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A process model to estimate the cost of industrial scale biodiesel production from waste cooking oil by supercritical transesterification

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Abstract

This paper describes the conceptual design of a production process in which waste cooking oil is converted via supercritical transesterification with methanol to methyl esters (biodiesel).

Since waste cooking oil contains water and free fatty acids, supercritical transesterification offers great advantage to eliminate the pre-treatment capital and operating cost.

A supercritical transesterification process for biodiesel continuous production from waste cooking oil has been studied for three plant capacities (125,000; 80,000 and 8000 tonnes biodiesel/year). It can be concluded that biodiesel by supercritical transesterification can be scaled up resulting high purity of methyl esters (99.8%) and almost pure glycerol (96.4%) attained as by-product.

The economic assessment of the biodiesel plant shows that biodiesel can be sold at US\$ 0.17/l (125,000 tonnes/year), US\$ 0.24/l (80,000 tonnes/year) and US\$ 0.52/l for the smallest capacity (8000 tonnes/year).

The sensitive key factors for the economic feasibility of the plant are: raw material price, plant capacity, glycerol price and capital cost.

Overall conclusion is that the process can compete with the existing alkali and acid catalyzed processes.

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Especially for the conversion of waste cooking oil to biodiesel, the supercritical process is an interesting technical and economical alternative.

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Keywords: Biodiesel; Waste cooking oil; Supercritical transesterification; Process design

1. Background

It is estimated that in the coming years, the fossil oil price will increase because the oil production cannot meet the projected demand due to oil depletion (Association of Peak Oil and Gas, 2004). This is a result of overconsumption in the developed countries and overpopulation in the developing countries (Korbitz, 1999).

A lot of efforts have been carried out to develop an alternative fuel for the current energy and transportation vehicle system, i.e.: fuel cell, electric power, hydrogen or natural gas for internal combustion engines, etc. One of the promising alternatives that are applied in small scale production is biodiesel.

The American Society for Testing and Materials (ASTM) defines biodiesel fuel as monoalkyl esters of long chain fatty acids derived from renewable lipid feed stocks, such as vegetable oil or animal fat. “Bio” represents its renewable and biological source in contrast to traditional petroleum based diesel fuel; “diesel” refers to its use in diesel engines. As an alternative fuel, biodiesel can be used in neat form or mixed with petroleum based diesel.

Several sources for producing biodiesel have been studied such as rape seed, coal seed, palm oil, sunflower oil, waste cooking oil, soybean oil, etc. Due to the high cost of the fresh vegetable oil, waste cooking oil gives interesting properties because it can be converted to biodiesel and it is available with relatively cheap price (Nisworo, 2005; Zhang et al., 2003).

The most common way to produce biodiesel is by transesterification, which refers to a catalyzed chemical reaction involving vegetable oil and an alcohol to yield fatty acid alkyl esters (biodiesel) and glycerol (by-product) as can be seen in Fig. 1.

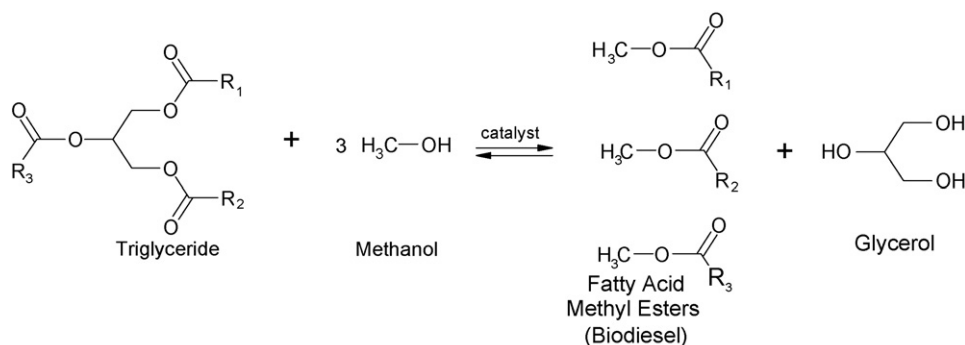


Fig. 1. Transesterification reaction of triglyceride and methanol to fatty acid methyl esters (biodiesel) and glycerol.

Transesterification reactions can be alkali-catalyzed, acid-catalyzed or enzyme catalyzed (Bunyakiat et al., 2006). An excess of methanol is used to shift the reaction to the right side in order to achieve high yield of methyl esters/biodiesel.

Most biodiesel industries use the alkali catalyzed process. One limitation to the alkali catalyzed process is its sensitivity to both water and free fatty acids. Free fatty acids can react with the alkali catalyst to produce soaps and water.

Therefore Freedman et al. (1984) stated that refined vegetable oils with free fatty acids content of less than 0.5% (acid value less than 1) should be used to maximize methyl esters formation.

The presence of water may cause ester saponification and can consume the catalyst and reduce the catalyst efficiency. The presence of water has a greater negative effect than that of the free fatty acids. Ma et al. (1998) stated that the water content should be kept below 0.06%.

Most industries use pre-treatment step to reduce the free fatty acid and water content of the feed stream. Usually free fatty acid is reduced via an esterification reaction with methanol in the presence of sulfuric acid. The pre-treatment step not only causes the production process to be less efficient (Kusdiana and Saka, 2004) but also increase the capital cost.

These facts hinder the efficient use of waste cooking oil, animal fats and crude oils as source for biodiesel since they generally contain water and free fatty acids.

There is an alternative for biodiesel production, namely the supercritical methanol method. The great advantages of supercritical methanol are:

- no catalyst required;
- not sensitive to both water and free fatty acid;
- free fatty acids in the oil are esterified simultaneously.

A comparison of the properties of the supercritical and conventional method can be seen in Table 1.

The absence of pre-treatment step, soap removal, and catalyst removal can significantly reduce the capital cost of a biodiesel plant, but the expected high operating cost due to high temperature and pressure can be a drawback for supercritical method. That is why it is interesting to see whether the supercritical methanol method is economically feasible to be applied in a biodiesel plant.

Table 1
Properties of supercritical and conventional transesterification

Properties	Supercritical	Conventional
Catalyst need	No (+)	Yes
Reaction time	Seconds–minutes	Minutes–hours
Temperature (°C)	200–300	50–80
Pressure (bar)	100–200	1
Free fatty acid sensitive	No (+)	Yes
Water sensitive	No (+)	Yes
Pre-treatment	No (+)	Yes
Catalyst removal	No (+)	Yes
Soap removal	No (+)	Yes

2. Design assumptions

- Production capacities are 125,000; 80,000 and 8000 tonnes methyl esters/year.
- 8000 working hours per year was used.
- Pressure drop of the process equipments is neglected.
- Water contamination was neglected as waste cooking oil contains low water content and the process is not water sensitive.
- Assumed waste cooking oil density is 953 kg/m³ and methyl esters (biodiesel) density of 840 kg/m³.
- Universal quasi-chemical (UNIQUAC) thermodynamic model was used due to the presence of highly polar components, i.e.: methanol and glycerol.
- The feed assumed to be 100% solid particle free.
- Assumed constant input of the waste oil feed for the whole production year.

3. Conceptual process design

The mass balance of the biodiesel production process is shown in Fig. 2.

The plant capacity was chosen based on the availability of waste cooking oil in The Netherlands (cbs; Dutch Central Bureau of Statistics, 2005). Based on the paid tax of waste cooking oil and animal fats value from the year 1999 to 2001 (20 Euro cent tax/l), a volume of 500 million liter of waste cooking oil and animal fat was calculated for The Netherlands. With the density of 953 kg/m³, the available waste cooking oil in The Netherlands is 457,440 tonnes/year.

Some of the waste cooking oil and animal fat is recycled and used as a fertilizer, soap, and filler for cosmetics industry. That is why design capacities of 125,000; 80,000 and 8000 tonnes/year are considered realistic for the process design and simulation. The costs of these capacities will be compared with the values of conventional biodiesel plant and will be studied to determine the effect of capacities on the economic feasibility of the plant.

Complete process simulation was carried out to assess the commercial feasibilities of the proposed processes.

The process simulation software, Aspen Plus[®] Version 11.1.1 developed by Aspen Technology Inc., Cambridge, Massachusetts, USA, was used in this research.

The procedures for process simulation mainly involve defining the chemical components, selecting a thermodynamic model, determining plant capacity, choosing proper operating units and setting up input conditions (flow rate, temperature, pressure and other conditions).

Information on most components, such as methanol, glycerol, propane, and water is available in the Aspen Plus[®] component library.

Regarding the waste cooking oil or animal fat feedstock, oleic acid is considered as the major component of the oils and fats used in the food industry in The Netherlands and Europe (Nisworo, 2005). Triolein (C₅₇H₁₀₄O₆) was chosen to represent the waste cooking oil or animal fat in the Aspen Plus[®] simulation. Methyl oleate (C₁₉H₃₆O₂) was chosen to represent the fatty acid methyl ester (biodiesel) product (as in agreement with Zhang et al., 2003).

Fig. 3 shows the process flow diagram (PFD) of the production plant. First, waste cooking oil is preheated in a heat exchanger (B17) to 40 °C to decrease the viscosity and improve

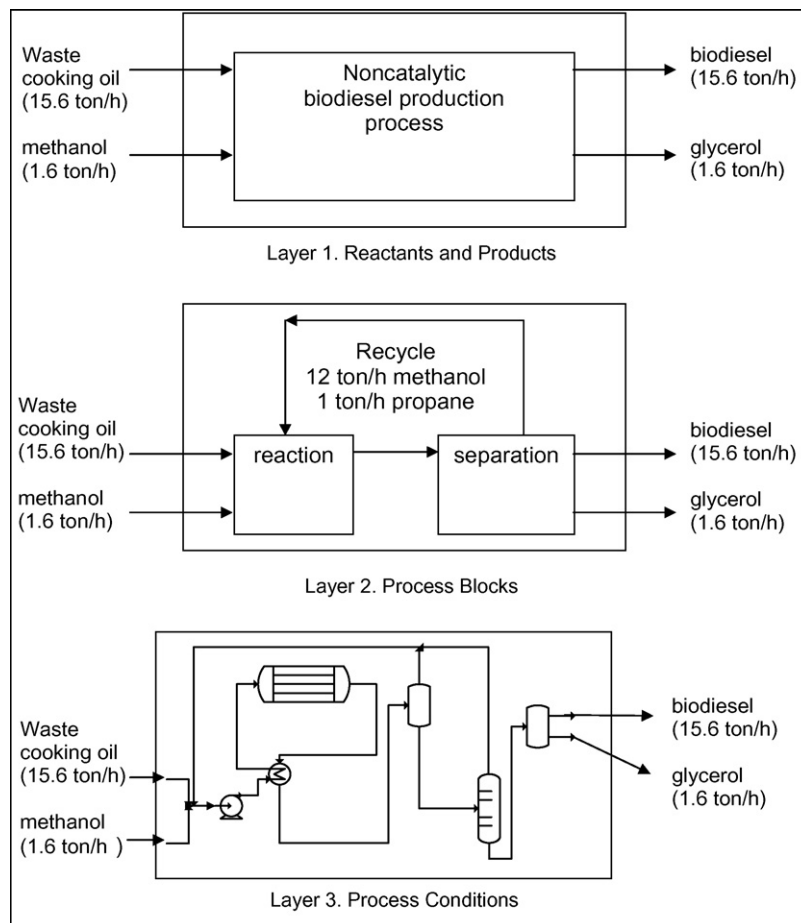


Fig. 2. Mass balance of supercritical transesterification process for waste cooking oil conversion to biodiesel, with a yearly capacity of 125,000 tonnes biodiesel/year.

the flow property. Oil methanol mol ratio used in this process design is 1:24 and propane (propane methanol molar ratio 1:20) used as co-solvent.

Propane is chosen as a co-solvent because it was proven to decrease the supercritical temperature from 320 °C to 280 °C, the supercritical pressure from 400 to 128 bar, and the methanol to oil ratio from 42 to 24 (mol base), respectively (Cao et al., 2005). According to the experiments (Cao et al., 2005) in pressurized autoclave, biodiesel yield was 98% in 10 min reaction time.

Fresh streams of oil and make up of methanol are pumped to 5 bar pressure and mixed in a mixer (B9) with the recycle stream of methanol and propane from the transesterification reaction and accommodated in the main reactor section (details can be seen in Nisworo (2005)). Propane solvent is soluble at 40 °C and 5 bar which leads to a reduction of a power consuming compressor.

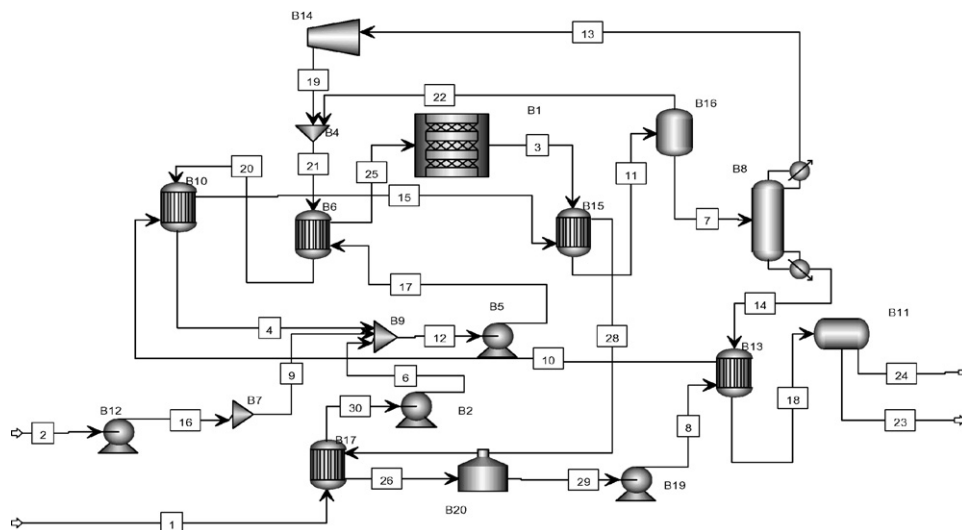


Fig. 3. Stream 1 is input fresh waste cooking oil, stream 2 is input of fresh methanol, stream 23 is output stream of glycerol and stream 24 is output stream of biodiesel product.

A cascade of heat exchangers is used to integrate heat of the process. The transesterification reaction is carried out in a tubular reactor (B1). Methanol and propane are recycled using a flash evaporator (B16) and a normal distillation column (B8). Finally biodiesel and glycerol are obtained from settler unit (B11). The operating units will be explained further in the coming sections.

Table 2
Design parameters of the supercritical transesterification reactor

Properties	Unit			
Design capacity	tonnes/year	125,000	80,000	8000
Temperature	°C		280	
Pressure	Bar		128	
Oil:methanol ratio	Molar ratio		1:24	
Propane:methanol ratio	Molar ratio		1:20	
Tubular reactor				
Tube internal diameter	cm	10	10	10
Tube thickness	mm	7	7	7
Tube length	m	96	58	6
Number of tubes		21	21	21
Activation energy	kJ/kmol		38,482	
Heat of reaction (slightly endothermic)	kJ/s		0.032	
Reaction kinetics constant	s ⁻¹		7×10^{-3}	
Residence time	min		17	

4. Supercritical transesterification and reactor

Knowing the yield and kinetics of supercritical experimental results of [Kusdiana and Saka \(2001\)](#), the residence time and the dimension (length, diameter) of the reactor was calculated and presented in [Table 2](#).

The reactor was modeled as an adiabatic plug flow reactor (RPlug) in Aspen Plus. The transesterification reaction, kinetics constant and activation energy were entered as the reaction input. The activation energy was obtained by the calculation of the data of the Arrhenius plot of [Kusdiana and Saka \(2001\)](#) (details in [Nisworo, 2005](#)).

5. Methanol and propane separation

The high pressure of the reactor output stream (11) was decreased to 5 bar inside a flash evaporator (B16). This pressure drop results in transfer of the liquid propane and methanol into gaseous form, which comes out upstream from the flash evaporator (22), containing mainly methanol (89%) and propane (11%).

A normal distillation column (B8) is needed to separate the remaining methanol and propane. The separation is carried out at atmospheric pressure with four stages and reflux ratio of 0.005. These operating conditions are chosen based on the sensitivity analysis results of the operating unit; it leads to the optimum separation of methanol and propane mixture which still delivers biodiesel product with methanol content lower than maximum allowable by the European biodiesel standard EN 14214 ([Nisworo, 2005](#)). The upstream 13 from distillation column (B8) contains 99% methanol and 1% propane.

Stream 13 is compressed to 5 bar before it enters mixer B4 with the stream 22. The high temperature of stream 21 is cooled immediately with the help of a heat exchanger (B6) using cold stream 17 (the feed stream of oil, methanol and propane). The stream 20 is 94 °C so it needs to be cooled down with the help of cooling water stream 10 in a heat exchanger (B10). Stream 4 contains liquid methanol and propane mixture at 40 °C and 5 bar and then mixed with the fresh feed of oil and make up of methanol in mixer B9.

The total recovery of the methanol and propane is 99.3%. The make up of methanol reacts with triglyceride to produce methyl esters and glycerol.

6. Glycerol separation

Stream 14 (17.2 tonnes/h) which contains mainly biodiesel as the end-product and glycerol as by-product needs to be cooled down to 25 °C using 17.2 tonnes/h cooling water in a heat exchanger B13.

The outlet of the cooling water stream is used further to cool the methanol–propane recycle stream, the stream leaving the reactor, and to preheat the cold feed stream of waste cooking oil. The stream is cooled down with the help of a cooling tower (B20). Then it is pumped back to heat exchanger B13.

Glycerol is separated using a settling tank as also very often and usually applied in the current biodiesel industries. Stream 23 contains pure glycerol (96.4%) as a by-product

Table 3
The properties of the biodiesel end-product stream

Component	End stream 24	European biodiesel standard (EN 14214)
Biodiesel (mass%)	99.82	96.50
Methanol (mass%)	0.17	0.20 (maximum)
Glycerol (mass%)	0.01	0.20 (maximum)
Triglyceride (mass%)	0.00	0.20 (maximum)
Propane (mass%)	0.00	–

and stream 24 contains high purity biodiesel (99.8%) and passes the European biodiesel standard EN 14214 as can be seen in Table 3.

7. Heat balance

To conclude the process design aspect, the energy requirements for the main processing units are described in Table 4.

The design of the process equipments are described in details in Nisworo (2005).

High reboiler duty is supplied by burning the biodiesel (assumed thermal efficiency 40% and well-known calorific value of 37 MJ/kg). A 4 wt.% of biodiesel produced used to supply the reboiler duty of the distillation column (Nisworo, 2005).

8. Economic evaluation

Variables in the cost calculation are: plant location, production capacity, bio-ethanol scenario. The plant locations were simulated in the average United States location and in The Netherlands.

These variables were studied for the sensitivity analysis. It is interesting to know the feasibility of using bio-ethanol instead methanol (which derived from natural gas, emits fossil CO₂ in the process).

Warabi et al. (2004) studied the reactivity of triglycerides and fatty acids of rapeseed oil in supercritical alcohols. Using supercritical ethanol, 98% yield of ethyl esters was obtained in 45 min instead of 15 min using supercritical methanol (at their lab experiments conditions).

Assuming that the process condition is similar to the ones of methanol, only residence time is longer (factor of 3), the bio-ethanol cost calculation was performed using multiplication of factor 3 of the purchased reactor cost.

8.1. The capital cost calculation

The equipments cost which contributes to the capital cost was calculated from the data of DACE price book (DACE (Dutch Association of Cost Engineers)), edition November 2003. The cost was corrected with the CEPCI ratio (CEPCI stands for Chemical Engineering's Plant Cost Index) as can be seen in Table 5.

Table 4
Energy requirements of operating units (Nisworo, 2005)

Block name	Description	125,000 (tonnes biodiesel/year)			80,000 (tonnes biodiesel/year)			8000 (tonnes biodiesel/year)		
		Input		Out	Input		Out	Input		Out
		kW _{th}	kW _e	kW _{th}	kW _{th}	kW _e	kW _{th}	kW _{th}	kW _e	kW _{th}
B1	Reactor	0		0	0		0		0	
B2	Pump		327			215		25		
B8	Distillation column	2483 reboiler		–33 Condenser	1609		–24	182		–21
B11	Settler			–43			–32			–25
B14	Compressor		655			429		52		
B16	Flash	0		0	0		0		0	
B19	Pump		10			8		4		
B20	Cooling tower			–1900			–1242			–148
Total		2483	992	–1976	1609	652	–1298	182	81	–194

Table 5
Chemical Engineering's Plant Cost Index

Year	CEPCI
1998	389.5
2003	402.0
2004	444.2
March 2005	468.3

Source: Chemical Engineering. Economic Indicators (July 2005).

The compressor cost which is not included in the DACE price book were estimated from the price data of process design course material given in Eindhoven University of Technology, The Netherlands (Dautzenberg, 2003).

Table 6 shows the purchase costs of operating units and the fixed capital of the plants.

Fixed capital for equipment cost or inside battery limit (ISBL) is the cost for processing units, i.e. reactors, mixers, heat exchangers, pumps, compressors, etc. This cost was calculated by multiplying the purchased total equipment cost with a factor of 5, so

$$\text{Fixed capital for equipment cost or ISBL} = \text{purchased cost} \times 5$$

This factor is in agreement with 4.7 Lang factor for fluids processing plant (Sinnott, 1998).

Table 6
Fixed capital of the biodiesel plants

Equipments	Code	Plant capacity (tonnes/year)					
		125,000 methanol	125,000 bio-ethanol	80,000 methanol	80,000 bio-ethanol	8000 methanol	8000 bio-ethanol
Reactor	B1	97,884	293,652	74,889	224,668	18,811	56,434
Flash evaporator	B16	78,074	78,074	59,733	59,733	15,004	15,004
Distillation column	B8	36,763	36,763	28,127	28,127	7,065	7,065
Settler tank	B11	53,102	53,102	40,627	40,627	10,205	10,205
HeatX 1	B6	398,204	398,204	304,659	304,659	76,527	76,527
HeatX 2	B10	59,445	59,445	45,481	45,481	11,424	11,424
HeatX 3	B15	54,537	54,537	41,725	41,725	10,481	10,481
HeatX 4	B17	34,445	34,445	26,353	26,353	6,620	6,620
Cooling tower	B20	118,272	118,272	90,488	90,488	22,730	22,730
Compressor	B14	709,527	709,527	542,846	542,846	136,357	136,357
Pump 1	B3	58,842	58,842	45,019	45,019	11,308	11,308
Pump 2	B5	13,060	13,060	9,992	9,992	2,510	2,510
Pump 3	B18	6,785	6,785	5,191	5,191	1,304	1,304
Pump 4	B12	6,785	6,785	5,191	5,191	1,304	1,304
Pump 5	B19	6,785	6,785	5,191	5,191	1,304	1,304
Equipments cost		1,732,510	1,928,278	1,325,512	1,475,291	332,954	370,576
ISBL		8,662,549	9,641,389	6,627,560	7,376,453	1,664,768	1,852,881
OSBL		1,732,510	1,928,278	1,325,512	1,475,291	332,954	370,576
Fixed capital		10,395,058	11,569,666	7,953,072	8,851,744	1,997,721	2,223,457

The values are given in US\$.

The cost calculation method also includes Outside Battery Limit (OSBL) which covers tankage, yards, roads, and other general facilities. The normal default value is 20% of ISBL.

$$\text{The fixed capital} = \text{ISBL} + \text{OSBL}$$

8.2. Operating cost calculation

$$\text{The total plant capital cost} = \text{fixed capital} + \text{working capital} + \text{start-up cost}$$

Working capital is the fund required for routine operation, including inventories, accounts receivable and payable and cash on hand.

The result of the calculation can be seen in Table 7.

S, G & A stands for sales, general and administrative cost which represents expenses, research and development (R&D), administrative cost beyond plant level and corporate overhead. It is 5% of the selling price (total operating cost and capital charges). Further details can be found in Nisworo (2005).

The required selling price (RSP) is the price of the product which is required to cover all costs (variable, fixed and overhead), recover the total investment and provide the specified return of the employed capital. It is also often called break even price.

Assumed that the density of the biodiesel (methyl esters) is 840 kg/m^3 , the RSP in 15 years project life for plant capacity of 125,000 tonnes/year is US\$ 0.17/l, for 80,000 tonnes/year is US\$ 0.24/l, and US\$ 0.52/l for 8000 tonnes/year. Using bio-ethanol for the reaction input, the prices are slightly more expensive, US\$ 0.18/l (125,000 tonnes/year), US\$ 0.25/l (80,000 tonnes/year), and US\$ 0.54/l (8000 tonnes/year).

With the same cost calculation method, the required selling price of biodiesel in The Netherlands is summarized in Fig. 4.

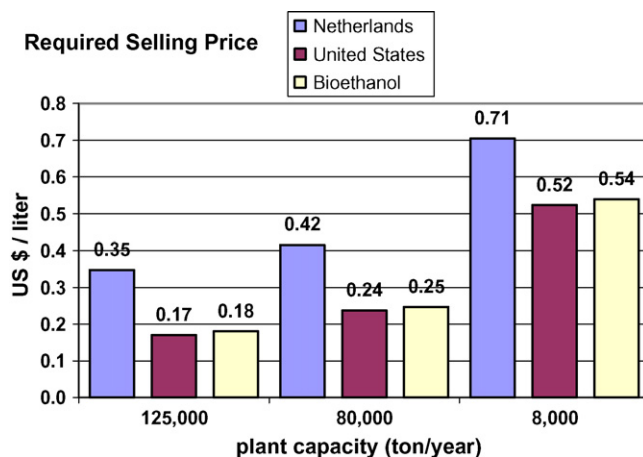


Fig. 4. Required selling price of biodiesel via supercritical transesterification.

Table 7
The required selling price of biodiesel by supercritical transesterification in US

Plant capacity/process condition	125,000 tonnes/year methanol	125,000 tonnes/year bio-ethanol	80,000 tonnes/year methanol	80,000 tonnes/year bio-ethanol	8000 tonnes/year methanol	8000 tonnes/year bio-ethanol
Fixed capital	10,395,058	11,569,666	7,953,072	8,851,744	1,997,721	2,223,457
Working capital	1,661,348	1,743,555	1,513,014	1,567,628	313,729	319,398
Start up cost	4,984,045	5,230,664	4,539,042	4,702,884	941,187	958,193
Total capital cost	17,040,452	18,543,885	14,005,128	15,122,255	3,252,638	3,501,048
Location	United States					
Annual variable cost						
Raw material						
Waste cooking oil	26,068,993	26,068,993	16,784,050	16,784,050	1,709,129	1,709,129
Methanol	4,218,750		2,736,000		278,400	
Bio-ethanol		4,990,494		3,236,502		329,328
Total raw material cost	30,287,743	31,059,487	19,520,050	20,020,552	1,987,529	2,038,457
Start up						
Methanol/bio-ethanol	14,400	17,040	9,050	10,710	924	1,093
Propane	4,409	4,409	2,672	2,672	269	269
Total start up cost	18,809	21,449	11,722	13,382	1,193	1,362
Utilities						
Electricity	713,592	713,592	456,699	456,699	45,670	45,670
Cooling water	102,708	102,708	67,103	67,103	8,217	8,217
Biodiesel for the reboiler	978,359	1,034,908	872,157	911,252	192,657	198,371
Total utilities cost	1,794,660	1,851,209	1,395,958	1,435,054	246,544	252,257
By-product credit						
Glycerol	15,937,500	15,937,500	6,234,000	6,234,000	1,017,600	1,017,600
Total by-product credit	15,937,500	15,937,500	6,234,000	6,234,000	1,017,600	1,017,600

Fixed cost						
Operating labor	1,020,000	1,020,000	1,020,000	1,020,000	1,020,000	1,020,000
Maintenance	485,103	539,918	371,143	413,081	371,143	371,143
Plant overhead	913,021	923,984	890,229	898,616	890,229	890,229
Taxes and insurance	207,901	231,393	159,061	177,035	39,954	44,469
Total fixed cost	2,626,024	2,715,295	2,440,433	2,508,733	2,321,326	2,325,841
Total operating cost	18,789,736	19,709,939	17,134,165	17,743,720	3,538,992	3,600,318
Capital charges ^a	5,314,381	5,787,437	4,353,483	4,707,127	1,207,569	1,287,014
S, G and A	1,205,206	1,274,869	1,074,382	1,122,542	237,328	244,367
Required selling price	25,309,323	26,772,245	22,562,030	23,573,389	4,983,890	5,131,699
RSP (US\$/tonnes)	202	214	282	295	623	641
RSP (US\$/kg)	0.20	0.21	0.28	0.29	0.62	0.64
RSP (US\$/l)	0.17	0.18	0.24	0.25	0.52	0.54

^a 20% return of investment (ROI) used.

From Fig. 4, it can be concluded that the biodiesel produced via supercritical transesterification which use no catalyst and no pre-treatment step is economically feasible since the biodiesel can be sold at 17 US cent/l for the 125,000 tonnes/year capacity.

Biodiesel produced from small plant (8000 tonnes/year) in The Netherlands is the most expensive compared with the others.

For all capacities, biodiesel price in The Netherlands is more expensive than in the United States. This can be attributed to the high price of waste cooking oil; 30 Euro cent/l (Rice et al., 1998) which is equal to 37 US cent/l. The price of the waste cooking oil in the United States is 20 US cent/l (Zhang et al., 2003).

Bio-ethanol hardly influences the biodiesel price as it only 1 US\$ cent more expensive per liter. This can be attributed to considerably small sensitivity of the methanol or bio-ethanol as the reactants ranging between 7 and 14% (Nisworo, 2005) although the bio-ethanol price is more expensive compared with methanol (bio-ethanol price US\$ 355/tonnes, methanol price US\$ 300/tonnes).

From Fig. 5, it can be seen that the biodiesel produced via non-catalytic way (49 US cent/l) can compete with the industrial way produced biodiesel (Zhang 01 and 02 bars) (Zhang et al., 2003a) as it is cheaper to sell. The method most used in biodiesel industries is alkali catalyst with acid pre-treatment step prior to main reaction.

The high cost of the biodiesel (72 US cent/l, second bar from the left) can be attributed to the high cost of the fresh vegetable oil.

Whereas the required selling price of 74 US cent/l is due to the catalyst cost and additional pre-treatment step to reduce the free fatty acid of the waste cooking oil although the cost of the waste cooking oil is lower than fresh vegetable oil.

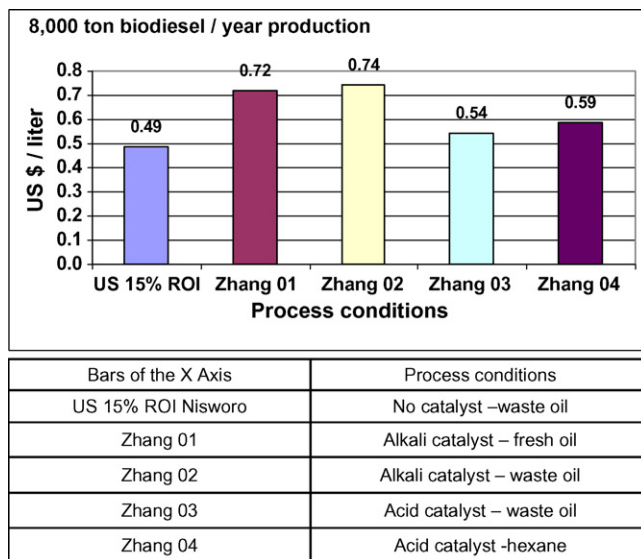


Fig. 5. The required selling prices of small biodiesel plants.

Table 8
Summary of the sensitive key factors as percentage of manufacturing cost

tonnes/year	The Netherlands	United States	Bio-ethanol
125,000	Waste oil (80%)	Waste oil (73%), capital (15%)	Waste oil (71%), capital (16%)
80,000	Waste oil (77%)	Waste oil (68%), capital (16%)	Waste oil (67%), capital (17%)
8000	Waste oil (49%), capital (18%), human labor (16%)	Waste oil (35%), capital (20%), human labor (21%)	Waste oil (34%), capital (21%), human labor (21%)

Table 9
Percentage reduction of operating cost by by-product sale

tonnes/year	The Netherlands	United States	Bio-ethanol
125,000	Glycerol (22%)	Glycerol (36%)	Glycerol (34%)
80,000	Glycerol (13%)	Glycerol (20%)	Glycerol (20%)
8000	Glycerol (12%)	Glycerol (16%)	Glycerol (15%)

Zhang et al. (2003) also carried out process design and economic feasibility with acid catalyst process which requires longer reaction time from waste cooking oil feed. It is insensitive to low free fatty acids in the waste cooking oil.

From Fig. 5, it is clear that biodiesel produced non-catalytically is 5 US cent cheaper than biodiesel produced with acid catalyst process (Zhang 03 bar).

Kusdiana and Saka (2001) experiment with acid catalyst shows that waste cooking oil which contains 10% of free fatty acids resulted in biodiesel yield drop to 71%. Whereas their supercritical experiment with the same waste cooking oil resulted in 98% yield.

Zhang et al. (2003) based their calculation on 97% yield which seems not realistic, so in reality the price of the acid catalyzed biodiesel will be much higher.

The major cost contributor to the price of biodiesel can be seen Table 8.

For big plants, the major cost contribution for the biodiesel price is the price of the raw material (71–80%) and capital charges (15–16%). Glycerol as the by-product also influences the price of the biodiesel as it contributes 22–36% reduction of the biodiesel price (Table 9).

For small plant capacity, the contribution of operating labor, maintenance, overhead become higher compared with bigger capacities.

This means that plant capacity changes the sensitive factors for cost contribution.

9. Conclusions

A supercritical transesterification process for biodiesel continuous production from waste cooking oil has been studied for three plant capacities (125,000; 80,000 and 8000 tonnes

biodiesel/year). It can be concluded that biodiesel by supercritical transesterification can be scaled up resulting high purity of methyl esters (99.8%) and almost pure glycerol (96.4%) attained as by-product.

The economic assessment of the biodiesel plant shows that biodiesel can be sold at US\$ 0.17/l (125,000 tonnes/year), US\$ 0.24/l (80,000 tonnes/year) and US\$ 0.52/l for the smallest capacity (8000 tonnes/year).

The sensitive key factors for the economic feasibility of the plant are: raw material price, plant capacity, glycerol price and capital cost.

Overall conclusion is that the process can compete with the existing alkali and acid catalyzed processes.

Especially for the conversion of waste cooking oil to biodiesel, the supercritical process is an interesting technical and economical alternative.

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