Available online at www.sciencedirect.com

SCIENCE DIRECT®

ELSEVIER

Bioresource Technology 89 (2003) 1–16

BIORESOURCE TECHNOLOGY

Review Paper

Biodiesel production from waste cooking oil: 1. Process design and technological assessment

Y. Zhang [a], M.A. Dubé [a], D.D. McLean [a,*], M. Kates [b]

[a] *Department of Chemical Engineering, University of Ottawa, Ottawa, Ont., Canada K1N 6N5*
[b] *Department of Biochemistry, University of Ottawa, Ottawa, Ont., Canada K1N 6N5*

Received 18 March 2002; received in revised form 22 October 2002; accepted 21 January 2003

Abstract

Four different continuous process flowsheets for biodiesel production from virgin vegetable oil or waste cooking oil under alkaline or acidic conditions on a commercial scale were developed. Detailed operating conditions and equipment designs for each process were obtained. A technological assessment of these four processes was carried out to evaluate their technical benefits and limitations. Analysis showed that the alkali-catalyzed process using virgin vegetable oil as the raw material required the fewest and smallest process equipment units but at a higher raw material cost than the other processes. The use of waste cooking oil to produce biodiesel reduced the raw material cost. The acid-catalyzed process using waste cooking oil proved to be technically feasible with less complexity than the alkali-catalyzed process using waste cooking oil, thereby making it a competitive alternative to commercial biodiesel production by the alkali-catalyzed process.

Keywords: Biodiesel; Waste cooking oil; Transesterification of triacylglycerols; Process design

1. Introduction

The American Society for Testing and Materials (ASTM) defines biodiesel fuel as monoalkyl esters of long chain fatty acids derived from a renewable lipid feedstock, 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.

Biodiesel, as an alternative fuel, has many merits. It is derived from a renewable, domestic resource, thereby relieving reliance on petroleum fuel imports. It is biodegradable and non-toxic. Compared to petroleum-based diesel, biodiesel has a more favourable combustion emission profile, such as low emissions of carbon monoxide, particulate matter and unburned hydrocarbons. Carbon dioxide produced by combustion of biodiesel can be recycled by photosynthesis, thereby minimizing the impact of biodiesel combustion on the greenhouse effect (Körbitz, 1999; Agarwal and Das, 2001). Biodiesel has a relatively high flash point (150 °C), which makes it less volatile and safer to transport or handle than petroleum diesel (Krawczyk, 1996). It provides lubricating properties that can reduce engine wear and extend engine life (Von Wedel, 1999). In brief, these merits of biodiesel make it a good alternative to petroleum-based fuel and have led to its use in many countries, especially in environmentally sensitive areas.

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 (i.e., biodiesel) and glycerol (Fig. 1). Triacylglycerols (triglycerides), as the main component of vegetable oil, consist of three long chain fatty acids esterified to a glycerol backbone. When triacylglycerols react with an alcohol (e.g., methanol), the three fatty acid chains are released from the glycerol skeleton and combine with the alcohol to yield fatty acid alkyl esters (e.g., fatty acid methyl esters or FAME). Glycerol is produced as a by-product. Methanol is the most commonly used alcohol because of its low cost and is the alcohol of choice in the processes developed in this

---

[*] Corresponding author. Tel.: +1-613-562-5800x6110; fax: +1-613-562-5172.

E-mail address: mclean@genie.uottawa.ca (D.D. McLean).

0960-8524/03/$ - see front matter © 2003 Elsevier Science Ltd. All rights reserved.
doi:10.1016/S0960-8524(03)00040-3

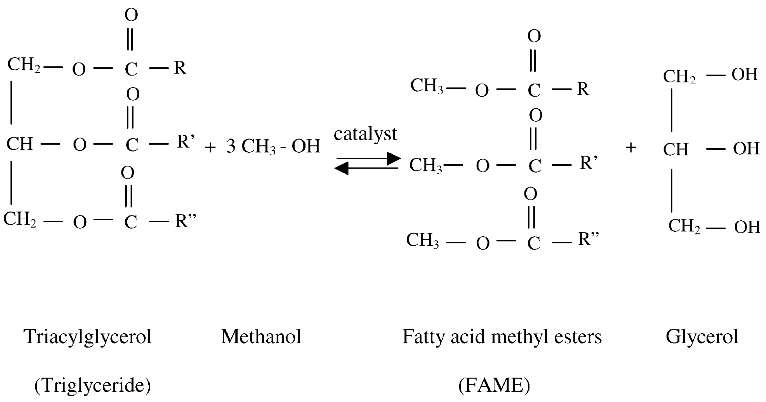


Fig. 1. A schematic representation of the transesterification of triglycerides (vegetable oil) with methanol to produce fatty acid methyl esters (biodiesel).

study. In general, a large excess of methanol is used to shift the equilibrium far to the right (Fig. 1).

Transesterification reactions can be alkali-catalyzed, acid-catalyzed or enzyme-catalyzed. The first two types have received the greatest attention and are the focus of this article. As for the enzyme-catalyzed system, it requires a much longer reaction time than the other two systems (Nelson et al., 1996; Watanabe et al., 2001). To date it has only been carried out on the laboratory scale and therefore will not be further discussed herein.

At present, the high cost of biodiesel is the major obstacle to its commercialization. Biodiesel usually costs over US\$0.5/l, compared to US\$0.35/l for petroleum-based diesel (Prokop, 2002; Lott, 2002). It is reported that the high cost of biodiesel is mainly due to the cost of virgin vegetable oil (Krawczyk, 1996; Connemann and Fischer, 1998). For example, in the United States, soybean oil was sold on average for \$0.36/l in June 2002 (Chemical Market Reporter, 2002). Therefore, it is not surprising that biodiesel produced from pure soybean oil costs much more than petroleum-based diesel. Exploring ways to reduce the high cost of biodiesel is of much interest in recent biodiesel research, especially for those methods concentrating on minimizing the raw material cost. The use of waste cooking oil instead of virgin oil to produce biodiesel is an effective way to reduce the raw material cost because it is estimated to be about half the price of virgin oil (Supple et al., 1999). In addition, using waste cooking oil could also help to solve the problem of waste oil disposal (Wiltsee, 1998).

Most current biodiesel research concentrates on the alkali-catalyzed technology carried out on a bench scale and no detailed technological information is available on overall continuous industrial processes in which both reactor and downstream separation units are continuously operated. Information on industrial process simulation and design is also unavailable. Apart from the transesterification reaction, the actual process of biodiesel production includes many process steps from raw material refining to product separation and purification. Evaluating the technological and economic feasibility of a biodiesel plant involves all operating units, not only one reactor. Therefore, there is a need to design a complete continuous process and assess its performance from the viewpoint of an entire plant. In this article, we aim to carry out process simulation on alkali- and acid-catalyzed transesterifications and develop continuous process flowsheets to produce biodiesel from virgin vegetable oil or waste cooking oil. A technical assessment of each process is also presented. This is an attempt to explore potential alternatives to current biodiesel production methods, thus contributing to biodiesel commercialization. In a subsequent article (Zhang et al., submitted for publication), an assessment of the relative economic feasibility of each process is undertaken.

2. Background

2.1. Alkali-catalyzed system

Many studies of alkali-catalyzed transesterification on the laboratory scale have been carried out. A reaction temperature near the boiling point of the alcohol (e.g., 60 °C for methanol) and a 6:1 molar ratio of alcohol to soybean oil were recommended (Freedman et al., 1984; Noureddini and Zhu, 1997). The kinetics of the alkali-catalyzed system were also studied by Freedman et al. (1986), Noureddini and Zhu (1997) and Darnoko and Cheryan (2000). Based on their results, approximately 90–98% oil conversion to methyl esters was observed within 90 min. In order to speed up the reaction, Boocock et al. (1998) suggested the addition of tetrahydrofuran (THF) as a co-solvent to minimize mass transfer resistance. After the reaction, different separation techniques to purify the biodiesel product from the other products were investigated by Karaosmanoğlu et al. (1996). In terms of the purity and yield of the biodiesel product, they concluded that the use of hot water washing at 50 °C was the best way to obtain a high purity (99%) and yield (86%) of the biodiesel product.

Apart from the bench-scale research, the alkali-catalyzed process for biodiesel production has been applied industrially. A commercial continuous alkali-catalyzed transesterification process to produce methyl esters on the industrial scale under high pressure (90 bar) and at high temperature (240 °C) was demonstrated by Kreutzer (1984). However, high energy consumption, a significant increase in equipment cost and process safety issues related to, for example, high pressure and high temperature, could make this process prohibitive. Krawczyk (1996) presented a flow diagram for producing biodiesel via transesterification on the industrial scale. The process mainly consisted of a transesterification reactor, a methanol/glycerol distillation column and a methyl ester distillation column. Aside from the flowsheet, no detailed description of the process was provided. A continuous deglycerolization process to produce biodiesel from refined rapeseed oil by alkali-catalyzed transesterification at ambient pressure and 65–70 °C was introduced by Connemann and Fischer (1998). They noted successful commercial applications of this process in Europe. In this process, a distillation column was also used to separate methanol from biodiesel and glycerol. The methanol was recycled to the transesterification reactor and multi-stage water washing was employed to purify the biodiesel product. The above industrial manufacturing information on biodiesel production formed the principle basis for the design of the alkali-catalyzed processes in this study.

One limitation to the alkali-catalyzed process is its sensitivity to the purity of reactants; the alkali-catalyzed system is very sensitive to both water and free fatty acids. The presence of water may cause ester saponification under alkaline conditions (Liu, 1994; Basu and Norris, 1996). Also, free fatty acids can react with an alkali catalyst to produce soaps and water. Saponification not only consumes the alkali catalyst, but also the resulting soaps can cause the formation of emulsions. Emulsion formation creates difficulties in downstream recovery and purification of the biodiesel. Thus, dehydrated vegetable oil with less than 0.5 wt.% free fatty acids, an anhydrous alkali catalyst and anhydrous alcohol are necessary for commercially viable alkali-catalyzed systems (Freedman et al., 1984; Jeromin et al., 1987). This requirement is likely to be a significant limitation to the use of waste cooking oil as a low-cost feedstock. Usually the level of free fatty acids in waste cooking oil is greater than 2 wt.% (Lepper and Friesenhagen, 1986; Watanabe et al., 2001). Lepper and Friesenhagen (1986) recommended a pretreatment step to reduce the free fatty acid content via an esterification reaction with methanol in the presence of sulfuric acid catalyst. Glycerine was employed as a liquid entraining agent to purify the refined oil. After such a treatment, the oil phase, having a low level of free fatty acids (less than 0.5 wt.%), was subjected to the alkali-catalyzed transesterification. Such a pretreatment step was applied to the alkali-catalyzed process using waste cooking oil in the present study.

2.2. Acid-catalyzed system

Despite its insensitivity to free fatty acids in the feedstock, acid-catalyzed transesterification has been largely ignored mainly because of its relatively slower reaction rate. Freedman et al. (1984) investigated the transesterification of soybean oil with methanol using 1 wt.% concentrated sulfuric acid (based on oil). They found that at 65 °C and a molar ratio of 30:1 methanol to oil, it took 69 h to obtain more than 90% oil conversion to methyl esters. Canakci and Gerpen (1999) studied the effects of the molar ratio of alcohol to soybean oil, the reaction temperature, the amount of catalyst, and the reaction time on the ester conversion by acid-catalyzed transesterification. Each effect was studied independently of the other effects. They found that increased ester conversions could be obtained at increased molar ratios of alcohol to oil, increased reaction temperatures, increased concentrations of sulfuric acid, and longer reaction times. However, possible interaction of these variables was not investigated and optimal conditions for the acid-catalyzed reaction were not recommended. The kinetics of the acid-catalyzed transesterification with butanol were also investigated by Freedman et al. (1986). They stated that the forward and reverse reactions followed pseudo-first-order and second-order kinetics, respectively. This conclusion of pseudo-first-order forward reaction is consistent with preliminary results in our laboratory (Ripmeester, 1998; McBride, 1999). Since soybean oil and butanol rather than canola oil and methanol were used in their work, the kinetic information given by Freedman et al. (1986) was not used as the basis of the present study.

In our laboratory, Ripmeester (1998) and McBride (1999) conducted pilot-scale transesterification reactions of waste cooking oil with an excess of methanol in the presence of sulfuric acid catalyst at 70 °C. A minimum molar ratio of 50:1 methanol to oil and acid concentrations of 1.5–3.5 mol% (based on the reaction mixture) were used. Such a high proportion of methanol was used to promote high equilibrium conversions of oil to esters. Recently, we obtained results at 80 °C. The reaction was carried out in a 15 L stainless steel reactor equipped with a heating jacket, at a 50:1 molar ratio of methanol to oil, pressure from 170–180 kPa and an agitation rate of 400 rpm. Under these conditions, a 97% oil conversion to FAME was reached within 240 min. An empirical first-order model was proposed and a rate constant was calculated. These preliminary results were used for reactor-sizing in the acid-catalyzed processes of this study. Further kinetic investigations are currently underway.

Instead of water washing, Nye et al. (1983) suggested using hexane as an extraction solvent to purify the methyl esters from other substances. This purification method was used in one of the designs of the acid-catalyzed process in this study.

Studies of the acid-catalyzed system have been very limited in number. No commercial biodiesel plants to date have been reported to use the acid-catalyzed process. Despite its relatively slow reaction rate, the acid-catalyzed process offers benefits with respect to its independence from free fatty acid content and the consequent absence of a pretreatment step. These advantages favour the use of the acid-catalyzed process when using waste cooking oil as the raw material.

3. Process simulation

To assess the commercial feasibilities of the proposed processes, complete process simulations were first carried out. Despite some expected differences between process simulation results and actual process operation, most current simulation software can provide reliable information on process operation because of their comprehensive thermodynamic packages, vast component libraries and advanced calculation techniques. The process simulation software, HYSYS.Plant NetVers 2.1.3 developed by Hyprotech Ltd., was used in this research.

The procedures for process simulation mainly involve defining chemical components, selecting a thermodynamic model, determining plant capacity, choosing proper operating units and setting up input conditions (flowrate, temperature, pressure, and other conditions). Information on most components, such as methanol, glycerol, sulfuric acid, sodium hydroxide and water, is available in the HYSYS™ component library. Regarding the vegetable oil feedstock, canola oil was considered as the raw material in either virgin or waste form because it is the major vegetable oil used in Canada. Because oleic acid is the major fatty acid in canola oil (Lawson, 1995), triolein ($C_{57}H_{104}O_6$) was chosen to represent canola oil in the HYSYS™ simulation. Accordingly, methyl oleate ($C_{19}H_{36}O_2$) was taken as the resulting biodiesel product and its properties were available in the HYSYS™ component library. For those components not available in the library, such as triolein, calcium oxide, calcium sulfate, phosphoric acid and sodium phosphate, they were defined using "the Hypo Manager" tool in HYSYS™. Detailed procedures for defining each component were presented by Zhang (2002).

Due to the presence of the highly polar components, methanol and glycerol, both the non-random two liquid (NRTL) and universal quasi-chemical (UNIQUAC) thermodynamic/activity models were recommended to predict the activity coefficients of the components in a liquid phase (Hyprotech Ltd., 2000). Detailed descriptions of these models were provided by Gess et al. (1991). Some unavailable interaction parameter coefficients, such as those for methanol/methyl-oleate, glycerol/methyl-oleate and sulfuric acid with any other component, were estimated using the UNIQAC liquid–liquid equilibrium module in HYSYS™.

The determination of plant capacity was based on the reported availability of waste cooking oil in the United States. Wiltsee (1998) analyzed data on urban waste grease resources in 30 randomly selected metropolitan areas in the United States. He concluded that on average, 9 pounds/person of yellow grease were produced annually in the United States. Assuming this statistic is applicable to Canada, approximately 120,000 tonnes/yr of yellow grease are produced in Canada, 45,000 tonnes/yr in Ontario, and 4000 tonnes/yr in the Ottawa Region. The same estimation method was also applied by (S & T)^2 Consulting Co. (2001). Thus, in order to provide a facility to handle regional waste oils, a plant capable of producing 8000 tonnes/yr biodiesel was simulated in the current work. This was also the same capacity as the existing continuous biodiesel plant described by Connemann and Fischer (1998).

The main processing units include reactors, distillation columns, extraction columns, heat exchangers, pumps and separators. Because detailed information on the kinetics was not available, a simple conversion reactor model with 97% and 95% oil conversion to FAME was used to describe the acidic and alkaline transesterification reactions, respectively. It was assumed that the reactor was a continuous, stirred tank reactor and the fill factor of the reactor (the ratio of reaction to reactor volumes) was set at 0.5. As has been observed in our laboratory, the theoretical reaction intermediates, diacylglycerols and monoacylglycerols, exist only in the early stages of the reaction, because of high methanol to oil ratios. Thus it was not appropriate to consider these intermediates in this work.

Multi-stage distillation was used for methanol recovery as well as purification of both the FAME and glycerine products. Although the boiling point of methanol (65 °C at 1 atm) is much lower than that of FAME (approximately 320 °C at 1 atm) or glycerol (300 °C at 1 atm), simulations suggested that the desired purities of biodiesel and glycerol (greater than 90 wt.%) could not be achieved by a simple flash unit. The ASTM standard for purity of biodiesel product (i.e., 99.65 wt.%) was applied to both the acid- and alkali-catalyzed processes in the present study. However, the large difference in the boiling points of the components facilitates distillation; only five or six theoretical stages in the columns are sufficient to yield high quality biodiesel and glycerine. In our simulations, we assumed a tray efficiency of 60–70%. Because FAME and glycerol are susceptible to thermal decomposition above 250 and 150 °C, respectively (Newman, 1968; Goodrum, 2002), vacuum operation for the FAME and glycerine purification was necessary to keep the temperature at suitably low levels. Liquid–liquid extraction was used to separate FAME from glycerol, methanol and catalyst (i.e., water washing column T-301). Detailed sizing calculations of the process equipment were presented by Zhang (2002).

After the input information and operating unit models were set up, the process steady-state simulation was executed by HYSYS™. Mass and energy balances for each unit, as well as operating conditions, were obtained. Pressure drops from heat exchangers and pipelines were not considered in this work.

4. Process design

Four different continuous processes were designed and simulated. Two of them were alkali-catalyzed processes, one using virgin oil (process I) and the other using waste cooking oil (process II). The remaining two (III and IV) were acid-catalyzed processes using waste cooking oil as the raw material. Process flowsheets along with the properties of main streams are presented in Figs. 2–5.

The materials of construction required for the main processing units in each of the four processes are summarized in Table 1. Freedman et al. (1986) pointed out that alkali-catalyzed transesterification was less corrosive to process equipment than the acid-catalyzed process. Davis et al. (2000) stated that, when the concentration of sodium hydroxide is less than 50 wt.%, from ambient temperature to 95 °C carbon steel could be used. Peterson (1993) studied a batch process to produce biodiesel from rapeseed oil using 0.2 wt.% potassium hydroxide, in which stainless steel was used for the transesterification reactor. Taking a conservative approach, stainless steel was used for the transesterification reactor in the designs for the alkali-catalyzed processes in this study. The material of construction of other equipment in the alkali-catalyzed processes was carbon steel. For the acid-catalyzed system, Norden (1973) recommended that stainless steel (type 316) should be used when sulfuric acid concentrations were below 5 wt.% or above 85 wt.% and temperatures were below the boiling point of the sulfuric acid solution. Davis et al. (2000) indicated that stainless steel 316 has an acceptable corrosion rate (less than 0.5 mm/yr) for 5 wt.% sulfuric acid under 100 °C; for a temperature between 50 and 100 °C, stainless steel (alloy 20) has good corrosion-resistance for sulfuric acid less than 60 wt.% or greater than 80 wt.%. These guidelines formed the basis for our choice of material in all the designs.

The use of two different thermodynamic/activity models (NRTL and UNIQUAC) led to some differences in the simulation results. In the following discussion, results from both NRTL and UNIQUAC are provided when there exists a big difference between them. Otherwise, the results shown are based only on the NRTL model. Unless specified, all percentages are expressed as mass percentages and the sizes of all process equipment are described as diameter × height.

4.1. Alkali-catalyzed process using virgin vegetable oil (process I)

4.1.1. Transesterification

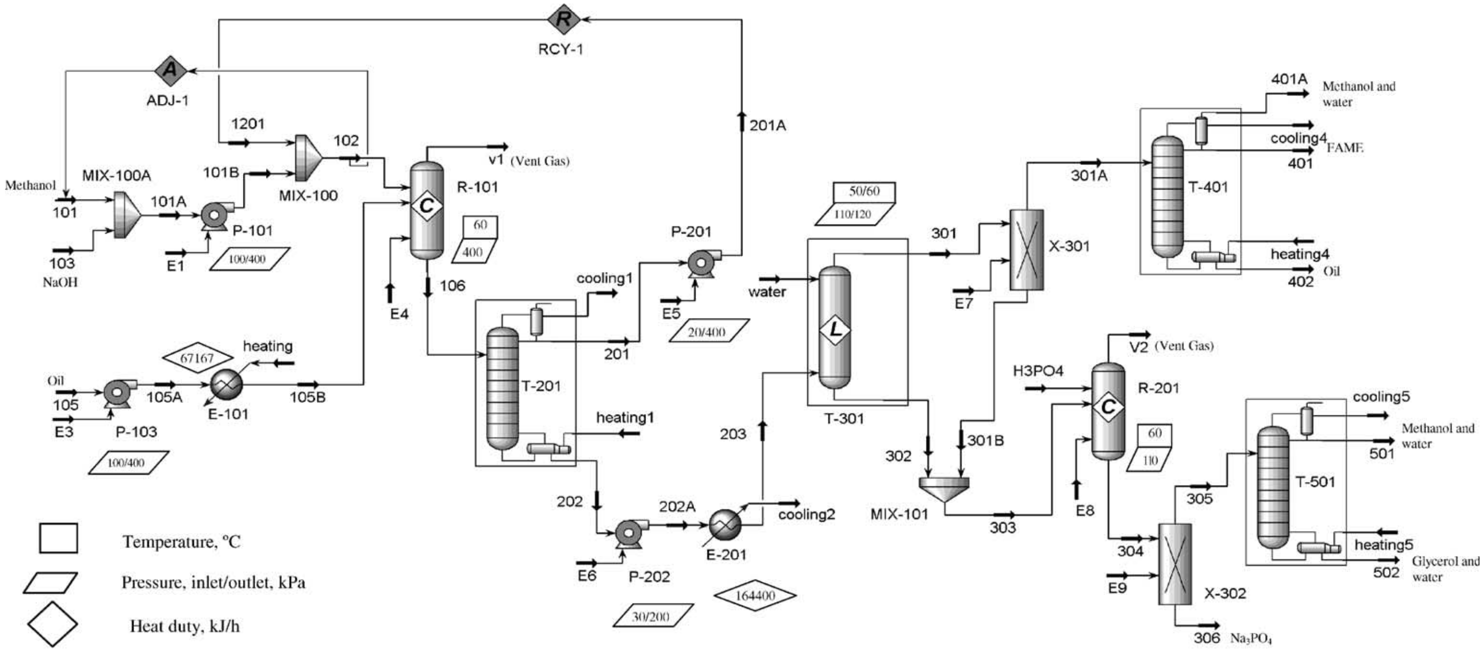
A continuous alkali-catalyzed process flowsheet using virgin oil was developed (Fig. 2). The reaction was carried out with a 6:1 molar ratio of methanol to oil, 1% sodium hydroxide (based on oil), 60 °C and 400 kPa. Fresh methanol (stream 101 at 117 kg/h), recycled methanol (stream 1201 at 111 kg/h) and anhydrous sodium hydroxide (stream 103 at 10 kg/h) were mixed prior to being pumped into reactor R-101 by pump P-101. Virgin vegetable oil (stream 105) was heated in exchanger E-101 before entering R-101. In R-101, 95% of oil was assumed to be converted to FAME, producing glycerol as a by-product. Stream 106 from the reactor was introduced to methanol distillation T-201.

4.1.2. Methanol recovery

In T-201, five theoretical stages and a reflux ratio of 2 were used to obtain a good separation between methanol and other components. Stream 201 was a pure methanol distillate, containing 94% of the total methanol in stream 106. Vacuum distillation was used to keep the bottom temperature under 150 °C. Pure methanol (stream 1201) was mixed with fresh make-up methanol (stream 101B) and then charged back into reactor R-101. Bottom stream 202 was sent to washing column T-301 after being cooled in exchanger E-201 to 60 °C.

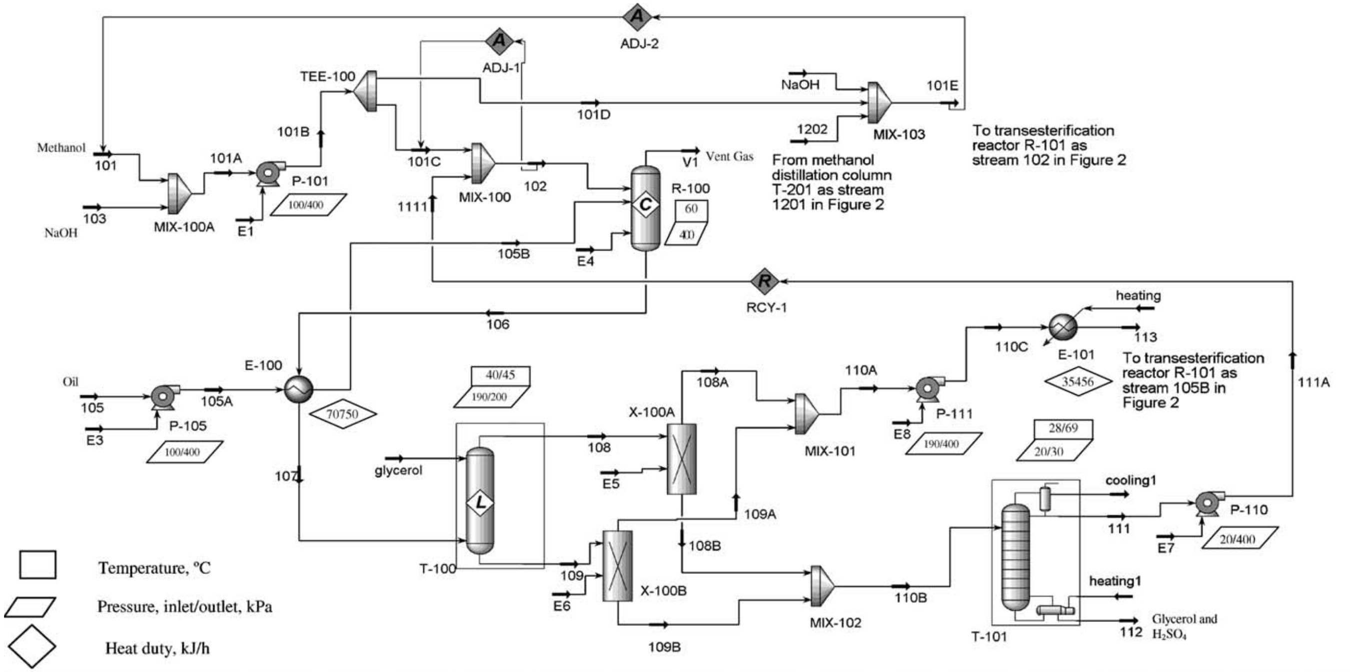
4.1.3. Water washing

The purpose of this step was to separate the FAME from the glycerol, methanol and catalyst. Although separation using a gravity settler was proposed by Krawczyk (1996), a complete separation could not be achieved based on our simulation results. Consequently, a water washing column (T-301) with four theoretical stages was used in this study (Connemann and Fischer, 1998). The FAME in stream 203 was separated from the glycerol, methanol and catalyst by adding 11 kg/h water (25 °C). The amounts of unconverted oil, methanol and water in stream 301A were all less than 6%. All of the glycerol remained in the bottom stream 303 (128 kg/h), which contained 81% glycerol, 8% water, 3% methanol and 9% sodium hydroxide.



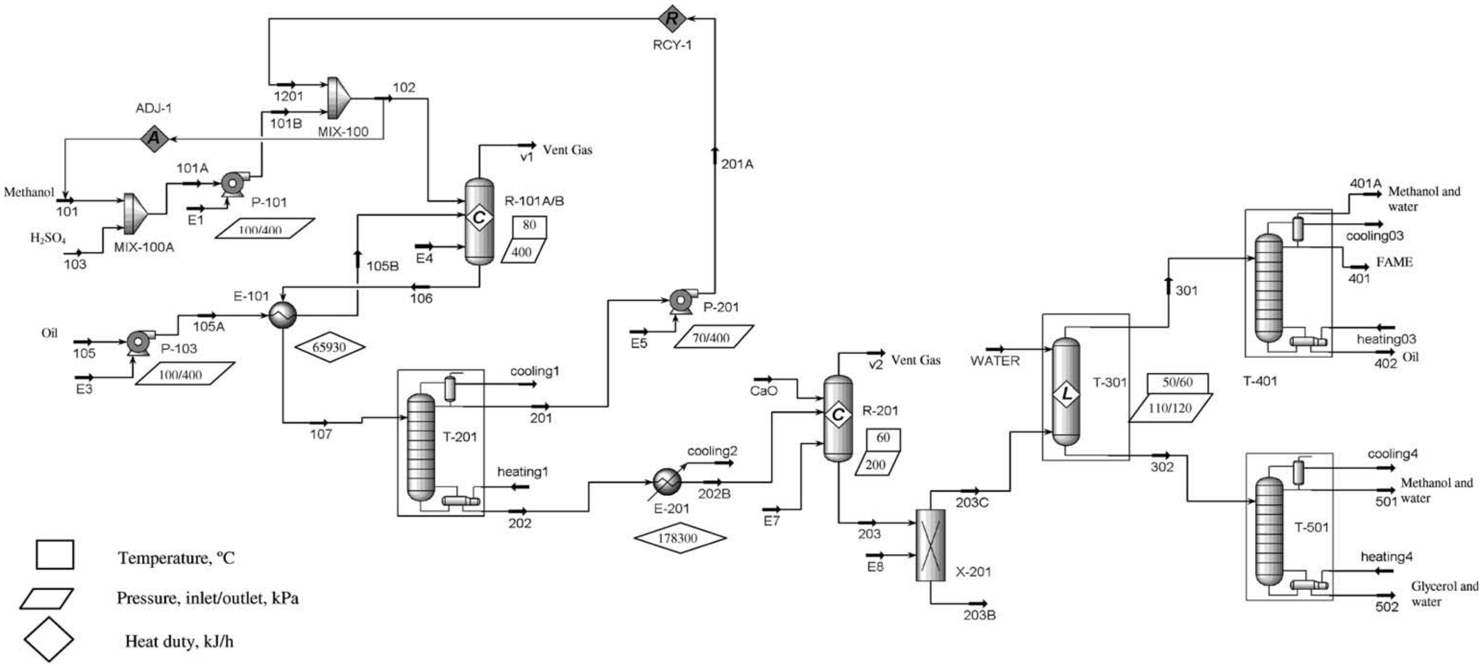
Stream name	101	102	103	105B	106	201	202	301A	305	306	401A	401	402	501	502
Temperature (°C)	25.0	26.7	25.0	60.0	60.0	28.2	122.34	60.0	60.0	60.0	193.7	193.7	414.7	56.2	112
Pressure (kPa)	100	400	100	400	400	20	30	110	110	110	10	10	20	40	50
Molar flow (kg-mol/h)	3.66	7.13	0.25	1.19	8.51	3.47	5.04	3.60	2.04	0.084	0.155	3.384	0.06	0.42	1.52
Mass flow (kg/h)	117.20	238.39	10.00	1050.00	1288.40	111.19	1177.20	1060.21	122.31	13.73	7.82	999.88	52.50	9.02	113.29
Liquid volume flow (m^3/h)	0.147	0.287	0.006	1.167	1.440	0.140	1.300	1.208	0.102	0.005	0.009	1.140	0.058	0.010	0.092
Component mass fraction															
Methanol	1.000	0.956	0.000	0.000	0.092	1.000	0.006	0.003	0.032	0.000	0.388	0.000	0.000	0.363	0.000
Triacylglycerol (oil)	0.000	0.000	0.000	1.000	0.041	0.000	0.045	0.050	0.000	0.000	0.000	0.000	1.000	0.000	0.000
FAME (biodiesel)	0.000	0.000	0.000	0.000	0.779	0.000	0.853	0.946	0.002	0.000	0.504	0.997	0.000	0.000	0.000
Glycerol	0.000	0.000	0.000	0.000	0.081	0.000	0.088	0.000	0.850	0.000	0.000	0.000	0.000	0.000	0.850
NaOH	0.000	0.044	1.000	0.000	0.008	0.000	0.008	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
H_2O	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.117	0.000	0.107	0.003	0.002	0.637	0.150
H_3PO_4	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.005	0.000	0.000	0.000	0.000	0.000
Na_3PO_4	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.995	0.000	0.000	0.000	0.000	0.000

Fig. 2. Alkali-catalyzed process to produce biodiesel from virgin oils.



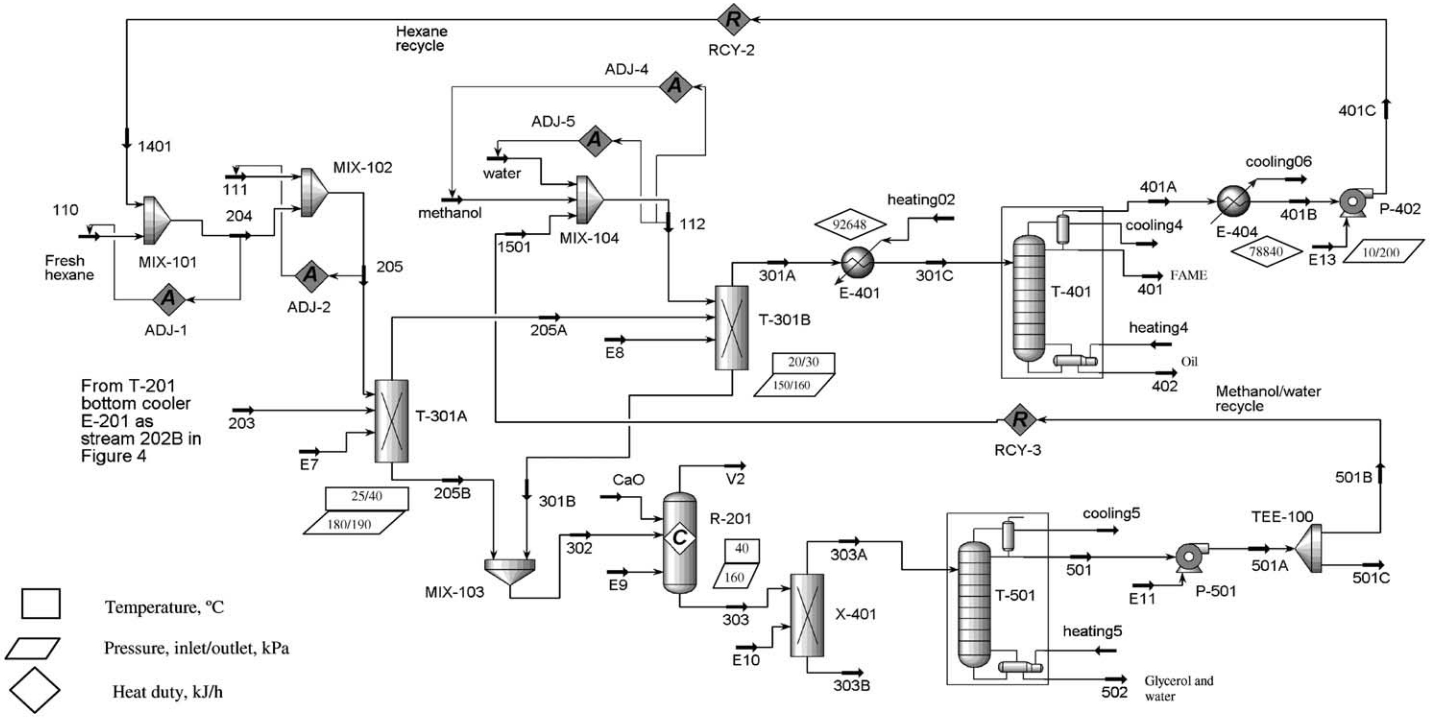
Stream name	101	102	103	105B	106	112	113	201	202	203	301A	305	306	401A	401	402	501	502
Temperature (ºC)	25.0	28.1	25.0	60.0	70.0	69.5	60.0	60.0	28.2	125.7	59.0	60.0	60.0	217.75	217.75	434.2	64.7	107.6
Pressure (kPa)	100	400	100	400	400	30	400	400	20	30	120	120	120	20	20	30	40	50
Molar flow (kg-mol/h)	4.00	6.60	0.10	1.34	7.94	1.91	1.32	8.05	3.10	4.95	3.48	3.97	0.092	0.04	3.38	0.05	2.02	1.95
Mass flow (kg/h)	128.10	218.01	10	1050.00	1268.01	147.16	1042.05	1261.32	99.52	1161.80	1048.19	152.61	15.03	2.27	997.29	48.62	38.87	113.74
Liquid volume flow (m^3/h)	0.161	0.266	0.005	1.167	1.434	0.124	1.160	1.409	0.125	1.284	1.194	0.134	0.006	0.003	1.137	0.054	0.040	0.094
Component mass fraction																		
Methanol	1.000	0.954	0.000	0.000	0.158	0.082	0.000	0.084	1.000	0.005	0.001	0.037	0.000	0.228	0.000	0.000	0.146	0.000
Triacylglycerol (oil)	0.000	0.000	0.000	0.940	0.778	0.071	0.937	0.008	0.000	0.042	0.047	0.000	0.000	0.000	0.001	1.000	0.000	0.000
FAME (biodiesel)	0.000	0.000	0.000	0.000	0.052	0.005	0.063	0.830	0.000	0.860	0.952	0.006	0.000	0.621	0.997	0.000	0.000	0.008
Glycerol	0.000	0.000	0.000	0.000	0.000	0.747	0.000	0.077	0.000	0.083	0.000	0.633	0.000	0.000	0.000	0.000	0.000	0.850
H_2SO_4	0.000	0.045	1.000	0.000	0.008	0.068	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
NaOH	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.008	0.000	0.009	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
H_2O	0.000	0.001	0.000	0.000	0.003	0.027	0.000	0.000	0.000	0.000	0.001	0.324	0.000	0.151	0.002	0.000	0.854	0.142
Oleic acid (Fatty acid)	0.000	0.000	0.000	0.060	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
H_3PO_4	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Na_3PO_4	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	1.000	0.000	0.000	0.000	0.000	0.000

Fig. 3. Acid-catalyzed process for pretreatment of waste oils prior to alkali-catalyzed production of biodiesel.



Stream Name	101	102	103	105B	106	201	202	203B	301	302	401A	401	402	501	502
Temperature (°C)	25.0	73.5	25.0	60.0	80.0	81.4	108.8	60.0	56.4	60.0	264.3	264.3	462.6	52.6	107.3
Pressure (kPa)	100	400	100	400	400	190	200	130	110	120	40	40	50	40	50
Molar flow (kg-mol/h)	6.75	59.03	1.53	1.16	59.06	49.75	9.31	1.53	3.46	10.86	0.04	3.386	0.035	8.63	2.22
Mass flow (kg/h)	216.28	1992.41	150.00	1030.00	2990.37	1593.99	1396.38	208.03	1035.24	328.86	4.31	1000.12	30.81	199.91	128.95
Liquid volume flow (m^3/h)	0.272	2.396	0.081	1.144	3.478	2.003	1.475	0.070	1.180	0.332	0.005	1.140	0.034	0.226	0.106
Component mass fraction															
Methanol	1.000	0.925	0.000	0.000	0.567	1.000	0.073	0.000	0.000	0.308	0.074	0.000	0.000	0.506	0.000
Triacylglycerol (oil)	0.000	0.000	0.000	1.000	0.010	0.000	0.022	0.000	0.030	0.000	0.000	0.000	0.999	0.000	0.000
FAME (biodiesel)	0.000	0.000	0.000	0.000	0.336	0.000	0.719	0.000	0.969	0.002	0.852	0.997	0.001	0.000	0.006
Glycerol	0.000	0.000	0.000	0.000	0.037	0.000	0.078	0.000	0.000	0.333	0.000	0.000	0.000	0.000	0.850
H_2SO_4	0.000	0.075	1.000	0.000	0.050	0.000	0.107	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
H_2O	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.356	0.074	0.003	0.000	0.493	0.143
CaO	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
$CaSO_4$	0.000	0.000	0.000	0.000	0.000	0.000	0.000	1.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000

Fig. 4. Acid-catalyzed process to produce biodiesel from waste oils.



Stream name	101	102	103	105B	106	201	203	205A	301C	303A	303B	401A	401	402	501	502
Temperature (°C)	25.0	58.9	25.0	60.0	80.0	64.1	60.0	25.0	60.0	40.0	40.0	149.7	149.7	414.7	46.6	114.49
Pressure (kPa)	100	400	100	400	400	100	200	180	150	160	160	10	10	20	40	50
Molar flow (kg-mol/h)	6.72	59.03	1.53	1.165	60.89	51.52	9.37	4.98	4.85	10.73	1.53	1.400	3.42	0.035	8.84	1.89
Mass flow (kg/h)	215.50	1992.41	150.00	1030.00	3046.44	1650.82	1395.61	1160.75	1153.50	369.37	208.13	118.62	1004.00	30.88	246.92	128.45
Liquid volume flow (m^3/h)	0.271	2.396	0.081	1.144	3.551	2.074	1.477	1.364	1.358	0.400	0.070	0.177	1.146	0.034	0.298	0.102
Component mass fraction																
Methanol	1.000	0.925	0.000	0.000	0.576	1.000	0.075	0.004	0.000	0.542	0.000	0.004	0.000	0.000	0.811	0.000
Triacylglycerol (oil)	0.000	0.000	0.000	1.000	0.010	0.000	0.022	0.027	0.027	0.000	0.000	0.000	0.000	1.000	0.000	0.000
FAME (biodiesel)	0.000	0.000	0.000	0.000	0.330	0.000	0.720	0.865	0.890	0.014	0.000	0.031	0.996	0.000	0.000	0.041
Glycerol	0.000	0.000	0.000	0.000	0.034	0.000	0.075	0.001	0.000	0.282	0.000	0.000	0.000	0.000	0.000	0.850
H_2SO_4	0.000	0.075	1.000	0.000	0.049	0.000	0.107	0.002	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
H_2O	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.162	0.000	0.008	0.000	0.000	0.189	0.109
n-Hexane	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.101	0.101	0.000	0.000	0.957	0.004	0.000	0.000	0.000
CaO	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
$CaSO_4$	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	1.000	0.000	0.000	0.000	0.000	0.000

Fig. 5. Alternative acid-catalyzed process to produce biodiesel from waste oils using hexane extraction.

Table 1
Materials of construction for main processing units

Main process equipment		Process I	Process II	Process III	Process IV
Pretreatment unit	R-100 esterification reactor	N/A	Stainless steel (type 316)	N/A	N/A
	T-100 glycerine washing		Stainless steel (type 316)		
	T-101 methanol recovery I		Stainless steel (alloy 20)		
Transesterification unit	R-101 transesterification reactor	Stainless steel[a]	Stainless steel[a]	Stainless steel (type 316)	Stainless steel (type 316)
Separation unit	T-201 methanol recovery II	Carbon steel	Carbon steel	Stainless steel (alloy 20)[b]	Stainless steel (alloy 20)[b]
	R-201 catalyst removal	Carbon steel	Carbon steel	Stainless steel (alloy 20)[b]	Stainless steel (alloy 20)
	T-301 water washing (or hexane extraction)	Carbon steel	Carbon steel	Carbon steel	Stainless steel (alloy 20 or type 316)
	T-401 FAME purification	Carbon steel	Carbon steel	Carbon steel	Carbon steel
	T-501 glycerine purification	Carbon steel	Carbon steel	Carbon steel	Carbon steel

[a] Carbon steel may be used.

[b] A nickel alloy (e.g., C-22 or G-30) as the material of construction may be used at a high temperature.

The results using the UNIQUAC model were somewhat different from the above using the NRTL model. The main components of stream 301A (1184 kg/h) were FAME (85%) and water (10%). Therefore, the load of T-401 was increased because of the presence of more water in the feed stream 301A. Bottom stream 303 (173 kg/h) contained 60% glycerol, 32% water and 6% sodium hydroxide. However, regardless of which model was used, the simulation results indicated that adding the proper amount of water could lead to almost complete separation between the FAME and glycerol phase.

4.1.4. FAME purification

In order to obtain a final biodiesel product adhering to ASTM specifications (greater than 99.6% pure), FAME distillation T-401 with four theoretical stages and a reflux ratio of 2 were used. Stream 301A from T-301 was forwarded to T-401. T-401 was operated under vacuum to keep temperatures low enough to prevent degradation of the FAME. A partial condenser was used to provide easy separation of the FAME from water and methanol in the column overhead. Water and methanol were removed as vent gases (stream 401A). FAME product (99.65% purity) was obtained in stream 401 as a liquid distillate (194 °C and 10 kPa). Unconverted oil remained at the bottom of T-401. Since only a small amount of unconverted oil (52 kg/h) was left, it was treated as a waste. When oil conversion in reactor R-101 was low and oil recycling was necessary for waste reduction, a cooler and a pump were required to pump the unconverted oil back to the transesterification reactor. Superheated high pressure steam was the heating medium for the reboiler.

When the UNIQUAC model rather than NRTL was employed, the load in T-401 increased. Accordingly, the size of T-401 and the energy requirement increased. However, the same desired purity of FAME product was obtained using either thermodynamic/activity model.

4.1.5. Alkali removal

Stream 303 (128 kg/h) was fed to neutralization reactor R-201 to remove sodium hydroxide by adding phosphoric acid (100% purity). The resulting Na_3PO_4 was removed in gravity separator X-302. When potassium hydroxide is used as an alkali catalyst, the resulting potassium phosphate may be used as a valuable by-product (e.g., fertilizer).

4.1.6. Glycerine purification

After removing the sodium hydroxide, stream 305 contained 85% glycerol. If a glycerine by-product with a higher grade (e.g., 92%) was preferred, this stream would pass to T-501 for further removal of water and methanol by distillation. When the UNIQUAC model was used, stream 305 contained 62% glycerol and was fed to T-501 to obtain 85% or 92% glycerine. Glycerine purification T-501 was designed with four theoretical stages and a reflux ratio of 2. Water and methanol were removed in distillate stream 501. At the bottom, 92% glycerine was obtained as a high quality by-product.

4.1.7. Waste treatment

The compositions of streams 401A, 402 and 501 are listed in Fig. 2. Because of their small flows, these streams were treated as hazardous gas or liquid wastes. However, reusing these streams may be advantageous in the future, especially for larger scale processes. For example, stream 501 can be returned to T-301 as a washing solvent instead of fresh water. Recovery of the solid waste stream 306 from X-302 as a possible fertilizer credit is also feasible. Overall, these changes offer potential approaches for reducing waste treatment loads.

4.2. Alkali-catalyzed process using waste cooking oil (process II)

To lower the cost of biodiesel, a continuous alkali-catalyzed process from waste cooking oil was developed. In comparison to process I, a pretreatment unit, including esterification of the free fatty acids, glycerine washing and methanol recovery, was added. The pretreatment unit is shown in Fig. 3 while the remainder of the process is identical to that shown in Fig. 2. The characteristics of the main streams in process II are shown in Fig. 3.

4.2.1. Esterification

The esterification reaction was carried out at 70 °C, 400 kPa and a 6:1 molar ratio of methanol to crude oil (Lepper and Friesenhagen, 1986). The fresh methanol stream 101 (128 kg/h), the recycled methanol stream 1111 (188 kg/h) and the H_2SO_4 stream 103 (10 kg/h) were mixed before being pumped into esterification reactor R-100 by pump P-101. The waste cooking oil stream 105A (1050 kg/h), containing 6% free fatty acids, was heated in exchanger E-100 to 60 °C before entering R-100. In R-100, all the free fatty acids were converted to methyl esters. After being cooled to 46 °C, stream 106 was forwarded to glycerine washing column T-100 to remove the sulfuric acid and water.

4.2.2. Glycerine washing

The resulting water and acid catalyst (H_2SO_4) from R-100 must be removed completely before proceeding to the alkali-catalyzed transesterification. By adding 110 kg/h of glycerine at 25 °C and 200 kPa, all of the resulting water was removed from oil stream 110A after three theoretical stages of washing. Stream 110A from T-100 was sent to downstream transesterification unit R-101. On the other hand, stream 110B (336 kg/h) contained 60% unreacted methanol, 33% glycerol, 3% sulfuric acid, 3% oil, 1% water and traces of esters. Recovering most of the methanol in this stream for reuse in R-100 was a logical step, which was realized in methanol recovery column T-101.

4.2.3. Methanol recovery

In T-101, five theoretical stages and a reflux ratio of 5 were used. At 28 °C and 20 kPa, 94% of the total methanol fed to the column was recovered in the distillate (i.e., stream 111) at the rate of 188 kg/h. It contained 99.94% methanol and 0.06% water and was recycled to R-100. At 70 °C and 30 kPa, bottom stream 112 (147 kg/h) was composed of 75% glycerol, 8% methanol, 7% sulfuric acid, 7% oil and 3% water. Due to the presence of sulfuric acid, this stream was not reused and was treated as waste. Nevertheless, neutralizing the sulfuric acid and then recovering the glycerol is a feasible alternative to reduce waste.

Once the refined oil without free fatty acids is obtained, the downstream units are identical to those in process I using virgin vegetable oil. Compared to process I, despite the decrease in raw material cost by using waste oil, the addition of a pretreatment unit to reduce the content of free fatty acids in the feedstock oil in process II would be expected to more than offset these savings.

4.3. Acid-catalyzed process using waste cooking oil (process III)

An acid-catalyzed system is insensitive to any free fatty acids in the oil. Consequently, process III, an acid-catalyzed continuous process from waste cooking oil (Fig. 4) appears to be a promising alternative to the alkali process. The description of process III concentrates on the differences from the previous processes I and II.

4.3.1. Transesterification

On the basis of discussions in Section 2.2, the reaction conditions were set to a 50:1 molar ratio of methanol to oil, a 1.3:1 molar ratio of sulfuric acid to waste oil, a reaction temperature of 80 °C and a pressure of 400 kPa.

Fresh methanol (stream 101 at 216 kg/h), recycled methanol (stream 1201 at 1594 kg/h) and sulfuric acid (stream 103 at 150 kg/h) were mixed first and fed to transesterification reactor R-101 by pump P-101. Waste cooking oil (stream 105 at 1030 kg/h) entered R-101 after being heated to 60 °C in exchanger E-101. In R-101, 97% of the oil was assumed to be converted to FAME after 4 h. Two identical reactors operated in series were used, indicated as R-101A/B in Fig. 4.

4.3.2. Methanol recovery

Because of the large excess of methanol in stream 106, methanol recovery was the first step following the reaction in order to reduce the load in the downstream units. In methanol distillation column T-201, five theoretical stages, a reflux ratio of 2 and vacuum distillation were employed. As in process I, a 94% methanol recovery rate was achieved in stream 201 and recycled to R-101. Bottom stream 202 was forwarded to acid removal unit R-201.

4.3.3. Acid removal

For acid removal, the design principle was the same as for alkali removal in process I. In reactor R-201, sulfuric acid was completely removed in a neutralization reaction by adding calcium oxide (CaO) to produce $CaSO_4$ and H_2O. Calcium oxide was used primarily due to its low-cost relative to other alkali substances. Also the water produced would be absorbed by the resulting $CaSO_4$ to form $CaSO_4 \cdot 2H_2O$. However, since absorption of water by $CaSO_4$ is relatively slow, in our current simulations $CaSO_4$ rather than $CaSO_4{\cdot}2H_2O$ was considered as a solid waste. A gravity separator, X-201, was employed to remove the $CaSO_4$. The resulting stream 203C (1247 kg/h) consisting of 79% FAME, 9% glycerol, 8% methanol, 2% unconverted oil and 2% water proceeded to water washing column T-301.

In terms of equipment sizing and operating conditions, the remaining water washing column (T-301) and purification units (i.e., FAME purification column T-401 and glycerol purification column T-501) were similar to those used for process I.

4.3.4. Other considerations

There are some other methods to increase oil conversion to the esters. Based on our recent experimental results, a 99% oil conversion to FAME was observed after 4 h when a 245:1 molar ratio of methanol to oil and 80 °C were used. A qualified biodiesel product was achieved, as well as the reduction of unconverted oil waste. However, such a huge excess of methanol in the system resulted in a very large increase in the sizes of the reactor, methanol distillation column and other separation units. Accordingly, its impact on economic feasibility of a biodiesel plant was expected to be significant.

4.4. Acid-catalyzed process using hexane extraction (process IV)

To avoid the formation of emulsions due to water washing, the use of hexane or petroleum ether as a solvent following the procedures of Nye et al. (1983) and McBride (1999), to separate the FAME from other components was proposed in process IV (Fig. 5). The operating conditions for the units from reactor R-101 to methanol distillation T-201 were the same as those in process III. The following discussion pertains to the units downstream of methanol distillation column T-201.

After T-201, the reaction mixture contained methanol, FAME, glycerol, sulfuric acid, unconverted oil. When hexane was added and a liquid–liquid extraction was used in simulating hexane extraction of FAME, the results showed incomplete recovery of FAME in hexane. This was due partly to the lack of information in the HYSYS on interaction parameters in such a complex multi-component system and also to the fact that hexane is soluble in anhydrous methanol. To decrease hexane solubility, water was added to the methanol in the ratio 1:10 by volume, resulting a clear-cut separation of hexane/FAME and methanol/water phases (McBride, 1999). In addition, instead of a liquid–liquid extraction unit, component splitters T-301A and T-301B were used in simulating the hexane extraction of FAME and the methanol/water washing in process IV. On the basis of our experimental results (McBride, 1999), we assumed that a good separation between the FAME/hexane and glycerol/methanol/water phases was achieved after the addition of hexane and water. Based on amounts of these components in feed streams 203 and 205, 100% of the hexane and the unconverted oil, 99.5% of the FAME, 4% of the methanol and the water, 2% of the sulfuric acid and 1% of the glycerol, were in the upper layer (stream 205A) from T-301A. The lower layer (stream 205B) consisted of the remaining glycerol, methanol, sulfuric acid and water. A second washing with methanol/water (T-301B) was applied to completely remove the water, glycerol and sulfuric acid from the hexane/FAME layer in stream 205A at room temperature. Detailed descriptions of these separations follow.

4.4.1. Hexane extraction

Based on the methanol volume in stream 203, an equal volume of hexane (0.13 m^3/h) and 0.01 m^3/h water (vol. ratio of water to methanol was 1:10) were added to T-301A at 25 °C and 200 kPa. After hexane extraction in T-301A, stream 205A was forwarded to a second washing unit (T-301B) at 25 °C and 150 kPa. The main components of bottom stream 205B were methanol (27%), glycerol (28%), sulfuric acid (40%) and FAME (1.4%). In T-301B, 0.14 m^3/h methanol–water (80:20 v/v) was added. After T-301B, neither glycerol nor sulfuric acid remained in the FAME and hexane stream 301A. It was then passed to the downstream FAME distillation column T-401 to remove the hexane. Stream 205B from T-301A was combined with stream 301B from T-301B. At a total flowrate of 492 kg/h, they entered R-201 for sulfuric acid removal by adding calcium oxide, as in process III.

4.4.2. FAME purification

Because most of the methanol remained in the glycerol stream after the hexane extraction and second methanol/water washing, T-401 was principally used for distilling the hexane from the FAME. At five theoretical stages and a reflux ratio of 3, vent gases (stream 401A) were discharged from the top of T-401 and recycled to T-301A to reduce the need for fresh solvent (stream 110). Distillate stream 401 was the FAME product (99.65%) and stream 402 from the bottom of T-401 contained any unconverted oil.

4.4.3. Glycerine purification

Stream 303A entered T-501 for a five-theoretical-stage distillation and a reflux ratio of 2. Glycerine with 85% or 92% purity, depending on the desired degree of purity, could be obtained in stream 502 by different energy requirements. A portion of top stream 501 (112 kg/h) was returned to T-301B as the solvent for the second washing.

Table 2
Description of operating conditions of main equipment (NRTL)

Main process equipment			Process I	Process II	Process III	Process IV	
Pretreatment unit	R-100	Temp., °C	N/A	70	N/A	N/A	
		Pressure, kPa		400			
		Size ($D \times H$), m		0.8 × 2.4			
	T-100	Temp., °C		42/45			
		Pressure, kPa		190/200			
		Size ($D \times H$), m		1 × 10			
	T-101	Temp., °C		28/69			
		Pressure, kPa		20/30			
		Size ($D \times H$), m		1 × 12			
Transesterification	R-101	Temp., °C	60	60	80	80	
		Pressure, kPa	400	400	400	400	
		Size ($D \times H$), m	1.8 × 5.4	1.8 × 5.4	2.1 × 6.3[a]	2.1 × 6.3[a]	
Separation unit	T-201	Temp., °C	28/122	28/126	81/116	81/116	
		Pressure, kPa	20/30	20/30	190/200	190/200	
		Condenser duty, MJ	0.4	0.3	5.1	5.1	
		Reboiler duty, MJ	0.5	0.5	5.3	5.3	
		Normal vapor flowrate, kg/h	330	300	4780	4780	
		Size ($D \times H$),	0.6 × 10	0.6 × 10	1 × 10	1 × 10	
	T-301	Total flowrate, kg/h	1190	1206	1364	T-301A	1530
						T-301B	1176
		Size ($D \times H$), m	0.8 × 10	0.8 × 10	1 × 10	T-301A	1 × 10
						T-301B	0.8 × 10
	T-401	Temp., °C	194/415	190/415	264/463	150/415	
		Pressure, kPa	10/20	10/20	40/50	10/20	
		Condenser duty, MJ	1.3	1.3	1.0	2.0	
		Reboiler duty, MJ	1.7	1.6	1.6	2.3	
		Normal vapor flowrate, kg/h	3100	3000	3000	4000	
		Size ($D \times H$), m	1.2 × 12	1.2 × 12	1 × 12	1.5 × 16	
	T-501	Temp., °C	N/A	64/108	52/107	46/114	
		Pressure, kPa		40/50	40/50	40/50	
		Condenser duty, MJ		0.2	1.0	1.0	
		Reboiler duty, MJ		0.3	1.0	1.0	
		Normal vapor flowrate, kg/h		150	600	740	
		Size ($D \times H$), m		0.5 × 10	0.6 × 10	0.8 × 10	

[a] Two reactors with the same sizes.

Table 3
Number of main processing units required for each process: total # (# requiring stainless steel)

Equipment	Process I	Process II	Process III	Process IV
Reactors	2 (2)	3 (3)	3 (3)	3 (3)
Columns	4 (0)	6 (2)	4 (1)	5 (3)
Exchangers	8 (0)	11 (1)	8 (3)	10 (3)
Pumps	6 (0)	8 (1)	5 (1)	6 (1)
Gravity separator(s)	1 (0)	1 (0)	1 (0)	1 (0)
Total	21 (2)	29 (7)	21 (8)	25 (10)

4.5. Process comparisons

A technical comparison of the four different processes is summarized in Tables 2 and 3. The sizes of major processing units in each process are presented in Table 2. The total number of major processing units in each process is summarized in Table 3.

4.5.1. Pre-esterification unit

The pretreatment required in the alkali-catalyzed process using waste cooking oil (process II) was not necessary in the other processes (Table 2). Virgin oil without free fatty acids was used in process I. Processes III and IV, being acid-catalyzed, were insensitive to free fatty acids and used waste cooking oil as raw material.

The pretreatment unit in process II included esterification reactor R-100, glycerine washing column T-100 (1×10 m) and methanol distillation column T-101 (1×12 m). Although R-100 was a small reactor compared to transesterification reactor R-101 in all of the processes, the sizes of columns T-100 and T-101 in process II were similar to other columns in all processes (Table 2). In addition, the use of pure glycerine as a washing solvent in T-100 would also offset a credit for selling the glycerine by-product from the transesterification unit. Moreover, the presence of sulfuric acid as a catalyst required the use of stainless steel materials in R-100, T-100, T-101 and their auxiliary equipment. There was an extra amount of waste in stream 112 (147 kg/h) from T-101 bottom in process II whereas it was absent from the other processes. Altogether, in process II these factors result in an increase in process complexity, with concomitant increases in equipment and operating costs.

4.5.2. Transesterification

The larger amount of methanol used in the acid-catalyzed processes III and IV led to increased reaction volumes. For example, the flowrate of effluent from R-101 (stream 106) in process I was 1228 kg/h but was 2990 kg/h in process III where total reactor capacities were 13.7 and 43.6 m^3, respectively.

4.5.3. Methanol distillation T-201

For methanol distillation column T-201, its operating loads (i.e., vapor flowrate) and energy requirements in processes III and IV were much higher than those in processes I and II (Table 2). The main reason was because a 50:1 molar ratio of methanol to oil was used in acid-catalyzed processes III and IV whereas only a 6:1 molar ratio was employed in alkali-catalyzed processes I and II. This resulted in larger column sizes and higher heat duties (Table 2). In addition, there was only 9 wt.% methanol in the feed stream of T-201 in processes I and II. Compared to the same stream containing 57 wt.% methanol in processes III and IV, it was more difficult to distill most of the methanol (e.g., 94% methanol recovery rate) in alkali-catalyzed processes I and II. Therefore, high vacuum distillation (20/30 kPa) was required in processes I and II. This showed that more methanol could be recovered with more rigid requirements in the operating conditions. If only 40% of the total methanol in the feed stream was recovered in process I, the operating pressure would be at normal pressure 110/120 kPa (top/bottom) with a bottom temperature at 100 °C. However, with a low methanol recovery rate, there would be more methanol entering the waste streams 401A and 501. More fresh make-up methanol (stream 101) would be required as well. As a result, waste disposal expenses and reactant costs would increase.

The construction material of T-201 was stainless steel (alloy 20) in processes III and IV whereas it was carbon steel in processes I and II (Table 1). This was because the concentration of sulfuric acid in the bottom of T-201 in processes III and IV was far higher than that of sodium hydroxide in processes I and II. Thus, the cost of material of construction of this column in processes III and IV would be higher than that in processes I and II.

4.5.4. Washing column T-301

As presented in Table 2, despite the different data resulting from the thermodynamic/activity model used, the operating load of T-301 in each process was similar, based on the same model (e.g., NRTL). Thus, similar column sizes were estimated for all four processes. Nevertheless, two washing columns were required in process IV rather than one column in the other processes. Because of the presence of sulfuric acid in T-301A/B in process IV, stainless steel was still used as the material of construction whereas carbon steel was sufficient in processes I, II and III (Table 1).

4.5.5. FAME purification column T-401

The sizes of FAME purification column T-401 were identical in processes I, II and III (Table 2). Most of the methanol was removed in T-201 in process III, which resulted in loads in the downstream units similar to those in processes I and II. In process IV, the addition of hexane/water (110 kg/h) in T-301A led to an increased load as well as higher energy needs in T-401. Thus, the size of this column was larger in process IV than in the other processes. In all processes, vacuum distillation was necessary to lower the column temperature.

4.5.6. Glycerine purification column T-501

In glycerine purification column T-501, the flowrate of the feed stream to T-501 was 120–160 kg/h in processes I and II. However, the flowrate of the feed stream was 328 kg/h in process III because of the presence of the large excess of methanol. Although 94% of the total methanol was recovered in T-201, the unrecovered 6% still played a major role in determining the amount of feed to T-501. For T-501 in process IV, its load and size were even larger than those in process III because of the addition of methanol/water (115 kg/h) as a washing solvent in T-301B. Vacuum distillation (40/50 kPa) was required in each process to obtain a high quality glycerine by-product. Although T-501 was unnecessary in process I when the NRTL model was used, it was needed when the UNIQUAC model was applied.

Overall, if the pretreatment unit is not taken into consideration, the sizes of the process equipment in alkali-catalyzed processes I and II are smaller than those in acid-catalyzed processes III and IV. The lowest number of units was in process I in which most of the equipment was made from carbon steel. Process II had the highest number of units with an extra nine pieces compared to process I. These nine pieces of equipment were related to the pretreatment unit. In acid-catalyzed processes III and IV, fewer units were required compared to process II but the number of those made from stainless steel was increased, especially in process IV. This represents a potential increase in the cost of construction material.

5. Conclusion

For a biodiesel production rate of 8000 tonnes/yr, four flowsheets for continuous alkali- and acid-catalyzed processes (I–IV) using virgin vegetable oil or waste cooking oil as the raw material were designed and simulated. From the technical assessment, all of these processes proved to be feasible for producing a high quality biodiesel product and a top-grade glycerine by-product under reasonable operating conditions. However, each process had its limitations. The alkali-catalyzed process using virgin oil (process I) was the simplest with the least amount of process equipment but had a higher raw material cost than other processes. Despite the reduced raw material cost in using waste cooking oil (process II), it was the most complex process with the greatest number of equipment pieces because of the addition of a pretreatment unit for free fatty acids removal. The acid-catalyzed process III using waste cooking oil had less equipment pieces than process II, but the large methanol requirement resulted in more and larger transesterification reactors, as well as a larger methanol distillation column. Methanol distillation was carried out immediately following transesterification to reduce the load in downstream units in process III but more pieces of equipment made from stainless steel material were necessary than in processes I and II. Acid-catalyzed process IV had the same merits and limitations as process III. However, the addition of hexane and methanol/water solvents increased the number of process equipment pieces and sizes of some separation units in process IV. In brief, for process simplicity, the alkali-catalyzed process using virgin vegetable oil (process I) is recommended. However, if raw material cost is of concern, the acid-catalyzed process using waste cooking oil (process III) is a relatively simple process and proved to be a competitive alternative to processes I and II.

In general, the feasibility of a plant includes both technological and economic aspects. Thus, aside from assessing the technological feasibility of the different process designs for biodiesel, an economic evaluation of these processes is needed, especially for processes I and III. Some differences in the simulation results were found when using the different thermodynamic/activity models NRTL and UNIQUAC. Consideration must be taken of the sensitivity of the results to the thermodynamic model used and the significance of model influences on the results. All of these points will be discussed in a subsequent article (Zhang et al., submitted for publication).

Acknowledgements

The authors acknowledge the support of Natural Sciences and Engineering Research Council of Canada and the help provided by Dr. A.Y. Tremblay with the HYSYS™ simulations and by Dr. B.C.-Y. Lu with the thermodynamic models.

References

Agarwal, A.K., Das, L.M., 2001. Biodiesel development and characterization for use as a fuel in compression ignition engines. J. Eng. Gas Turbines Power 123, 440–447.

Basu, H.N., Norris, M.E., 1996. Process for production of esters for use as a diesel fuel substitute using a non-alkaline catalyst. US Patent 5525126.

Boocock, D.G.B., Konar, S.K., Mao, V., Lee, C., Buligan, S., 1998. Fast formation of high-purity methyl esters from vegetable oils. J. Am. Oil Soc. Chem. 75 (9), 1167–1172.

Canakci, M., Gerpen, J.V., 1999. Biodiesel production via acid catalysis. Trans.: Am. Soc. Agric. Eng. 42 (5), 1203–1210.

Chemical Market Reporter, 2002. 261(24), 30–31.

Connemann, J., Fischer, J., 1998. Biodiesel in Europe 1998: Biodiesel processing technologies. Paper presented at the International Liquid Biofuels Congress, Brazil, 15 pp.

Darnoko, D., Cheryan, M., 2000. Kinetics of palm oil transesterification in a batch reactor. J. Am. Oil Soc. Chem. 77 (12), 1263–1267.

Davis, J.R. et al., 2000. Corrosion: Understanding the Basics. ASM International, Materials Park, OH (Chapters 2–5).

Freedman, B., Pryde, E.H., Mounts, T.L., 1984. Variables affecting the yields of fatty esters from transesterified vegetable oils. J. Am. Oil Soc. Chem. 61, 1638–1643.

Freedman, B., Butterfield, R.O., Pryde, E.H., 1986. Transesterification kinetics of soybean oil. J. Am. Oil Soc. Chem. 63, 1375–1380.

Gess, M.A., Danner, R.P., Nagvekar, M., 1991. Thermodynamic Analysis of Vapor–Liquid Equilibria: Recommended Models and a Standard Data Base. Design Institute for Physical Property Data and American Institute of Chemical Engineers, University Park, PA (Chapter 3).

Goodrum, J.W., 2002. Volatility and boiling points of biodiesel from vegetable oils and tallow. Biomass Bioenergy 22, 205–211.

Hyprotech Ltd., 2000. HYSYS.PLANT 2.2 documentation.

Jeromin, L., Peukert, E., Wollmann, G., 1987. Process for the pre-esterification of free fatty acids in fats and oils. US Patent 4698186.

Karaosmanoğlu, F., Cigizoglu, K.B., Tuter, M., Ertekin, S., 1996. Investigation of the refining step of biodiesel production. Energy Fuels 10, 890–895.

Körbitz, W., 1999. Biodiesel production in Europe and North American, an encouraging prospect. Renew. Energy 16, 1078–1083.

Krawczyk, T., 1996. Biodiesel. INFORM 7 (8), 801–822.

Kreutzer, U.R., 1984. Manufacture of fatty alcohols based on natural fats and oils. J. Am. Oil Soc. Chem. 61 (2), 343–348.

Lawson, H., 1995. Food oils and fats. Chapman & Hall, New York (Chapter 2).

Lepper, H., Friesenhagen, L., 1986. Process for the production of fatty acid esters of short-chain aliphatic alcohols from fats and/or oils containing free fatty acids. US Patent 4608202.

Liu, K.S., 1994. Preparation of fatty acid methyl esters for gas-chromatographic analysis of lipids in biological materials. J. Am. Oil Soc. Chem. 71 (11), 1179–1187.

Lott, M., 2002. QSS Group Inc., 4500 Forbes Boulevard, Suite 200, Lanham, MD 20706.

McBride, N., 1999. Modeling the production of biodiesel from waste frying oil. B.A.Sc. thesis, Department of Chemical Engineering, University of Ottawa.

Nelson, L.A., Foglia, T.A., Marmer, W.N., 1996. Lipase-catalyzed production of biodiesel. J. Am. Oil Soc. Chem. 73 (8), 1191–1195.

Newman, A.A., 1968. Glycerol. CRC Press, Cleveland (Chapter 6).

Norden, R.B., 1973. Materials of construction. In: Carberry, J.J., Peters, M.S., Schowalter, W.R., Wei, J. (Eds.), Chemical Engineers' Handbook, fifth ed. McGraw-Hill Book Company. (Section 23).

Noureddini, H., Zhu, D., 1997. Kinetics of transesterification of soybean oil. J. Am. Oil Soc. Chem. 74, 1457–1463.

Nye, M.J., Williamson, T.W., Deshpande, S., Schrader, J.H., Snively, W.H., 1983. Conversion of used frying oil to diesel fuel by transesterification: preliminary test. J. Am. Oil Soc. Chem. 60 (8), 1598–1601.

Peterson, C.L., 1993. Commercial process feasibility analysis and bench scale process system design. University of Idaho, Departments of Agricultural Engineering and Chemical Engineering, US Department of Energy Agreement No. DE-B179-93BPO9233. NTIS, Springfield, VA, 15 pp.

Prokop, T., 2002. Imperial Western Products, 14970 Chandler St., Coachella, CA 91720.

Ripmeester, W.E., 1998. Modeling the production of biodiesel oil from waste cooking oil. B.A.Sc. thesis, Department of Chemical Engineering, University of Ottawa.

(S & T)^2 Consulting Company, 2001. Economic opportunities in renewable bio-resource utilization. Unpublished report for industry Canada, 65 pp.

Supple, B., Howard-Hildige, R., Gonzalez-Gomez, E., Leahy, J.J., 1999. The effect of steam treating waste cooking oil on the yield of methyl ester. J. Am. Oil Soc. Chem. 79 (2), 175–178.

Von Wedel, R., 1999. Technical handbook for marine biodiesel in recreational boats. Prepared for National Renewable Energy Laboratory, US Department of Energy, Subcontract No. ACG-7-16688-01 under Prime Contract No. DE-AC36-83CH10093, 32 pp.

Watanabe, Y., Shimada, Y., Sugihara, A., Tominaga, Y., 2001. Enzymatic conversion of waste edible oil to biodiesel fuel in a fixed-bed bioreactor. J. Am. Oil Soc. Chem. 78 (2), 703–707.

Wiltsee, G., 1998. Waste grease resource in 30 US metropolitan areas. In: The Proceedings of Bioenergy 98 Conference, Wisconsin, 1998. pp. 956–963.

Zhang, Y., 2002. Design and economic assessment of biodiesel production from waste cooking oil. M.A.Sc. thesis, Department of Chemical Engineering, University of Ottawa.

Zhang, Y., Dubé, M.A., McLean, D.D., Kates, M., submitted for publication. Biodiesel production from waste cooking oil: 2. Economic assessment and sensitivity analysis. Bioresour. Technol.