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Review on biodiesel production by two-step catalytic conversion

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ABSTRACT

Many researchers have done intensive efforts to enhance the biodiesel yield through two-step reaction in the production process. These processes have been applied under various conditions; including the type of feedstock oil, alcohol, catalyst, heating mode and reaction time. Chemical property of feedstock oil is the most important factor related to the selection of the best suitable two-step reaction technology. This review discusses two double-step reaction technologies; the first step esterification followed by the second step transesterification (called E + T technology), and two-step transesterification (denominated T1 + T2 technology). The purpose of the two-step reaction is to optimize the operating cost of the production process such as lowering alcohol ratio, reducing reaction time, and minimizing yield loss. If free fatty acid content is more than 2 wt% then the first step esterification will be followed by the second step transesterification (E + T technology). The target of the first step esterification is to decrease the free fatty acid content in feedstock oils as much as possible in order to reduce the soap formation in the second step transesterification. Soap formation prevents the separation of biodiesel and glycerol phase and also needs higher amount of water for washing. It is the main reason of biodiesel loss because of turning ester to soap. The T1 + T2 technology should be applied to low free fatty acid content feedstock oils (< 2 wt%) to reduce the production cost. This review highlights the present status and challenges for these technologies, recommendations are also given for future research in two-step reaction technologies.

1. Introduction

Nowadays, the human society is essentially dependent on energy resources. In 2015, fossil fuel was the biggest source of energy (79.34%), whereas, the percentage of nuclear power and renewable energy sources were only 9.91% and 10.75%, respectively (U.S. Energy Administration, 2016). The widespread usage of fossil fuel is one of the major causes of greenhouse gas emission which leads to severe environmental hazards and global warming (Soltani et al., 2015; Woch et al., 2014). The impacts of global warning include warming temperatures, changes in precipitation, increases in the frequency or intensity of some extreme weather events, and rising sea levels. These impacts threaten health by affecting the food, drinking water, air, and the changes in weather.

The most urgent requirement of producing energy from non-fossil and eco-friendly energy resources is to avoid the disastrous consequences of fossil-fuel energy. Renewable energy resources include hydroelectric power, geothermal, solar, wind, biomass etc. (U.S. Energy Administration, 2016; Soltani et al., 2015; Woch et al., 2014; Hernik et al., 2016). These energy resources will play noteworthy roles in the future. Biodiesel is one of the most promising liquid fuels with high quality, derived from renewable resources. It is suitable to substitute for petroleum-based diesel without engine modification (Enweremadu and Mbarawa, 2009; Leung et al., 2010). In comparison with petroleum diesel, biodiesel has proved many outstanding advantages for the environment because it is safe, renewable, biodegradable, and non-toxic (Sharma et al., 2008; Srivastava and Prasad, 2000).

Biodiesel is a mixture of mono alkyl esters obtained through the transesterification of different feedstock (edible oil, non-edible oil, algae) in the presence of alcohol and catalyst (Knothe and Gerpen, 2005). Some edible oils are palm, sunflower, canola, soybean, coconut oil, used as feedstock for biodiesel production. High biodiesel production process cost is the main drawback of these feedstock oils as compared to the petroleum-based diesel (Borges and Díaz, 2012). As a result, non-edible oils including jatropha oil and waste oils are more economical. These feedstock have been encouraged to be used for biodiesel production industries (Tiwari et al., 2007; Huynh et al., 2011). Algae is also a potential feedstock for biodiesel production (Nautiyal et al., 2014; Chisti, 2007).

Methanol and ethanol are the most suitable alcohols in the biodiesel

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Nomenclature

E + T	First step esterification and second step transesterification
T1 + T2	First step transesterification and second step transesterification
WCO	Waste Cooking Oil
FFA	Free Fatty Acid
TDSP	Transesterification Double Step Process

production, however, each has its own pros and cons. Most of biodiesel produces through transesterification of feedstock oils with methanol due to its suitable physicochemical properties, low price, gentle reaction condition, higher activity and easy phase separation. Though, Reid Vapor Pressure (RVP) of methanol is low due to its low boiling temperature which leads to an explosion risk. Another disadvantage of methanol is that it is more dangerous to human than ethanol (Leung et al., 2010). The next suitable alcohol is to use ethanol because it is crafted from renewable resources and not as toxic as methanol (Nikhom and Tongurai, 2014). Though, it is difficult to separate ethyl esters because of the formation of unexpected emulsion in the product (Kim et al., 2010).

Catalyst plays an important role in biodiesel production. These are three categories comprised of (i) acid catalyst, (ii) base catalyst, and (iii) enzyme catalyst based on their active sites (Avhad and Marchetti, 2015; Yaakob et al., 2013). Catalysts maintain the same (liquid) phase status with reactants during reaction process is known as homogeneous catalyst. On the contrary, if the catalysts remain in the different phases (solid or immiscible liquid) with reactants then they are called heterogeneous catalysts. The choice of an appropriate catalyst mainly depends on the free fatty acid and water content in the feedstock oil. The base catalyst has been known for strengthening reaction rate, creating the maximum value of ester content and producing biodiesel yield with mild reaction condition (Zabeti et al., 2009; Helwani et al., 2009).

Homogeneous and heterogeneous acid catalysts are chosen if feedstock oils contain the high free fatty acid (FFA) and water content. They catalyze both esterification and transesterification reaction, but its long reaction time is the biggest drawback (Avhad and Marchetti, 2015). Homogeneous acid catalysts are commonly used for biodiesel production. Nevertheless, they involve more complexity in separation and purification steps, consume a large amount of water for washing process and discharge large waste water as well. Another disadvantage of base homogeneous catalyst is easy occurrence of saponification reaction, especially for high FFA feedstock oils (Lam et al., 2010; Pisarello and Querini, 2013). Soap formation is further another reason of yield loss.

Although the heterogeneous acid catalysts convert feedstock into biodiesel slowly, biodiesel separation process from the reaction mixture is easy. Moreover, the ability of regeneration and reusability of this catalyst is a major advantage in comparison with the homogeneous catalyst (Avhad and Marchetti, 2015). The enzyme catalyst, for instance lipase enzymes, has been demonstrated to be an effective catalyst for biodiesel production. It overcomes all of the challenges of high FFA feedstock as separates glycerol easily due to no soap formation which produces high quality biodiesel (Yaakob et al., 2013).

Some technologies including one-step reaction (Pisarello and Querini, 2013; Loong and Idris, 2016) and two-step reaction (Dubey et al., 2015; Kumar et al., 2014; Samios et al., 2009; Cai et al., 2015; Thanh et al., 2010) have been developed to reduce biodiesel production cost from various feedstock. Firstly, one-step reaction, called transesterification reaction, is suitable for the feedstock oils with a low FFA content. Transesterification reaction will not take place if FFA content in feedstock oils is more than 3 wt% (Canakci and Gerpen, 2001). Higher consumption of catalyst and alcohol content as compare to the two-step transesterification is major shortcoming of the one-step reaction (Pisarello and Querini, 2013; Mendow et al., 2011).

Secondly, the two-step reaction includes first step esterification and second step transesterification (Cai et al., 2015; Suppalakpanya et al., 2010; Nakpong and Wootthikanokkhan, 2010; Jaliliannosrati et al., 2013; Wang et al., 2010; Patil et al., 2010), two-step esterification (Math and Irfan, 2007) and two-step transesterification (Kumar et al., 2014; Samios et al., 2009; Thanh et al., 2010; Mendow et al., 2011; Guzatto et al., 2011; Predojevic, 2008). Some researchers have used more than two-step esterification process (Photaworn et al., 2017). The two-step reaction can be applied to any feedstock oils, especially in case of high FFA content feedstock oils. If the FFA content is more than 2 wt % then the first step esterification will be followed by the second step transesterification. The aim of the first step is to decrease the FFA content as much as possible and to become an appropriate feedstock oils for the second step transesterification. This two-step reaction has been proven the most effective technology for any feedstock oils in biodiesel production process (Kumar et al., 2014; Samios et al., 2009; Cai et al., 2015; Thanh et al., 2010; Canakci and Gerpen, 2001; Mendow et al., 2011; Suppalakpanya et al., 2010; Nakpong and Wootthikanokkhan, 2010; Jaliliannosrati et al., 2013; Wang et al., 2010; Patil et al., 2010; Math and Irfan, 2007; Guzatto et al., 2011; Predojevic, 2008).

The heating system for the two-step reaction is a noticeable issue relates to technological conditions and production cost (Thanh et al., 2010; Mendow et al., 2011; Worapun et al., 2010). Typically, the biodiesel production process operates with a conventional heating system. It often uses oil bath for heating process. The outstanding advantage of the conventional heating is the easy condition about equipment as well as its operation. However, heat transfer is only occurred on the surface of the materials which leads to decreasing the effective heating and consumes higher energy.

The technology of two-step reaction assisted by ultrasonic irradiation efficiently emulsifies the immiscible liquids. It increases contact area between reactants and contributes to gain in biodiesel yield (Dubey et al., 2015; Thanh et al., 2010; Worapun et al., 2010; Deng et al., 2010). Recently, microwave-assisted two-step reaction has been demonstrated as a promising technology for efficient biodiesel production process (Suppalakpanya et al., 2010, 2011; Jaliliannosrati et al., 2013). A microwave assisted reactor significantly reduces the energy consumption and reaction time for the process, especially for the heterogeneous catalysis reaction (Suppalakpanya et al., 2011).

By contrast, so far the microwave assisted technology could not be implemented at industrial scale. It is too difficult to scale up the microwave assisted two-step reaction technology to the industrial scale due to its short penetration of radiation into material (Hernando et al., 2007; Leadbeater et al., 2008; Lertsathapornsuk et al., 2008). A large sealed container has to be used to the low penetration of microwave irradiation. It causes a huge concern about the security. These disadvantages are the major obstacles to use this technology at industrial scale.

As mentioned above, the biodiesel production process via two-step reaction has been demonstrated as an effective technology in favor of decreasing the production cost, increasing the competitiveness of biodiesel with petroleum diesel. There is no consolidated source of information on two-step reaction implantation in biodiesel production. Present review paper carefully analyzes, summarizes this technology and several new approaches are also discussed.

2. First step esterification followed by second step transesterification (E + T technology)

2.1. Sources of feedstock oil for E + T technology

The E + T technology is applied to feedstock oils such as crude palm oil (Suppalakpanya et al. (2010); Suppalakpanya et al. (2011), sludge palm oil (Hayyan et al., 2010), crude coconut oil (Nakpong and Wootthikanokkhan, 2010), Jatrophacurcas L. oil (Jaliliannosrati et al., 2013; Worapun et al., 2010; Bouaid et al., 2012), salmon oil and waste oil (Cai et al., 2015; Wang et al., 2010; Patil et al., 2010; Math and Irfan, 2007; Liu et al., 2010; Martı et al., 2010; Dias et al., 2009; Banani et al., 2015). Waste oil (WO) is one of the potential sources for the production of low-cost biodiesel. It can be obtained from cooking oil, animal fat and yellow or brown grease. The most important WO source is derived from waste cooking oil (WCO). The perfect solution for WCO reuse is to apply E + T technology. The common feature of these feedstock oils is their high FFA content. The first step esterification is chosen to convert high FFA in feedstock oil into alkyl esters and this reaction step reduces the FFA content to less than 2 wt%. The feedstock from the first step esterification is appropriate for the second step transesterification.

2.2. E + T technology by conventional heating process

The FFA content plays a prominent role in yield of the first step esterification and it varies from 7 to 30 wt% depending on the type of feedstock. The first step esterification has been done with conventional heating process in order to reduce its content in the feedstock oil. Experimental setup with conventional heating process is shown in Fig. 1. The common pretreatment involves esterification of FFA by alcohol in the presence of acid catalyst. Methanol is the most appropriate alcohol for pretreatment because of its high solubility. Cai et al. have suggested glycerol as a suitable alcohol (Cai et al., 2015). Reaction occurs at vacuum pressure (5000 Pa) for a specified period. Glycerol was refluxed under ambient temperature and the water formed by the esterification reaction was taken out by the vacuum to decrease the boiling point of glycerol (from 290 °C to 210 °C). Acid catalysts, such as H_2SO_4 (Nakpong and Wootthikanokkhan, 2010; Banani et al., 2015), $Fe_2(SO_4)_3$ (Patil et al., 2010; Wang et al., 2007), toluene-4-sulfonic monohydrate acid ‘PTSA’ (Hayyan et al., 2010) and polyferric sulfate ‘PFS’ (Wang et al., 2010) are used in this process. H_2SO_4 has proven to be the most appropriate catalyst among these catalysts (Nakpong and Wootthikanokkhan, 2010; Banani et al., 2015). The efficiency of the first step esterification process is affected by MeOH/FFA molar ratio, H_2SO_4/FFA weight percentage, temperature and reaction time.

Stoichiometry of the esterification requires one molecule of methanol to react with one molecule of FFA. However, an excess of the methanol is used to promote the FFA conversion. Therefore, a high molar ratio about 10–30 between methanol and FFA is required for an effective reaction. The molar ratio of about 10–20 should be used for crude oils (palm oil, coconut oil). The FFA content in crude palm oil decreased significantly from 10 wt% to less than 1 wt% by using the molar ratio about 10. The FFA content in coconut oil reduced from 13 wt% to 0.6 wt% by increasing this molar ratio till 20 (Nakpong and Wootthikanokkhan, 2010). The highest molar ratio about 30 is commonly used in the case of WCO (Wang et al., 2010; Patil et al., 2010; Banani et al., 2015).

Catalyst plays a vital role and its content depends on the type of catalyst as well as other conditions in the reaction (MeOH/FFA molar ratio, time and temperature). H_2SO_4 is the most suitable catalyst for esterification process with FFA content in the range from 5 to 30 wt% (Nakpong and Wootthikanokkhan, 2010; Bouaid et al., 2012; Banani et al., 2015). P-toluene sulfonic acid (PTSA) showed the highest catalytic activity in comparison with benzene sulfonic acid and sulfuric acid. FFA content reduced significantly from 22.33 to less than 2 wt% by using 3.4 wt% of PTSA to FFA (Hayyan et al., 2010). $Fe_2(SO_4)_3$ is also considered as a suitable catalyst used with the content in a range from 5 to 23 wt% to FFA in order to decrease FFA content until below 1 wt% (Patil et al., 2010; Wang et al., 2007). In another study, polyferric sulfate (PFS) produced from ferrous sulfate via three stages (oxidation, hydrolysis, and polymerization) is introduced to catalyze the esterification of FFA in WCO with methanol (Wang et al., 2010). FFA content in WCO could decrease to 1.68 wt% in the presence of 9 wt % of PFS to FFA.

Temperature and time are also important factors which affect the esterification under conventional heating process. Most researches were done at temperature under boiling point of methanol (about 60 °C) to avoid unexpected evaporation of methanol in the reactor. Therefore, a long reaction time was requested to ensure the target of this stage.

Esterified feedstock oil is converted into biodiesel by the second step transesterification process. The main reaction is transesterification reaction between esterified oil and alcohol in the presence of base catalyst (NaOH, KOH, CH_3OK). The time for this stage is less than the first step process due to higher catalytic activities of base catalyst as compared to acid catalyst.

The stoichiometry of the transesterification requires 3 mol of methanol and 1 mol of triglyceride to get 3 mol of ester and 1 mol of glycerol. However, transesterification reaction is reversible; the reaction rate is significantly slow and then rapidly reaches an equilibrium state. Hence, a high MeOH/Oil molar ratio about 5–10 is required in order to drive the forward reaction to achieve the highest product yield. A large amount of methanol interferes with the glycerol separation due to increasing the solubility of glycerol in ester phase. The remaining glycerol in the biodiesel provokes the reverse reaction and thus causes the loss of biodiesel yield. This can be seen clearly in two studies (Cai et al., 2015; Hayyan et al., 2010). Hayyan reported that using 10 by mole between MeOH and oil (in the presence of 1 wt% KOH to oil, 60 °C, 1 h), the biodiesel yield and ester content were only 76.62% and 96%, respectively (Hayyan et al., 2010). Cai showed that the biodiesel yield and ester content could reach 93.1% and 98.6%, respectively in a smoother condition (MeOH/Oil molar ratio: 6, 0.3 wt% of NaOH to oil, 40 °C, 1 h) (Cai et al., 2015). Therefore, a 6:1 molar ratio of methanol to oil is the best condition (Cai et al., 2015; Wang et al., 2007, 2010; Bouaid et al., 2012). Comparisons of esters content and yield of biodiesel under conventional heating E + T technology are given in Table 1.

2.3. E + T technology by modern heating technology

Longer reaction time is required in conventional heating process. Hence, novel heating technologies have been studied and developed to create biodiesel in smaller reaction time. Some modern heating technologies such as microwave irradiation (Suppalakpanya et al., 2010, 2011; Jaliliannosrati et al., 2013), ultrasonic irradiation (Worapun et al., 2010; Deng et al., 2010) and radio frequency (Liu et al., 2010) were applied.

The E + T technology process with microwave irradiation was applied to make biodiesel from the high FFA feedstock oil. The

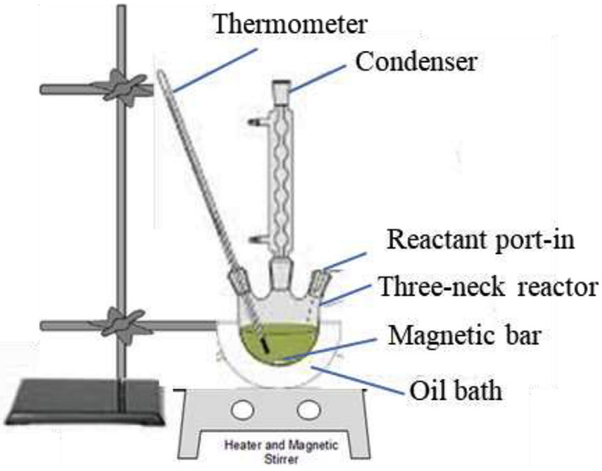

Fig. 1. Experimental setup for the conventional heating process.

Table 1
Summarized E + T technology under conventional heating process.

Raw material	Optimum condition for the first step esterification	Optimum condition for the second step transesterification	Ester content (wt %)	Yield of biodiesel (%)	Reference
WCO	Glycerol/FFA molar ratio = 1.4, NaOH/FFA = 0.8 wt%, 210 °C, 4 h	MeOH/Oil molar ratio = 6, NaOH/Oil = 0.3 wt%, 40 °C, 1 h	98.6	93.1	[Cai et al., 2015]
Crude coconut oil	MeOH/FFA molar ratio = 21.8, H_2SO_4/FFA = 11.3 wt%, 60 °C, 60 min	MeOH/Oil molar ratio = 10, KOH/Oil = 1.7 wt%, 60 °C, 60 min	98.4	ND	[Nakpong and Wootthikanokkhan, 2010]
WCO	MeOH/FFA molar ratio = 28.8, PFS/FFA = 9 wt%, 67 °C, 4 h	MeOH/Oil molar ratio = 6, KOH/Oil = 1.2 wt%, 40 °C, 1 h	95.08	ND	[Wang et al., 2010]
WCO	MeOH/FFA molar ratio = 32.9, $Fe_2(SO_4)_3$/FFA = 22.9 wt%, 100 °C, 1 h	MeOH/Oil molar ratio = 9, KOH/Oil = 0.5 wt%, 100 °C, 1 h	96	ND	[Patil et al., 2010]
Crude palm oil	MeOH/FFA molar ratio = 10, H_2SO_4/FFA = 10 wt%, 60 °C, 11 h	MeOH/Oil molar ratio = 6, NaOH/Oil = 0.7 wt%, 60 °C, 35 min	96.5	95	[Jansri and Prateepchaikul, 2011]
Sludge palm oil	MeOH/FFA molar ratio = 14.3, PTSA/FFA = 3.4 wt%, 60 °C, 1 h	MeOH/Oil molar ratio = 10, KOH/Oil = 1 wt%, 60 °C, 1 h	96	76.62	[Hayyan et al., 2010]
Jatrophacurcas L. oil	MeOH/FFAmolar ratio = 20, H_2SO_4/FFA = 5 wt%, 60 °C, 60 min	MeOH/Oil molar ratio = 6, CH_3OK/Oil = 0.95 wt%, 45 °C, 30 min	98	ND	[Bouaid et al., 2012]
Salmon oil	MeOH/FFA molar ratio = 31.8, H_2SO_4/FFA = 16.7 wt%, 52 °C, 60 min	MeOH/Oil molar ratio = 9, KOH/Oil = 0.5 wt%, 52 °C, 30 min	99	ND	[El-Mashad et al., 2008]
WCO	MeOH/FFA molar ratio = 26.7, H_2SO_4/FFA = 12.6 wt%, 60 °C, 1 h	MeOH/Oil molar ratio = 5, KOH/Oil = 1.1 wt%, 60 °C, 30 min	98	ND	[Banani et al., 2015]
WCO	MeOH/FFA molar ratio = 8.4, $Fe_2(SO_4)_3$/FFA = 5.3 wt%, 95 °C, 4 h	MeOH/Oil molar ratio = 6, KOH/Oil = 1 wt%, 65 °C, 1 h	97.02	ND	[Wang et al., 2007]
WCO	MeOH/FFA molar ratio = 25.9, H_2SO_4/FFA = 37.4 wt%, 82 °C, 3 h	MeOH/Oil molar ratio = 6, KOH/Oil = 1 wt%, 65 °C, 1.5 h	96.66	ND	[Hassania et al., 2013]

ND: not determined.

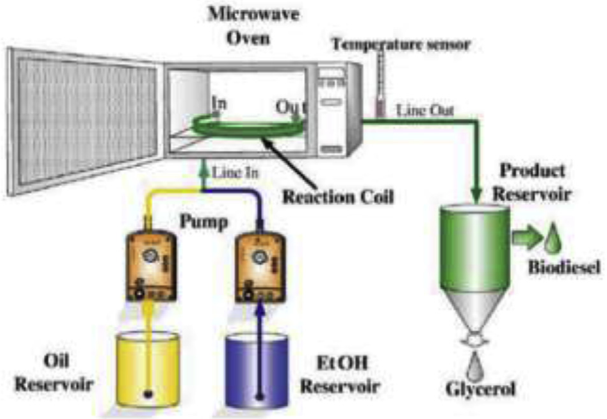

Fig. 2. Microwave irradiation heating technology [Enweremadu and Mbarawa, 2009].

microwave irradiation can provide strong heat and reach reaction temperature in a short time. The FFA content was reduced from 7.5 wt % to less than 2 wt% by using 24 of EtOH/FFA molar ratio with 4 wt% of H_2SO_4/FFA. This esterification process was conducted at 70 W of microwave power for 60 min (Suppalakpanya et al., 2010). A higher reaction condition (EtOH/FFA molar ratio of 54, 5 wt% of H_2SO_4/FFA, 110 W of microwave power) was done to decrease the reaction time for the first step (Jaliliannosrati et al., 2013). FFA content could be decreased from 14 wt% to less than 1 wt% in only 35 min in this study. Microwave irradiation heating technology is shown in Fig. 2.

In the second step, transesterification of esterified feedstock oil has been carried out in short time (about 5–12 min) with smoother reaction condition (EtOH/Oil molar ratio: 5–8, KOH/Oil: 1.5–1.7 wt%). The ester content could be reached more than 97% in comparison with the EN 14103 standard (96.5% min).

Ultrasonic irradiation energy can also enhance the E + T process in biodiesel production and reducing the reaction time (Worapun et al., 2010; Deng et al., 2010). Earlier, FFA was reduced from 5.23 wt% to 0.6 wt% at 60 °C in 60 min in the presence of 60 of MeOH/FFA molar ratio and 1.6 wt% of H_2SO_4/FFA at the first step (Deng et al., 2010). In the later step, 96.4% of ester content was obtained in a quite lightly reaction condition (MeOH/Oil molar ratio: 6, NaOH/Oil: 1.4 wt%, 60 °C, 60 min). Recently, only 20 min was needed to reduce FFA from 12.5 to less than 2.8 wt% at ambient temperature (30 °C) and other conditions (MeOH/FFA molar ratio: 10, H_2SO_4/FFA: 24 wt%) (Worapun et al., 2010). However, only 90% of ester content was gained at 30 °C. This low yield of ester can be improved by reaction conditions at the second step (MeOH/Oil molar ratio: 4, KOH/Oil: 1 wt%, 40 min). An experimental set-up for ultrasonic irradiation heating technology is shown in Fig. 3.

Radio frequency (RF) heating is another promising dielectric heating technology which provides fast heat generation through a direct interaction between a RF electromagnetic field and the object. RF heating technology was applied to create biodiesel from WCO by E + T technology (Liu et al., 2010). In the first step, FFA content was decreased from 34.1 wt% to 0.82 wt% within 8 min at 65 °C by using 20 of MeOH/FFA molar ratio, 8.8 wt% of H_2SO_4/FFA. In the second step, esterified feedstock oil reacted with MeOH followed a MeOH/Oil molar ratio (14.2) and 0.91 wt% of NaOH/Oil at 65 °C under RF heating for 5 min. Ester content could be achieved to 98.8%. The modern heated E + T technology is summarized in Table 2.

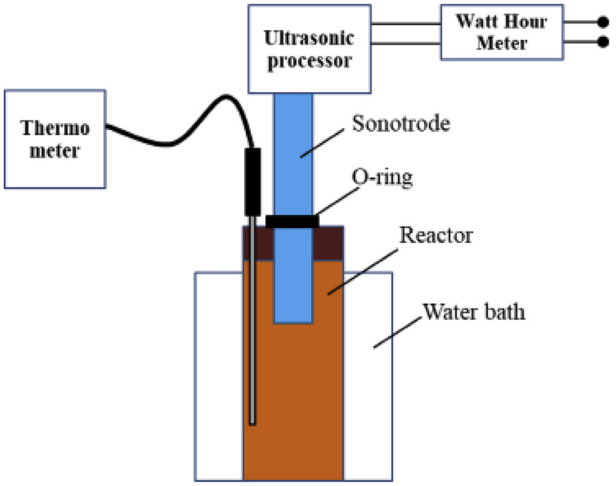

Fig. 3. Experimental set-up for ultrasonic irradiation heating technology.

3. Two-step transesterification (T1 + T2 technology)

3.1. T1 + T2 process catalyzed by base catalyst on both stages

Mendow studied an efficient T1 + T2 two-step process for ethyl esters production using solid sodium methoxide catalyst (Mendow et al., 2011) (Table 3). This process consists of two reaction steps with glycerol separation and an additional part of mixture ethanol and catalyst in each of stages. The optimum condition is listed as EtOH/Oil molar ratio of 4.25:1 (2.55:1 for T1 and 1.7:1 for T2), CH_3ONa content of 1.1 wt% (0.55 wt% for each step) in the same temperature and time (55 °C and 30 min). Biodiesel with ester content of 99% was attained and meets the required international standards.

In order to extend the ability of using non-edible feedstock for this process, Predojevíc produced biodiesel by two-step alkali transesterification of WCO using methanol and KOH as base catalyst (Predojevic, 2008). Each stage of this process was followed by glycerol separation, purification and drying. The two-step transterification utilized a total molar ratio of methanol to oil of 6:1 (3:1 for each step), a total catalyst content of KOH to oil of 1 wt% (0.5 wt% for each step) in the same reaction time (30 min) at 30 °C and 60 °C, respectively. Three different methods have been chosen for the purification of the product mixture after the transesterification reaction: washing the mixture with (a) silica gel, (b) 5% phosphoric acid, and (c) hot distilled water. The comparison of three purification methods showed similar biodiesel yield after silica gel or acid washing (about 92%). A lower yield was achieved after the washing process by hot distilled water (about 89%). The ester content was obtained more than 97% after purification process and absolutely suitable for the minimum acceptable biodiesel purity according to standard EN 14103 (96.5 min).

Ultrasonic irradiation assisted technology is considered as a modern method in a two-step transesterification process to approach economic and efficient biodiesel production (Thanh et al., 2010). The transesterification was carried out with the molar ratio of methanol to WCO of 2.5:1 and 1.5:1, the content of KOH to WCO to 0.7 wt% and 0.3 wt%, time of 25 min and 20 min at ambient temperature (30 °C) for first step and second step, respectively. The ester content of 99% achieved in the short time and at low temperature is a remarkable proof for this technology.

3.2. T1 + T2 process catalyzed by base catalyst in first step and acid catalyst on second step

The applications of base catalyst for both steps in T1 + T2 process have advantages of fast reaction rate with low alcohol/oil molar ratio

Table 2
Summarized E + T technology under modern heating technology.

Raw material	Heating technology	Optimum condition for the first step esterification	Optimum condition for the second step transesterification	Ester content (wt%)	Yield of biodiesel (%)	Reference
Crude palm oil	Microwave irradiation	EtOH/FFA molar ratio = 24, H_2SO_4/FFA = 4 wt%, 70 W, 60 min	EtOH/Oil molar ratio = 4, KOH/Oil = 1.5 wt%, 70 W, 5 min	97.4	80	[Suppalakpanya et al., 2010]
Jatrophacurcas L. oil	Microwave irradiation	EtOH/FFA molar ratio = 54, H_2SO_4/FFA = 5 wt%, 110 W, 35 min	5N KOH (in EtOH)/Oil = 16.3 wt%, 110 W, 12.21 min	97.29	90.01	[Jaliliannosrati et al., 2013]
Crude Jatrophacurcas L. oil	Ultrasonic irradiation (40 KHz, 400 W)	MeOH/FFA molar ratio = 10, H_2SO_4/FFA = 24 wt%, 30 °C, 20 min	MeOH/Oil molar ratio = 4, KOH/Oil = 1 wt%, 30 °C, 40 min	90	ND	[Worapun et al., 2010]
Jatrophacurcas L. oil	Ultrasonic irradiation	MeOH/FFA molar ratio = 60, H_2SO_4/FFA = 1.6 wt%, 60 °C, 1 h	MeOH/Oil molar ratio = 6, NaOH/Oil = 1.4 wt%, 60 °C, 1 h	96.4	ND	[Deng et al., 2010]
Crude palm oil	Microwave irradiation	EtOH/FFA molar ratio = 26, H_2SO_4/FFA = 16.7 wt%, 78 W, 90 min	EtOH/Oil molar ratio = 8.5, KOH/Oil = 1.7 wt%, 78 W, 7 min	97.4	78	[Suppalakpanya et al., 2011]
WCO	Radio frequency	MeOH/FFA molar ratio = 20, H_2SO_4/FFA = 8.8 wt%, 65 °C, 8 min	MeOH/Oil molar ratio = 14.2, NaOH/Oil = 0.91 wt%, 65 °C, 5 min	98.8	ND	[Liu et al., 2010]

ND: not determined.

and high ester content. However, the base catalyst causes saponification and leads to loss of yield. In order to overcome this difficulty, T1 + T2 two-step transesterification procedure which included base transesterification followed by acid transesterification was indicated clearly in some studies (Kumar et al., 2014; Samios et al., 2009; Guzatto et al., 2011; Thoai et al., 2017). A typical process diagram of two-step transesterification process (T1 + T2) is shown in Fig. 4.

Microalgae was considered as an alternative feedstock for T1 + T2 two-step direct transesterification process (Kumar et al., 2014). Conventional lipid extraction (Bligh and Dyer, 1959) and transesterification method were found to underestimate the total biodiesel yield. This novel two-step direct transesterification technology can bypass the solvent extraction steps. This decreases using chloroform and methanol which leads to reduction of adverse effects on health and environment (Cheng et al., 2011). A two-step direct transesterification method using NaOH in first step and H_2SO_4 in second step was reported (Kumar et al., 2014). It experimented with three types of biomass (wet, oven dried and lyophilized biomass). With lyophilized biomass, the ester content was gained up to 94.5% under optimum condition, including methanol to biomass weight ratio 51.59 (w/w) and 51.3 (w/w), catalyst to biomass weight ratio 0.67 (w/w) and 3.81 (w/w), reaction time 19.33 min and 10 min at 90 °C in first step and second step, respectively.

The significant development of this technology was mentioned in two research works of Samios et al. which was called “Transesterification Double Step Process” (TDSP) (Samios et al., 2009; Guzatto et al., 2011). This process includes continuous homogeneous base–acid catalyst steps. Also it proved the effectiveness by high reaction rate, easy separation process as well as high conversion (Samios et al., 2009). The ester content can be higher than 97% at 60 °C by adding 10 and 15 of MeOH/Oil molar ratio, 1.15 wt% of KOH and 15.9 wt% of H_2SO_4 to Oil for first step and second step, respectively, for each step. The improved TDSP process involves the reduction of reaction conditions (catalyst content in both steps, MeOH/Oil molar ratio in second step, reaction time in first step) and direct adding of MeOH/H_2SO_4 solution without cooling the reaction system between first and second step (Guzatto et al., 2011).

4. Conclusions and recommendations

The two-step reaction technology in biodiesel production was carefully analyzed, summarized and discussed. Following conclusions and recommendations are drawn:

- ➢ Even though lot of research has been conducted on biodiesel synthesis, the cost of biodiesel production is still a question because it is somewhat higher than petroleum-diesel.
- ➢ In order to reduce the production cost, the two-step reaction technology has proven its superiority over one step reaction process in biodiesel production in term of using various feedstock, decreasing of alcohol and catalyst content, and acquiring smoother reaction conditions, higher conversion, higher ester content, and biodiesel yield.
- ➢ Moreover, future studies should be focused on finding cost effective biodiesel production process by exploring a novel and cost effective feedstock. The WCO and biomass are potential as economical feedstock for biodiesel production.
- ➢ Two-step technology uses base catalyst for the second step. It increases the conversion and lead to improve the ester content. Nevertheless, base catalyst also accelerates the saponification reaction. Soap formation prevents from the separation of biodiesel, glycerol and washed water and is also crucial reason of biodiesel loss.
- ➢ In order to overtake on this unexpected problem, H_2SO_4 is considered as a homogeneous acid catalyst for second step in some studies.
- ➢ Homogeneous acid catalyst causes corrosion on equipment, it is

Table 3
Summary T1 + T2 technology.

Raw material	Heating system	Optimum condition for T1	Optimum condition for T2	Ester content (%)	Yield of biodiesel (%)	Reference
Microalgae (biomass)	Oil bath	MeOH/Biomass (wt/wt) = 41.59, NaOH/Biomass (wt/wt) = 0.67, 90 °C, 19.33 min	MeOH/Biomass (wt/wt) = 51.3, H_2SO_4/Biomass (wt/wt) = 3.81 wt%, 90 °C, 10 min	94.5	ND	[Kumar et al., 2014]
Vegetable oil (Sunflower and linseed oil)	Oil bath	MeOH/Oil molar ratio = 10, KOH/Oil = 1.15 wt%, 60 °C, 60 min	MeOH/Oil molar ratio = 15, H_2SO_4/Oil = 15.9 wt%, 60 °C, 60 min	97	85	[Samios et al., 2009]
WCO	Ultrasonic irradiation	MeOH/Oil molar ratio = 2.5, KOH/Oil = 0.7 wt%, 30–32 °C, 25 min	MeOH/Oil molar ratio = 1.5, KOH/Oil = 0.3 wt%, 27–29 °C, 20 min	99	93.8	[Thanh et al., 2010]
Refined palm oil	Oil bath	EtOH/Oil molar ratio = 2.55, CH_3ONa/Oil = 0.55 wt%, 55 °C, 30 min	EtOH/Oil molar ratio = 1.7, CH_3ONa/Oil = 0.55 wt%, 55 °C, 30 min	99	ND	[Mendow et al., 2011]
Vegetable oil (Sunflower and linseed oil) and WCO	Oil bath	MeOH/Oil molar ratio = 10, KOH/Oil = 0.63 wt%, 60 °C, 30 min	MeOH/Oil molar ratio = 5, H_2SO_4/Oil = 5.3 wt%, 60 °C, 60 min	97–98	87–93	[Guzatto et al., 2011]
WCO (waste sunflower oil)	Oil bath	MeOH/Oil molar ratio = 3, KOH/Oil = 0.5 wt%, 30 °C, 30 min	MeOH/Oil molar ratio = 3, KOH/Oil = 0.5 wt%, 60 °C, 30 min	97–98	89–92	[Predojevic, 2008]
WCO	Oil bath	EtOH/Oil molar ratio = 12, KOH/Oil = 1 wt%, 78 °C, 120 min	EtOH/Oil molar ratio = 5, KOH/Oil = 0.75 wt%, 78 °C, 120 min	94.5	ND	[Encinar, 2007]
Sunflower oil	Oil bath	EtOH/Oil molar ratio = 12, NaOH/Oil = 1 wt%, 80 °C, 150 min	EtOH/Oil molar ratio = 6, NaOH/Oil = 0.75 wt%, 80 °C, 30 min	96.5	ND	[Anastopoulos et al., 2009]

ND: not determined.

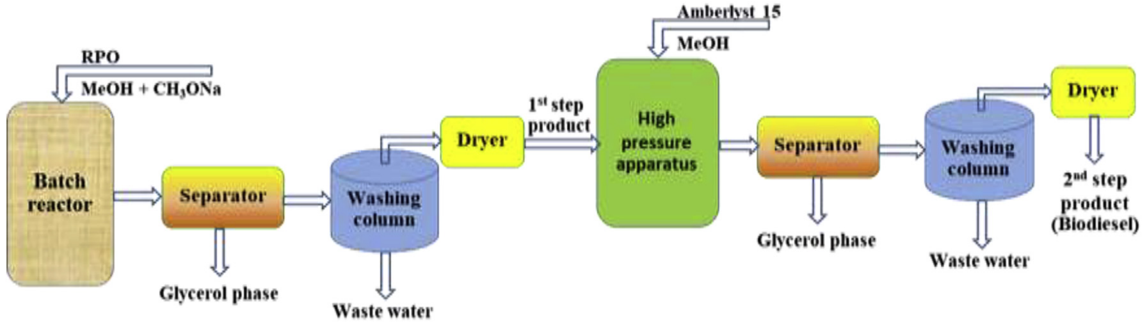

Fig. 4. Schematic diagram of two-step transesterification process [Thoai et al., 2017].

recommended that researches on heterogeneous acid catalyst should be carried out extensively to develop this two-step technology in biodiesel production. Two more advantages of heterogeneous acid catalyst are its reusability and stability. These strengths contribute to decrease the production cost and strengthen the competition of biodiesel with petroleum diesel.

- The two-step transesterification via the first step using homogeneous base catalyst and the second step using heterogeneous acid catalyst may lead to upcoming research interest.
- In the two-step transesterification, the second step transesterification using heterogeneous catalyst is the rate-limiting step. Therefore, the second step transesterification should be studied first in order to find the optimum composition of second step feedstock that supports a mild condition of using solid catalyst and results in better quality of commercial biodiesel product (96.5% ester min.). After that, study of the first step transesterification using homogeneous base catalyst should be carried out in order to determine the optimum condition for this step. This will incorporate the advantage of both catalysts in biodiesel production process.

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