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Techno-economic analysis of biodiesel production from waste cooking oil using supercritical and subcritical processes

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ABSTRACT

In this study, design of biodiesel production process from waste cooking oil through supercritical and subcritical processes with co-solvent methods was studied. The processes with production capacity of 10,000 tons a year were designed and simulated using the simulation software Aspen Plus. Simulation results showed that both processes can provide purity of fatty acid methyl ester as biodiesel standard. Furthermore, economic analysis was performed using Aspen Process Economic Analyzer. Results showed that the subcritical with co-solvent process is more economically promising, that is, the process has lower capital cost, lower payout period, and higher internal rate of return.

Keywords: biodiesel; transesterification; supercritical condition; technical study; economic study

1. INTRODUCTION

An increase in world energy demand results in depletion of fossil fuel and highlights the need for alternative fuel sources. Biodiesel is an alternative resource that is renewable, biodegradable, non-toxic, and can be used directly in diesel engines without modification (Srivastava and Prasad, 2000). In Thailand, biodiesel is also an important fuel as the production rate has increased continually over a decade.

Biodiesel can be produced from many types of oils such as sunflower, jatropha, and palm oil, but it is not competitive in the market due to its high production cost. The main reason is the price of feedstock oils (Zhang et al., 2003a,b), which can be up to 80% of the total cost when virgin oil is used (Marchetti et al., 2008). Using cheaper feedstock such as waste cooking oil is interesting. Nevertheless, waste cooking oil contains a certain amount of free fatty acids (FFAs) that can produce soap through saponification, causing difficulties in the purification process when conventional alkali-catalyzed transesterification is used (Freedman et al., 1984).

Acid-catalyzed transesterification is a possible way to produce biodiesel from waste cooking oil. Acid can catalyze esterification and transesterification simultaneously, that is, both FFAs and triglycerides (TGs) can be converted to fatty acid methyl ester (FAME) or biodiesel. However, a major drawback of this method is its slow reaction rate. For 80% conversion, the reaction time required might be up to 48 hours (Canakci and Gerpen, 2001). To solve this problem, a two-step method (Canakci and Gerpen, 2001; Marchetti et al., 2008) is proposed by using the acid-catalyzed method for removal of FFAs and then

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applying alkali-catalyzed method for fast reaction. Nevertheless, the process of biodiesel production via the two-step method can be extremely complex.

Another promising way to produce biodiesel from waste cooking oil is supercritical transesterification (Kusdiana and Saka, 2004; He et al., 2007; Kasteren and Nisworo, 2007; West et al., 2008). Using supercritical condition can improve solubility between oils and methanol, thereby resulting in short reaction time for transesterification. This method does not use catalysts and therefore is not sensitive to the amount of FFAs. Furthermore, separation step of catalysts is reduced compared with conventional processes. However, the major disadvantage of supercritical transesterification is the operation at very high pressure and temperature. To have a mild condition, we proposed inclusion of co-solvents in the reaction to improve solubility of oils and methanol.

Cao et al. (2005) have shown that the supercritical methanol with propane as co-solvent is superior to the conventional supercritical methanol method. Yin et al. (2008) investigated biodiesel synthesis from soybean oil using supercritical and subcritical methanol in the presence of hexane, carbon dioxide, and potassium hydroxide as co-solvents. The results indicated that the yield of methyl ester was significantly improved. Jiang and Tan (2012) have tested eight co-solvents, namely, heptane, ether, cyclohexane, carbon dioxide, n-hexane, dimethyl ether, toluene, and propane, for the supercritical methanol method. The effects of temperature, pressure, molar ratio of methanol to oil, and molar ratio of methanol to co-solvent to methyl ester yield were also investigated.

The objective of this study was to examine biodiesel production from supercritical and subcritical approaches with co-solvent transesterification processes. Propane was selected as co-solvent because it is more attractive in terms of product purification and co-solvent recycling (Sawangkaew et al., 2010). The process design was conducted using simulation software Aspen Plus. Technical and economic assessments of the two processes were performed and discussed in this paper.

2. MATERIALS AND METHODS

In Thailand, the Ministry of Energy estimated that 100 million liters of waste cooking oil a year are produced. Thus, waste cooking oil is a potential feedstock for biodiesel production. In this study, the production rate is set as 10,000 tons a year. As waste cooking oil can contain 2-10% w/w of FFAs (Lepper and Friesenhagen, 1986), the 5.2% w/w of FFAs in waste-cooking oil is assumed. As palm oil is a major source of cooking oil in Thailand, the composition of palm oil adopted from Che Man et al. (1999) is used in this study. The process of biodiesel production is designed to meet the European standard EN 14214 (96.5% w/w of FAME) for biodiesel and technical grade (98% w/w of glycerol) for the byproduct glycerol.

In the process design, a process simulator called Aspen Plus was used. The Redlich-Kwong-Aspen equation of state (RK-Aspen EOS) was selected as property method due to the polarity interaction and critical operating condition (Weber et al., 1999; Glisic and Skala, 2010; Almagrbi et al., 2012). Aspen Economic Analyzer was used for equipment sizing and economic calculation.

3. RESULTS AND DISCUSSION

3.1 Supercritical transesterification processes

In transesterification, as shown in Figure 1, one mole of triglyceride (TG) reacts with three moles of methanol (MeOH) to produce three moles of FAME or biodiesel as product and one mole of glycerol (GL) as byproduct.

As the transesterification reaction is reversible, an excess amount of methanol is typically required for high conversion. In conventional transesterification, an alkali catalyst, such as NaOH, is usually preferred compared with an acid catalyst due to shorter reaction time (Freedmann et al., 1984). However, when waste cooking oil was used as feedstock, saponification of NaOH and free fatty acid to produce soap could reduce reaction efficiency (e.g., consumed catalyst) and cause difficulties in separation processes. Although pre-treatment of cooking oil to remove free fatty acid is possible, it makes the process more complex (Zhang et al., 2003a,b).

TG + MeOH	<=>	DG + FAME
DG + MeOH	<=>	MG + FAME
MG + MeOH	<=>	GL + FAME

TG + 3MeOH	<=>	GL + 3FAME

Figure 1 Transesterification of triglycerides and methanol (MeOH = methanol; TG = triglyceride; DG = diglyceride; MG = monoglyceride; GL = glycerol)

A promising method to solve this problem is catalyst-free supercritical transesterification. At the supercritical condition of methanol (critical points of methanol: 239°C and 8.09 MPa), the dielectricity is decreased, thereby resulting in higher solubility between methanol and oils. Transesterification can be completed within 2-4 minutes at 350°C (Kusdiana and Saka, 2001, 2004) and methanol to oil molar ratio 42:1. The conversion from the simulation of the reactor is almost 0.97, which is in accordance with the results reported by Kusdiana and Saka (2001).

When waste cooking oil was used as feedstock in the supercritical methanol method, free fatty acid can react with methanol through esterification to produce FAME and water as product, as shown in Figure 2.

FFA + MeOH <=> FAME + H_2O

Figure 2 Esterification of free fatty acid and methanol

In supercritical transesterification, transesterification and esterification can proceed simultaneously in the reactor. In this study, the kinetic information of supercritical transesterification was taken from Kusdiana and Saka (2001), whereas esterification converted free fatty acid completely due to its fast reaction (Warabi et al., 2004).

After the transesterification, the outlet stream usually consisted of mixtures, including excess methanol, unconverted oils, FAME, and GL. Thus, further separation tasks were required for recovery of methanol to reuse in transesterification, purification of FAME to biodiesel standard, and purification of GL to technical grade. Note that an advantage of the supercritical transesterification process compared with the conventional alkali-catalyzed method was that the former does not require separating catalysts.

Although methanol has a much lower boiling point than the other components, our simulation shows that flash vessel cannot provide satisfaction in methanol recovery. Thus, a distillation column was selected as methanol recovery column. After methanol separation, the mixture stream tended to be in the state of two phases of FAME and GL phases. The phase separation can be achieved using a decanter. Then, each phase was further purified to have the purity of FAME 96.5% w/w and GL 98% w/w.

Remark 1 Although separation of FAME and GL phases before methanol separation was possible, this process required two methanol recovery columns for each phase. Thus, this study proposed to perform methanol separation before the phase separation.

Remark 2 Myint et al. (2009) discussed that separation of methanol before the phase separation of FAME and GL can cause a reversible pathway of transesterification. However, in this study, the supercritical condition was relieved before the separation section and thus, this problem was addressed.

Biodiesel production process using supercritical transesterification is shown in Figure 3. The waste cooking oil (stream 105) and methanol (stream 101) were pressurized and heated to supercritical condition (350°C and 25 MPa) before entering the tubular reactor R-100 with the methanol to oil molar ratio 42:1 and 4-minute reaction time. Esterification of free fatty acid and transesterification of TGs will proceed in the reactor to produce FAME and GL as products.

In the separation section, because no catalyst is involved in the reaction, a separation unit was not needed to remove it. The outlet stream from the reactor was adjusted to a mild condition and then sent to a methanol recovery column T-200 to recover excess methanol for reuse in the reaction. Thereafter, decanter X-300 was used to separate the FAME and glycerol phases. The FAME phase was further purified to meet EN 14214 biodiesel standard using the distillation column T-400. For the glycerol phases, the simulation shows that 98% w/w of glycerol can be achieved without further purification.

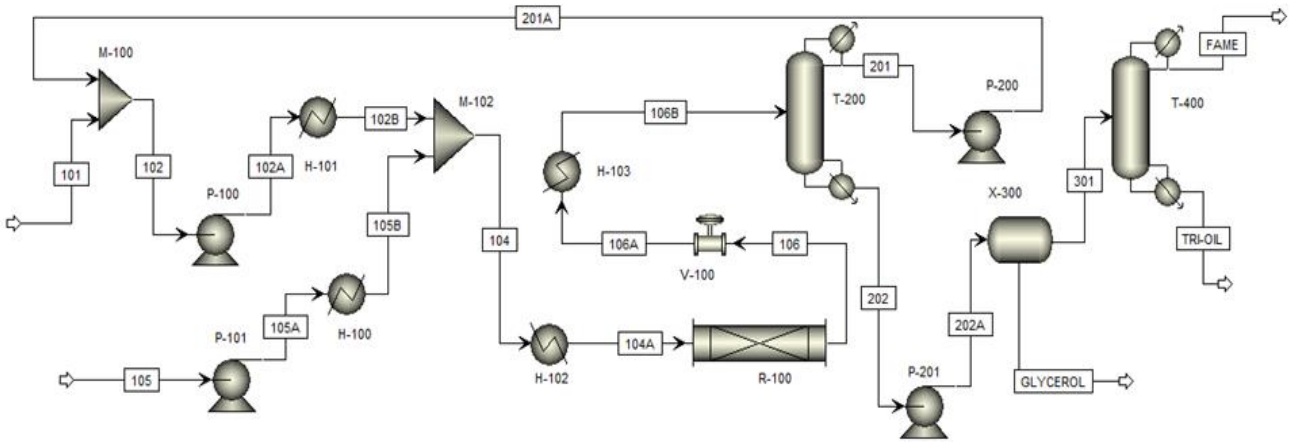

Figure 3 Biodiesel production process using supercritical transesterification

3.2 Subcritical transesterification with co-solvent processes

A drawback of supercritical transesterification is the supercritical operating condition. Using co-solvents, such as carbon dioxide, propane, and hexane, can improve the solubility of oils in methanol, and thus, a milder operating condition of subcritical transesterification is possible (Cao et al., 2005; Yin et al., 2008; Sawangkaew et al., 2010). In this study, propane was selected as co-solvent in subcritical transesterification with co-solvent process because propone is more attractive than other co-solvents in terms of product purification and recycling (Sawangkaew et al., 2010).

Addition of co-solvent improved the solubility of oils in methanol without affecting the reaction. Thus, the reaction pathways in Figures 1 and 2 remain valid in this section. The reaction information for the simulation was adapted from Cao et al. (2005) in which 0.05 molar ratio of propane to methanol was used. The other operating conditions were molar ratio of methanol to oils 24:1, temperature 280°C, pressure 12.8 MPa, and reaction time 10 minutes. The conversion from the simulation of the reactor was almost 0.99, which is in agreement with the findings of Cao et al. (2005).

In the separation section, the only additional component from the reactor to be considered was the co-solvent propane. Thus, the separation section in the subcritical process was slightly modified from the separation section in the supercritical process by addition of a propane separation unit. As propane has a much lower boiling point than the other components, a simple flash unit can be used for propane recovery.

Figure 4 shows biodiesel process using subcritical transesterification with co-solvent. The waste cooking oil (stream 105), propane (stream 103), and methanol (stream 101) were pressurized and heated to subcritical condition (280°C and 12.8 MPa) before entering the tubular reactor R-100 with the methanol to oil molar ratio 24:1 and 10-minute reaction time. Esterification of free fatty acid and transesterification of TGs proceeded simultaneously in the reactor to produce FAME and GL as products.

The outlet stream from the reactor was adjusted to a milder condition. Thereafter, propane and methanol were recovered using a flash unit X-200 and methanol recovery column T-300, respectively, for reuse in the reaction. Then, the decanter X-400 separated the FAME and GL phases. The FAME phase was further purified to meet EN 14214 biodiesel standard using the distillation column T-500. For the GL phase, the simulation showed that 98% w/w of GL can be achieved without need of further purification. Compared with the supercritical transesterification process, the subcritical process required only a flash unit as additional equipment in the separation section for propane recovery.

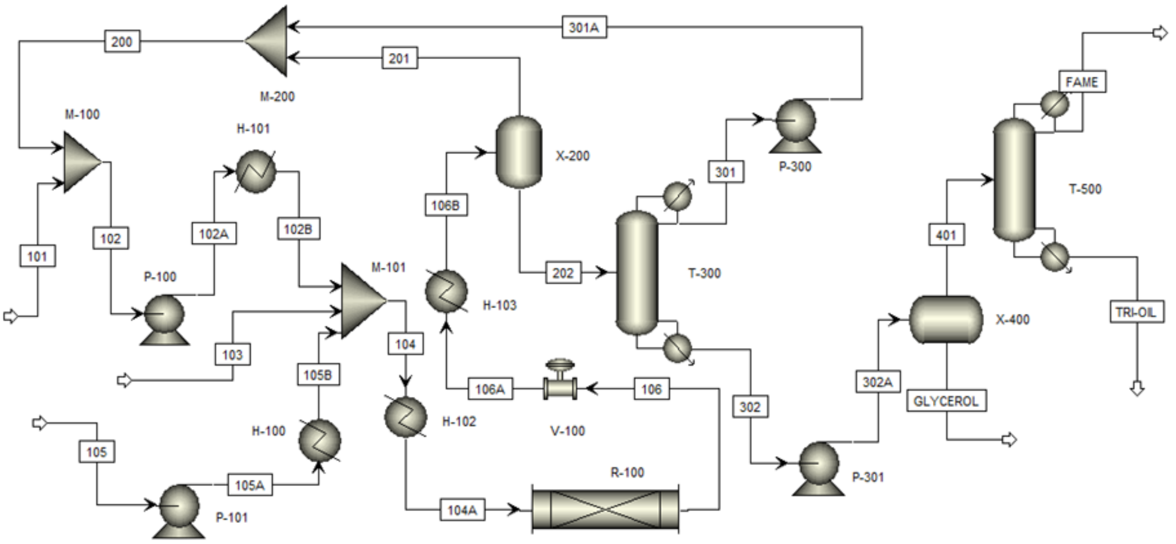

Figure 4 Biodiesel production process using subcritical transesterification with co-solvent

3.3 Technical assessment of biodiesel production processes

Simulation results showed that supercritical transesterification and subcritical transesterification with co-solvent processes were feasible, that is, both processes can provide purity of FAME as the standard EN 14214 and purity of GL as the technical grade.

A comparison of major equipment in the processes showed that both processes required a transesterification reactor, a methanol recovery column, and a FAME purification column. However, the subcritical process requires an additional equipment of flash unit for propane recovery.

The presence of co-solvent improved the solubility of oils and methanol (Cao et al., 2005), thereby resulting in milder operating condition and lower molar ratio of methanol to oils. Table 1 shows operating conditions, size, and material of major equipments of the two processes. The reactor of the subcritical process had a milder operating condition than the reactor of the supercritical process. Furthermore, the lower molar ratio of methanol to oils in the subcritical process compared with the supercritical process resulted in a smaller size of the reactor and methanol recovery column. For material selection, budget carbon steel was chosen for all equipments except the reactor operating at high pressure and temperature in which stainless steel 316 was more appropriate.

Table 1 Comparison of operating condition, size, and material of equipment in each process

Equipment		**Supercritical transesterification process**	**Subcritical transesterification with co-solvent process**
Reactor	Operating condition	350°C /25bar	280°C /12.8bar
	Size (DxH)	0.37 m x 5.00 m (5 tubes)	0.2 m x 3.00 m (5 tubes)
	Material	316SS	316SS
Methanol recovery column	Operating condition	22.86°C /136.09°C 0.15 bar	19.47°C /140.80°C 0.35 bar
	Size (DxH)	3.54 m x 5.9 m	3.81 m x 3.12 m
	Material	CS	CS
Mythylester purification column	Operating condition	208.54°C /493.91°C 0.5 bar	207.56°C /515.57°C 1 bar
	Size (DxH)	2.74 m x 6.71 m	2.90 m x 7.24 m
	Material	CS	CS

Energy usage in supercritical transesterification and subcritical transesterification with co-solvent processes is shown in Table 2. The supercritical process required 7,152 kW for cooling and 10,597 kW for heating, which is almost twofold of the heat duty required in the subcritical process. More heat duty was required for higher operating temperature. Furthermore, a higher amount of methanol involved in the reaction implied that greater reboiler duty was required for vaporization of methanol in the recovery column.

Table 2 Comparison of energy usage in each process

Energy usage in	**Supercritical transesterification**	**Subcritical transesterification with co-solvent**
Reaction section	0/3036 kW	0/1816 kW
Methanol recovery column	5716/5946 kW	1803/1902 kW
Mythylester purification column	1436/1615 kW	1646/1822 kW

*Cooling/Heating

Technical assessment revealed that the subcritical process was more promising because it required a milder operating condition and was safer in terms of process operation point of view. The process also required smaller equipment and less energy usage.

Although the subcritical process required less energy usage than the supercritical process, net specific energy usage was still much higher than that in other biodiesel production processes. For example, a recent heterogeneous process using hybridization of esterification and transesterification in a single reactive distillation (Petchsoongsakul et al., 2017) required 666 kWh/ton of biodiesel while the proposed supercritical and subcritical processes required 9,283 and 4,853 kWh/ton of biodiesel, respectively.

3.4 Economic assessment of biodiesel production processes

The prices of chemicals used in the calculation are listed in Table 3.

Table 3 Prices of chemicals used in the economic evaluation

Chemicals	Price	Unit
Waste cooking oil	20.00	(Baht/kg)
Methanol	14.92	(Baht/kg)
Biodiesel	31.53	(Baht/kg)
Glycerol (98% w/w)	28.00	(Baht/kg)
Propane	10.79	(Baht/L)

For economic calculation, Aspen Economic Analyzer was used, which included mapping and sizing of process equipment, and evaluation of economic factors, as summarized in Tables 4-5. The results showed that the cost of transesterification reactor and methanol recovery column in the supercritical process was higher than that in the subcritical process. This condition corresponded with the larger reactor and column required in the supercritical process, as shown in Table 1. In terms of total capital investment, the subcritical process was almost 155 million baht cheaper than the supercritical process.

Table 4 Equipment cost of each process (million bahts)

Equipment	Supercritical transesterification process	Subcritical transesterification with co-solvent process
Transesterification reactor	34.39	6.94
Methanol recovery column	74.10	33.96
FAME purification column	47.66	49.36
Other equipment[1]	132.21	115.00
Total equipment cost[2]	288.36	205.26
Total capital investment[3]	681.37	526.41

[1] Other equipment include heat exchangers, pumps, and separators.

[2] Total equipment cost includes the cost of major equipment, other equipment, contingency and fees.

[3] Total capital investment includes the cost of total equipment cost, equipment setting, piping, instrumentation, etc.

Table 5 Cost and revenue and economic indices of each process

	Supercritical transesterification process	Subcritical transesterification with co-solvent process
Cost and revenue		
Total capital investment (million bahts)	681.37	526.41
Total manufacturing cost (million bahts)	649.56	643.01
Revenue from biodiesel (million bahts)	882.99	884.06
Economic indices		
Internal rate of return (%)	31.89	36.74
Modified internal rate of return (%)	20.52	20.60
Net return rate (%)	9.11	10.46
Payout period (yrs)	7.55	6.13
Accounting rate of return (%)	187.81	227.51
Profitability index	1.09	1.10

Table 5 shows cost and revenue and economic indices of each process. The total manufacturing cost that includes direct manufacturing cost (e.g., raw material, utility, and man hours) and indirect manufacturing cost (e.g., depreciation and taxes) of the supercritical process was 649.56 million baht, which was slightly higher than the cost in process #2. Although process #1 had higher energy consumption that was almost two times as shown in Table 2, the major cost of manufacturing cost was feedstock oil. In our results, the cost of feedstock oil was almost 90% of the total manufacturing cost. At a glance, both processes were economically feasible because revenue from biodiesel was higher than total manufacturing cost.

All economic indices showed that both processes were economically feasible. For example, if accounting rate of return was more than the internal rate of return, then the project was acceptable. Profitability index ≥ 1 also revealed that both plants were acceptable. However, comparison of the two processes showed that process #2 was more promising in terms of all economic indices, that is, higher internal rate of return, higher net return rate, lower payout period, higher accounting rate of return, and higher profitability index.

4. CONCLUSION

In this study, the design of biodiesel production process from waste cooking oil with capacity of 10,000 tons a year via supercritical and subcritical with co-solvent methods was analyzed. The processes were designed and simulated using the simulation software Aspen Plus. The simulation results showed that both processes can provide purity of FAME as biodiesel standard and GL as technical grade. However, comparison of the two processes showed that the subcritical with co-solvent method has a smaller reactor, smaller methanol recovery column, and milder and safer operating conditions. Furthermore, economic analysis of the processes was performed using Aspen Economic Analyzer. The results showed that the subcritical with co-solvent process is more economically promising, that is, the process has lower capital cost, lower payout period, and higher internal rate of return.

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