณฑ์พลอยได้ยังเป็นตัวแปรที่ส่งผลมากที่สุดสำหรับกรณีที่ I III และ IV

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Napat Olarachin : Techno-Economic Analysis of Monoglyceride and Diglyceride Production from Waste Cooking Oil . Advisor: MERIKA CHANTHANUMATAPORN, Ph.D. Co-advisor: Prof. SUTTICHAI ASSABUMRUNGRAT, Ph.D.,Assoc. Prof. Kanokwan Ngaosuwan, Ph.D.

Monoglycerides (MGs) and their derivatives are widely used and considered the most important group of emulsifiers. These emulsifiers can be produced from waste cooking oils (WCOs) via two-step transesterification-glycerolysis or hydrolysis-glycerolysis processes. The transesterification-glycerolysis process has the advantages in terms of a high reaction rate and a high process yield. For hydrolysis, triglycerides are converted to free fatty acids (FFA) at higher reaction temperature, but water is used as a reactant. Therefore, the separation process is not complicated. This study simulated the techno-economic comparison of four different scenarios of MG and DG production using ASPEN Plus V11 simulation software. In both scenarios I and IV, MG and DG are synthesized from WCO via transesterification and glycerolysis. Scenario I used a homogenous catalyst and scenario IV used a heterogenous catalyst. In scenarios II and III, MG and DG are synthesized from WCO via hydrolysis and glycerolysis. Scenario III, the make-up glycerol was added to achieve the glycerol to FFA molar ratio of 1:1 for improvement from scenario II. From the simulation results, transesterification-glycerolysis processes provided higher MG production than that of hydrolysis-glycerolysis process. The maximum MG productivity was obtained from the scenario I while the scenario IV can reduce one distillation for separation and recycle of unreacted glycerol to reduced energy consumption in the glycerolysis and purification sections as compared with scenario I. Moreover, the make-up glycerol for glycerolysis in scenario III increased overall energy consumption as well as productivity of MG compared with scenario II. The scenario IV presented the lowest COM_d and the minimum MG production cost. The MG production cost per ton of MG was lower than the current MG price for scenarios I, III, and IV, indicating that these processes can be feasible economically. Moreover, by-product price was the most sensitive parameter for scenarios I, III, and IV.

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Chapter 1

Introduction

1.1 Background and rationale

Although the total world production of food emulsifiers is not known exactly due to the lack of statistical information from many countries, the estimated amount of produced food-grade emulsifiers is about 250,000 metric tons per year. Mono- and diglycerides, including distilled monoglycerides and their organic acid esters, are approximately 75% of the total production of emulsifiers [1]. Applications of monoglycerides (MGs) and diglycerides (DGs) that are widely used in various industries (e.g., food, detergent, plasticizer, cosmetic and pharmaceutical formulations) make them the most important chemicals based on the economic and the functional point of view [1]. The mixture of MGs and DGs can be produced via glycerolysis of fats/oils using a base catalyst at the reaction temperature of 250 °C. However, this reaction requires a high reaction temperature and long reaction time due to the less solubility of glycerol and oil [2].

Hydrolysis of triglycerides (TGs) using lipase at high temperature, a water and free fatty acids (FFAs) are produced which is a major form of dietary lipid in fats and oils, via the breaking of ester bonds. Apart from direct oxidation, lipid hydrolysis is the most common cause of FFAs formation when oils reach the second stage of lipid oxidation. Fatty acid methyl esters (FAMEs) are esters of fatty acids. The physical characteristics of FAMEs are closer to those of fossil diesel fuels than that of pure vegetable oils, but properties depend on the type of vegetable oil. A mixture of different FAMEs is commonly referred to as biodiesel, which is a renewable alternative fuel. It is also non-toxic and biodegradable [3]. As mentioned before, the glycerolysis of oils (TGs) as the conventional MG and DG production is limited by the solubility between glycerol and oil. Therefore, it should be interesting to use the TG derivatives (FFAs or FAMEs), instead of TGs, as a reactant to increase the glycerol miscibility.

Glycerolysis of FFAs is an esterifying FFAs with glycerol or hydroxyl groups presenting in the parent reactant to produce MGs, DGs, TGs and water. From this perspective, it is the esterification process in which glycerol acts as the alcohol to convert FFAs into the respective glycerides, and water as a by-product. The process is usually applied as a pretreatment step for biodiesel production when the FFAs content is higher than 5% [4]. For glycerolysis of FAMEs is also a reversible reaction of the methanolysis of fats, which is a major route for biodiesel production. MGs, DGs and TGs are produced together with a by-product of methanol through this reaction, which is carried out at the reaction temperature of 135 °C [5]. Glycerolysis of FAMEs is an interesting route for MGs synthesis. Because using methyl esters instead of the corresponding oils and glycerol in the preparation of MGs has several advantages. For instance, methyl esters that are prepared from fats by energy preserving fat methanolysis are easily purified and less corrosive. Furthermore, glycerolysis of methyl ester occurs more rapidly than esterification of fatty acids with glycerol [6]. There are many routes to produce MGs and DGs which depends on the feedstocks, such as oils/fats, FFAs and FAMEs.

The upstream reactions to produce FFAs and FAMEs are required as hydrolysis of TGs and transesterification of TGs, respectively. The hydrolysis of oils and fats is an important industrial operation: worldwide 1.6×10^6 tons of fatty acids are produced every year by this process [7]. Oils and fats are part of a group of compounds known as fatty esters or TGs, and their hydrolysis essentially involves reactions with water to produce valuable FFAs and glycerol [8]. The conventional hydrolysis process to produce FFAs (fat splitting process) is carried out reacting vegetable oils and/or fats with superheated water (100-260 °C and 100-7000 kPa using 0.4-1.5 %wt of water/oil ratio). This process requires a high-energy input; breakdown of products may also occur, especially in the case of highly unsaturated fatty acids [9]. The by-products dissolved in the water phase cause a problem in the isolation of glycerol from this phase [7]. FAMEs or biodiesel has been considered interesting alternative energy since it is renewable, less flammable, non-toxic, and environmentally friendly. Biodiesel consisting of mono alkyl esters of long-chain fatty acids is produced through a transesterification of TGs derived from vegetable oils or animal fats. In the transesterification, TGs are reacted with low molecular weight alcohol in a presence of catalyst, producing biodiesel and glycerol as a by-product. For instance, the optimum reaction conditions were found to methanol to waste cooking oil (WCO) molar ratio of 14:1, 60 °C temperature and pressure 1 atm using calcium carbonate ($CaCO_3$) catalyst [10]. Transesterification of TGs process offers advantages such as lower reaction temperature, short reaction time, and higher conversion [11].

WCOs are important food-chain by-products that can be used as green raw materials for chemical synthesis. The concerning amount of WCOs available throughout the world causes major environmental, economic, and social issues. More than 15 million tons of WCOs are generated globally each year, with the European Union (EU) producing close to 1 million tons [12]. WCOs are often discharged into municipal sewers, necessitating extra maintenance and increasing water treatment costs [12]. The main composition of WCOs are TGs and FFAs. Therefore, this research aims to simulate techno-economic analysis of MGs and DGs production using WCO as a feedstock via two possible routes including: 1) hydrolysis of WCOs to produce FFAs and glycerol, and then glycerol and FFAs are esterified to produce MGs and DGs; and 2) transesterification of WCOs to produce FAMEs and glycerol, and then glycerolysis of FAMEs to produce MGs and DGs. The simulation results will be performed in Aspen Plus simulation software.

1.2 Research objective

To perform techno-economic analysis of MG and DG production from WCOs via two different scenarios: transesterification of TG and glycerolysis of FAME; and hydrolysis of TG and glycerolysis of FFA using Aspen Plus simulation software.

1.3 Research scope

1.3.1 Aspen Plus V11 will be used to comparatively study on MG and DG production processes.

1.3.2 This study aims to perform techno-economic analysis of MG and DG production from WCOs via four different scenarios:

Scenario I: Transesterification of TG using K/CeO_2 catalyst at a condition of 65 ℃ and 1 atm followed by glycerolysis of FAME using CH_3ONa as a homogeneous catalyst at the reaction temperature of 135 ℃ and 1 atm. Triolein and oleic acid are used as a model compound of WCO for this simulation.

Scenario II: Hydrolysis of TG using subcritical water at a condition of 350 ℃ and 20 MPa followed by glycerolysis of FFA using a CH_3SO_3H as a homogeneous catalyst at the reaction temperature of 120 ℃ and 1 atm. Triolein and oleic acid are used as a model compound of WCO for this simulation.

Scenario III: Hydrolysis of TG using subcritical water at a condition of 350 ℃ and 20 MPa followed by glycerolysis of FFA with the make-up glycerol using a CH_3SO_3H catalyst at the reaction temperature of 120 ℃ and 1 atm. Triolein and oleic acid are used as a model compound of WCO for this simulation.

Scenario IV: Transesterification of TG using K/CeO_2 catalyst at a condition of 65 ℃ and 1 atm followed by glycerolysis of FAME using a heterogeneous catalyst of MgO at the reaction temperature of 250 ℃ and 1 atm. Triolein and oleic acid are used as a model compound of WCO for this simulation.

1.3.3 The feedstock of waste cooking oil (WCO) consisting of triglyceride 90%, free fatty acid 6%, and water 4%. The plant capacity is set at feedstock supply of 81,457.3 kg/hr and the purity of MG product set at 90%wt.

1.3.4 The process performance will be reported in terms of product yields of MG, energy consumption and cost analysis, respectively.

1.3.5 The cost analysis will be presented in manufacturing cost, fixed capital investment, and sensitivity analysis of the process.

1.4 Expected benefits

1.4.1 The feasibility of the MG and DG production processes via scenario I: transesterification of TG-glycerolysis of FAME used a homogeneous catalyst of CH_3ONa, scenario II: hydrolysis of TG-glycerolysis of FFA, scenario III: hydrolysis of TG-glycerolysis of FFA with adding glycerol and scenario IV: transesterification of TG-glycerolysis of FAME used a heterogeneous catalyst of MgO can be analyzed.

1.4.2 Able to analyze and compare the energy consumption and the cost-effectiveness for the MG and DG production process via scenario I: transesterification of TG-glycerolysis of FAME used a homogeneous catalyst of CH_3ONa, scenario II: hydrolysis of TG-glycerolysis of FFA, scenario III: hydrolysis of TG-glycerolysis of FFA with adding glycerol and scenario IV: transesterification of TG-glycerolysis of FAME used a heterogeneous catalyst of MgO.

Chapter 2

Theory and literature review

This chapter presents theory and literature reviews, which include information of feedstocks for MG and DG production, MG and DG synthesis and kinetic parameters of the related reactions for MG and DG production.

2.1 Feedstocks for MG and DG production

WCO is an interesting feedstock to produce MGs. WCO is obtained by immersing foods, oils or fats in the presence of oxygen, moisture, pro-oxidant, and antioxidants of food at high temperature (150-200 °C). Generally, the composition of WCO is 94-98% TG, 2-6% FFA, 1-3% water, and a trace amount of other compounds [13, 14]. Composition of WCO feedstock from different country sources are summarized in Table 1 [15].

Table 1 WCO feedstock composition from different country sources.

Source of waste cooking oil	Composition						Ref.
	FFA (%wt)	Water content (%wt)	C16:0 (%)	C18:0 (%)	C18:1 (%)	C18:2 (%)	
Bakery oil (Brazil)	1.5	6.2	11.6	3.9	25.5	51.9	[16]
Chinese Restaurant (United Kingdom)	1.53	1.2	6.1	1.8	64.2	19.4	[17]
Waste frying oil (Malaysia)	5.5	6	60.1	10.8	27.2	1.14	[18]
Local restaurant (Mexico)	1.05	0.4	17.82	5.75	40.98	28.77	[14]

The different physicochemical properties of used and unused WCO are determined by the established ASTM standard test method and shown in Table 2 [19].

Table 2 Properties of used and unused cooking oil [19].

Properties	Unused cooking oil values	Used cooking oil values
Acid value (mg KOH/g)	0.3	4.03
Calorific value (J/g)	-	39658
Saponification value (mg KOH/g)	194	177.97
Peroxide value (meq/kg)	<10	10
Density (gm/cm^3)	0.898	0.9013
Kinematic viscosity (mm^2 /s)	39.994	44.956
Dynamic Viscosity (mPa.s)	35.920	40.519
Flash point (°C)	161-164	222-224
Moisture content (%wt)	0.101	0.140

Triacylglycerol or triglyceride (TG) is a major form of dietary lipid in fats and oils, whether derived from plants or animals. Triacylglycerol is composed of three fatty acids esterified to a glycerol molecule as presented in Fig 1. The physical properties of the triacylglycerol are determined by the specific fatty acids esterified to the glycerol moiety and the actual position the fatty acids occupy [20].

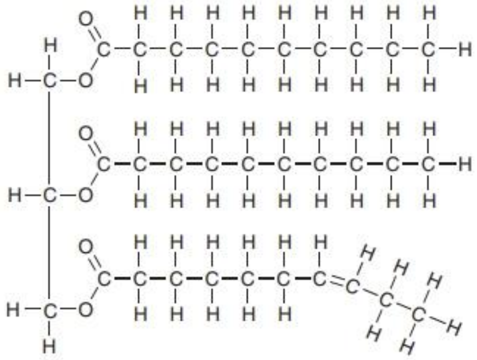
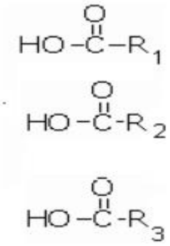


Fig. 1 The structure of triglyceride [20]

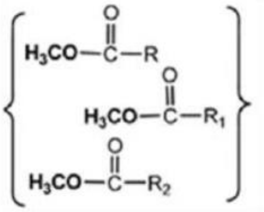
Free fatty acids (FFA) are derived from triacylglycerol by cleavage of ester bonds due to the action of lipase, high temperature, and moisture. Besides the direct oxidation, lipid hydrolysis is the dominant reason for the generation of FFA when the oils were entered the second stage of lipid oxidation. FFA can act as pro-oxidants in oils by speed up the rate of hydroperoxide decomposition. Thus, high FFA content in the oil may cause further oxidation and lead to development of offensive taste and flavor in the oil. FFA content is one of the most important concerns in the refining of edible oil. FFA is often used to indicate the oil quality and its suitability for edible [21].



$$HO-\overset{O}{\overset{\|}{C}}-R_1 \qquad HO-\overset{O}{\overset{\|}{C}}-R_2 \qquad HO-\overset{O}{\overset{\|}{C}}-R_3$$

Fig. 2 The structure of FFA [22]

Biodiesel is a renewable, alternative diesel fuel produced from vegetable oils, animal fats, or recycled restaurant grease. This biodiesel is non-toxic, biodegradable liquid fuel consisting of mono alkyl esters of long chain fatty acids (also known as fatty acid methyl esters, or FAMEs as presented in Fig 3.) and may be used alone or blended with petroleum-based diesel fuels. The most common process for producing biodiesel involves two steps: In the first, the transesterification, TGs (i.e. oils or fats) are chemically reacted with an alcohol, usually methanol, in the presence of a catalyst, like sodium or potassium hydroxide, yielding FAMEs and by-product glycerol. In the second, the FAMEs and by-product glycerol are then separated and purified. Biodiesel is the name given to the FAME fraction retained for use as fuel. The glycerol fraction is sold for use in soaps and other products [23].



$$\left\{ H_3CO-\overset{O}{\overset{\|}{C}}-R \quad H_3CO-\overset{O}{\overset{\|}{C}}-R_1 \quad H_3CO-\overset{O}{\overset{\|}{C}}-R_2 \right\}$$

Fig. 3 The structure of FAME [23]

Glycerol has three hydroxyl groups attached to the carbon back bone (Fig. 4) and it is a hydrophilic molecule and hence it is decidedly less soluble in organic solutions; for example, it is only 4–5% soluble in common fats which are hydrophobic themselves [24]. This low solubility hinders the glycerolysis reaction and unless the reaction is carried out with a catalyst. It takes a longer reaction time at higher temperatures around 250 °C, where glycerol solubility is approximately 45% [24].

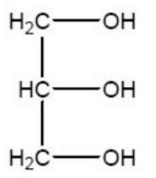


Fig. 4 The structure of glycerol [25]

2.2 MGs and DGs: Use and synthesis

Monoglycerides (MGs), also known as monoacylglycerol, is the most widespread and important type of glycerides. It consists of a chain of fatty acids that bind covalently to a glycerol molecule via ester linkage. The types of MGs are classified according to the location of the ester bonds on the glycerol as 1-monoacylglycerols and 2-monoacylglycerols [6].

The structures of monoglyceride are shown in Fig 5. and the physical properties of monoglyceride are presented in Table 3.

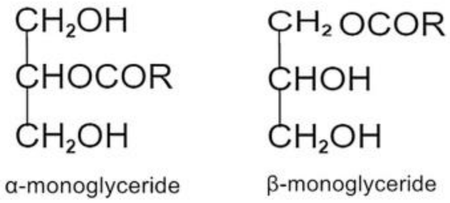


Fig. 5 The structures of monoglyceride [26]

Table 3 Physical properties of monoglyceride (monoolein) [27].

Properties of MGs	
Molecular formula	$C_{21}H_{42}O_4$
Density	0.914
Boiling point	417.1 [°C] at 760mmHg
Melting point	70.5 [°C]
Flash point	238.7 [°C]

Diglycerides (DGs) is a glyceride composed of two fatty acid chains that are covalently bound to a single glycerol molecule via an ester linkage [28]. The structure of DG is shown in Fig 6. The physical properties of diglyceride are also presented in Table 4.

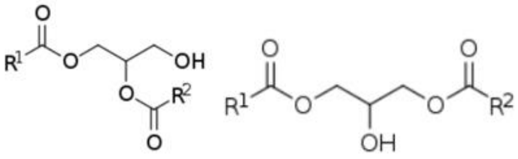


Fig. 6 The structure of diglyceride [29]

Table 4 Physical properties of diglyceride (diolein) [30].

Properties of DGs	
Molecular formula	$C_{39}H_{72}O_5$
Density	0.934
Boiling point	678.3 [°C] at 760mmHg
Melting point	12 [°C]
Flash point	189.2 [°C]

The conventional chemical method to produce MGs and DGs involves the glycerolysis of fats and oils at higher temperatures (220 – 260 ˚C) and elevated pressure under nitrogen atmosphere while employing inorganic alkaline catalysts [6]. In addition, there are two alternative main synthetic routes for obtaining MGs and DGs: direct esterification of glycerol with fatty acids; and transesterification of glycerol with fatty acid methyl esters (FAME) as illustrated in Fig. 7. In both routes the commercial processes use homogeneous catalysts. Former method requires an acid catalyst such as sulfuric, phosphoric, or organic sulfonic acid [31, 32] whereas later case is a basic catalyzed reaction with a strong base such as KOH or $Ca(OH)_2$ at high temperatures [24].

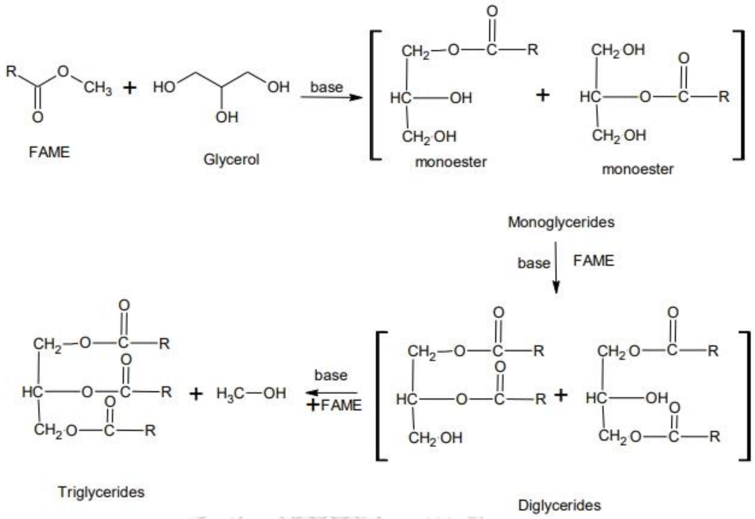


Fig. 7 MGs and DGs synthesis [6]

2.2.1 MGs and DGs synthesis from glycerolysis of oils/fats

Glycerolysis of fats and oils produces industrially important MGs and DGs. MGs and their derivatives have many applications as surfactants and emulsifiers in a wide range of foods, cosmetics, and pharmaceutical products [33, 34]. MGs are commercially manufactured by the glycerolysis in which fats and oils undergo a transesterification with glycerol. This is a physicochemical process and requires high temperatures (210 – 260 °C) and the use of an inorganic catalyst, such as sodium hydroxide (NaOH), potassium hydroxide (KOH), or calcium hydroxide ($Ca(OH)_2$) [24, 35]. Noureddini et al. [36] studied the transesterification of glycerol with triglyceride at 245 °C to MGs and DGs products were obtained using an alkaline catalyst. The main reaction steps are:

$$\text{Triglyceride} + \text{Glycerol} \leftrightarrow \text{Diglyceride} + \text{Monoglyceride} \tag{2.1}$$

$$\text{Diglyceride} + \text{Glycerol} \leftrightarrow 2\ \text{Monoglyceride} \tag{2.2}$$

$$\text{Triglyceride} + \text{Monoglyceride} \leftrightarrow 2\ \text{Diglyceride} \tag{2.3}$$

2.2.2 MGs and DGs synthesis from glycerolysis of FAME with homogeneous catalyst

The main reaction steps glycerolysis of FAME using homogeneous catalyst are:

Fatty acid methyl ester + Glycerol ↔ Monoglyceride + Methanol (2.4)

Monoglyceride + Monoglyceride ↔ Diglyceride + Glycerol (2.5)

Fatty acid methyl ester + Diglyceride ↔ Triglyceride + Methanol (2.6)

The reaction was reported to carry out at temperature of 135 °C and the used catalyst is sodium methoxide (1 %wt of total reactant) [5].

2.2.3 MGs and DGs synthesis from glycerolysis of FAME with heterogeneous catalyst

The main reaction steps glycerolysis of FAME with heterogeneous catalyst are:

Fatty acid methyl ester + Glycerol → Monoglyceride + Methanol (2.7)

Monoglyceride + Fatty acid methyl ester → Diglyceride + Methanol (2.8)

The reaction was reported to carry out at temperature of 250 °C and the used catalyst is Magnesium oxide (30 g/mol of mole FAME). Moreover, TGs did not observed at any reaction time using this heterogeneously catalyzed conditions [37].

2.2.4 MGs synthesis from glycerolysis of FFA

The main reaction of glycerolysis of FFAs are shown as follows:

Glycerol + Fatty fatty acid ↔ Monoglyceride + Water (2.9)

Monoglyceride + Fatty fatty acid ↔ Diglyceride + Water (2.10)

Diglyceride + Fatty fatty acid ↔ Triglyceride + Water (2.11)

The temperature reaction condition is 120 °C using methanesulfonic acid (MSA) as a homogeneous catalyst [38].

2.3 Kinetic parameters of the related reactions for MGs and DGs production

2.3.1 Glycerolysis of FFAs

Maquirriain et al. [38] proposed esterification of glycerol by FFAs using homogeneous catalysts. Three catalysts: p-toluene sulfonic acid (PTSA), methane sulfonic acid (MSA), and sulfuric acid (SA) were compared. The product distribution in Fig. 8 shows the evolution of MG, DG, TG, FFA, glycerol (GOH) and water (W) as a function of time obtained with a catalyst concentration of 0.35 equiv/kg.

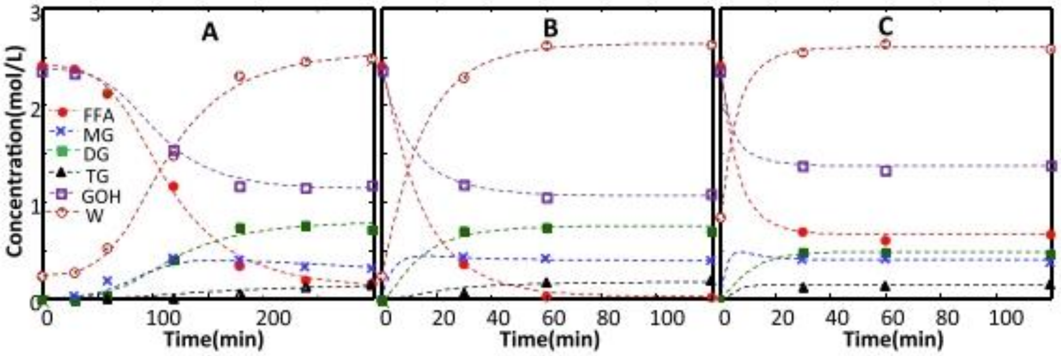


Fig. 8 Product distribution obtained with: (A) SA; (B) MSA; (C) PTSA, at 120°C, molar ratio FFA:GOH = 1:1, catalyst concentration 0.35 equiv/kg [38]

Fig. 8 provides evidence that the sulfuric acid (SA) has a more stable state in the bulk of the glycerol phase. In this part, there is a high surface tension resulting in low reaction rate. Due to the well-known function of these compounds acting as emulsifiers, MGs reduce surface tension. Therefore, the interfacial area increases and consequently the reaction rate increases generating the induction period. In the case of the catalysts of methane sulfonic acid (MSA) and p-toluene sulfonic acid (PTSA), they tend to active because they have a non-polar head which reduces the surface tension. It is important that although all three acids have similar strengths, the activity increases when the surface tension of the glycerol-catalyst of the system decreases. The curves shown in Fig. 8 was used to determine the kinetic model.

The reaction rate constants of Eqs. (2.9) - (2.11) are presented in Table 5. Similar behaviors could be observed when reaction rate constants are compared the reaction of DG formation and TG formation. The reaction rate constants of the glycerol esterification with FFA are results in high conversion and low residence time.

Table 5 Kinetic constants of the glycerol esterification with FFA at 120 °C [38].

Reaction	k_i	FFA/GL = 1:1
		MSA
(2.9)	k_1	2.06e-02
	k_{-1}	1.53e-04
(2.10)	k_2	6.87e-02
	k_{-2}	2.59e-04
(2.11)	k_3	1.23e-02
	k_{-3}	9.86e-05

2.3.2 Glycerolysis of FAME with homogeneous catalyst

Negi et al. [5] investigated the glycerolysis of FAMEs. This work aims to develop and test a kinetic model that can be used reliably simulate different alternative processes for this reaction. To definition of conversion, the ester phase was analyzed without methanol and glycerol. The ester molar conversion based on the methyl ester, X, at time t was calculated as shown in Eq (2.12):

$$x = 1 - \frac{x'_{FAME}}{(x'_{FAME} + x'_{MG} + 2x'_{DG} + 3x'_{TG})} \tag{2.12}$$

where x' are the mole fractions calculated on a glycerol- and methanol-free basis.

Thermodynamic models of UNIFAC and UNIFAC-Dortmund were reported to qualitatively predict that the concentration of glycerol in the ester phase increases with increasing monoglyceride concentrations [39]. The values of the rate constant for Eqs. (2.4) - (2.6) are shown in Table 6.

Table 6 Parameters used in the kinetic model [5].

Parameter	Value
k_{1f}	0.074 kg.mol^{-1} min^{-1}
k_{1b}	0.645 kg.mol^{-1} min^{-1}
k_{2f}	0.348 kg.mol^{-1} min^{-1}
k_{2b}	0.717 kg.mol^{-1} min^{-1}
k_{3f}	0.004 kg.mol^{-1} min^{-1}
k_{3b}	0.227 kg.mol^{-1} min^{-1}

2.3.3 Glycerolysis of FAME with heterogeneous catalyst obtained from Ferretti et al. [37]. They proposed the synthesis of monoglycerides by glycerolysis of fatty acid methyl ester using strongly basic high surface area MgO. The effect of the reaction temperature is investigated by carrying out the catalytic tests on MgO at 473, 483, 493, and 523 K as shown in Fig. 9.

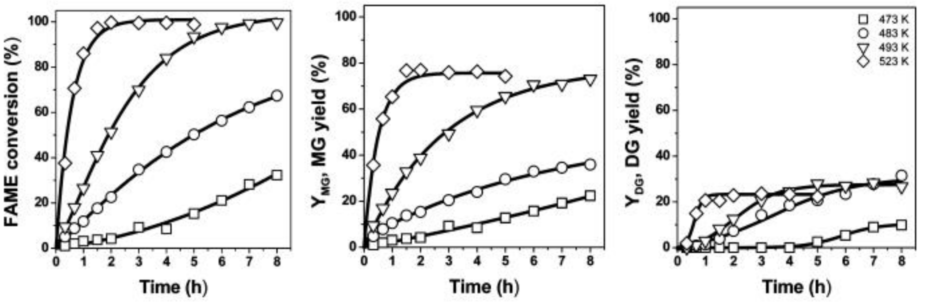


Fig. 9 Effect of the reaction temperature on FAME conversion and MG and DG yields

Fig. 9 provides FAME conversion significantly increased with the reaction temperature so that complete conversion is achieved in 2 hr at 523 K in contrast to 51% reached in 2 hr at 493 K, 23% at 483 K, and 4% at 473 K. That MG yield is enhanced by increasing the reaction temperature. This is due not only to the increasing conversion but also to the fact that the selectivity to MG improved at higher reaction temperatures at the expense of DG selectivity when compared at similar FAME conversion levels. The activation energy and pre-exponential factor are computed. Table 7 lists the kinetic parameters of A_1 (pre-exponential factor of Eq

2.7), A_2 (pre-exponential factor of Eq 2.8), Ea_1 (activation energy of Eq 2.7) and Ea_2 (activation energy of Eq 2.8), respectively.

Table 7 The kinetic parameters of glycerolysis of FAME with heterogeneous catalyst [37].

Pre-exponential factor (h^{-1})	A_1	A_2
	7.4	1.36
Activation energy (kJ/mol)	Ea_1	Ea_2
	26	19

2.3.4 Transesterification of WCOs

Roy et al. [40] proposed the biodiesel production from waste material using heterogeneous to achieve a sustainable source of fuel. Heterogeneous base-catalyzed transesterification attracts more attention as it overcomes the flaws regarding homogeneous catalysis

The effect of oil to methanol molar ratio on FAME conversion is investigated by two sets of batch reactions using two feedstocks of WCO and castor oil as shown in Fig. 10. The catalyst weight percentage predominantly influences the transesterification process as the optimum catalyst amount ensures access of active sites for reactants. The impact of catalyst dose on FAME conversion (%) is examined by differing catalyst amount from 0.5 to 3 wt% (w/w) with 0.5 wt% steady increment as shown in Fig. 11. The influence of temperature in FAME conversion has been shown in Fig. 12.

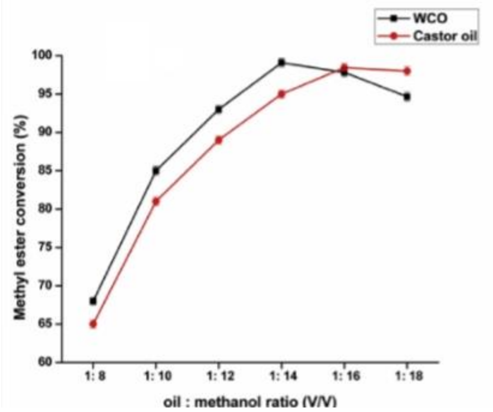


Fig. 10 Optimization of oil:methanol molar ratio [40]

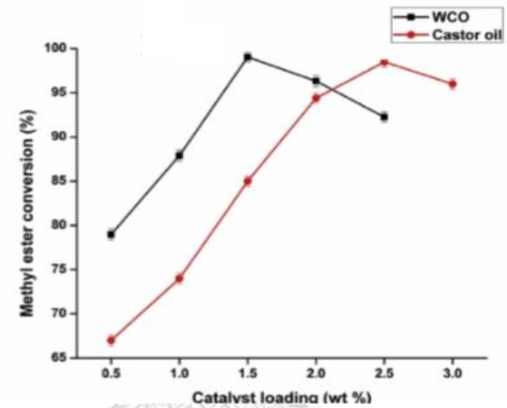


Fig. 11 Optimization of catalyst loading (wt%) [40]

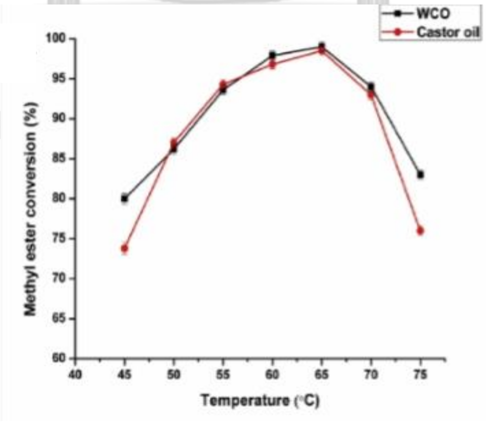


Fig. 12 Optimization of reaction temperature (°C) [40]

Fig. 10 illustrates the highest conversions of 99.09% was corresponding 1:14 WCO to methanol molar ratio. Fig. 11 has depicted that increasing catalyst loading enhanced the conversion till the optimum catalyst loading of 1.5 wt% in the corresponding methyl ester formation. Fig. 12 shows that the FAME conversion was accelerated with increasing temperature. Maximum conversion of WCO was obtained at 65 °C quite near to boiling temperature of methanol. The overall reaction is as follows:

Transesterification of TG:

$$\text{Triglyceride} + 3\ \text{Methanol} \longrightarrow 3\ \text{Fatty acid methyl ester} + \text{Glycerol} \qquad (2.12)$$

The activation energy and pre-exponential factor are computed. Table 8 lists the kinetic parameters.

Table 8 Parameters for the transesterification of WCOs [40].

Parameter	Values
Pre-exponential factor (A) (min^{-1})	3.54×10^{5}
Activation energy (E_a) (kJ/mol)	50.10

2.3.5 Hydrolysis of WCOs

Alenezi et al. [41] investigated the hydrolysis of sunflower oil under subcritical water. Number of hydrolysis experiments was carried out in a tubular reactor at 20 MPa, temperature range of 270-350°C. They reported that the water also acts as a solvent, the concentration of water is sufficient to affect the hydrolysis of the oil to produce >90 %wt fatty acid (FA). The reaction is a pseudo-homogenous first-order reversible reaction with an excess of one reactant, mainly water, in an oily phase. The hydrolysis reaction consists of three stepwise reactions represented by Eqs. (2.13), (2.14), and (2.15). In the first step, TG is hydrolyzed to DG, which is converted to MG in the second step. In the final step, the produced MG is hydrolyzed to glycerol, while in each step FFA is also generated. The amount of collected FFA product is equivalent to the sum of three times the moles of TG reacted, two times the moles of DG reacted, and one times the mole of MG, or equivalent to the total moles of consumed water. FFA can act as an acid catalyst in the hydrolysis in the subcritical water and yield up to 90% conversion.

Hydrolysis is a crucial reaction in the chemical industry's processing of oils and fats. Using superheated steam, this reaction can be carried out thermally as a liquid–liquid or gas–liquid reaction [42]. A mass transfer regulated chemical reaction in which water combines with oil (TG) to generate FFA and glycerol may be characterized as hydrolysing oil with water. FFA and glycerol are important intermediate raw ingredients with a wide range of applications, including biodiesel, soap, synthetic detergents, greases, and cosmetics [43]. Lascaray [44] reported that the degree of hydrolysis in water and oil at equilibrium is unaffected by reaction temperature. Some studies have discovered that employing pressures more than 20 MPa and temperatures greater than 250 °C can remove the need for acidic or alkaline catalysts. A kinetic study for the continuous flow thermal hydrolysis of sunflower oil in subcritical water at 20 MPa, between 270 and 350 °C [41]. The influence of temperature on the kinetic parameters was determined based on the Arrhenius equation to the optimum evaluated rate constants. The energy of activation was found to be highest in the first-step hydrolysis reaction (TG). It is evident that the Ea_1 value for first reaction of TG conversion to DG is higher than the Ea_2 and Ea_3 values. This is because the hydrolysis needs higher energy to start the reaction. Since reactions of organic compounds involve the making and breaking of chemical bonds. The strength of bonds becomes an important consideration. A high value of Ea_3 is required in the third reaction, but it is smaller activation energy as compared to the start of the reaction. The activation energy required in the second step of the hydrolysis reaction (converting from DG to MG) was observed to be almost half of the Ea_1 indicating the forward driving force for the progression of reaction. The kinetic parameters of hydrolysis are listed in Table 9 as obtained from the previous report [41]. The reaction of hydrolysis of TG is:

$$\text{Triglyceride + Water} \longrightarrow \text{Diglyceride + Free fatty acid} \tag{2.13}$$

$$\text{Diglyceride + Water} \longrightarrow \text{Monoglyceride + Free fatty acid} \tag{2.14}$$

$$\text{Monoglyceride + Water} \longrightarrow \text{Glycerol + Free fatty acid} \tag{2.15}$$

Table 9 The kinetic parameters of hydrolysis [41].

Pre-exponential factor (min^{-1})	A_1	A_2	A_3
	5.2×10^6	1.1×10^1	2.8×10^6
Activation energy (kJ/mol)	Ea_1	Ea_2	Ea_3
	98	68	90

Chapter 3
Experimental design

3.1 Process modeling and simulation

The comparative process simulation is performed using Aspen Plus software by defining appropriate thermodynamic model and specifying operating conditions. Four different process scenarios of MG and DG production from WCO are examined and compared in terms of performance analysis including required feed MG and DG productivities energy consumption, cost analysis and sensitivity analysis. In the first scenario, MG and DG are synthesized via two combined reactions of transesterification of TG with methanol and glycerolysis of FAME. In the second scenario, MG and DG are synthesized via hydrolysis of TG and glycerolysis of FFA. In the third scenario, MG and DG are synthesized via hydrolysis of TG-glycerolysis of FFA using make-up glycerol. The four scenarios, MG and DG are synthesized transesterification of TG-glycerolysis of FAME using a heterogeneous catalyst in order to improve the process perfomance.

3.2 Key components

The feedstock of waste cooking oil (WCO) consisting of triglyceride 90%, free fatty acid 6%, and water 4% is used for each scenarios [45]. The plant capacity is set at feedstock supply of 81,457.3 kg/hr or 787,110 ton/y according to EU WCO quantitation [46]. For scenario I, the feed molar ratio of methanol:oil was used at 14:1 for transesterification [40]. For scenario II, the feed molar ratio of water:oil was 17:1 for hydrolysis [41]. For scenario III, the feed molar ratio of water:oil was 17:1 and using make-up glycerol to obtain glycerol to FFA molar ratio of 1:1 [41]. For scenario IV, the feed molar ratio of methanol:oil was used at 14:1 for transesterification and using MgO as a heterogeneous catalyst for glycerolysis of FAME [40].

3.3 Thermodynamic selection

The thermodynamic characteristics of non-polar - polar chemical components is determined using the regressed UNIQUAC model. According to a study of Gaurav et al. [47], all chemical components were linked to the UNIQUAC model.

3.4 Process description

3.4.1 Scenario I: Transesterification of TG-glycerolysis of FAME

In the first scenario, MG and DG are synthesized from WCO via two combined processes of the transesterification with methanol and glycerolysis of FAME. The kinetic parameters of pre-exponential factor A_1 (s^{-1}) and activation energy Ea_1 (J/mol) are shown in Table 8. The concentration of glycerol in the ester phase increases with increasing monoglyceride concentrations, resulting in kinetic suitable for use in glycerolysis of FAME. The mixture of oleic acid and triolein is used as a model compound of WCO consisting of triolein 90%, oleic acid 6%, and water 4% [45]. The oleic acid and palmitic acid have similar kinetic result because the initial rate of reaction decreased slightly with increasing the carbon chain length of the fatty acids, possibly resulting from the steric hindrance effect of the carbon chains [48]. The main reaction is transesterification of TG as presented in Eq. (2.12). The values of the rate constant for glycerolysis of FAME are shown in Table 6 obtained from a report by Negi et al. [5] and the reaction steps illustrated in Eqs. (2.4) - (2.6) are modeled as glycerolysis of FAME.

The WCO and the methanol (MTOH) feed steams were mixed in MIX-100. It was heated to 65 °C in heater (E-100) before sent to the reactor (TRANS). Transesterification was carried out in reactor (TRANS) using a K/CeO_2 to produce FAME, glycerol. The resulting mixture of reactants and products (MTOH, FAME, glycerol, FFA, water) was increased the pressure to 1.5 atm (P-100) and sent to distillation (T-100). Methanol was recovery from T-100 and then it was reduced pressure to 1 atm (VAL-100) before sent back to the TRANS reactor. It was reduced pressure to 1 atm (VAL-101) after that the water was removed via flash distillation (V-100). For, the glycerolysis of FAME process, the stream No.7 (TRI, MTOH, FAME, glycerol, water, FFA) and stream of CH_3ONa (No.8) were mixed in MIX-101, after that reduced the temperature to 135 °C in E-101 before sent to the reactor (GLYCERO). Glycerolysis of FAME was carried out in reactor (GLYCERO) to produce MG, DG, TRI and the un reacted of MTOH, FAME and glycerol. Then it was increased the pressure to 1.5 atm (P-101) before sent to the distillation (T-101). Methanol was recovery from T-101 and then it was reduced pressure to 1 atm (VAL-102) before sent back to the TRANS reactor. Glycerol was recovery from T-102 and then it was reduced pressure to 1 atm (VAL-103) before sent back to the reactor (GLYCERO). The stream No.14 (MG, DG, TRI, FAME, glycerol, FFA, CH_3ONa) was reduced the pressure to 1 atm (VAL-104) and then it was heated to 135 °C in heater (E-102). The stream H_3PO_4 (No.17) was heated to 135 °C in heater (E-103) before sent to the neutralized reactor (R-NUTR). Neutralization was carried out in a reactor (R-NUTR) and then separated Na_3PO_4 from SEP. Pump (P-102) was used to increase the pressure of stream No.21 (MG, DG, TRI, MTOH, FAME, glycerol, FFA) to 1.5 atm. And the last step of the scenario I was purification through the distillation (T-103) to make FAME to 96.5%wt purity and the distillation (T-104) to achieve MG to 90%wt purity.

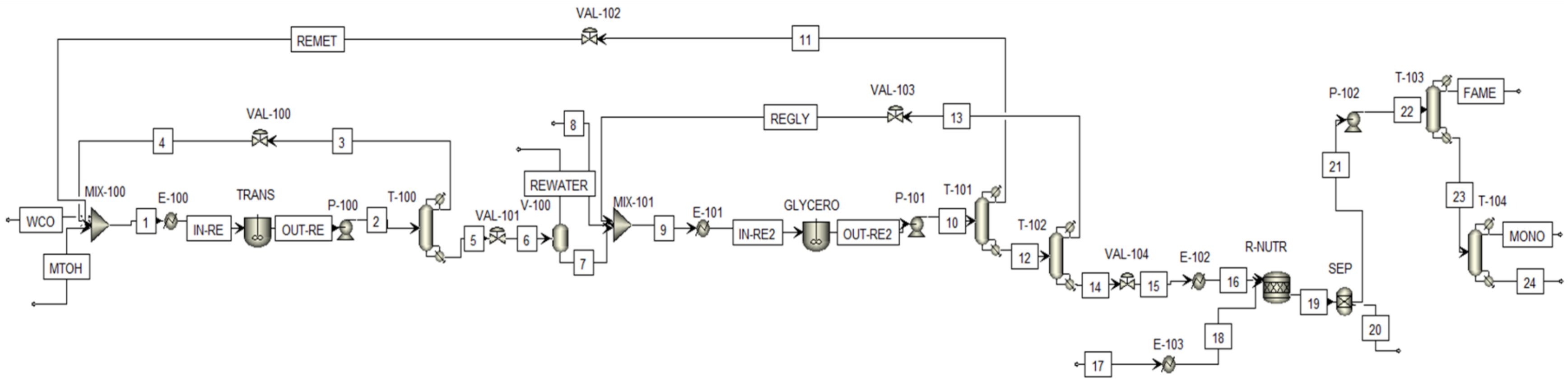


Fig. 13 Process flow diagram of Scenario I

3.4.2 Scenario II: Hydrolysis of TG-glycerolysis of FFA

In the second scenario, MG and DG are synthesized from WCO via hydrolysis of TG and glycerolysis of FFA. The kinetic parameters of hydrolysis are listed in Table 9 obtained from a report by Alenezi et al. [41]. The main and side reactions of hydrolysis of TG are presented in Eqs. (2.13) - (2.15). FFA can act as an acid catalyst in the hydrolysis in the subcritical water and yield up to 90% conversion.

The forward reaction rate constants of glycerolysis of oleic acid are presented in Table 5. The highest reaction rate constant of MG formation is found in the MSA catalyst. Similar behaviors could be observed when kinetic constants were compared between the reaction of DG formation and TG formation. The main reaction of glycerolysis of oleic acid are expressed in Eqs. (2.9) - (2.11). The reaction rate constants of the glycerol esterification with FFA are results in high conversion and low residence time.

The process in scenario II was shown in Fig 14. The WCO and the water were mixed in MIX-100. Pump (P-100) was used to increase the pressure of mixed feedstocks to 20 MPa and then it was heated to 350 °C in a heater (E-100) before sent to a reactor (HYDRO). Hydrolysis was carried out in the reactor (HYDRO) to produce MG, DG, glycerol, FFA and water. Then, the temperature was reduced to 119 °C in E-101 after that it was increased pressure to 1.5 atm (VAL-100) sent to distillation (T-100). Water was recovery from T-100 and it was reduced pressure to 1 atm (VAL-101) before sent back to the HYDRO reactor. It was reduced pressure to 1 atm (VAL-102). For the glycerolysis of FFA process, the stream No.6 (glycerol, FAME, water) was reduced the temperature to 120 °C in E-102 before sent to the reactor (GLYCERO). The water was removed via flash distillation (V-100). Pump (P-101) was used to increase the pressure of stream No.9 to 1.5 atm and sent to distillation (T-101). Glycerol was recovery from T-101 and then it was reduced pressure to 1 atm (VAL-103) before sent back to the reactor (GLYCERO). The stream No.11 (MG, DG, TRI, glycerol, FFA) was reduced the pressure to 1 atm (VAL-104) and then it was heated to 120 °C in heater (E-103). The stream NAOH and stream MSA was heated to 120 °C in heater (E-104) before sent to the neutralized reactor (R-NUTR). Neutralization was carried out in a reactor (R-NUTR). The water was removed via flash distillation (V-101) and then separated CH_3NaO_3S from SEP. Pump (P-102) was used to increase the pressure of stream No.19 to 1.5 atm. The last step of the scenario II was purification through the distillation (T-102) to separate FFA from the product stream and the distillation (T-103) to obtain 90%wt purity of MG. The stream DI was purified via distillation (T-104) to achieve DG to 97%wt purity.

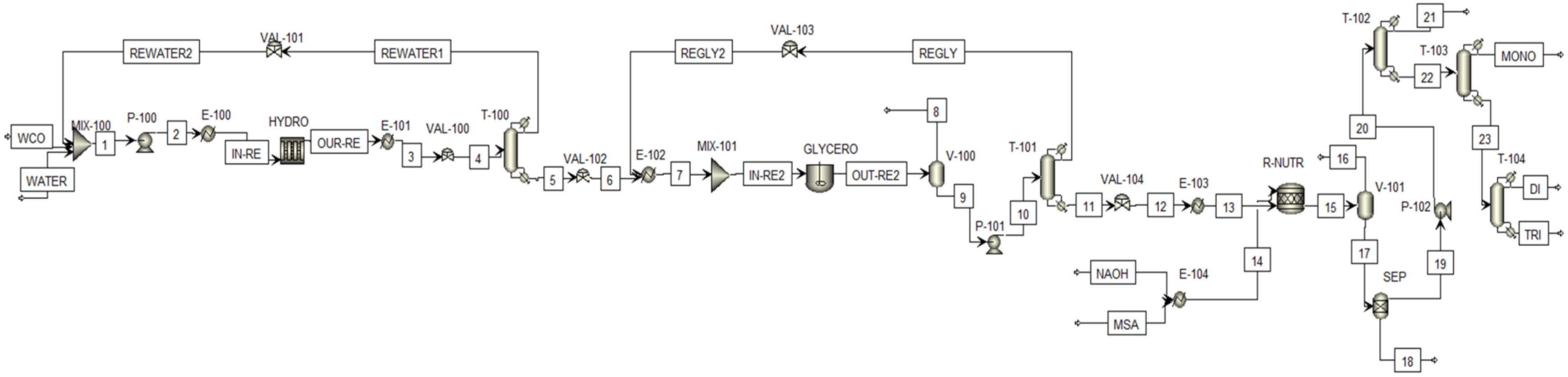


Fig. 14 Process flow diagram of Scenario II

3.4.3 Scenario III: Hydrolysis of TG-glycerolysis of FFA with make-up glycerol

The process in scenario III was shown in Fig 15. The WCO and the water were mixed in MIX-100. Pump (P-100) was used to increase the pressure of mixed feedstocks to 20 MPa and then it was heated to 350 °C in a heater (E-100) before sent to a reactor (HYDRO). Hydrolysis was carried out in the reactor (HYDRO) to produce MG, DG, glycerol, FFA and water. Then, the temperature was reduced to 119 °C in E-101 after that it was increased pressure to 1.5 atm (VAL-100) sent to distillation (T-100). Water was recovery from T-100 and it was reduced pressure to 1 atm (VAL-101) before sent back to the HYDRO reactor. It was reduced pressure to 1 atm (VAL-102). For the glycerolysis of FFA process, the stream GLY as a make-up was feed glycerol 64,570.5 ton/y to obtain glycerol to oleic acid molar ratio of 1:1. The stream No.6 was reduced the temperature to 120 °C in E-102 before sent to the reactor (GLYCERO). The water was removed via flash distillation (V-100). Pump (P-101) was used to increase the pressure of stream No.9 to 1.5 atm and sent to distillation (T-101). Glycerol was recovery from T-101 and then it was reduced pressure to 1 atm (VAL-103) before sent back to the reactor (GLYCERO). The stream No.11 (MG, DG, TRI, glycerol, FFA) was reduced the pressure to 1 atm (VAL-104) and then it was heated to 120 °C in heater (E-103). The stream NAOH and stream MSA was heated to 120 °C in heater (E-104) before sent to the neutralized reactor (R-NUTR). Neutralization was carried out in a reactor (R-NUTR). The water was removed via flash distillation (V-101) and then separated CH_3NaO_3S from SEP. Pump (P-102) was used to increase the pressure of stream No.19 to 1.5 atm. The last step of the scenario III was purification through the distillation (T-102) to separate FFA from the product stream and the distillation (T-103) to obtain 90%wt purity of MG. The stream DI was purified via distillation (T-104) to achieve DG to 97%wt purity.

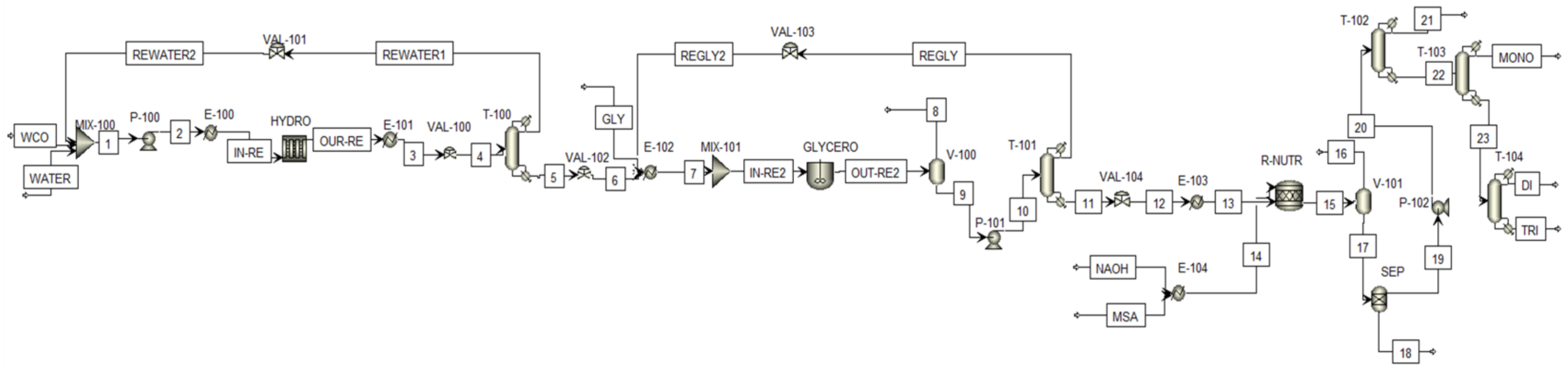


Fig. 15 Process flow diagram of Scenario III

3.4.4 Scenario IV: Transesterification of TG-glycerolysis of FAME heterogeneous catalyst.

In the fourth scenario, MG is synthesized from WCO via transesterification of TG and glycerolysis of FAME. The kinetic parameters of transesterification reaction are listed in Table 8 obtained from a report by Roy et al. [40] The main reaction is transesterification of TG as presented in Eq. (2.12). The WCO and the MTOH feed steams were mixed in MIX-100. It was heated to 65 °C in heater (E-100) before sent to the reactor (TRANS). Transesterification was carried out in reactor (TRANS) using a K/CeO_2 to produce FAME, glycerol. The resulting mixture of reactants and products (MTOH, FAME, glycerol, FFA, water) was increased the pressure to 1.5 atm (P-100) and sent to distillation (T-100). Methanol was recovery from T-100 and then it was reduced pressure to 1 atm (VAL-100) before sent back to the TRANS reactor. It was reduced pressure to 1 atm (VAL-101) after that the water was removed via flash distillation (V-100). For, the glycerolysis of FAME process, the stream No.7 (TRI, MTOH, FAME, glycerol, water, FFA) and stream of MGO were mixed in MIX-101, after that reduced the temperature to 135 °C in E-101 before sent to the reactor (GLYCERO). Glycerolysis of FAME was carried out in reactor (GLYCERO) to produce MG, DG, MTOH and then it was increased the pressure to 1.5 atm (P-101) before sent to the distillation (T-101). Methanol was recovery from T-101 and then it was reduced pressure to 1 atm (VAL-102) before sent back to the TRANS reactor. The stream No.11 was heated to 350 °C in heater (E-102) before sent to the separation (SEP). And the last step of the scenario I was purification through the distillation (T-102) to make FAME to 96.5%wt purity and the distillation (T-103) to make MG to 90%wt purity.

Table 10 summarizes the temperature and pressure of all units for 4 scenarios.

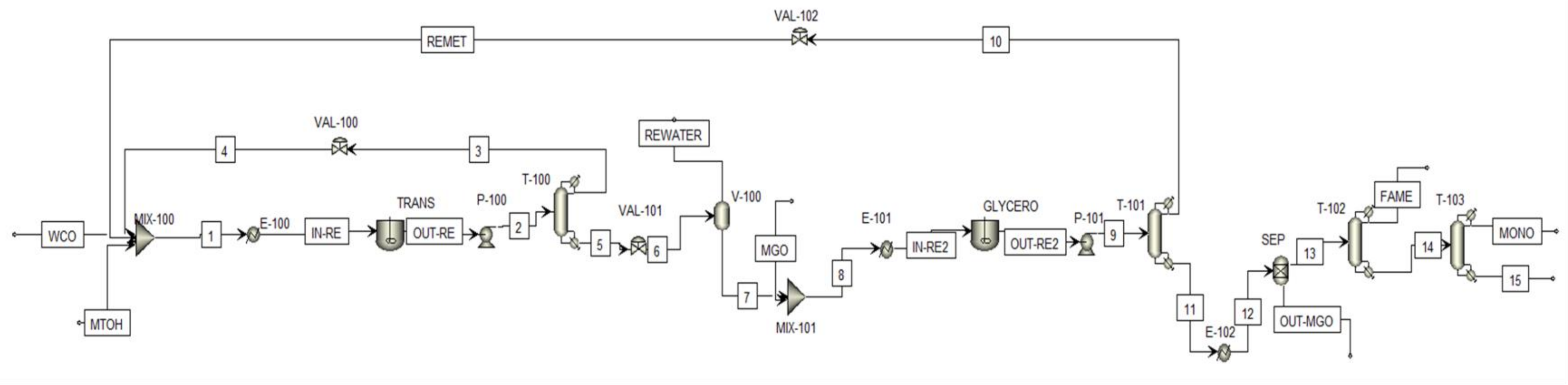


Fig. 16 Process flow diagram of Scenario IV

Operating conditions for analyzed processes are given in Table 10. Triolein and oleic acid are used as model compounds for TG and FFA, respectively.

Table 10 Operating conditions for analyzed processes of each scenario.

Scenario I	T (°C)	P (atm)	Scenario II	T (°C)	P (atm)	Scenario III	T (°C)	P (atm)	Scenario IV	T (°C)	P (atm)
TRANS	65	1	HYDRO	350	200	HYDRO	350	200	TRANS	65	1
GLYCERO	135	1	GLYCERO	120	1	GLYCERO	120	1	GLYCERO	250	1
R-NUTR	135	1	R-NUTR	120	1	R-NUTR	120	1	SEP	350	1.5
SEP	135	1	SEP	120	1	SEP	120	1	V-100	250	1
V-100	250	1	V-100	165	1	V-100	165	1	T-100		
T-100			V-101	200	1	V-101	200	1	Condenser	75.35	1.5
Condenser	75.24	1.5	T-100			T-100			Reboiler	188.54	1.5
Reboiler	143.00	1.5	Condenser	111.79	1.5	Condenser	111.79	1.5	T-101		
T-101			Reboiler	224.93	1.5	Reboiler	224.93	1.5	Condenser	76.91	1.5
Condenser	75.90	1.5	T-101			T-101			Reboiler	413.61	1.5
Reboiler	337.00	1.5	Condenser	140.14	1.5	Condenser	157.23	1.5	T-102		
T-102			Reboiler	378.95	1.5	Reboiler	408.00	1.5	Condenser	363.757	1.5
Condenser	303.37	1.5	T-102			T-102			Reboiler	451.61	1.5
Reboiler	380.22	1.5	Condenser	201.37	1.5	Condenser	159.2	1.5	T-103		
T-103			Reboiler	488.81	1.5	Reboiler	501.65	1.5	Condenser	438.78	1.5
Condenser	141.84	1.5	T-103			T-103			Reboiler	590.58	1.5

Table 10 Operating conditions for analyzed processes of each scenario (continue).

Scenario I	T (°C)	P (atm)	Scenario II	T (°C)	P (atm)	Scenario III	T (°C)	P (atm)	Scenario IV	T (°C)	P (atm)
Reboiler	432.41	1.5	Condenser	433.09	1.5	Condenser	443.24	1.5	E-100	65	1
T-104			Reboiler	589.09	1.5	Reboiler	590.48	1.5	E-101	250	1
Condenser	428.57	1.5	T-104	120		T-104			E-102	350	1
Reboiler	535.65	1.5	Condenser	583.23	1.5	Condenser	583.36	1.5	P-100		1.5
E-100	65	1	Reboiler	622.72	1.5	Reboiler	622.36	1.5	P-101		1.5
E-101	135	1	E-100	350	200	E-100	350	200	VAL-100		1
E-102	135	1	E-101	119	200	E-101	119	200	VAL-101		1
E-103	135	1	E-102	120	1	E-102	120	1	VAL-102		1
P-100		1.5	E-103	120	1	E-103	120	1			
P-101		1.5	E-104	120	1	E-104	120	1			
P-102		1.5	P-100		200	P-100		200			
VAL-100		1	P-101		1.5	P-101		1.5			
VAL-101		1	P-102		1.5	P-102		1.5			
VAL-102		1	VAL-100		1	VAL-100		1			
VAL-103		1	VAL-101		1	VAL-101		1			
VAL-104		1	VAL-102		1	VAL-102		1			
			VAL-103		1	VAL-103		1			
			VAL-104		1	VAL-104		1			

3.5 Cost analysis

The cost analysis for the MG and DG producing techniques is shown in the section below. The cost of manufacturing was calculated by estimating the capital investment, operational labor cost, utility cost, waste treatment cost, and raw material cost, respectively.

3.5.1 Equipment and capital cost

The capital cost of the MG and DG manufacturing processes is calculated using the module costing approach. The simulation data from Aspen Plus V11 software is used to estimate the sizing of the equipment. From the acquired equipment and installation charges, the bare module cost (CBM) is computed. To account for inflation, the chemical engineering plant cost index (CEPCI = 801.3, 2022) [49] is employed (year 2022).

$$\log C_p^o = K_1 + K_2 \log_{10}(A) + K_3[\log_{10}(A)]^2 \quad (3.1)$$

where C_p^o is equipment purchasing cost at carbon steel construction and ambient pressure, Jan 2001 (CEPCI = 394.3 ,2001). K_1, K_2, K_3 are cost constants, and A is equipment capacity as indicated in Table 11.

Table 11 Parameters of estimated equipment cost [50].

Equipment	**Unit for A**	K_1	K_2	K_3
Pumps (Centrifugal)	kW	3.8696	0.3161	0.1220
Pressure vessel (cs)	m^3	3.4974	0.4485	0.1074
Reactor (agitated, jacketed)	m^3	4.1052	0.5320	-0.0005
Sieve trays	m^2	2.9949	0.4465	0.3961
Heat exchanger (Floating head)	m^2	4.8306	-0.8509	0.3187

Eq. (3.2) was used to evaluate bare module cost of each equipment. Eqs. (3.3) and (3.4) showed the fixed cost investment (FCI) and the total capital investment (TCI), respectively. The FCI is combination of direct costs (purchasing equipment and installation cost) and indirect costs (freight, overhead, and engineering). In addition, TCI is summarization of FCI and working capital (WC) that is capital needed for the initial operation of the plant. Working capital was assumed at 15% of total capital investment.

Bare module cost of equipment:

$$C_{BM}=C_{p}^{o}[B_{1}+B_{2}F_{p}F_{m}] \tag{3.2}$$

Fixed capital investment (FCI):

$$FCI = 1.18\sum_{i=1}^{n}C_{BM,i} \tag{3.3}$$

Total capital investment (TCI):

$$TCI = \frac{100}{85}FCI \tag{3.4}$$

where C_{BM} is equipment bare module cost. B_1, B_2 are constants for bare module estimation. F_p is pressure factor and F_m is material factor. $F_m = 1$ when material of construction is carbon steel. *FCI* is fixed capital investment and *TCI* is total capital investment.

3.5.2 Cost of manufacturing (COM)

The manufacturing cost of MG and DG production process, including non-depreciable production costs (COM_d), is calculated by investing in fixed costs. Operating labor cost (C_{OL}), utility cost (C_{UT}), waste treatment (C_{WT}) and raw material cost (C_{RM}) is calculated using Eq. (3.5). The cost of operating labor cost was estimated from Eq. (3.6)

$$COM_{d}=0.180FCI+2.73C_{OL}+1.23\left(C_{UT}+C_{WT}+C_{RM}\right) \tag{3.5}$$

$$N_{OL}=\left(6.29+31.7P^{2}+0.23N_{np}\right)^{0.5} \tag{3.6}$$

where COM_d is manufacturing cost, FCI is fixed cost investment, C_{OL} is cost of operating labor, C_{UT} is cost of utility, C_{WT} is cost of waste treatment, C_{RM} is cost of raw material, N_{OL} is number of operators per shift, N_{np} is unit that non-particulate processing (compression, heating/cooling, separation, mixing and reaction), and P is particulate processing unit (transportation, distribution and particle size control).

Depreciation is not included in the computed production cost in Eq. (3.5). The operating labor cost was assumed at 24,600 USD/y [50] with a single operator works 49 weeks/y, 5 shifts/week and 8 hr/shift [51]. Thailand's operational labor rate was used as a comparison. It should be noted that the labor rate can be significantly different in other countries.

3.5.3 Cost of raw materials

The cost of raw materials and products which are used to calculate in this study are presented in Table 12.

Table 12 Cost of raw materials and products.

Component name	Price (USD/ton)	Ref.
WCO	224	[52]
Methanol	600	[53]
Sodium methoxide	1,150	[54]
Phosphoric acid	340	[55]
K/CeO_2	78,520	[56, 57]
Water	2.84	[58]
Sodium hydroxide	200	[54]
Methanesulfonic acid	1,600	[59]
Glycerol	1,260	[60]
Magnesium oxide	1,500	[61]
Monoglyceride	800	[62]
Diglyceride	600	[63]
Biodiesel (FAME)	524	[64]

3.5.4 Cost of utilities

Operation of the MG and DG production processes are provided by utilities. Hot utilities are such as low-pressure steam, medium-pressure steam, and high-pressure steam. The utility cost is presented in Table 13

Table 13 Utility cost [51].

Utility	Unit	Cost of utility
Cooling water	USD/GJ	0.21
LP steam	USD/GJ	1.90
MP steam	USD/GJ	2.20
HP steam	USD/GJ	2.50
Hot oil	USD/GJ	3.50
Fired temperature	USD/GJ	4.25
Very high temperature	USD/GJ	8.90
Electricity	USD/GJ	16.9

3.6 MG production cost and sensitivity analysis

3.6.1 MG production cost

Economic analysis was carried out based on the finding of the process simulation in terms of itemized cost estimation and sensitivity analysis of net present value (NPV). The total annual costs and the annual MG production were used to calculated itemized cost estimation per unit of MG production, as given in Eq. (3.7).

$$\text{MG production cost}\left(\frac{\text{USD}}{\text{kg}}\text{of MG}\right)=\frac{\text{Total annual cost }(\frac{\text{USD}}{\text{y}})}{\text{Annual MG production (kg of}\frac{\text{MG}}{\text{y}})} \tag{3.7}$$

The total annual costs are summation of the annualized capital costs and the annual operating costs.

3.6.2 Sensitivity analysis

The influence of uncertainty on input parameters, such as raw material cost, utility cost, total capital investment, and MG and DG selling prices, are investigated using sensitivity analysis. The net present value (NPV) is the total discounted cash flow at the conclusion of the project. The output NPV of the processes is influenced by the input parameters. The range of price study was selected in the proximity of 0 to selected price of each parameter or proximity of -100% to +100% from the base condition (0%) to each parameter, while the values of other parameters remain fixed. The NPV in this study is calculated using a 10-year plant life and a 10% internal rate of return. Eq. (3.8) is used to compute the NPV.

$$\mathrm{NPV} = \sum_{n=0}^{10} \frac{\text{net cash flow at year n}}{(1+0.10)^n} \tag{3.8}$$

Chapter 4

Results and discussion

A techno-economic analysis of MG and DG production process was presented in this study. The simulation results were discussed in following aspects: performance analysis, energy consumption, cost analysis and sensitivity analysis.

4.1 Performance analysis

4.1.1 Comparisons of required feedstock amount

Based on material balance, 100 kmol/hr of WCO was fed to the process, which corresponded to 787,110 ton/year of WCO consisting of triolein 90%, oleic acid 6%, and water 4% for all scenarios in this study. The number of other reactants are required for each scenario as shown in Fig. 17.

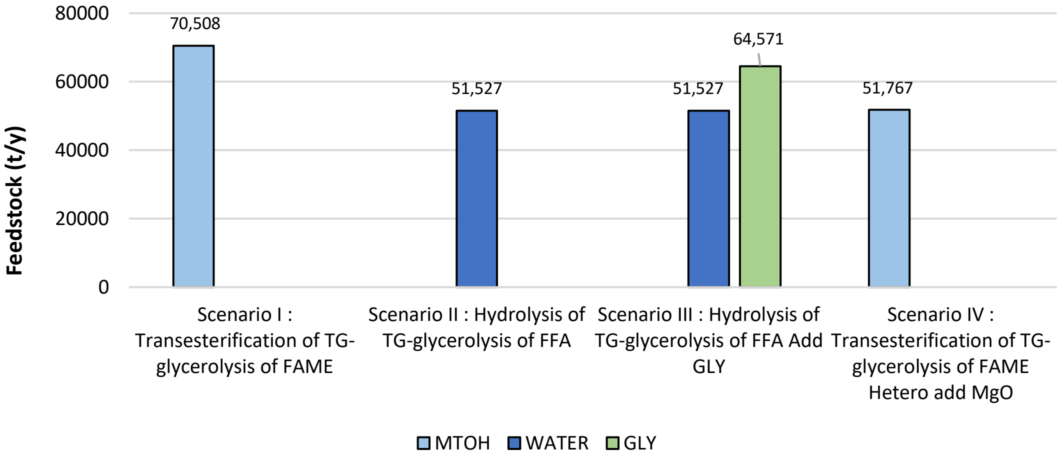


Fig. 17 The required amount of feedstocks calculated based on supplied WCO of 787,110 ton/year

After mixing with the recycle stream, the methanol feed was based on a molar ratio 14:1 of triglyceride at inlet of the reactor for scenario I and IV (Transesterification of TG-glycerolysis of FAME), while the water feed was based on a molar ratio 17:1 of triglyceride at inlet of the reactor for scenario II and III (Hydrolysis of TG-glycerolysis of FFA). Considering of scenarios I and IV, scenario IV presented lower required methanol amount than that of scenario I because the heterogeneous catalyst of MgO provided the higher glycerol conversion per pass (99.0%) compared to the scenario I, which used the homogeneous catalyst of CH_3ONa (34.7%). This result is agreed with the results of Ferretti et. Al [37] and Negi et. Al [5]. Higher glycerol conversion produced higher amount of methanol for recycling to transesterification reactor and led to reduce the required amount of methanol. The make-up glycerol was not required for cases I, II and VI since the first reaction step produce the available glycerol for the consecutive glycerolysis. For scenario III, the make-up glycerol was added to achieve the glycerol to FFA molar ratio of 1:1 [38], which was improved from scenario II because scenario II produced less glycerol from hydrolysis and resulted in the lower MG production.

4.1.2 Comparisons of MG and DG productivities

100 kmol/hr of WCO was fed to the process, which corresponded to 787,110 ton/year of WCO in all scenarios. The MG and DG productivity of each scenario is shown in Fig. 18.

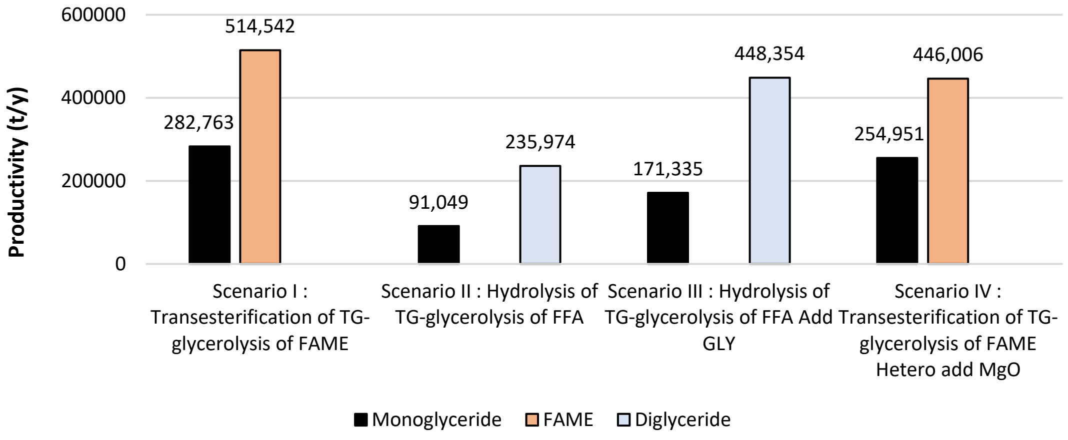


Fig. 18 The MG and DG productivity of each scenario

Comparison of transesterification of TG and glycerolysis of FAME in the scenario I and IV with hydrolysis of TG and glycerolysis of FFA in the scenario II and III, transesterification-glycerolysis processes provided higher MG production than hydrolysis-glycerolysis processes because the higher yield of MG form glycerolysis of FAME. The maximum MG productivity (282,763 ton/year) was obtained in scenario I, followed by scenario IV, III, and II, respectively.

Considering the MG productivity of scenario I and IV, the scenario I gave more recycled unreacted glycerol (142,377 ton/year) resulting in higher reactant inlet the glycerolysis reactor of and leading to higher MG productivity than that of scenario IV. For the MG productivity of scenario II and III, scenario III provided higher MG productivity than that of scenario II because the make-up glycerol was added to the glycerol to FFA molar ratio of 1:1 in scenario III which can improve the MG production rate in scenario II. Considering the by-product of all process, FAME was a by-product from transesterification for scenarios I and IV, while DG was a by-product from hydrolysis and glycerolysis reaction for scenarios II and III. Thus, they have a market value which is positive effect in economics of the process. In addition, scenario I provided higher FAME productivity than that of scenario IV because scenario IV consumed more FAME for glycerolysis (overall glycerol conversion was 99.83%) than scenario I (overall glycerol conversion was 98.01%).

4.1.3 Comparison of energy consumption

Energy consumption for scenario I was divided into 4 sections: transesterification section (E-100, TRAN, P-100, T-100, and V-100), glycerolysis section (E-101, GLYCERO, P-101, T-101 and T-102), separation section for washing homogeneous catalyst (E-102, E-103, R-NUTR, and SEP), and product purification section (P-102, T-103 and T-104). For scenario II and III, energy consumption was divided into 4 sections: hydrolysis section (E-100, HYDRO, P-100, E-101, and T-100), glycerolysis section (E-102, GLYCERO, V-100, P-101 and T-101), separation section for washing homogeneous catalyst (E-103, E-104, R-NUTR, V-101, and SEP), and product purification section (P-102, T-102, T-103, and T-104). For scenario IV, energy consumption was divided into 3 sections: transesterification section (E-100, TRANS, P-100, T-100, and V-100), glycerolysis section (GLYCERO, P-101, and T-101), and product purification section (T-102 and T-103). The energy consumption was considered only hot duties and electricity which were the amount of energy that we have to provide to the system. The divided energy consumption was presented in Fig. 19 and Table 14. The order of energy consumption is required as scenario I (167,547.76 kW), followed by scenario III (161,900.02 kW), scenario II (154,981.59 kW) and scenario IV (83,710.99 kW), respectively. Production process in scenario IV can reduce one distillation column for separation and a recycle line of unreacted glycerol, thus leading to the reduction of energy consumption in the glycerolysis and purification sections as compared to the scenario I. Moreover, the energy glycerolysis section was decreased for scenario IV since the total inlet reactant including recycle stream was lower than that of scenario I. Whereas, the overall energy consumption for scenario III was higher compared to the scenario II due to the addition of glycerol stream to accelerate glycerolysis rate resulting to increase the energy consumption in the glycerolysis section from 27,662.94 to 39,058.71 kW.

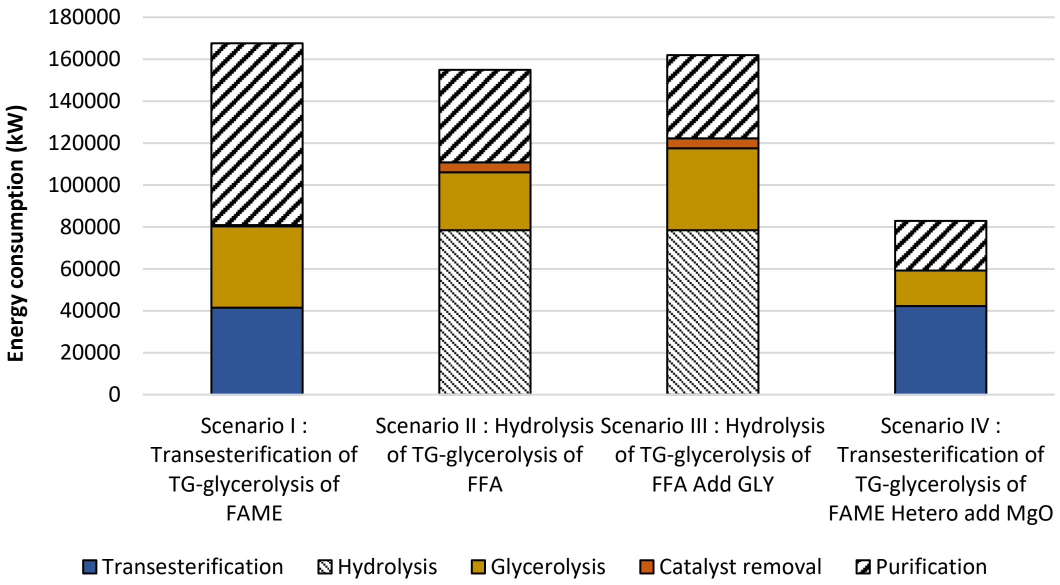


Fig. 19 Energy consumptions in each scenario

Table 14 Comparisons of energy consumptions was divided into 4 sections for each scenario.

Parameters	Unit	Scenario I	Scenario II	Scenario III	Scenario IV
Transesterification	kW	41,490.22	-	-	42,219.56
Hydrolysis	kW	-	78,423.70	78,423.70	-
Glycerolysis	kW	38,802.88	27,662.94	39,058.71	16,972.95
Catalyst removal	kW	636.53	4,643.82	4,731.38	-
Purification	kW	86,618.12	44,240.09	39,675.23	23,714.73

The details of energy consumption of each unit operation as presented in Fig. 20 and Table 15. The unit operation for purification of FAME (T-103 distillation column) for scenario I required the highest energy consumption since the energy was used to heat a large amount of low purity FAME. While the unit operation for separation of water in hydrolysis process (T-100 distillation column) for scenario II and III required the highest energy consumption for separation the excessive amount of water and recycled back to hydrolysis reactor. For scenario IV, the unit operation for separation of methanol in transesterification process (T-100) also required the highest energy consumption for using to separate an excessive amount of methanol and recycled back to transesterification process.

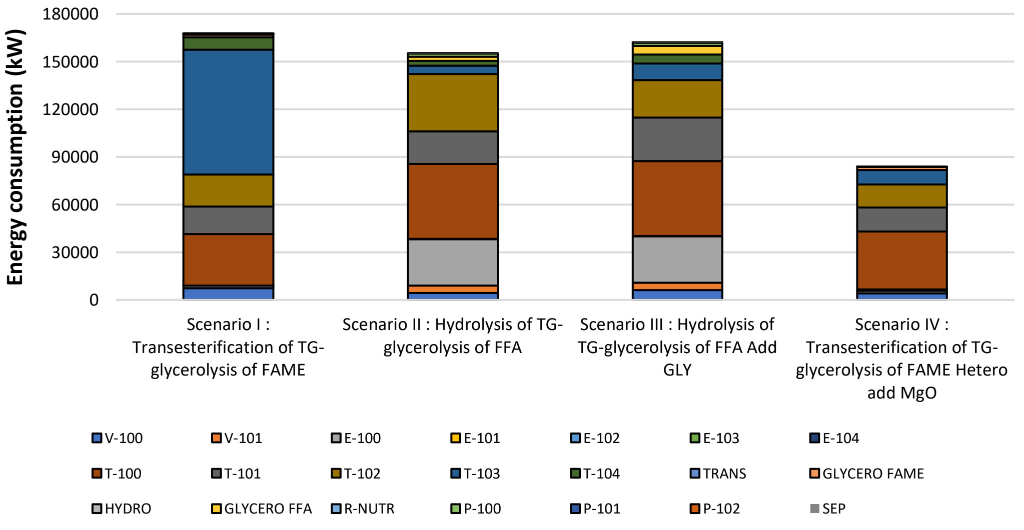


Fig. 20 Details of energy consumptions for each unit operation of all scenarios

Table 15 Comparisons of energy consumptions for each unit operation.

Parameters	Unit	Scenario I	Scenario II	Scenario III	Scenario IV
V-100	kW	7,415.12	4,400.37	6,092.39	4,234.33
V-101	kW	-	4,558.59	4,646.15	-
E-100	kW	1,556.66	29,339.9	29,339.9	1,452.26
E-101	kW	-	-	-	806.749
E-102	kW	-	-	-	-
E-103	kW	51.05	-	-	-
E-104	kW	-	85.23	85.23	-
T-100	kW	32,515.70	47,172.00	47,172.00	36,530.20
T-101	kW	17,325.40	20,533.30	27,402.50	15,054.20
T-102	kW	19,946.80	36,177.10	23,677.90	14,503.90
T-103	kW	78,722.80	5,134.36	10,356.10	9,210.83
T-104	kW	7,893.41	2,925.33	5,637.78	-
TRANS	kW	-	-	-	-
GLYCERO FAME	kW	1,512.82	-	-	1,913.58
HYDRO	kW	-	-	-	-
GLYCERO FFA	kW	-	2,726.56	5,560.51	-
R-NUTR	kW	585.476	-	-	-
P-100	kW	2.74	1,911.80	1,911.80	2.77
P-101	kW	17.86	2.71	3.31	2.17
P-102	kW	1.91	3.30	3.45	-
SEP	kW	-	11.03	10.98	-

4.1.4 Comparison of energy consumption per MG productivity.

The divided energy consumption per MG productivity was presented in Fig 21 and Table 16. Overall energy consumption per MG productivity of scenario IV was the lowest (0.33 kW/ton) due to scenario IV provided the lowest energy consumption and high MG productivity, followed by scenario I (0.59 kW/ton), scenario III (0.94 kW/ton) and scenario II (1.70 kW/ton), respectively.

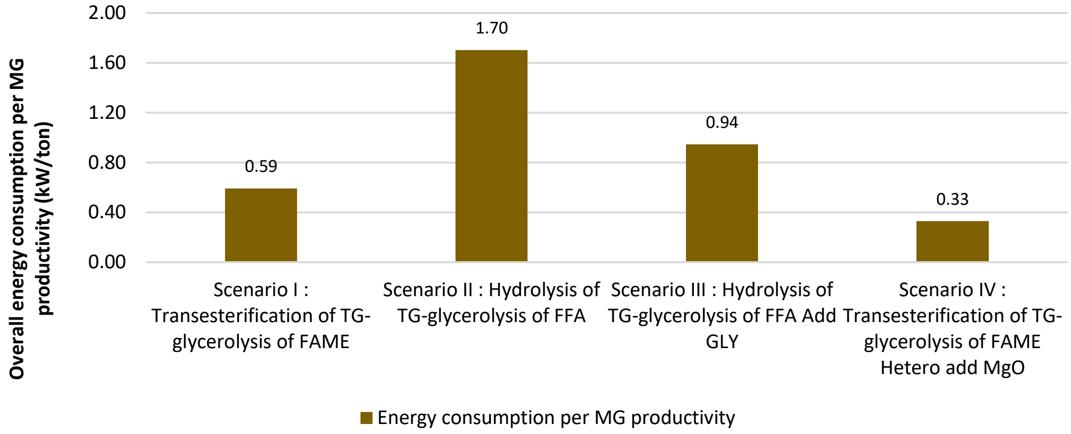


Fig. 21 Energy consumption per MG productivity

Table 16 Comparison of energy consumption per MG productivity.

Parameters	Unit	Scenario I	Scenario II	Scenario III	Scenario IV
MG productivity	ton/year	282,763.00	91,049.20	171,335.00	254,951.00
Energy consumption	kW	167,547.76	154,981.59	161,900.02	83,710.99
Overall energy consumption per MG productivity	kW/ton	0.59	1.70	0.94	0.33

4.2 Cost analysis

4.2.1 Comparison of capital investment

The capital investment of different scenarios was shown in Fig. 22 and Table 17 which summarized the capital investment for economic evaluation. This can be seen that scenario I gave the highest MG productivity as well as required the highest capital investment cost. Most cost of capital investment in scenario I was derived from the reactor cost based on the size of the reactor including reactor for neutralization process of homogenous catalyst. Moreover, the highest cost of reactor was obtained in scenario I because transesterification was carried out for the longest residence time as well as glycerolysis using homogeneous catalyst. Thus, large volume of reactors was installed resulting to the highest cost of reactor. In addition, the cost of the distillation significantly increased for scenario I due to it required more distillation column to separate unreacted glycerol for recovery as compared to scenario IV which applied heterogenous catalyst on glycerolysis. The scenario I required the highest total capital investment (20.12 Million USD), followed by scenario III (19.64 Million USD), II (19.03 Million USD) and I (12.22 Million USD), respectively. The high pump cost is acquired for scenario II and III because the hydrolysis condition was carried out at high operating pressure, resulting in the requirement of high cost of operated reactor. From the result, scenario IV provided the lowest total capital investment (TCI) and presented the lowest TCI per ton of MG produced due to the high MG production obtained from scenario IV.

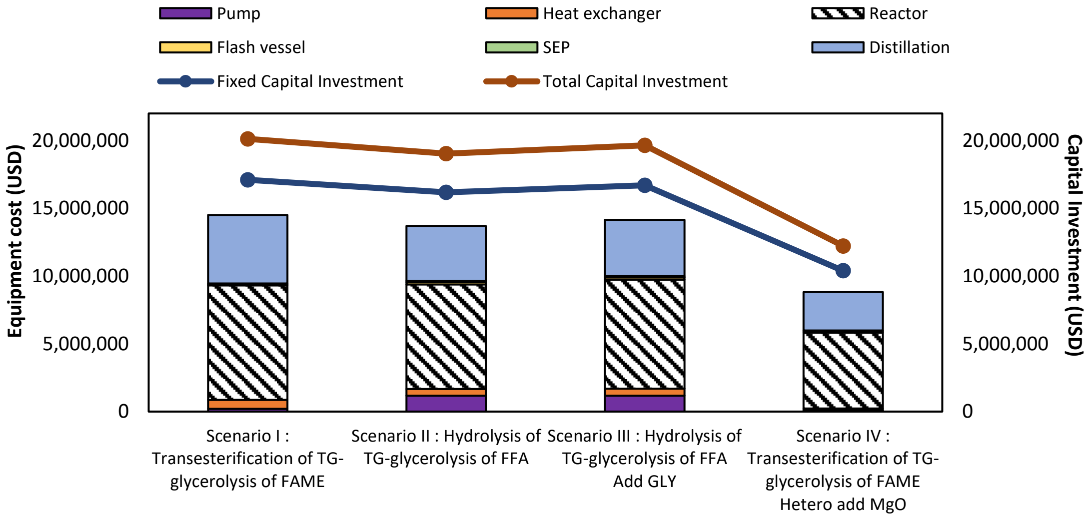


Fig. 22 Capital investment of each scenario

Table 17 Capital investment costs of MG and DG production processes.

Parameters	Unit	Scenario I	Scenario II	Scenario III	Scenario IV
MG productivity	ton/year	282,763.00	91,049.20	171,335.00	254,951.00
Pump	USD	201,359.80	1,179,077.48	1,184,504.60	118,046.34
Heat exchanger	USD	656,439.50	485,793.18	496,445.81	103,263.45
Reactor	USD	8,449,154.04	7,801,743.71	8,053,337.46	5,590,431.28
Separator	USD	76,652.06	78,553.09	85,332.54	85,332.17
Distillation	USD	5,034,004.62	4,081,171.73	4,154,515.41	2,825,222.68
Fixed capital investment	USD	17,105,472.48	16,272,465.29	16,694,336.41	10,393,001.15
Total capital investment	USD	20,124,085.27	19,144,076.81	19,640,395.77	12,227,060.18

4.2.2 Comparisons of manufacturing cost

The cost of manufacturing of different scenarios was shown in Fig. 23 and Table 18. Scenario III required the highest cost of manufacturing without depreciation (COM_d). Mostly COM_d for all scenarios was derived from the raw material cost and utility cost. The scenario IV presented the lowest COM_d (296.17 Million USD), followed by scenario II (301.58 Million USD), I (329.99 Million USD) and III (392.11 Million USD), respectively. Moreover, the lowest COM_d per ton of produced MG after deduction of the revenue from by-product was included in scenario I since scenario I providing the highest MG productivity as presented in Table 17. The minimum MG production cost (213.51 USD/ton) was obtained in scenario I, followed by scenario IV (244.26 USD/ton), III (718.67 USD/ton), and II (1,757.50 USD/ton), respectively. For scenario I, III and IV, MG production cost per ton of MG was still lower than currently MG price (800 USD/ton) [62], indicating that these processes can be feasible economically.

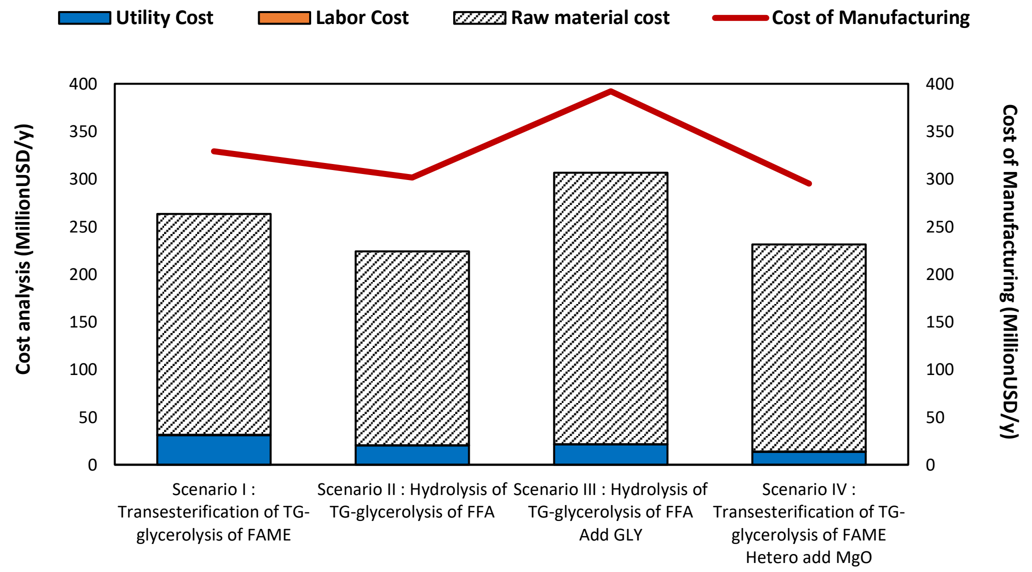


Fig. 23 Cost of manufacturing of each scenario

Table 18 Cost of manufacturing of MG and DG production processes.

Parameters	Unit	Scenario I	Scenario II	Scenario III	Scenario IV
Raw material					
WCO	USD/y	176,312,640.00	176,312,640.00	176,312,640.00	176,312,640.00
MTOH	USD/y	40,370,760.00	-	-	31,057,200.00
CH_3ONa	USD/y	15,020,150.00	-	-	-
K/CeO_2	USD/y	906,949.19	-	-	906,949.19
Water	USD/y	-	146,337.82	146,337.82	-
NaOH	USD/y	-	2,512,160.00	2,512,160.00	-
MSA	USD/y	-	24,584,320.00	24,584,320.00	-
Glycerol	USD/y	-	-	81,358,830.00	-
MgO	USD/y	-	-	-	9,143,280.00
Utility					
LP Steam[a]	USD/y	85,371.41	1,605,484.80	1,605,484.80	79,490.07
MP steam[a]	USD/y	2,194,774.08	218,588.48	357,714.72	-
HP steam[a]	USD/y	-	3,521,970.00	4,170,334.00	2,630,180.00
Hot oil	USD/y	748,991.60	-	-	426,820.80
FIRED[b]	USD/y	4,794,370.60	2,026,903.20	3,354,066.00	234,192.00
VERY[c]	USD/y	22,284,866.64	11,013,963.60	10,168,719.92	9,937,248.72
Cooling water	USD/y	946,551.36	793,599.90	778,181.96	357,341.11
Electricity	USD/y	11,417.80	933,443.73	933,809.53	3,869.55
Total utility cost	USD/y	31,066,343.50	20,113,953.71	21,368,310.93	13,669,142.25
Operating labor cost	USD/y	369,000.00	369,000.00	369,000.00	344,400.00
Waste management cost	USD/y	2,004,980.40	18,334,303.20	9,244,119.60	7,417,270.80

Table 18 Cost of manufacturing of MG and DG production processes (continue).

Parameters	Unit	Scenario I	Scenario II	Scenario III	Scenario IV
Cost of manufacturing	USD/y	329,991,714.27	301,584,688.88	392,110,214.12	296,173,925.36
COM_d per ton MG	USD/t	1,167.03	3,312.90	2,289.21	1,160.70
COM_d per ton methanol (Deduct from revenue of selling value)	USD/t	213.51	1,757.50	718.67	244.26

[a]LP, MP and HP are low pressure, medium pressure and high pressure, respectively

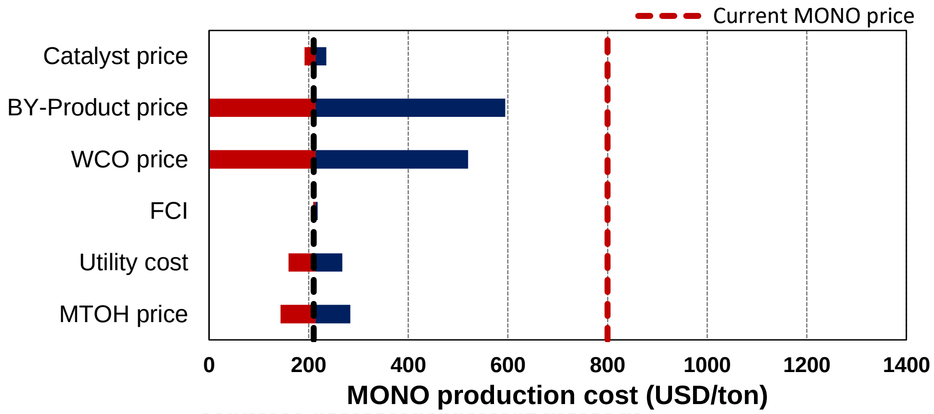
[b]FIRED is fired heat

[c]VERY is very high temperature fired heat

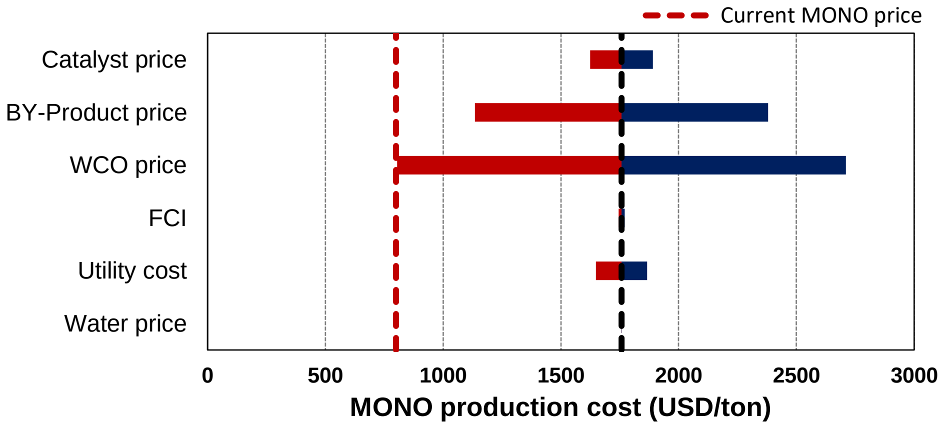
4.3 Sensitivity analysis

Sensitivity analysis was performed to investigate the impact of input parameters on the MG production cost of the MG production processes, as shown in Fig. 24. Sensitivity analysis based on a 10-year project were undertaken by varying by-product price, WCO price, fixed capital investment (FCI), utility costs, methanol price, catalyst price in scenario I and IV, and water price in scenario II and III. Each parameter was varied from -40% to +40% from the based scenario (0%). The sensitivity analysis can reveal the most sensitive factor to the process, providing significant influence. At the current conditions, the MG production cost of the MG production plant was lower than the current MG price in scenario I, III, and IV. Therefore, these processes can return a profit which corresponded to positive net present value (NPV) of 803.14, 52.02, and 691.63 Million USD for scenario I, III, and IV, respectively. By-product price was also being the most sensitive parameter for scenario I, III, and IV. The subsequent parameters of scenario I and IV were WCO price, methanol price, utility cost, and FCI, while the subsequent parameters of scenario II and III were WCO price, utility cost, water price, and FCI. Moreover, WCO price was the most sensitive parameter for scenario II followed by by-product price, utility cost, water price, and FCI. For payback period of scenario I, III, and IV was 0.17, 1.88, and 0.12 year, respectively. In summary, transesterification of TG and glycerolysis of FAME in the scenario I and IV not only provided the high productivity but also achieved the great value for investment. The scenario I provided the highest productivity and lowest MG production cost and scenario IV when applied transesterification followed by glycerolysis process with heterogenous catalyst presented high productivity, low MG production cost and lowest energy consumption.

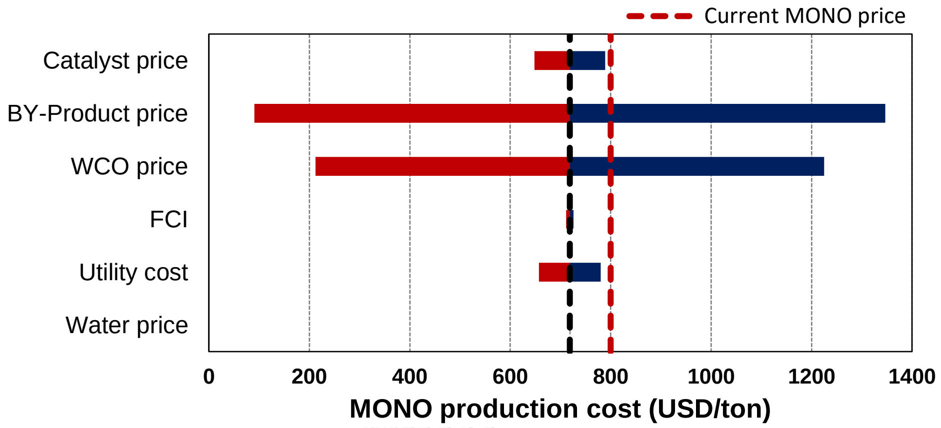
(a)



(b)



(c)



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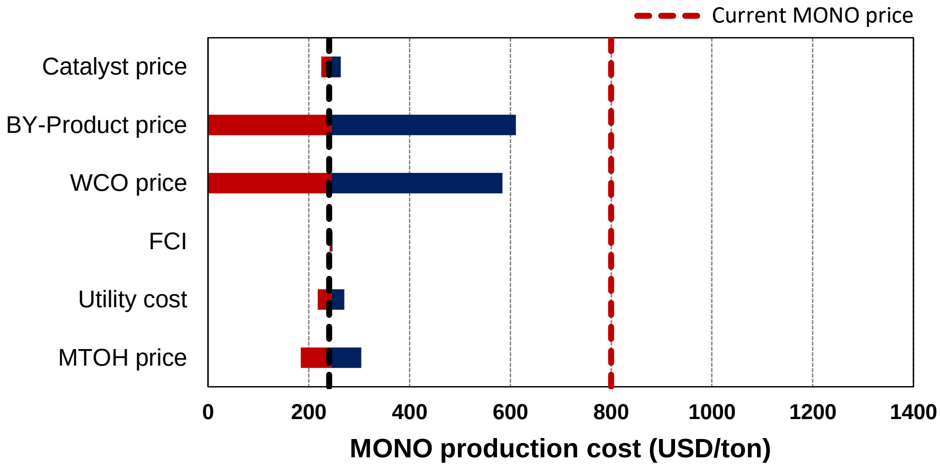

Fig. 24 Sensitivity analysis (SA) in term of MG production cost in (a) scenario I, (b) scenario II, (c) scenario III, and (d) scenario IV

Chapter 5

Conclusion

5.1 Conclusions

A techno-economic analysis of MG and DG production process was presented in this study. The simulation results were discussed in following aspects: performance analysis, energy consumption, cost analysis and sensitivity analysis. 100 kmol/hr of WCO was fed to the process, which corresponded to 787,110 ton/year of WCO as a basis of calculation for all scenario in this study. In both scenarios I and IV, MG is synthesized from WCO via transesterification of TG and glycerolysis of FAME then scenarios II and III, MG is synthesized from WCO via hydrolysis of TG and glycerolysis of FFA, Therefore, it is divided into four scenarios including of scenario I: transesterification of TG-glycerolysis of FAME using a homogeneous catalyst of CH_3ONa, scenario II: hydrolysis of TG-glycerolysis of FFA, scenario III: hydrolysis of TG-glycerolysis of FFA with make-up glycerol and scenario IV: transesterification of TG-glycerolysis of FAME using a heterogeneous catalyst of MgO. After mixing with the recycle stream, the methanol feed was based on a molar ratio 14:1 of TG at inlet of the reactor for scenario I and IV, while the water feed was based on a molar ratio 17:1 of TG at inlet of the reactor for scenario II and III. For scenario I and IV (Transesterification of TG-glycerolysis of FAME), scenario IV presented lower required methanol feed than scenario I. In addition, scenario III which make-up glycerol was added to obtain the glycerol to FFA molar ratio of 1:1 as an improvement from scenario II.

Comparison of transesterification of TG-glycerolysis of FAME scenarios (scenario I and IV) and hydrolysis of TG-glycerolysis of FFA scenarios (scenario II and III), transesterification-glycerolysis processes provided higher MG production than hydrolysis-glycerolysis processes. Considering the MG productivity, the maximum MG productivity (282,763 ton/year) was obtained in scenario I, followed by scenario IV, III, and II, respectively. For by-product of all processes, FAME was a by-product from transesterification for scenarios I and IV, while DG was a by-product from hydrolysis and glycerolysis for scenarios II and III. In addition, scenario I provided higher FAME productivity than that of scenario IV since the scenario IV consumed FAME for glycerolysis reaction more than scenario I.

For the energy consumptions, scenario I required the highest energy consumption (167,547.76 kW), followed by scenario III (161,900.02 kW), scenario II (154,981.59 kW) and scenario IV (83,710.99 kW), respectively. Production process in scenario IV can reduce one distillation column for separation and a recycle stream of unreacted glycerol, leading to reduce energy consumption in glycerolysis and purification section compared to the scenario I. Moreover, the energy glycerolysis section was decreased for scenario IV since the total inlet reactant including recycle stream was lower than that of scenario I. Whereas the overall energy consumption for scenario III was higher compared to the scenario II due to the addition of make-up glycerol stream to enhance glycerolysis rate.

For the capital investment of different scenarios, although scenario I achieved the highest MG productivity, scenario I also required the highest capital investment cost (TCI). Most cost of capital investment in scenario I was derived from the reactor cost due to the size of reactor including neutralization reactor for homogenous catalyst. In addition, the cost of the distillation significantly increased for scenario I due to it required one distillation column for separation and unreacted glycerol recovery as compared with scenario IV which applied heterogenous catalyst for glycerolysis. Scenario II and III presented the high pump cost because hydrolysis condition was carried out high pressure. Although scenario II provided the lowest TCI while scenario IV provided the lowest TCI per ton of MG produced due to high MG production of scenario IV.

For the cost of manufacturing without depreciation (COM_d), scenario III presented the highest cost of manufacturing without depreciation (COM_d). The scenario IV achieved the lowest COM_d (296.17 Million USD), followed by scenario II (301.58 Million USD), I (329.99 Million USD) and III (392.11 Million USD), respectively. Moreover, the minimum MG production cost (213.51 USD/ton) was obtained in scenario I, followed by scenario IV (244.26 USD/ton), III (718.67 USD/ton), and II

(1,757.50 USD/ton), respectively. For scenario I, III and IV, MG production cost per ton of MG was also lower than currently MG price, indicating that these processes can be feasible economically.

Sensitivity analysis based on a 10-year project were undertaken by varying of by-product price, WCO price, fixed capital investment (FCI), utility costs, methanol price in scenario I and IV, and water price in scenario II and III. The sensitivity analysis can reveal that the factor is the most sensitive to the process, providing significant influence. At the current conditions, the MG production cost of the MG plant was lower than the current MG price in scenario I, III, and IV. Therefore, these processes returned the profit which corresponded to positive net present value (NPV) of 803.14, 52.02, and 691.63 Million USD for scenario I, III, and IV, respectively. By-product price was the most sensitive parameter for scenario I, III, and IV. For payback period of scenario I, III, and IV were 0.17, 1.88, and 0.12 year, respectively. This simulation results suggested that using transesterification of TG and glycerolysis of FAME in the scenario I and IV are potential processes for MG production based on the MG productivity and economic assessment.

5.2 Suggestions

5.2.1 Effect of types of catalyst should be further used to investigate due to it directly results in the productivity of MG from glycerolysis. In addition, the heterogeneous catalyst can decrease energy consumption of the process as can be seen from scenario IV.

5.2.2 Operating conditions and parameters of hydrolysis should be further optimized to improve the productivity and decrease of energy consumptions such as using heterogeneous catalyst instead of subcritical water.

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APPENDIX A

Process flow diagram and stream properties of MG and DG production processes

Scenario I: Transesterification of TG-glycerolysis of FAME

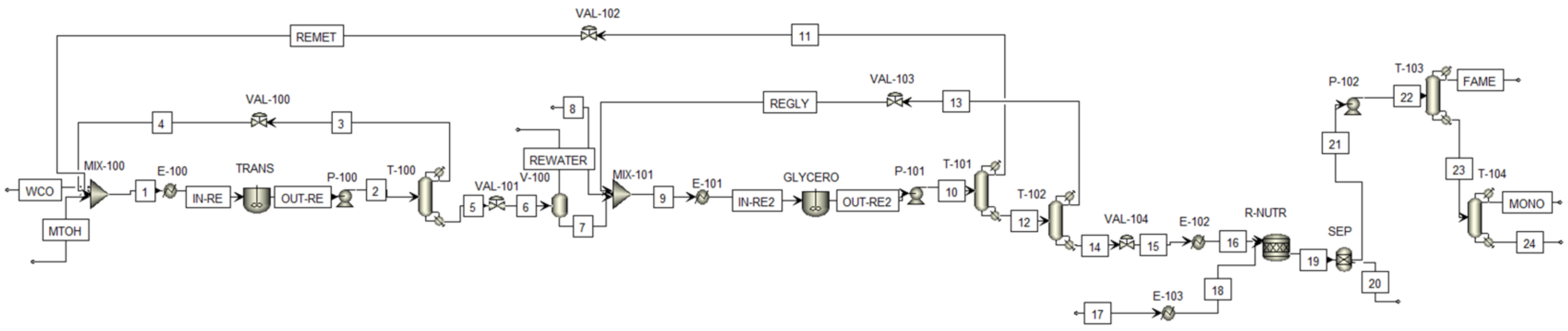

Fig. A-1 Process flow diagram of Transesterification of TG-glycerolysis of FAME

Table A-1 Stream properties of Transesterification of TG-glycerolysis of FAME (scenario I).

Name	**WCO**	**MTOH**	**1**	**IN-RE**	**OUT-RE**	**2**	**3**	**4**	**5**
From			MIX-100	E-100	TRANS	P-100	T-100	VAL-100	T-100
To	MIX-100	MIX-100	E-100	TRANS	P-100	T-100	VAL-100	MIX-100	VAL-101
Temperature (°C)	25.00	25.00	45.36	65.00	65.00	65.03	75.25	64.57	143.00
Pressure (bar)	1.01	1.01	1.01	1.01	1.01	1.52	1.52	1.01	1.52
Mole flows (kmol/h)	100.00	227.72	1,364.72	1,364.72	1,364.72	1,364.72	960.00	960.00	404.72
Mass flows (kg/h)	81,457.29	7,296.75	122,028.56	122,028.56	122,028.56	122,028.56	30,727.91	30,727.91	91,300.64
Mass fractions									
MONO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
DI	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
TRI	0.98	0.00	0.65	0.65	0.04	0.04	0.00	0.00	0.05
MET	0.00	1.00	0.33	0.33	0.26	0.26	1.00	1.00	0.02
FAME	0.00	0.00	0.00	0.00	0.62	0.62	0.00	0.00	0.83
GLY	0.00	0.00	0.00	0.00	0.07	0.07	0.00	0.00	0.09
H_2O	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
FFA	0.02	0.00	0.01	0.01	0.01	0.01	0.00	0.00	0.02
CH_3ONa	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
H_3PO_4	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Na_3PO_4	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Table A-1 Stream properties of Transesterification of TG-glycerolysis of FAME (continue).

Name	**6**	**REWATER**	**7**	**8**	**9**	**IN-RE2**	**OUT-RE2**	**10**	**11**
From	VAL-101	V-100	V-100		MIX-101	E-101	GLYCERO	P-101	T-101
To	V-100		MIX-101	MIX-101	E-101	GLYCERO	P-101	T-101	VAL-102
Temperature (°C)	140.84	250.00	250.00	25.00	255.49	135.00	135.00	137.93	75.90
Pressure (bar)	1.01	1.01	1.01	1.01	1.01	1.01	1.01	1.52	1.52
Mole flows (kmol/h)	404.72	56.53	348.19	19.37	535.77	535.77	535.77	535.77	77.00
Mass flows (kg/h)	91,300.64	2,869.60	88,431.04	1,046.55	104,655.48	104,655.48	104,655.48	104,655.48	2,546.61
Mass fractions									
MONO	0.00	0.00	0.00	0.00	0.00	0.00	0.25	0.25	0.00
DI	0.00	0.00	0.00	0.00	0.00	0.00	0.03	0.03	0.00
TRI	0.05	0.00	0.05	0.00	0.04	0.04	0.00	0.00	0.00
MET	0.02	0.50	0.00	0.00	0.00	0.00	0.02	0.02	0.94
FAME	0.83	0.33	0.84	0.00	0.71	0.71	0.51	0.51	0.00
GLY	0.09	0.15	0.09	0.00	0.21	0.21	0.15	0.15	0.06
H_2O	0.00	0.03	0.00	0.00	0.00	0.00	0.00	0.00	0.01
FFA	0.02	0.00	0.02	0.00	0.02	0.02	0.02	0.02	0.00
CH_3ONa	0.00	0.00	0.00	1.00	0.01	0.01	0.01	0.01	0.00
H_3PO_4	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Na_3PO_4	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Table A-1 Stream properties of Transesterification of TG-glycerolysis of FAME (continue).

Name	**REMET**	**12**	**13**	**REGLY**	**14**	**15**	**16**	**17**	**18**
From	VAL-102	T-101	T-102	VAL-103	T-102	VAL-104	E-102		E-103
To	MIX-100	T-102	VAL-103	MIX-101	VAL-104	E-102	R-NUTR	E-103	R-NUTR
Temperature (°C)	65.21	337.00	303.37	303.37	380.23	366.10	135.00	25.00	135.00
Pressure (bar)	1.01	1.52	1.52	1.01	1.52	1.01	1.01	1.01	1.01
Mole flows (kmol/h)	77.00	458.77	160.00	160.00	298.77	298.77	298.77	9.20	9.20
Mass flows (kg/h)	2,546.61	102,108.87	14,734.44	14,734.44	87,374.43	87,374.43	87,374.43	901.56	901.56
Mass fractions									
MONO	0.00	0.26	0.00	0.00	0.30	0.30	0.30	0.00	0.00
DI	0.00	0.03	0.00	0.00	0.04	0.04	0.04	0.00	0.00
TRI	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
MET	0.94	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
FAME	0.00	0.52	0.00	0.00	0.61	0.61	0.61	0.00	0.00
GLY	0.06	0.15	1.00	1.00	0.01	0.01	0.01	0.00	0.00
H_2O	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
FFA	0.00	0.02	0.00	0.00	0.02	0.02	0.02	0.00	0.00
CH_3ONa	0.00	0.01	0.00	0.00	0.02	0.02	0.02	0.00	0.00
H_3PO_4	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.00	1.00
Na_3PO_4	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Table A-1 Stream properties of Transesterification of TG-glycerolysis of FAME (continue).

Name	**19**	**20**	**21**	**22**	**FAME**	**23**	**MONO**	**24**
From	R-NUTR	SEP	SEP	P-102	T-103	T-103	T-104	T-104
To	SEP		P-102	T-103		T-104		
Temperature (°C)	135.00	135.00	135.00	135.03	141.84	432.41	428.57	535.66
Pressure (bar)	1.01	1.01	1.01	1.52	1.52	1.52	1.52	1.52
Mole flows (kmol/h)	307.97	9.19	298.78	298.78	207.60	91.18	84.00	7.18
Mass flows (kg/h)	88,275.99	1,507.18	86,768.81	86,768.81	53,249.42	33,519.38	29,262.86	4,256.52
Mass fractions								
MONO	0.30	0.00	0.31	0.31	0.00	0.79	0.90	0.10
DI	0.04	0.00	0.04	0.04	0.00	0.10	0.00	0.81
TRI	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.09
MET	0.01	0.00	0.01	0.01	0.02	0.00	0.00	0.00
FAME	0.60	0.00	0.61	0.61	0.96	0.06	0.07	0.00
GLY	0.01	0.00	0.01	0.01	0.01	0.00	0.00	0.00
H_2O	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
FFA	0.02	0.00	0.02	0.02	0.01	0.03	0.04	0.00
CH_3ONa	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
H_3PO_4	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Na_3PO_4	0.02	1.00	0.00	0.00	0.00	0.00	0.00	0.00

Scenario II: Hydrolysis of TG-glycerolysis of FFA

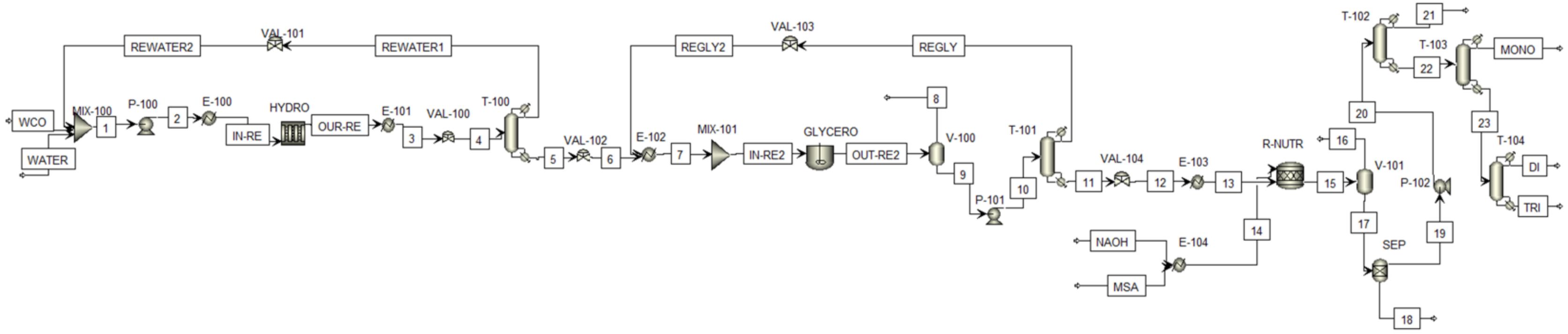

Fig. A-2 Process flow diagram of Hydrolysis of TG-glycerolysis of FFA

Table A-2 Stream properties of Hydrolysis of TG-glycerolysis of FFA (scenario II).

Name	WCO	WATER	1	2	IN-RE	OUR-RE	3	4	REWATER1
From			MIX-100	P-100	E-100	HYDRO	E-101	VAL-100	T-100
To	MIX-100	MIX-100	P-100	E-100	HYDRO	E-101	VAL-100	T-100	VAL-101
Temperature (°C)	25.00	25.00	56.97	82.04	350.00	350.00	119.00	119.00	111.80
Pressure (bar)	1.01	1.01	1.01	200.00	200.00	200.00	200.00	1.52	1.52
Mole flows (kmol/h)	100.00	296.00	1,626.00	1,626.00	1,626.00	1,626.00	1,626.00	1,626.00	1,230.00
Mass flows (kg/h)	81,457.29	5,332.52	108,948.60	108,948.60	108,948.60	108,950.13	108,950.13	108,950.13	22,158.79
Mass fractions									
MONO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
DI	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
TRI	0.98	0.00	0.73	0.73	0.73	0.00	0.00	0.00	0.00
MET	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
FAME	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
GLY	0.00	0.00	0.00	0.00	0.00	0.08	0.08	0.08	0.00
FFA	0.02	0.00	0.02	0.02	0.02	0.72	0.72	0.72	0.00
H_2O	0.00	1.00	0.25	0.25	0.25	0.21	0.21	0.21	1.00
MSA	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
NaOH	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
SFS	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Table A-2 Stream properties of Hydrolysis of TG-glycerolysis of FFA (continue).

Name	**REWATER2**	**5**	**6**	**7**	**IN-RE2**	**OUT-RE2**	**8**	**9**	**10**
From	VAL-101	T-100	VAL-102	E-102	MIX-101	GLYCERO	V-100	V-100	P-101
To	MIX-100	VAL-102	E-102	MIX-101	GLYCERO	V-100		P-101	T-101
Temperature (°C)	111.80	224.94	223.42	120.00	120.00	120.00	165.00	165.00	165.05
Pressure (bar)	1.01	1.52	1.01	1.01	1.01	1.01	1.01	1.01	1.52
Mole flows (kmol/h)	1,230.00	396.00	396.00	516.00	516.00	516.00	158.03	357.97	357.97
Mass flows (kg/h)	22,158.79	86,791.34	86,791.34	93,424.44	93,424.44	93,424.44	2,884.85	90,539.59	90,539.59
Mass fractions									
MONO	0.00	0.00	0.00	0.00	0.00	0.09	0.00	0.10	0.10
DI	0.00	0.00	0.00	0.00	0.00	0.27	0.00	0.28	0.28
TRI	0.00	0.00	0.00	0.00	0.00	0.07	0.00	0.07	0.07
MET	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
FAME	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
GLY	0.00	0.10	0.10	0.14	0.14	0.07	0.01	0.08	0.08
FFA	0.00	0.90	0.90	0.84	0.84	0.45	0.00	0.47	0.47
H_2O	1.00	0.01	0.01	0.02	0.02	0.04	0.98	0.01	0.01
MSA	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
NaOH	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
SFS	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Table A-2 Stream properties of Hydrolysis of TG-glycerolysis of FFA (continue).

Name	**REGLY**	**REGLY2**	**11**	**12**	**13**	**NAOH**	**MSA**	**14**	**15**
From	T-101	VAL-103	T-101	VAL-104	E-103			E-104	R-NUTR
To	VAL-103	E-102	VAL-104	E-103	R-NUTR	E-104	E-104	R-NUTR	V-101
Temperature (°C)	140.15	140.15	378.95	368.71	120.00	25.00	25.00	120.00	120.00
Pressure (bar)	1.52	1.52	1.52	1.01	1.01	1.01	1.01	1.01	1.01
Mole flows (kmol/h)	120.00	120.00	237.97	237.97	237.97	32.50	16.21	48.71	286.68
Mass flows (kg/h)	6,633.10	6,633.10	83,907.05	83,907.05	83,907.05	1,299.91	1,590.13	2,890.04	86,797.08
Mass fractions									
MONO	0.00	0.00	0.10	0.10	0.10	0.00	0.00	0.00	0.10
DI	0.00	0.00	0.30	0.30	0.30	0.00	0.00	0.00	0.29
TRI	0.00	0.00	0.08	0.08	0.08	0.00	0.00	0.00	0.07
MET	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
FAME	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
GLY	0.79	0.79	0.02	0.02	0.02	0.00	0.00	0.00	0.02
FFA	0.04	0.04	0.50	0.50	0.50	0.00	0.00	0.00	0.48
H_2O	0.17	0.17	0.00	0.00	0.00	0.00	0.00	0.00	0.01
MSA	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
NaOH	0.00	0.00	0.00	0.00	0.00	0.00	1.00	0.55	0.00
SFS	0.00	0.00	0.00	0.00	0.00	1.00	0.00	0.45	0.00

Table A-2 Stream properties of Hydrolysis of TG-glycerolysis of FFA (continue).

Name	**16**	**17**	**18**	**19**	**20**	**21**	**22**	**MONO**	**23**
From	V-101	V-101	SEP	SEP	P-102	T-102	T-102	T-103	T-103
To		SEP		P-102	T-102		T-103		T-104
Temperature (°C)	200.00	200.00	200.00	200.00	200.25	201.38	488.82	433.10	589.10
Pressure (bar)	1.01	1.01	1.01	1.01	1.52	1.52	1.52	1.52	1.52
Mole flows (kmol/h)	13.11	273.57	16.05	257.52	257.52	182.00	75.52	27.02	48.50
Mass flows (kg/h)	248.25	86,548.83	2,279.87	84,268.96	84,268.96	43,041.80	41,227.16	9,422.59	31,804.57
Mass fractions									
MONO	0.00	0.10	0.00	0.10	0.10	0.00	0.21	0.90	0.00
DI	0.00	0.29	0.00	0.30	0.30	0.00	0.62	0.00	0.80
TRI	0.00	0.07	0.00	0.08	0.08	0.00	0.16	0.00	0.20
MET	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
FAME	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
GLY	0.02	0.02	0.00	0.02	0.02	0.04	0.00	0.00	0.00
FFA	0.04	0.48	0.00	0.50	0.50	0.95	0.02	0.10	0.00
H_2O	0.95	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00
MSA	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
NaOH	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
SFS	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Table A-2 Stream properties of Hydrolysis of TG-glycerolysis of FFA (continue).

Name	**DI**	**TRI**
From	T-104	T-104
To		
Temperature (°C)	583.23	622.73
Pressure (bar)	1.52	1.52
Mole flows (kmol/h)	39.00	9.50
Mass flows (kg/h)	24,420.72	7,383.85
Mass fractions		
MONO	0.00	0.00
DI	0.97	0.22
TRI	0.03	0.78
MET	0.00	0.00
FAME	0.00	0.00
GLY	0.00	0.00
FFA	0.00	0.00
H_2O	0.00	0.00
MSA	0.00	0.00
NaOH	0.00	0.00
SFS	0.00	0.00

Scenario III: Hydrolysis of TG-glycerolysis of FFA added glycerol

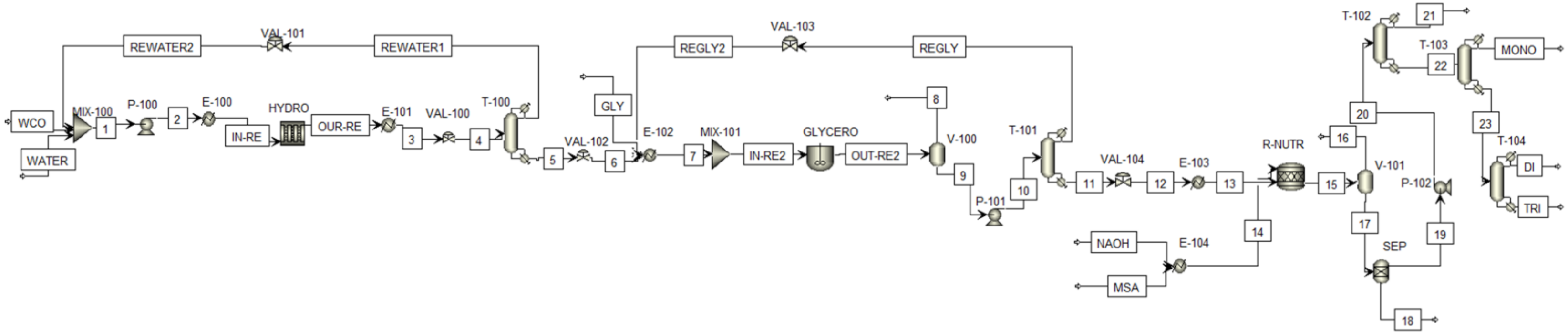

Fig. A-3 Process flow diagram of Hydrolysis of TG-glycerolysis of FFA added glycerol

Table A-3 Stream properties of Hydrolysis of TG-glycerolysis of FFA added glycerol (scenario III).

Name	WCO	WATER	1	2	IN-RE	OUR-RE	3	4	REWATER1
From			MIX-100	P-100	E-100	HYDRO	E-101	VAL-100	T-100
To	MIX-100	MIX-100	P-100	E-100	HYDRO	E-101	VAL-100	T-100	VAL-101
Temperature (°C)	25.00	25.00	56.97	82.04	350.00	350.00	119.00	119.00	111.80
Pressure (bar)	1.01	1.01	1.01	200.00	200.00	200.00	200.00	1.52	1.52
Mole flows (kmol/h)	100.00	296.00	1,626.00	1,626.00	1,626.00	1,626.00	1,626.00	1,626.00	1,230.00
Mass flows (kg/h)	81,457.29	5,332.52	108,948.60	108,948.60	108,948.60	108,950.13	108,950.13	108,950.13	22,158.79
Mass fractions									
MONO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
DI	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
TRI	0.98	0.00	0.73	0.73	0.73	0.00	0.00	0.00	0.00
MET	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
FAME	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
GLY	0.00	0.00	0.00	0.00	0.00	0.08	0.08	0.08	0.00
FFA	0.02	0.00	0.02	0.02	0.02	0.72	0.72	0.72	0.00
H_2O	0.00	1.00	0.25	0.25	0.25	0.21	0.21	0.21	1.00
MSA	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
NaOH	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
SFS	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Table A-3 Stream properties of Hydrolysis of TG-glycerolysis of FFA added glycerol (continue).

Name	**REWATER2**	**5.00**	**6**	**GLY**	**7**	**IN-RE2**	**OUT-RE2**	**8**	**9**
From	VAL-101	T-100	VAL-102		E-102	MIX-101	GLYCERO	V-100	V-100
To	MIX-100	VAL-102	E-102	E-102	MIX-101	GLYCERO	V-100		P-101
Temperature (°C)	111.80	224.94	223.42	25.00	120.00	120.00	120.00	165.00	165.00
Pressure (bar)	1.01	1.52	1.01	1.01	1.01	1.01	1.01	1.01	1.01
Mole flows (kmol/h)	1,230.00	396.00	396.00	72.56	653.56	653.56	653.56	291.45	362.11
Mass flows (kg/h)	22,158.79	86,791.34	86,791.34	6,682.34	105,270.72	105,270.72	105,270.73	5,336.10	99,934.63
Mass fractions									
MONO	0.00	0.00	0.00	0.00	0.00	0.00	0.16	0.00	0.17
DI	0.00	0.00	0.00	0.00	0.00	0.00	0.47	0.00	0.49
TRI	0.00	0.00	0.00	0.00	0.00	0.00	0.15	0.00	0.16
MET	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
FAME	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
GLY	0.00	0.10	0.10	1.00	0.24	0.24	0.11	0.02	0.12
FFA	0.00	0.90	0.90	0.00	0.74	0.74	0.04	0.00	0.04
H_2O	1.00	0.01	0.01	0.00	0.02	0.02	0.06	0.98	0.01
MSA	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
NaOH	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
SFS	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Table A-3 Stream properties of Hydrolysis of TG-glycerolysis of FFA added glycerol (continue).

Name	**10**	**REGLY**	**REGLY2**	**11**	**12**	**13**	**NAOH**	**MSA**	**14**
From	P-101	T-101	VAL-103	T-101	VAL-104	E-103			E-104
To	T-101	VAL-103	E-102	VAL-104	E-103	R-NUTR	E-104	E-104	R-NUTR
Temperature (°C)	165.05	157.24	157.24	408.01	405.27	120.00	25.00	25.00	120.00
Pressure (bar)	1.52	1.52	1.52	1.52	1.01	1.01	1.01	1.01	1.01
Mole flows (kmol/h)	362.11	185.00	185.00	177.11	177.11	177.11	32.50	16.21	48.71
Mass flows (kg/h)	99,934.63	11,797.05	11,797.05	88,137.58	88,137.58	88,137.58	1,299.91	1,590.13	2,890.04
Mass fractions									
MONO	0.17	0.00	0.00	0.19	0.19	0.19	0.00	0.00	0.00
DI	0.49	0.00	0.00	0.56	0.56	0.56	0.00	0.00	0.00
TRI	0.16	0.00	0.00	0.18	0.18	0.18	0.00	0.00	0.00
MET	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
FAME	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
GLY	0.12	0.89	0.89	0.02	0.02	0.02	0.00	0.00	0.00
FFA	0.04	0.00	0.00	0.05	0.05	0.05	0.00	0.00	0.00
H_2O	0.01	0.11	0.11	0.00	0.00	0.00	0.00	0.00	0.00
MSA	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
NaOH	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.00	0.55
SFS	0.00	0.00	0.00	0.00	0.00	0.00	1.00	0.00	0.45

Table A-3 Stream properties of Hydrolysis of TG-glycerolysis of FFA added glycerol (continue).

Name	**15**	**16**	**17**	**18**	**19**	**20**	**21**	**22**	**MONO**
From	R-NUTR	V-101	V-101	SEP	SEP	P-102	T-102	T-102	T-103
To	V-101		SEP		P-102	T-102		T-103	
Temperature (°C)	120.00	200.00	200.00	200.00	200.00	200.24	159.20	501.66	443.25
Pressure (bar)	1.01	1.01	1.01	1.01	1.01	1.52	1.52	1.52	1.52
Mole flows (kmol/h)	225.82	17.37	208.45	16.05	192.40	192.40	46.00	146.40	49.40
Mass flows (kg/h)	91,027.62	320.73	90,706.89	2,279.87	88,427.02	88,427.02	5,895.49	82,531.53	17,731.30
Mass fractions									
MONO	0.19	0.00	0.19	0.00	0.19	0.19	0.00	0.20	0.95
DI	0.54	0.00	0.54	0.00	0.56	0.56	0.00	0.60	0.03
TRI	0.18	0.00	0.18	0.00	0.18	0.18	0.00	0.19	0.00
MET	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
FAME	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
GLY	0.02	0.02	0.02	0.00	0.02	0.02	0.26	0.00	0.00
FFA	0.05	0.01	0.05	0.00	0.05	0.05	0.69	0.00	0.02
H_2O	0.01	0.97	0.00	0.00	0.00	0.00	0.05	0.00	0.00
MSA	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
NaOH	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
SFS	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Table A-3 Stream properties of Hydrolysis of TG-glycerolysis of FFA added glycerol (continue).

Name	**23**	**DI**	**TRI**
From	T-103	T-104	T-104
To	T-104		
Temperature (°C)	590.49	583.36	622.36
Pressure (bar)	1.52	1.52	1.52
Mole flows (kmol/h)	97.00	74.00	23.00
Mass flows (kg/h)	64,800.24	46,399.72	18,400.52
Mass fractions			
MONO	0.00	0.00	0.00
DI	0.75	0.97	0.21
TRI	0.25	0.03	0.79
MET	0.00	0.00	0.00
FAME	0.00	0.00	0.00
GLY	0.00	0.00	0.00
FFA	0.00	0.00	0.00
H_2O	0.00	0.00	0.00
MSA	0.00	0.00	0.00
NaOH	0.00	0.00	0.00
SFS	0.00	0.00	0.00

Scenario IV: Transesterification of TG-glycerolysis of FAME using heterogeneous catalyst

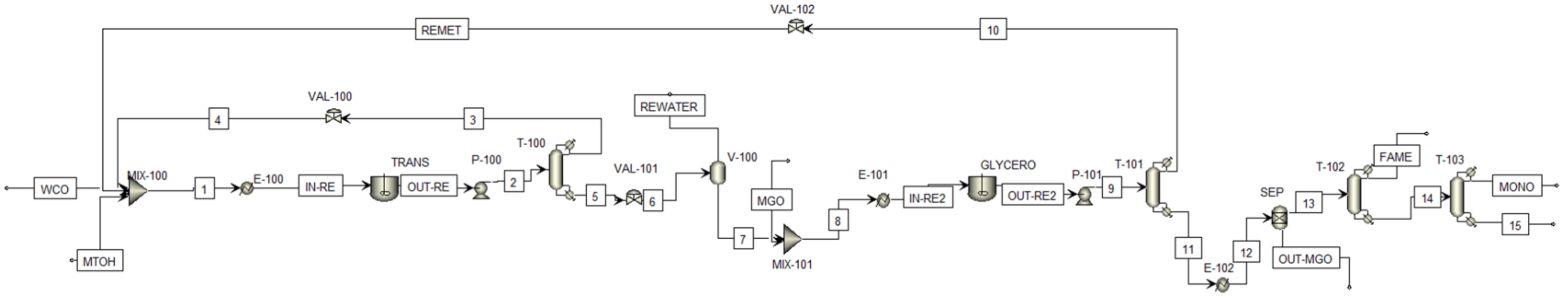

Fig. A-4 Process flow diagram of Transesterification of TG-glycerolysis of FAME using heterogeneous catalyst

Table A-4 Stream properties of Transesterification of TG-glycerolysis of FAME using heterogeneous catalyst (scenario IV).

Name	**WCO**	**MTOH**	**1**	**IN-RE**	**OUT-RE**	**2**	**3**	**4**	**5**
From			MIX-100	E-100	TRANS	P-100	T-100	VAL-100	T-100
To	MIX-100	MIX-100	E-100	TRANS	P-100	T-100	VAL-100	MIX-100	VAL-101
Temperature (°C)	25.00	25.00	46.91	65.00	65.00	65.03	75.35	64.68	188.54
Pressure (bar)	1.01	1.01	1.01	1.01	1.01	1.52	1.52	1.01	1.52
Mole flows (kmol/h)	100.00	167.19	1,377.19	1,377.19	1,377.19	1,377.19	1,000.00	1,000.00	377.19
Mass flows (kg/h)	81,457.29	5,357.28	123,215.99	123,215.99	123,215.99	123,215.99	31,912.92	31,912.92	91,303.07
Mass fractions									
MONO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
DI	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
TRI	0.98	0.00	0.65	0.65	0.04	0.04	0.00	0.00	0.05
MET	0.00	1.00	0.33	0.33	0.26	0.26	0.99	0.99	0.01
FAME	0.00	0.00	0.01	0.01	0.62	0.62	0.00	0.00	0.84
GLY	0.00	0.00	0.00	0.00	0.06	0.06	0.00	0.00	0.09
H_2O	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.00
FFA	0.02	0.00	0.01	0.01	0.01	0.01	0.00	0.00	0.02
MGO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Table A-4 Stream properties of Transesterification of TG-glycerolysis of FAME using heterogeneous catalyst (continue).

Name	**6**	**REWATER**	**7**	**MGO**	**8**	**IN-RE2**	**OUT-RE2**	**9**	**10**
From	VAL-101	V-100	V-100		MIX-101	E-101	GLYCERO	P-101	T-101
To	V-100		MIX-101	MIX-101	E-101	GLYCERO	P-101	T-101	VAL-102
Temperature (°C)	187.86	250.00	250.00	25.00	238.69	250.00	250.00	250.08	76.92
Pressure (bar)	1.01	1.01	1.01	1.01	1.01	1.01	1.01	1.52	1.52
Mole flows (kmol/h)	377.19	18.74	358.46	193.60	552.06	552.06	552.06	552.06	110.00
Mass flows (kg/h)	91,303.07	912.44	90,390.63	7,803.00	98,193.63	98,193.63	98,193.63	98,193.63	4,488.50
Mass fractions									
MONO	0.00	0.00	0.00	0.00	0.00	0.00	0.24	0.24	0.00
DI	0.00	0.00	0.00	0.00	0.00	0.00	0.10	0.10	0.00
TRI	0.05	0.00	0.05	0.00	0.05	0.05	0.05	0.05	0.00
MET	0.01	0.43	0.00	0.00	0.00	0.00	0.03	0.03	0.73
FAME	0.84	0.34	0.84	0.00	0.78	0.78	0.47	0.47	0.22
GLY	0.09	0.15	0.09	0.00	0.08	0.08	0.00	0.00	0.04
H_2O	0.00	0.08	0.00	0.00	0.00	0.00	0.00	0.00	0.01
FFA	0.02	0.00	0.02	0.00	0.02	0.02	0.02	0.02	0.00
MGO	0.00	0.00	0.00	1.00	0.08	0.08	0.08	0.08	0.00

Table A-4 Stream properties of Transesterification of TG-glycerolysis of FAME using heterogeneous catalyst (continue).

Name	**REMET**	**11**	**12**	**OUT-MGO**	**13**	**FAME**	**14**	**MONO**	**15**
From	VAL-102	T-101	E-102	SEP	SEP	T-102	T-102	T-103	T-103
To	MIX-100	E-102	SEP		T-102		T-103		
Temperature (°C)	66.20	413.61	350.00	350.00	350.00	363.76	451.62	438.78	590.59
Pressure (bar)	1.01	1.52	1.52	1.52	1.52	1.52	1.52	1.52	1.52
Mole flows (kmol/h)	110.00	442.06	442.06	193.60	248.46	156.00	92.46	72.80	19.66
Mass flows (kg/h)	4,488.50	93,705.13	93,705.13	7,803.00	85,902.13	46,153.25	39,748.88	26,229.50	13,519.38
Mass fractions									
MONO	0.00	0.25	0.25	0.00	0.28	0.00	0.60	0.90	0.00
DI	0.00	0.11	0.11	0.00	0.12	0.00	0.26	0.05	0.66
TRI	0.00	0.05	0.05	0.00	0.05	0.00	0.11	0.00	0.33
MET	0.73	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
FAME	0.22	0.49	0.49	0.00	0.53	0.97	0.02	0.04	0.00
GLY	0.04	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
H_2O	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
FFA	0.00	0.02	0.02	0.00	0.02	0.03	0.01	0.01	0.00
MGO	0.00	0.08	0.08	1.00	0.00	0.00	0.00	0.00	0.00

APPENDIX B

Total energy requirement

Table B-1 Energy requirement of Transesterification of TG-glycerolysis of FAME.

Process	Symbol	Equipment	Type	Utility	Duty (kW)
Scenario I	P-100	Centrifugal pump	-	Electricity	2.75
	P-101				17.86
	P-102				1.92
	E-100	Heat exchanger	Heater	LP steam	1,560.16
	E-101		Cooler	Cooling water	8,410.87
	E-102				15,811.29
	E-103		Heater	MP steam	51.06
	TRANS	Reactor	Isothermal	Cooling water	1,775.26
	R-NUTR			MP steam	585.47
	GLYCERO FAME				1,516.28
	SEP	Separate	Cooler	Cooling water	0.002
	V-100	Flash vessel	Heater	HOT steam	7,430.53
	T-100	Condenser	Cooler	Cooling water	27,664.36
		Reboiler	Heater	MP steam	32,487.20
	T-101	Condenser	Cooler	Cooling water	2,166.00
		Reboiler	Heater	FIRED	14,186.75
	T-102	Condenser	Cooler	Cooling water	20,267.08
		Reboiler	Heater	FIRED	24,983.26
	T-103	Condenser	Cooler	Cooling water	70,898.62
		Reboiler	Heater	VERY	78,470.35
	T-104	Condenser	Cooler	Cooling water	8,037.79
		Reboiler	Heater	VERY	8,471.93
Total cooling					15,5031.27
Total heating					169,743.00
Total electricity					22.52

Table B-2 Energy requirement of Hydrolysis of TG-glycerolysis of FFA.

Process	Symbol	Equipment	Type	Utility	Duty (kW)
Scenario II	P-100	Centrifugal pump	-	Electricity	1,911.80
	P-101				2.72
	P-102				3.31
	E-100	Heat exchanger	Heater	LP steam	29,340.23
	E-101		Cooler	Cooling water	18,657.54
	E-102				6,390.63
	E-103				15,853.07
	E-104		Heater	MP steam	85.22
	HYDRO	Reactor	Isothermal	Cooling water	157,292.00
	R-NUTR			Cooling water	2,886.77
	GLYCERO FFA			MP steam	3,364.75
	SEP	Separate	Heater	HP steam	10.83
	V-100	Flash vessel	Heater	HP steam	4,603.68
	V-101				4,496.81
	T-100	Condenser	Cooler	Cooling water	41,119.77
		Reboiler	Heater	HP steam	39805.32
	T-101	Condenser	Cooler	Cooling water	7,166.45
		Reboiler	Heater	FIRED	16,559.80
	T-102	Condenser	Cooler	Cooling water	26,954.02
		Reboiler	Heater	VERY	33,470.82
	T-103	Condenser	Cooler	Cooling water	2,671.49
		Reboiler	Heater	VERY	3,381.61
	T-104	Condenser	Cooler	Cooling water	2,818.74
		Reboiler	Heater	VERY	6,117.49
Total cooling					129,980.06
Total heating					141,236.57
Total electricity					1,917.83

Table B-3 Energy requirement of Hydrolysis of TG-glycerolysis of FFA added glycerol.

Process	Symbol	Equipment	Type	Utility	Duty (kW)
Scenario III	P-100	Centrifugal pump	-	Electricity	1,911.80
	P-101				3.32
	P-102				3.46
	E-100	Heat exchanger	Heater	LP steam	29,340.23
	E-101		Cooler	Cooling water	26,024.68
	E-102				6,219.27
	E-103				18,034.37
	E-104		Heater	MP steam	85.22
	HYDRO	Reactor	Isothermal	Cooling water	157,292.00
	R-NUTR			Cooling water	2,886.25
	GLYCERO FFA			MP steam	5,560.57
	SEP	Separate	Heater	HP steam	10.83
	V-100	Flash vessel	Heater	HP steam	6,092.44
	V-101				4,646.18
	T-100	Condenser	Cooler	Cooling water	41,119.77
		Reboiler	Heater	HP steam	47,172.32
	T-101	Condenser	Cooler	Cooling water	11,811.32
		Reboiler	Heater	FIRED	27,402.72
	T-102	Condenser	Cooler	Cooling water	4,569.26
		Reboiler	Heater	VERY	23,678.08
	T-103	Condenser	Cooler	Cooling water	5,949.27
		Reboiler	Heater	VERY	10,356.22
	T-104	Condenser	Cooler	Cooling water	5,379.07
		Reboiler	Heater	VERY	5,637.99
Total cooling					129,980.06
Total heating					159,982.81
Total electricity					1,918.57

Table B-4 Energy requirement of Transesterification of TG-glycerolysis of FAME using heterogeneous catalyst.

Process	Symbol	Equipment	Type	Utility	Duty (kW)
Scenario IV	P-100	Centrifugal pump	-	Electricity	2.77
	P-101				2.18
	E-100	Heat exchanger	Heater	LP steam	1,452.68
	E-101			HOT steam	806.76
	E-102		Cooler	Cooling water	4,965.10
	TRANS	Reactor	Isothermal	Cooling water	1,773.82
	GLYCERO FAME			FIRED	1,913.35
	SEP	Separate	Heater	VERY	0.00
	V-100	Flash vessel	Heater	HOT steam	4,234.37
	T-100	Condenser	Cooler	Cooling water	28,865.23
		Reboiler	Heater	HP steam	36,530.57
	T-101	Condenser	Cooler	Cooling water	4,499.95
		Reboiler	Heater	VERY	15,054.29
	T-102	Condenser	Cooler	Cooling water	10,613.36
		Reboiler	Heater	VERY	14,504.03
	T-103	Condenser	Cooler	Cooling water	7,809.78
		Reboiler	Heater	VERY	9,210.91
Total cooling					58,527.25
Total heating					82,900.19
Total electricity					4.95

APPENDIX C

Cost evaluation

Total capital investment can be calculated from Eqs (3.1)-(3.4)

Table C-1 Total capital investment of Transesterification of TG-glycerolysis of FAME.

Process	Symbol	Equipment	A (Eq. 3.1)	Unit	C_{BM}
Scenario I	P-100	Centrifugal pump	2.75	kW	52,721.35
	P-101		17.86		101,737.33
	P-102		1.92		46,901.13
	E-100	Heat exchanger	31.47	m^2	40,655.02
	E-101		78.86		25,538.46
	E-102		93.42		23,631.14
	E-103		0.77		566,614.88
	TRANS	Reactor	348.16	m^3	2,330,520.97
	R-NUTR		13.79		418,316.84
	GLYCERO FAME		1,870.39		5,700,316.22
	SEP	Separate	17.85	m^3	76,652.06
	V-100	Flash vessel	18.79	m^3	78,553.09
	T-100	Vessel	532.83	m^3	522,003.14
		Sieve	10.06(5)	diameter(trays)	607,689.58
		Condenser	641.04	m^2	116,84.59
		Reboiler	770.05	m^2	117,446.82
	T-101	Vessel	54.04	m^3	140,520.44
		Sieve	2.74(8)	diameter(trays)	82,158.10
		Condenser	49.97	m^2	31,872.19
		Reboiler	738.03	m^2	115,603.53
	T-102	Vessel	490.39	m^3	461,587.88
		Sieve	6.40(15)	diameter(trays)	403,217.23
		Condenser	96.19	m^2	23,322.24
		Reboiler	2,865.41	m^2	216,253.72

Table C-1 Total capital investment of Transesterification of TG-glycerolysis of FAME (continue).

Process	Symbol	Equipment	A (Eq. 3.1)	Unit	C_{BM}
Scenario I	T-103	Vessel	1,174.55	m^3	781,962.41
		Sieve	9.91(15)	diameter(trays)	948,262.75
		Condenser	463.69	m^2	12,856.06
		Reboiler	619.12	m^2	108,563.95
	T-104	Vessel	105.24	m^3	200,980.48
		Sieve	3.96(7)	diameter(trays)	132,703.55
		Condenser	26.5482	m^2	44,670.78
		Reboiler	71.4742	m^2	70,645.10
FCI (USD)		1.18*(ΣC_{BM})			17,105,472.48
TCI (USD)		(100/85)*FCI			20,124,085.27
FCI per ton MG		MG productivity = 282,763 ton/year			60.49
TCI per ton MG					71.17

Table C-2 Total capital investment of Hydrolysis of TG-glycerolysis of FFA.

Process	Symbol	Equipment	A (Eq. 3.1)	Unit	C_{BM}
Scenario II	P-100	Centrifugal pump	1,911.80	kW	1,055,676.09
	P-101		2.72		67,320.43
	P-102		3.31		56,080.95
	E-100	Heat exchanger	1,506.42	m^2	12,510.53
	E-101		115.63		28,343.37
	E-102		144.71		19,565.89
	E-103		98.70		23,054.91
	E-104		1.13		408,367.04
	HYDRO	Reactor	76.96	m^3	6,138,268.20
	R-NUTR		14.13		423,712.82
	GLYCERO FFA		106.30		1,239,762.68
	SEP	Separate	18.79	m^3	78,553.09
	V-100	Flash vessel	18.79	m^3	78,553.09
	V-101		22.34		85,332.53

Table C-2 Total capital investment of Hydrolysis of TG-glycerolysis of FFA (continue).

Process	Symbol	Equipment	A (Eq. 3.1)	Unit	C_{BM}
Scenario II	T-100	Vessel	883.76	m^3	718,536.64
		Sieve	12.95(5)	diameter(trays)	1,048,098.64
		Condenser	367.89	m^2	13,842.58
		Reboiler	854.38	m^2	122,207.66
	T-101	Vessel	76.45	m^3	171,015.86
		Sieve	3.81(5)	diameter(trays)	103,748.25
		Condenser	48.96	m^2	32,204.16
		Reboiler	2,036.34	m^2	180,405.40
	T-102	Vessel	328.97	m^3	378,088.85
		Sieve	6.55(9)	diameter(trays)	353,016.94
		Condenser	144.71	m^2	19,565.89
		Reboiler	289.84	m^2	86,843.89
	T-103	Vessel	113.02	m^3	205,128.62
		Sieve	3.35(12)	diameter(trays)	128,618.21
		Condenser	8.75	m^2	87,955.14
		Reboiler	43.39	m^2	69,997.68
	T-104	Vessel	39.85	m^3	120,227.32
		Sieve	2.43(7)	diameter(trays)	65,784.26
		Condenser	6.83494	m^2	103,815.07
		Reboiler	24.9971	m^2	72,070.57
FCI (USD)		1.18*(ΣC_{BM})			16,181,943.16
TCI (USD)		(100/85)*FCI			19,037,580.19
FCI per ton MG		MG productivity = 91,049.2 ton/year			177.75
TCI per ton MG					209.12

Table C-3 Total capital investment of Hydrolysis of TG-glycerolysis of FFA added glycerol.

Process	Symbol	Equipment	A (Eq. 3.1)	Unit	C_{BM}
Scenario III	P-100	Centrifugal pump	1,911.80	kW	1,055,676.09
	P-101		3.32		71,908.28
	P-102		3.46		56,920.22
	E-100	Heat exchanger	1,506.42	m^2	12,510.53
	E-101		208.93		22,294.63
	E-102		53.14		30,902.46
	E-103		105.65		22,371.13
	E-104		1.13		408,367.04
	HYDRO	Reactor	76.96	m^3	6,138,268.20
	R-NUTR		14.46		429,050.60
	GLYCERO FFA		149.43		1,486,018.65
	SEP	Separate	22.34	m^3	85,332.53
	V-100	Flash vessel	23.97	m^3	88,274.35
	V-101		22.34		85,332.53
	T-100	Vessel	883.76	m^3	718,536.64
		Sieve	12.95(5)	diameter(trays)	1,048,098.64
		Condenser	367.89	m^2	13,842.58
		Reboiler	1,009.13	m^2	130,638.29
	T-101	Vessel	205.62	m^3	296,242.70
		Sieve	6.24(5)	diameter(trays)	239,504.30
		Condenser	75.15	m^2	26,120.05
		Reboiler	2,752.76	m^2	211,526.06
	T-102	Vessel	64.23	m^3	153,493.59
		Sieve	2.89(9)	diameter(trays)	93,292.83
		Condenser	29.14	m^2	42,411.09
		Reboiler	190.85	m^2	79,409.45
	T-103	Vessel	256.47	m^3	319,451.26
		Sieve	4.72(14)	diameter(trays)	232,032.94
		Condenser	18.87	m^2	54,385.01
		Reboiler	87.55	m^2	71,599.64

Table C-3 Total capital investment of Hydrolysis of TG-glycerolysis of FFA added glycerol (continue).

Process	Symbol	Equipment	A (Eq. 3.1)	Unit	C_{BM}
Scenario III	T-104	Vessel	82.35	m^3	176,076.80
		Sieve	3.50(7)	diameter(trays)	109,813.72
		Condenser	13.0373	m^2	68,103.20
		Reboiler	48.1838	m^2	69,936.50
FCI (USD)		1.18*(ΣC_{BM})			16,694,336.41
TCI (USD)		(100/85)*FCI			19,640,395.77
FCI per ton MG		MG productivity = 171,371 ton/year			97.46
TCI per ton MG					114.66

Table C-4 Total capital investment of Transesterification of TG-glycerolysis of FAME using heterogeneous catalyst.

Process	Symbol	Equipment	A (Eq. 3.1)	Unit	C_{BM}
Scenario IV	P-100	Centrifugal pump	2.77	kW	52,900.01
	P-101		2.18		65,146.32
	E-100	Heat exchanger	29.61	m^2	42,036.89
	E-101		1,094.58		10,182.87
	E-102		21.03		51,043.68
	TRANS	Reactor	348.16	m^3	2,330,520.96
	GLYCERO FAME		654.25		3,259,910.30
	SEP	Separate	22.34		85,332.17
	V-100	Flash vessel	22.34	m^3	85,332.17
	T-100	Vessel	582.37	m^3	551,593.33
		Sieve	10.51(5)	diameter(trays)	667,077.84
		Condenser	666.64	m^2	11,557.61
		Reboiler	474.36	m^2	99,493.24
	T-101	Vessel	142.83	m^3	233,897.96
		Sieve	3.96(11)	diameter(trays)	161,170.54
		Condenser	46.87	m^2	32,928.40
		Reboiler	117.97	m^2	73,770.28
	T-102	Vessel	156.93	m^3	246,957.62
		Sieve	4.26(10)	diameter(trays)	175,041.92
		Condenser	42.33	m^2	34,704.31

Table C-4 Total capital investment of Transesterification of TG-glycerolysis of FAME using heterogeneous catalyst (continue).

Process	Symbol	Equipment	A (Eq. 3.1)	Unit	C_{BM}
Scenario IV	T-102	Reboiler	115.38	m^2	73,576.31
	T-103	Vessel	115.29	m^3	208,718.24
		Sieve	3.65(10)	diameter(trays)	137,286.79
		Condenser	24.76	m^2	46,468.64
		Reboiler	77.55	m^2	70,979.59
FCI (USD)		1.18*(ΣC_{BM})			10,393,001.15
TCI (USD)		(100/85)*FCI			12,227,060.18
FCI per ton MG		MG productivity = 255,168 ton/year			40.73
TCI per ton MG					47.92

Cost of manufacturing can be obtained from Eq (3.5) and (3.6) and Table 14.

Table C-5 Cost of manufacturing of Transesterification of TG-glycerolysis of FAME.

Component	Cost/Unit	Unit	Cost (USD/year)
WCO (t/y)	224.00	787,110.00	176,312,640.00
MTOH (t/y)	600.00	67,284.60	40,370,760.00
CH_3ONa (t/y)	1,150.00	10,100.00	11,615,000.00
H_3PO_4 (t/y)	340.00	7,903.04	2,687,033.60
K/CeO_2 (kg/y)	78.52	11,550.55	906,949.19
Labor (person)	15.00	24,600.00	369,000.00
LP steam (GJ/y)	1.90	44,932.32	85,371.41
Hot oil (GJ/y)	3.50	213,997.60	748,991.60
Cooling water (GJ/y)	0.21	4,464,864.92	946,551.36
Electricity (GJ/y)	16.90	675.60	11,417.80
MP steam (GJ/y)	2.20	997,624.58	2,194,774.08
VERY (GJ/y)	8.90	2,503,917.60	22,284,866.64
FIRED (GJ/y)	4.25	1,128,087.20	4,794,370.60
Waste management (t/y)	36.00	55,693.90	2,004,980.40
FCI (USD)			17,105,472.48
Total cost of manufacturing (USD/y)			329,991,714.27
Total cost of manufacturing per ton of MG (USD/t)			1,167.03

Table C-6 Cost of manufacturing of Hydrolysis of TG-glycerolysis of FFA.

Component	Cost/Unit	Unit	Cost (USD/year)
WCO (t/y)	224.00	787,110.00	176,312,640.00
Water (t/y)	2.84	51,527.40	146,337.82
NaOH (t/y)	200.00	12,560.80	2,512,160.00
MSA (t/y)	1,600.00	15,365.200	24,584,320.00
Labor (person)	15.00	24,600.00	369,000.00
LP steam (GJ/y)	1.9	844,992.00	1,605,484.80
HP steam (GJ/y)	2.5	1,408,788.00	3,521,970.00
Cooling water (GJ/y)	0.212	3,586,103.76	793,599.90
Electricity (GJ/y)	16.9	55,233.36	933,443.73
MP steam (GJ/y)	2.2	99,358.40	218,588.48
VERY (GJ/y)	8.9	1,237,524.00	11,013,963.60
FIRED (GJ/y)	4.25	476,918.40	2,026,903.20
Waste management (t/y)	36.00	509286.20	18,334,303.20
FCI (USD)			16,181,943.16
Total cost of manufacturing (USD/y)			301,584,688.88
Total cost of manufacturing per ton of MG (USD/t)			3,312.72

Table C-7 Cost of manufacturing of Hydrolysis of TG-glycerolysis of FFA added glycerol.

Component	Cost/Unit	Unit	Cost (USD/year)
WCO (t/y)	224.00	787,110.00	176,312,640.00
Water (t/y)	2.84	51,527.40	146,337.82
NaOH (t/y)	200.00	12,560.80	2,512,160.00
MSA (t/y)	1,600.00	15,365.200	24,584,320.00
Glycerol (t/y)	1,260.00	64,570.50	81,358,830.00
Labor (person)	15.00	24,600.00	369,000.00
LP steam (GJ/y)	1.9	844,992.00	1,605,484.80
HP steam (GJ/y)	2.5	1,668,133.60	4,170,334.00
Cooling water (GJ/y)	0.212	3,513,377.60	778,181.96
Electricity (GJ/y)	16.9	55,255.00	933,809.53
MP steam (GJ/y)	2.2	162,597.60	357,714.72
VERY (GJ/y)	8.9	1,142,552.80	10,168,719.92
FIRED (GJ/y)	4.25	789,192.00	3,354,066.00

Table C-7 Cost of manufacturing of Hydrolysis of TG-glycerolysis of FFA added glycerol (continue).

Component	Cost/Unit	Unit	Cost (USD/year)
Waste management (t/y)	36.00	256,781.00	9,244,119.60
FCI (USD)			16,694,336.41
Total cost of manufacturing (USD/y)			392,110,214.12
Total cost of manufacturing per ton of MG (USD/t)			2,289.21

Table C-8 Cost of manufacturing of Transesterification of TG-glycerolysis of FAME using heterogeneous catalyst.

Component	Cost/Unit	Unit	Cost (USD/year)
WCO (t/y)	224.00	787,110.00	176,312,640.00
MTOH (t/y)	600.00	51,762.00	31,057,200.00
MgO (kg)	1.50	6,095.52.00	9,143,280.00
K/CeO_2 (kg/y)	78.52	11,550.55	906,949.19
Labor (person)	14.00	24,600.00	344,400.00
LP steam (GJ/y)	1.9	41,836.88	79,490.07
Hot oil (GJ/y)	3.5	121,948.80	426,820.80
Cooling water (GJ/y)	0.212	1,685,571.28	357,341.11
Electricity (GJ/y)	16.9	228.97	3,869.55
HP steam (GJ/y)	2.5	1,052,072.00	2,630,180.00
VERY (GJ/y)	8.9	1,116,544.80	9,937,248.72
FIRED (GJ/y)	4.25	55,104.00	234,192.00
Waste management (t/y)	36.00	206,035.30	7,417,270.80
FCI (USD)			10,393,001.15
Total cost of manufacturing (USD/y)			296,173,925.36
Total cost of manufacturing per ton of MG (USD/t)			1,160.70

APPENDIX D

Sensitivity analysis

Sensitivity analysis (SA) was used to explore the effect of ±40% variation in WCO price, by-product price, MTOH price, FCI, water, and Utility cost on the profit abilities of the four process schemes. The NPV can be obtained from Eq (3.8).

Table D-1 MG production cost of Transesterification of TG-glycerolysis of FAME.

MG production cost (USD)						
Parameter	WCO price	BY-PRODUCT	MTOH price	FCI	Utility cost	Catalyst price
-40%	-93.27	594.91	143.26	209.15	159.45	191.71
0%	213.50	213.50	213.50	213.50	213.50	213.50
40%	520.28	-167.90	283.75	217.86	267.56	235.29

Table D-2 MG production cost of Hydrolysis of TG-glycerolysis of FFA.

MG production cost (USD)						
Parameter	WCO price	BY-PRODUCT	FCI	Utility cost	Water	Catalyst price
-40%	804.83	2379.76	1744.81	1648.98	1756.89	1624.64
0%	1757.68	1757.68	1757.68	1757.68	1757.68	1757.68
40%	2710.53	1135.59	1770.55	1866.38	1758.47	1890.36

Table D-3 MG production cost of Hydrolysis of TG-glycerolysis of FFA added glycerol.

MG production cost (USD)						
Parameter	WCO price	BY-PRODUCT	FCI	Utility cost	Water	Catalyst price
-40%	212.22	1346.88	711.65	657.29	718.24	648.05
0%	718.66	718.66	718.66	718.66	718.66	718.66
40%	1225.10	90.45	725.68	780.04	719.08	789.28

Table D-4 MG production cost of Transesterification of TG-glycerolysis of FAME using heterogeneous catalyst.

MG production cost (USD)						
Parameter	WCO price	BY-PRODUCT	MTOH price	FCI	Utility cost	Catalyst price
-40%	-95.69	610.83	184.37	241.32	217.90	224.87
0%	244.26	244.26	244.26	244.26	244.26	244.26
40%	584.21	-122.32	304.13	247.18	270.61	263.63

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