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DESIGN AND ECONOMIC ASSESSMENT OF BIODIESEL PRODUCTION FROM WASTE COOKING OIL

by

Yi Zhang

A thesis submitted to the Faculty of Graduate and Postdoctoral Studies in partial fulfillment of the requirements for the degree of

Master of Applied Science, Chemical Engineering

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Abstract

Biodiesel is a recommended petroleum-based diesel substitute mainly because it is environmentally friendly and is a renewable, domestic resource. However, compared to petroleum-based diesel, biodiesel has a higher cost, which is the major obstacle to its commercialization.

In this thesis, four different continuous alkali- and acid-catalyzed processes to produce biodiesel from virgin vegetable oil and waste cooking oil were designed and simulated. Process flowsheets, along with detailed operating conditions and equipment designs for each process were created. Technical assessment of these processes showed that the alkali-catalyzed process using virgin oil required the least amount of process equipment and no significant requirement for special materials of construction but had the highest raw material cost. The acid-catalyzed process using waste cooking oil proved to be technically feasible with a significantly lower raw material cost but required forty percent of the process equipment to be constructed from stainless steel.

An economic assessment was also performed based on the results of process simulations. The alkali-catalyzed process using virgin vegetable oil was found to have the lowest fixed capital cost. However, in terms of total manufacturing cost, aftertax rate of return and break-even price of biodiesel, the acid-catalyzed process using waste cooking oil had the lowest operating cost, the best aftertax rate of return (i.e., 10%) and the lowest break-even price (i.e., $590/tonne). In summary, the acid-catalyzed process to produce biodiesel from waste cooking oil is technically feasible and economically attractive. Results from the sensitivity analyses of the various processes indicated that plant capacity, the price of feedstock oil and biodiesel price were the factors that most significantly affected the economic feasibility of biodiesel production.

Résumé

Le biodiesel est recommandé en tant que subsitut pour le diesel à base pétrolière, principalement parce que c'est une ressource domestique renouvelable qui est sensible à l'environnement. Par contre, l'obstacle le plus important pour la commercialisation du biodiesel est son coût plus élevé comparativement au diesel à base pétrolière.

Au cours de cette thèse, quatre procédés continus catalysés d'acide et de base pour produire du biodiesel à partir d'huile végétale vierge et d'huile de cuisine superflue ont été dévelopés et simulés. Des flowsheets de procédés ainsi que des conditions d'opération détaillées et des conceptions d'équipement ont été créés. Une évaluation technique de ces procédés a démontré que le procédé catalysé de base utilisant l'huile vierge nécessitait le moins d'équipement de production et n'avait aucun besoin significatif de matériaux de construction spécialisés, mais avait le coût de matière première le plus élevé. Le procédé catalysé d'acide utilisant l'huile de cuisine superflue s'est avéré être techniquement faisable tout en ayant un coût de matière première significativement plus bas, mais nécessitait que quarante pourcent de l'équipement soit construit en acier inoxidable.

Une étude de faisabilité économique a aussi été conduite basée sur les résultats des simulations de procédés. Il a été découvert que le procédé catalysé de base utilisant l'huile végétale vierge avait le coût capital fixe le plus bas. Par contre, en termes du coût de production total, du taux après-taxes de retour et du prix de rentabilité du biodiesel, le procédé catalysé d'acide utilisant l'huile de cuisine superflue avait le coût d'opération le plus bas, le meilleur taux après-taxes de retour (c'est-à-dire 10%) et le prix de rentabilité du biodiesel le plus bas (c'est-à-dire 590$/tonne). En somme, le procédé catalysé d'acide produisant du biodiesel à partir d'huile de cuisine superflue est techniquement faisable et économiquement attrayant. Les résultats des analyses de sensibilité de divers procédés ont indiqué que la capacité d'usine, le prix d'huile feedstock et le prix du biodiesel étaient les facteurs les plus importants affectant la faisabilité économique de la production du biodiesel.

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Table of Contents

List of Tables

List of Figures

Chapter 1 INTRODUCTION

1.1 What is biodiesel?

According to the American Society for Testing and Materials (ASTM), biodiesel can be defined as monoalkyl esters of long chain fatty acids derived from a renewable lipid feedstock, such as vegetable oil or animal fat, for use in diesel engines. "Bio" represents its biological source and "diesel" implies its use as a fuel. It is typically produced by a catalyzed transesterification reaction in which vegetable oil or animal fat reacts with an alcohol. As an alternative fuel, biodiesel can be in the neat form or mixed with petroleum-based diesel.

Relative to conventional petroleum-based fuels, biodiesel has gained acceptance as an alternative fuel because:

- It is a renewable, domestic resource. Biodiesel is derived from vegetable oil or animal fat. Every country has the ability to produce biodiesel, thus relieving reliance on petroleum fuel imports.
- It is biodegradable and non-toxic. European tests of biodiesel produced from rapeseed oil indicated that it is 99.6% biodegradable within 21 days and should completely decompose within one month (Congressional Research Service, 1993).
- It emits less carbon monoxide, lower particulate matter (e.g. smoke), unburned hydrocarbons (e.g. soot) and almost no sulfur or aromatic compounds compared to petroleum-based diesel. For an engine running on biodiesel, Korbitz (1999) found a 20% reduction in carbon monoxide emissions, 99% reduction in sulfur compounds, and 39-50% reduction in particulate matter and soot emissions.
- It has insignificant contribution to the accumulation of carbon dioxide compared to petroleum-based diesel. Thus, this will not aggravate the

greenhouse effect. Agarwal and Das (2001) reported that the cycle time of carbon dioxide (fixed by plants and released during combustion) in biodiesel is quite smaller than that of petroleum oils.

- It has a high flash point (approximately 150°C). Petroleum-based diesel has a much lower flash point (approximately 50°C) (Krawczyk, 1996). Fuels with higher flash points are less volatile and thus, safer to transport or handle.
- It requires few modifications when biodiesel is used in diesel engine and it provides more lubrication than petroleum-based diesel (Knothe et al., 1996; Krawczyk, 1996; Wedel, 1999).

The fuel properties of common vegetable oils, their methyl esters (biodiesel) and #2 petroleum-based diesel are compared in Table 1.1.

Table 1.1 Fuel properties of some vegetable oils, their methyl esters (biodiesel) and #2 diesel fuel (Knothe et al., 1996)

Property	Soybean oil	Soy esters	Sunflower oil	Sunflower esters	Canola oil	Canola esters	#2 Diesel
Viscosity (mPa.s)	31.9	4.6	30.0	4.4	33.7	5.2	2.6
Density (kg/cm^3)	910.78	922.77	910.78	874.83	910.78	862.85	850.86
Heat energy (kJ/kg)	39,623	39,800	39,575	39,800	39,709	40,449	45,343
Cloud point (°C)	-3.9	2	7.2	0	-3.9	10	-15
Flash point (°C)	254	171	274	164	>250	180	52
Boiling point (°C, atm.)	380	350	380	-	400	340	350
Cetane No.	38	46.2	37	46.6	37	54	47

Apart from these good features, biodiesel has some limitations:

- It has a slightly lower heat value than that of petroleum-based diesel fuel (see Table 1.1). This implies that less power is provided when biodiesel is burned (Knothe et al., 1996).

- It has poorer low-temperature properties (e.g., higher cloud point) than petroleum-based diesel fuels, which might be a barrier to its use in cold climates (see Table 1.1). One effective way to overcome this shortcoming is to produce a blend of biodiesel with petroleum-based diesel fuel, such as B20 (20% biodiesel, 80% diesel) (Krawczyk, 1996).
- It has slightly higher (2-4%) emissions of nitrogen oxide (NO_x) than petroleum-based diesel (Krawczyk, 1996; Korbitz, 1999). However, such small increases could be overcome by adjusting combustion temperature or engine timing (Krawczyk, 1996).

In spite of the above limitations, biodiesel appears to be a good alternative to petroleum-based fuel and is employed in many countries around the world.

1.2 History of biodiesel

In 1900, Rudolf Diesel succeeded in running a combustion engine using peanut oil as fuel and demonstrated it at the World Exhibition in Paris. In 1911, he stated that "the diesel engine can be fed with vegetable oils and would help considerably in the development of agriculture of the countries which use it". In 1912 he claimed that "the use of vegetable oils for engine fuels may seem insignificant today. But such oils may become in course of time as important as petroleum and coal tar products of the present time" (Krawczyk, 1996). However, with the appearance of low viscosity petroleum-based diesel, interest in the higher viscosity vegetable oils, which tend to stick to the fuel injector in the engine, waned. Better engine performance, easy availability and favourable economics led to a steady growth in the use of petroleum-based fuels for most of the 20th century.

In recent years, especially after the Gulf War in 1991, interest began to turn towards non-petroleum, domestic and renewable fuels, so as to relieve the occasional period of "petroleum anxiety". At the same time, the state of the environment has become an issue of great concern. Stricter environmental requirements for the reduction in pollutants demand the appearance of fuels having a minimal impact on the environment. Once again, vegetable or animal oils have gained attention and are seriously considered as alternative fuel sources.

Problems with substituting virgin vegetable or animal oil for petroleum-based fuels are mostly associated with their high viscosities. The fuel injection system in the engine is sensitive to high fuel viscosity, which easily causes coking in the injector and engine deposits. The viscosity of vegetable oil is nearly 10 times that of #2 Diesel (petroleum-based) (see Table 1.1). Attempts have been made to reduce its viscosity, thus making it more attractive as an alternative fuel.

Generally, there are at least four potential ways to reduce the viscosity of vegetable oils: dilution, pyrolysis, microemulsion and transesterification. Schwab et al. (1987), Knothe et al. (1996) and Ma and Hanna (1999) described these four methods in detail. Dilution involves blending vegetable oils with petroleum-based diesel. For example, at 40°C, a blend of petroleum-based diesel and sunflower oil at a ratio of 75:25 (vol.%) has a viscosity at 4.44 mPa.s (Knothe et al., 1996). Pyrolysis refers to a chemical process in which one compound is broken into simpler compounds by heating, similar to the crude oil cracking process used to produce petroleum-based fuels. A microemulsion is defined as a system consisting of a liquid dispersed with or without an emulsifier in an immiscible liquid, usually in droplets smaller than colloidal size. Finally, transesterification refers to the process of transesterifying vegetable oil with an alcohol to fatty acid alkyl esters in the presence of a catalyst. It has the effect of reducing the molecular weight of the oil by approximately one third and the resulting viscosity is similar to petroleum-based diesel fuel (see Table 1.1). Transesterification is the most useful of the fuel viscosity-reduction processes and is the focus of this thesis.

1.3 Biodiesel production

At present, biodiesel is produced commercially in Europe and the United States. The main biodiesel producers are shown in Table 1.2. In Europe, biodiesel has been in commercial use in Austria, Italy, Germany and France since 1988. Reduction of the tax on biodiesel stimulated its commercial use so that its price remained competitive with that of petroleum-based diesel. In Europe it is estimated that biofuels will reach five percent of the market share of total fuel consumption by the year 2005 (Connemann and Fischer, 1999). Despite its high price, the market for biodiesel continues to develop because of environmental concerns. In Canada, biodiesel is still being produced only on

the laboratory or pilot-plant scale and no commercial biodiesel facilities to date are reported. Interest in biodiesel is remarkably growing all over the world. Some biodiesel producers and information sources are listed in Table 1.3.

Table 1.2 Biodiesel production in Europe and U.S.A (Korbitz, 1999)

Country	Annual production (tones)		
	1996	1997	Predicted*
Austria	17,000	22,000	
Belgium	20,000	20,000	
France	227,000	250,000	100,000
Germany	63,000	83,000	30,000
Italy	141,000	109,000	
Czech Republic	22,000	45,000	
U.S.A	5,000	8,000	300,000

* No indication of the basis of this prediction is given in the source.

The price of biodiesel is about 3 to 5 times that of petroleum-based diesel fuels (Connemann and Fischer, 1999). Bender (1999) reported that biodiesel costs over $0.60 per litre, compared to $0.20 per litre for petroleum-based diesel. It is reported that approximately 75% or more of the cost of biodiesel is due to the cost of raw material (Krawczyk, 1996; Connemann and Fischer, 1999). Exploring effective ways to reduce biodiesel cost has become the focus of biodiesel research, especially for methods to reduce the raw material cost. Thus, the use of waste cooking oil to produce biodiesel is of interest because its price is much lower than virgin oil. This was a focus of this work.

Table 1.3 Biodiesel producers in the world

Biodiesel Producers	Website
Ag Environmental Products, USA	http://www.soygold.com
American Biofuels Inc, USA	http://americanbiofuels.com
Australian Renewable Fuels Pty Ltd., Australia	http://www.ausrf.com.au
Biodiesel Industries, USA	http://www.pipeline.to
Biodiesel International, German	http://www.biodiesel-intl.com
Columbus Foods, USA	http://www.columbusfoods.com
Ekoil, Slovakia	http://www.ekoil.sk
Griffin Industries, USA	http://www.griffinind.com
Ocean Air Environmental, USA	http://www.oceanairenvironmental.com
Oelmühle Leer Connemann GmbH& Co., German	http://www.biodiesel.de
NOPEC Corporation, USA	http://www.nopec.com
Pacific Biodiesel, USA	http://biodiesel.com
Peter Cremer N.A., USA	http://www.cremer-gruppe.com
Southern States Power, USA	http://www.sspowerco.com
Stepan Company, USA	http://www.stepan.com
Twin Rivers Technologies, USA	http://www.twinriverstechnologies.com
West Central Soy, USA	http://www.soypower.net
World Energy Alternatives, USA	http://www.worldenergy.net
Biodiesel Organizations	**Website**
Alternative Fuels Data Center, USA	http://www.afdc.doe.gov
American soybean association, USA	http://www.soygrowers.com
Austrian Biofuels Institute, Austria	http://www.biodiesel.at
Dancing Rabbit, USA	http://dancingrabbit.org
Journey to Forever, Hong Kong	http://www.jtforever.org
National Biodiesel Board, USA	http://www.biodiesel.org
National Renewable Energy Laboratory, USA	http://www.nrel.gov
The Veggie Van, USA	http://www.veggievan.org
The Office of Transportation Technologies, USA	http://www.ott.doe.gov
United Soybean Board, USA	http://www.unitedsoybean.org

1.4 Objectives

The objectives of this thesis consist mainly of two parts. The first one is to develop different alkali- and acid-catalyzed continuous process flowsheets to produce biodiesel using virgin vegetable oil or waste cooking oil and to evaluate their technical benefits and limitations. The second main objective is to carry out an economic assessment of these processes, to determine their economic feasibilities and to identify those factors having the greatest impact on the economics of biodiesel production.

1.5 Thesis structure

The remainder of this thesis begins by presenting necessary background and a review of the literature relevant to the objectives (Chapter 2). It continues with two articles to be submitted for publication (Chapters 3 and 4).

Chapter 3 (paper 1) concentrates on the process design. Alkali-catalyzed technologies using virgin vegetable oil or waste cooking oil as the raw material are presented first. Then, acid-catalyzed processes using waste cooking oil are described, followed by a technical comparison between all of these processes.

Chapter 4 (paper 2) presents an economic assessment of both the acid- and alkali-catalyzed processes. Fixed capital cost, total manufacturing cost and aftertax rate of return are chosen as the main economic criteria to evaluate the different processes. Sensitivity analyses of these processes are also discussed.

Finally, general discussion, conclusions and recommendations are presented in Chapter 5. References for each chapter are provided at the end of the chapter.

1.6 References

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Schwab, A.W., M.O. Bagby and, B. Freedman, "Preparation and Properties of Diesel Fuels from Vegetable Oils", FUEL 66, 1372-1378 (1987).

Wedel, R.V., "Technical handbook for marine biodiesel in recreational boats", CytoCulture International, Inc. http://www.cytoculture.com (1999).

Chapter 2 LITERATURE BACKGROUND

This chapter mainly concentrates on a review of transesterification technology. The relevant research activities, commercial development of the alkali- and acid-catalyzed transesterification processes and the corresponding economic studies are presented herein. The limitations of current research are summarized, which lead to the specific objectives of this work.

2.1 Transesterification

Vegetable oil, expressed chemically as triglyceride or triacylglycerol, reacts with an alkyl alcohol in the presence of a catalyst, to produce alkyl esters and glycerol. This reaction is called transesterification, which involves converting one ester to another ester. Methanol, ethanol and butanol are the recommended alcohols (Freedman et al., 1984). Due to its lower price, methanol is commonly used. Thus, the resulting esters are called fatty acid methyl esters (i.e., FAME or biodiesel). Glycerol is produced as a by-product. Transesterification is illustrated in Figure 2.1. Triglyceride is composed of three long chain fatty acids esterified to a glycerol backbone. When triglyceride reacts with an alcohol (e.g. methanol), three fatty acid chains are released from the glycerol and are combined with methanol to yield FAME (i.e., biodiesel). In general, to shift the equilibrium to the right side, a large excess of methanol is required. The reaction is normally carried out close to the boiling point of the alcohol under a pressure slightly above that of the atmosphere, so as to guarantee that the reaction is carried out in the liquid state (Nye et al., 1983).

Transesterification can be alkali-catalyzed, acid-catalyzed or enzyme-catalyzed. Sodium hydroxide or potassium hydroxide are the commonly used alkali catalysts; sulfuric acid is the typical acid catalyst; and lipase is used for the enzyme-catalyzed system. Among these systems, the alkali-catalyzed process is most widely used in current commercial biodiesel plants.

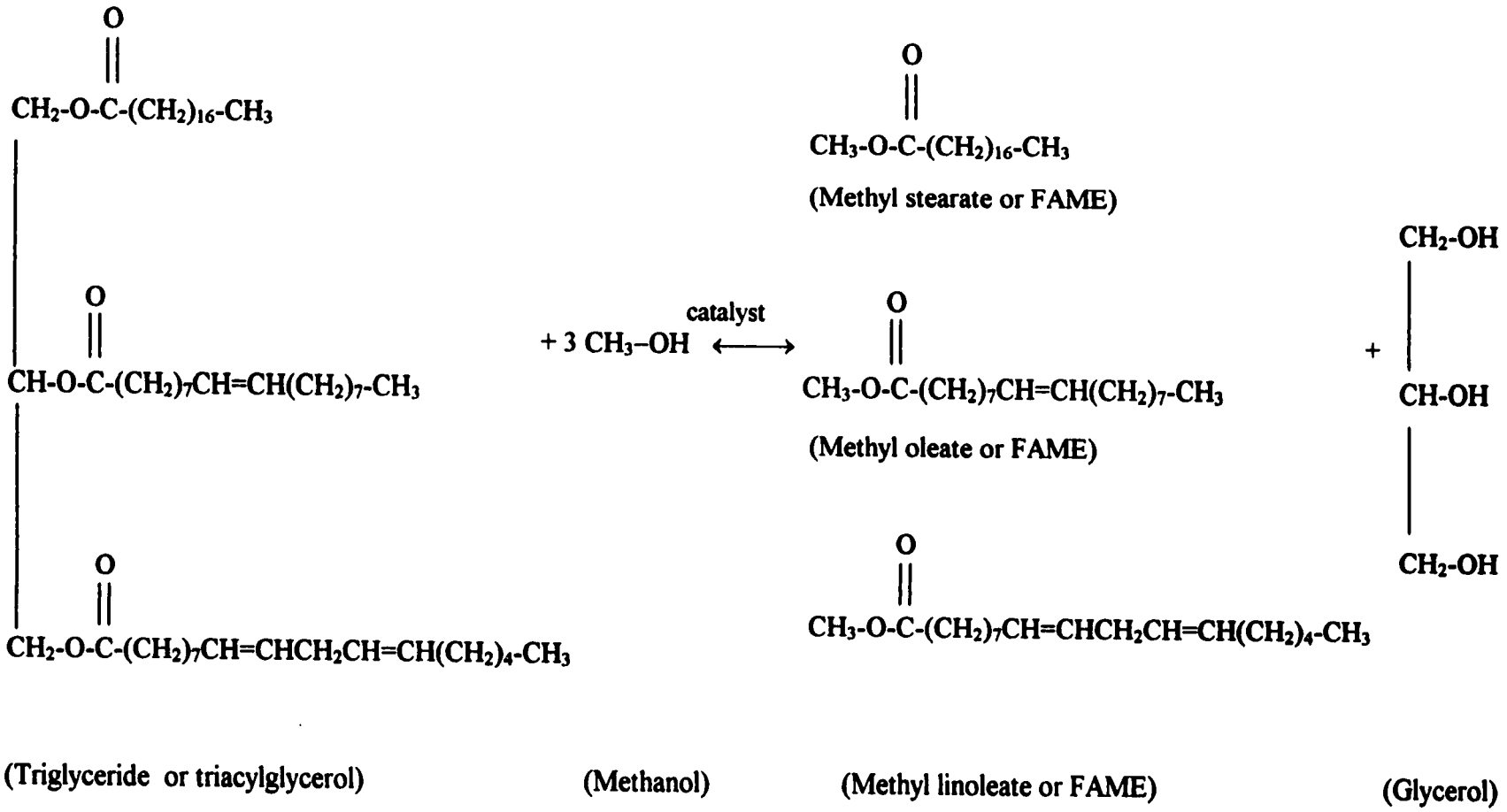

Figure 2.1 Transesterification reaction (Krawczyk, 1996)

With respect to the transesterification reaction mechanism, three issues of importance arise (Liu, 1994). Firstly, vegetable oil usually contains 2-10 wt% free fatty acids (Lepper and Friesenhagen, 1986; Reed, 1997). These free fatty acids can react with an alcohol in the presence of acid catalyst to produce alkyl ester and water, as described in Equation 2.1. This reaction is called esterification. $R' - CO - OH$ represents a long chain fatty acid. It reacts with an alcohol (e.g., $CH_3 - OH$) in the presence of an acid catalyst (H^+), to yield fatty acid methyl esters ($R' - CO - O - CH_3$) and water ($H - OH$).

$$R' - CO - OH + CH_3 - OH \xleftrightarrow{H^+} R' - CO - O - CH_3 + H - OH \qquad (2.1)$$

Strictly speaking, both transesterification and esterification are reversible reactions and happen simultaneously under certain conditions. According to their polarity, free fatty acids dissolve easily in methanol and their esterification is more rapid than that of triglyceride. One difference between transesterification and esterification is that the former reaction can be catalyzed by either an acid catalyst or an alkali catalyst, while esterification can only be catalyzed by an acid catalyst. In both transesterification and esterification, alkyl esters are produced under acidic conditions. In other words, the acid-catalyzed system is insensitive to free fatty acids.

Secondly, when an alkali catalyst is used to catalyze the transesterification reaction, free fatty acids can react with the alkali catalyst in a neutralization reaction to yield soaps and water, in which the alkali catalyst is consumed as a reactant. This neutralization reaction is expressed in Equation 2.2. $R' - CO - OH$ and $NaOH$ represent a long chain free fatty acid and an alkali catalyst, respectively. The resulting soap and water are represented by $R' - CO - ONa$ and $H - OH$, respectively.

$$R' - CO - OH + NaOH \longleftrightarrow R' - CO - ONa + H - OH \qquad (2.2)$$

Basu et al. (1996) concluded that soap emulsifies and solubilizes fat and oil materials in the feedstock, thereby promoting dissolution of these materials in a glycerol layer. This in turn introduces many challenges to the separation of the reaction products in biodiesel production and should be eliminated if possible. This means that the efficiency of the alkali-catalyzed transesterification is very sensitive to free fatty acids.

Thirdly, it is worth noting that the presence of water interferes with both transesterification and esterification. In the presence of an acid catalyst, the ester, once formed, can be hydrolyzed as the reverse reaction of esterification (see Equation 2.1). However, for the alkali-catalyzed system, alkali hydrolysis is depicted as:

$$R'-CO-OR''+H-OH \xrightarrow{Na^+OH^-} R'-CO-O^-Na^+ + H-OR'' + H^+OH^- \qquad (2.3)$$

where, $R'-CO-OR''$ is the free fatty alcohol ester, and is hydrolyzed in the presence of an alkali catalyst (Na^+OH^-), to get a long chain carboxylic acid soap $R'-CO-ONa$ and an alcohol ($H-OR''$). This reaction is irreversible. Equations 2.2 and 2.3 are also known as saponifications.

Therefore, the presence of water in the alkali-catalyzed system promotes formation of soaps. In other words, the alkali-catalyzed system is more sensitive to water than the acid-catalyzed system.

Feedstock

Vegetable oil or animal fat is commonly used as feedstock (e.g. soybean oil, canola oil, rapeseed oil, sunflower oil, cottonseed oil and beef tallow). In the United States, most biodiesel is produced from soybean oil, whereas rapeseed oil is the general raw material in Europe. There are other raw materials such as palm oils in Malaysia, and sunflower oils in France and Italy. In Canada, canola oil is preferred as a major feedstock.

As mentioned previously, the cost of raw material is the major factor in determining the cost of biodiesel. Various feedstock oils have different effects on the price of biodiesel. For example, when using beef tallow as feedstock, its cost is 70% of total production costs. When using soybean oil as feedstock, its cost amounts to 90% of the total biodiesel production costs (Krawczyk, 1996). Knothe et al. (1996) reported that in the United States, a gallon of soybean oil costs approximately two to three times as much as a gallon of petroleum-based diesel fuel. Accordingly, the use of low cost raw material will go a long way towards reducing biodiesel price. They suggested that waste cooking oil is a potential source for biodiesel production. Its cost can be regarded as nearly zero. In addition, this provides a promising alternative for waste treatment (Wiltsee, 1998).

Legally, waste cooking oil belongs to a special type of waste that should be collected and treated separately from other types of waste. Unfortunately, in reality only a very small amount of waste oil is collected separately. Most of it is disposed of with other wastes. If waste cooking oil were collected exclusively for biodiesel production, its disposal problem would largely be solved. On the whole, waste cooking oil appears to be a promising feedstock for biodiesel production and its use should substantially reduce the biodiesel price.

Product

Pure biodiesel is specified by the ASTM standard shown in Table 2.1.

Table 2.1 ASTM specification of biodiesel (National Biodiesel Board, 1999)

Property	ASTM Method	Limits	Units
Flash Point	D93	100.0 (min.)	°C
Water & Sediment	D1796	0.050 (max.)	% vol.
Kinematic Viscosity, 40°C	D445	1.9-6.0	$mm^2/sec.$
Sulfated Ash	D874	0.020 (max.)	% mass
Sulfur	D2622	0.05 (max.)	% mass
Copper Strip Corrosion	D130	No.3 (max.)	
Cetane Number	D613	40 (min.)	
Cloud Point	D2500	By Customer	°C
Carbon Residue, 100% sample	D4530	0.050 (max.)	% mass
Acid Number	D664	0.80 (max.)	mg KOH/gm
Free Glycerin	GC	0.020 (max.)	% mass
Total Glycerin	GC	0.240 (max.)	% mass

Glycerine (or glycerin, glycerol, 1,2,3-propanetriol) is produced as a by-product of biodiesel production. It has very extensive applications in foods and beverages, drugs, cosmetics and toiletries, tobacco, paper and printing, and textiles (Jungermann and Sonntag, 1991). Crude glycerine from biodiesel plants costs $250-750/tonne whereas top-grade glycerine (99.7% purity) could be up to $2000/tonne (Krawczyk, 1996). However,

the glycerine market tends to fluctuate. Bender (1999) reported that the price of technical glycerine in 1990 was US$3520/tonne. By December, 1991, it fell to US$1760/tonne. More recently, for glycerine with 99+ wt% purity, its price rose from $1300/tonne in 1997 up to $2600/tonne in 2001 (Chemical Market Reporter, 1997-2001). The fluctuation of glycerine price is believed to have a potential economic effect on biodiesel plant profitability. There is a need to determine how strong an effect the glycerine price has on biodiesel production costs. This point was discussed in Chapter 4.

2.2 Alkali-catalyzed system

The alkali-catalyzed process to produce biodiesel has been widely applied industrially. Freedman et al. (1984, 1985) studied both the acid- and alkali-catalyzed systems and concluded that the alkali-catalyzed transesterification was more rapid than the acid-catalyzed reaction. They found that, at 60°C, 1 wt% sodium hydroxide (based on oil) and a 6:1 molar ratio of methanol to soybean oil, 95% oil was converted to methyl esters within an hour. When a 30:1 molar ratio of methanol to oil and 1 wt% sulfuric acid were used, greater than 90% conversion to methyl esters was observed to at 65°C after 60 hours. They also investigated different variables affecting the alkali-catalyzed transesterification, such as the molar ratio of alcohol to oil, moisture and free fatty acids in the raw material, reaction time, etc. The molar ratio of alcohol to oil was found to significantly affect the yield of esters. A 6:1 molar ratio was recommended in the alkali-catalyzed system. Furthermore, they suggested the use of an anhydrous alcohol and refined oil containing less than 0.5 wt% free fatty acids as the starting materials in the alkali-catalyzed system. These factors were considered in the design of the alkali-catalyzed transesterification processes in the current work.

Freedman et al. (1985) studied the kinetics of the alkali-catalyzed transesterification of soybean oil with butanol in the presence of sodium butoxide. Because methanol and sodium hydroxide rather than butanol and sodium butoxide were used in the current process design, their kinetic results were not considered for the transesterification reactor in the alkali-catalyzed system.

Noureddini and Zhu (1997) studied the kinetics of the alkali-catalyzed transesterification of soybean oil with methanol. Their reaction conditions were 60°C, a 6:1 molar ratio of methanol to oil and 0.2 wt% sodium hydroxide as the catalyst. Ninety percent of oil was converted to methyl esters within 90 minutes. In the present study, 1 wt% sodium hydroxide and canola oil rather than soybean oil were considered. Thus, the data provided by these authors were used in a preliminary estimation of the alkali-catalyzed transesterification reactor.

Boocock et al. (1998) suggested that the use of tetrahydrofuran (THF) as a co-solvent should further speed up the alkali-catalyzed reaction by increasing mass transfer. They conducted an alkali-catalyzed reaction at 23°C, with a 6:1 molar ratio of methanol to soybean oil, 1.3 wt% sodium hydroxide and a 5:4 volume ratio of THF to methanol. Ninety-five percent conversion of oil to methyl esters was obtained within 20 minutes. Despite the significant improvement in kinetics through the use of a co-solvent, this is a relatively untested procedure and necessary information required for the more complex separations involving THF is not available. Thus, their approach was not utilized in the process designs in this thesis.

Methods to separate the biodiesel product from the reaction mixture were investigated by Karaosmanoglu et al. (1996). They compared three methods: one was to wash the reaction mixture with hot water; the second was to wash the mixture using petroleum ether and water; the last one was to use sulfuric acid to neutralize the mixture followed by an evaporation to remove the methanol. They concluded that hot water washing at 50°C was the best way to separate and purify the biodiesel product. Consequently, the use of water washing was chosen to be the principal means to purify the biodiesel product in this thesis. In addition, there are some other alternatives to purify the biodiesel product. For example, Nye et al. (1983) suggested the use of hexane (a 3:1 volume ratio of hexane to reaction mixture) to separate the esters from the glycerine. The resulting light phase containing the ester was washed three times with sodium bicarbonate followed by three times with water. A modified hexane extraction (McBride, 1999) was presented in one of the process designs in this thesis.

Bam et al. (1995) described an alkali-catalyzed transesterification of rapeseed oil with methanol. Rather than the use of water washing to purify the resulting esters, they

advocated the use of a portion of the glycerine by-product as a solvent to wash impurities from the methyl esters. The volume ratio of glycerine to esters was 1:1 to 1:4. Undoubtedly, this glycerine washing reduces the by-product credit. Hayafuji et al. (1999) suggested the use of a solid absorbent, such as activated carbon, activated carbon fiber, activated clay, etc. After the alkali-catalyzed transesterification, adding the solid absorbent could replace the water-washing step for removing impurities, such as residual catalyst, odourous material, colouring material and moisture, from the esters. However, the suggestions of using glycerine washing or solid absorbent have only been tested on the laboratory scale and were not used this study.

To this point, discussion has focused on laboratory-scale investigations. At the industrial scale, Connemann and Fischer (1999) described an alkali-catalyzed continuous process to produce biodiesel from rapeseed oil at ambient pressure and 65-70°C. In this process, a distillation column was used to recover the methanol and reuse it in the reactor. A countercurrent multi-stage water washing was employed to purify the biodiesel product. The content of free fatty acids in the raw material was required to be less than 2 wt% in this process. A typical alkali-catalyzed process described by Marc-IV Consulting Company (1997) formed the basis of our designs for the alkali-catalyzed processes.

One of the critical characteristics of the alkali-catalyzed process is its rigid requirement of a low content of free fatty acids in the feedstock oil. As mentioned previously, the presence of free fatty acids results in the production of soaps and water, which could affect the quality and the yield of biodiesel. Consequently, vegetable oil containing less than 0.5 wt% free fatty acids is a requirement for the alkali-catalyzed transesterification (Freedman et al. 1984; Jeromin et al., 1987). However, it is generally not practical to achieve such a low content of free fatty acids in oil. More than 3 wt% of free fatty acids are usually present in vegetable oil or animal fats. For waste cooking oil, the free fatty acid content reaches 2-10 wt% (Lepper and Friesenhagen, 1986; Reed, 1997). To solve this problem, a pre-treatment step has been suggested to be used prior to transesterification (Kawahara and Ono, 1979; Lepper et al., 1986; Basu et al., 1996). In this pre-treatment step, an acid-catalyzed esterification of free fatty acids with an alcohol is carried out. Kawahara et al. (1979) suggested that the preliminary step should be used to esterify the free fatty acids in unrefined oils with methanol in the presence of sulfuric

acid at around 65-70°C. Lepper et al. (1986) conducted the esterification of coconut oil with methanol using p-toluene sulfonic acid or sulfuric acid as the catalyst. The reactions were carried out below 120°C and 5 bar for 30 minutes. After the reaction, pure glycerine was added as a liquid entraining agent to separate the refined oil from the acid-catalyst and water. Basu et al. (1996) concluded that the acid catalysts commonly used in esterification are concentrated sulfuric acid, p-toluene sulfonic acid, methane sulfonic acid and strong acidic sulfonated ion exchange resins. Hence, the addition of a pre-treatment step was considered in the development of the alkali-catalyzed process flowsheet using waste cooking oil in this thesis.

A commercial, continuous alkali-catalyzed transesterification process to produce methyl esters at 90 bar and 240°C was mentioned by Kreutzer et al. (1984) This technology was claimed to be suitable for dealing with raw materials having high free fatty acid contents without requiring the addition of a pre-treatment step. However, such a high pressure and temperature leads to problems of high-energy consumption, a significant increase in equipment cost and process safety.

2.3 Acid-catalyzed system

Development of an acid-catalyzed process has received less attention than that of the alkali-catalyzed system. This is likely due to the relatively long reaction time of the acid-catalyzed system compared to the alkali-catalyzed system. Freedman et al. (1984) studied the acid-catalyzed transesterification of soybean oil with methanol, ethanol and butanol at the temperatures just below the boiling point of the alcohol (i.e., 65°C, 78°C and 117°C, respectively). A 30:1 molar ratio of alcohol to oil and 1 wt% concentrated sulfuric acid (based on the oil) were used. It took 3, 22 and 69 hours to reach 90% conversions to butyl, ethyl and methyl esters, respectively. When the reactions using each of the alcohols were conducted at 65°C for 69 hours, similar oil conversions (90%) were obtained. They concluded that reaction temperature rather than the alcohol type was the major factor contributing to the original differences in conversions.

Freedman et al. (1985) continued to investigate the kinetics of the acid-catalyzed transesterification of soybean oil with butanol. Their kinetics information was not

considered because the transesterification of canola oil with methanol was used in the acid-catalyzed processes in this study.

Canakci and Gerpen (1999) studied the effects of different process variables on the acid-catalyzed transesterification, such as the molar ratio of alcohol to soybean oil, the reaction temperature, the catalyst amount, and the reaction time. In each experiment, they investigated the effect by varying one variable at a time. For example, at 60°C, 3 wt% sulfuric acid and at alcohol to oil molar ratios of 3.3:1, 3.9:1, 6:1, 20:1 and 30:1, the ester conversion was observed after 48 hours. A 98.4% ester conversion was reached at a 30:1 molar ratio of methanol to oil. They concluded that a higher oil conversion could be obtained by using a higher molar ratio of alcohol to oil, a higher reaction temperature, an increase in the concentration of sulfuric acid catalyst, or a longer reaction time. Interaction effects among these factors were not studied and recommended conditions for the acid-catalyzed transesterification were not provided.

In the 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. A minimum molar ratio of 50:1 methanol to oil and an acid concentration of 1.5-3.5 mol% (based on the reaction mixture) were used. The reaction was carried out in a 15 L stainless steel reactor equipped with a heating jacket, at a temperature of 70°C, a pressure of 170-180 kPa and an agitation rate of 300 rpm. Under these conditions, nearly 100% conversion was reached within 200 minutes. These preliminary results were used in the design for the sizing of the transesterification reactor in the acid-catalyzed processes.

Unfortunately, largely due to the relatively slow reaction, there are no published reports of the development of a complete continuous biodiesel process using an acid-catalyzed system, including both the transesterification reaction and the subsequent separation units.

2.4 Other processes

Early in 1961, Metcalfe and Schmitz (1961) used boron trifluoride in methanol as the catalyst to prepare the FAME from free fatty acids. In their experiment, they reported that fatty acid methyl esters were produced in 2 minutes with BF_3-methanol as the catalyst. It

was found that boron trifluoride in methanol has a higher capability in esterification than in transesterification. This method was once a popular method for FAME preparation. However, BF_3 has received little interest by recent researchers due to its toxicity, high cost and limited stability (Christie, 1994; Liu, 1994).

Jham et al. (1982) specified another method for obtaining fatty esters from soybean lipids by using anhydrous HCl/methanol at a volume ratio of 4:1. The method involved the saponification of soybean lipids with KOH/methanol for 5 minutes at 100°C, followed by esterification with anhydrous HCl/methanol for 15 minutes at 100°C. Soybean lipids were first converted to free fatty acids by the KOH/methanol hydrolysis reaction, and then free fatty acids were reacted with methanol in the presence of the HCl catalyst to produce fatty esters and water. But, as discussed earlier, in the alkali saponification step, soap formation could not be avoided. Hence, this method has not been advocated in recent years.

The use of an enzyme-catalyzed process was discussed by Nelson et al. (1996). They stated that product separation and waste disposal problems could be simplified using an enzyme-catalyzed system. They studied different lipases as catalysts in the transesterification reaction involving various oils and alcohols and found that the lipases exhibited different catalysis efficiencies with various alcohols. Watanabe et al. (2001) investigated an enzymatic conversion of waste edible oil to biodiesel. They conducted a three-step methanolysis of waste oils using lipases in a fixed-bed bioreactor. Around 95 wt% conversion was achieved after 50 hours. Presently, the use of enzyme-catalyzed systems has been limited to laboratory scale investigations. Commercialization of enzyme-catalyzed biodiesel production has not been reported to date.

In the present study, alkali- and acid-catalyzed processes were the focus of the process designs in this thesis because they are currently the principle ways to produce biodiesel. Other methods will not be discussed further in the remainder of the thesis.

2.5 Economic assessment and sensitivity analysis

In previous economic studies of biodiesel production, capital cost, operating cost and biodiesel break-even price are the main economic criteria used. Nelson et al. (1994) indicated that the total capital cost for a 100,000 tonnes/year biodiesel production facility

from beef tallow was 12 million dollars and for a 10,000 tonnes/year biodiesel facility was 3 million dollars. However, they did not present sufficient information to determine the type of the reaction or the nature of the separations, nor did they provide any details of their economic calculations.

Noordam and Withers (1996) claimed that for a 7600 tonnes/year biodiesel plant using canola oilseed as raw material, the estimated equipment cost of the transesterification unit was approximately $0.7 million and the break-even price of biodiesel was $0.68/litre ($0.76/kg). Their results were compared to those determined in this study and were discussed in Chapter 4. However, oilseed as the raw material was not considered in this study, which results in some differences in the process design. Moreover, some other expenses, such as the costs of supervision, patents and royalties, research and development were not discussed in their study. Neither process flowsheets nor detailed process descriptions were provided. As well, explanations of the economic assessments were not given. Overall, these limitations make it difficult to compare their results with the results determined in this study.

Bender (1999) compared seven plants of three different capacities using various oilseeds (i.e. soybean oilseed, canola oilseed, sunflower oilseed) or animal fats as the raw material. He concluded that for a continuous plant with a 10,000 tonnes/year biodiesel production capability (i.e., 12 million litres/year) from animal fats, the capital cost was $3.12 million. Glycerine credit was $0.72 million at the price of $ 660/tonne or $1.2 million at the price of $1470/tonne.

Korus et al. (1993) carried out a sensitivity analysis of a batch alkali-catalyzed transesterification with rape oil and methanol or ethanol. They suggested that the cost of feedstock oil should be an important factor in determining the economic feasibility of a biodiesel process. Similarly, Nelson et al. (1994) concluded that the feedstock cost, plant size and glycerine credit should be the significant factors in determining the economics of biodiesel production.

Noordam and Wither (1996) performed a price sensitivity analysis. By varying the values of the raw material cost, canola meal or glycerine cost, they reported that a $0.01/kg increase in the canola seed cost would increase the biodiesel price by $0.03/kg. A $0.11/kg increase in glycerine price would reduce the biodiesel price by $0.01/kg.

2.6 Limitations of existing research

Based on the previous discussion, the main limitations of existing biodiesel research are summarized below.

First, the use of waste cooking oil to produce biodiesel should gain more attention because of its potential to significantly reduce the high cost of biodiesel. However, the presence of free fatty acids in waste oil makes the alkali-catalyzed process unfavourable unless a pre-treatment step is added. In contrast, the acid-catalyzed system is insensitive to free fatty acids but, due to its slower rate of reaction for virgin oils, few investigations have been undertaken and its commercial application has not been reported.

Secondly, most of the literature to date concentrates on batch transesterification in the alkali-catalyzed system. There is no detailed review and discussion of continuous processes on an industrial scale, including both the transesterification reaction and subsequent separation units. However, the process of biodiesel production is not limited to the transesterification reactor, but includes many units from raw material refining to product separation and purification. Thus, there is a need to design a complete continuous process and assess its technical performance from the viewpoint of an entire plant.

The lack of a detailed economic evaluation is another limitation to the assessment of the feasibility of one process over another. Sufficient information concerning process type, process description and detailed economic calculations are not presented in the current economic studies. There are no comprehensive economic analyses for a continuous biodiesel plant from vegetable oil or waste cooking oil, including studies on fixed capital cost, total manufacturing cost, aftertax rate of return and break-even price of biodiesel product. In particular, an economic evaluation on the acid-catalyzed process is unavailable. Furthermore, a more reliable quantitative sensitivity analysis is also needed. Therefore, carrying out a detailed economic analysis will assist us in detecting potential problems and determining or optimizing the economic feasibility of biodiesel production. Moreover, for a commercial biodiesel plant with continuous production, the main factor(s) contributing to the whole plant cost could be calculated provided that an effective economic analysis is set up. Thus, the need for a preliminary economic

evaluation of both the alkali- and acid-catalyzed continuous processes for biodiesel production from waste cooking oils is clear.

In this work, a chemical process simulator, HYSYS™, was used to develop a continuous acid-catalyzed process to produce biodiesel from waste cooking oil. Major process equipment including reactors, utilities and the required separation units were considered from the viewpoint of an industrial plant. Technical evaluations of the acid- and alkali-catalyzed processes were carried out. A detailed economic assessment was also performed for each alkali- or acid-catalyzed process using virgin vegetable oil or waste cooking oil. The economic feasibilities of the plants using these technologies were evaluated on the basis of fixed capital cost, total manufacturing cost and aftertax rate of return. A quantitative sensitivity analysis of these processes was conducted to explore those factors having significant economic impact on biodiesel production. These analyses demonstrated the commercial feasibility of the technologies.

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Chapter 3 PAPER 1

Biodiesel Production from Waste Cooking Oil: 1. Process Design and Technological Assessment

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Abstract

Four different continuous process flowsheets to produce biodiesel from virgin vegetable oil or waste cooking oil under alkaline or acidic conditions were developed. Detailed operating conditions and equipment designs for each process were presented. A technological assessment of these four processes was carried out to evaluate their technical benefits and limitations. Results showed that the commercial alkali-catalyzed process using virgin vegetable oil as the raw material required the least 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 can reduce 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 biodiesel production from waste cooking oil.

Keywords: Biodiesel; Waste cooking oil; Transesterification of triglycerides; 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 renewable lipid feedstock, such as vegetable oil or animal fat, for use in diesel engines. "Bio" represents its renewable and biological source in contrast to traditional petroleum-based diesel fuel; "diesel" refers to its use in diesel engines similar to petroleum-based diesel. As an alternative fuel, biodiesel can be used in neat form or mixed with petroleum-based diesel.

The main merits of biodiesel as an alternative fuel are:

- It is derived from a renewable, domestic resource, namely vegetable oil or animal fat, thereby relieving reliance on petroleum fuel imports.
- It is biodegradable and non-toxic.
- It has a favourable combustion emission profile. Compared to petroleum-based diesel, carbon monoxide in biodiesel emissions is greatly reduced (Gerpen et al., 1995). Levels of particulate matter and unburned hydrocarbons in the emissions, such as smoke and soot, are less than those in traditional fuels and almost no sulfur or aromatic compounds are produced (Knothe et al., 1996; Wedel, 1999). Moreover, emissions of carbon dioxide are also insignificant, lessening the impact of biodiesel combustion on the greenhouse effect (Agarwal and Das, 2001).
- It 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 can reduce engine wear and extend engine life (Wedel, 1999).

In brief, biodiesel appears to be a good alternative to petroleum-based fuel and is being used 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 (see Figure 3.1). Triglyceride (i.e., triacylglycerol), as the main component of vegetable oil, consists of three long chain fatty acids esterified to a glycerol backbone. When the triglyceride reacts with an alcohol (e.g.

methanol), the three fatty acid chains are released from the glycerol skeleton and combined with methanol to yield fatty acid methyl esters (i.e., FAME or biodiesel). 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 study. In general, to shift the equilibrium to the right (see Figure 3.1), a large excess of methanol is used.

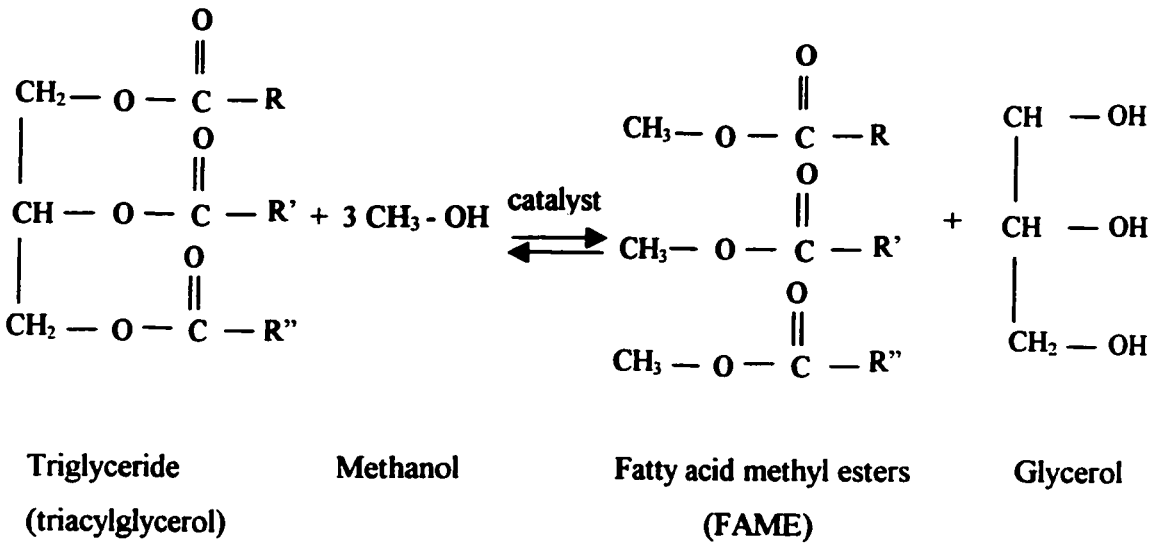


Figure 3.1 Transesterification reaction

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$0.60/litre, compared to US$0.20/litre for petroleum-based diesel (Bender, 1999). It is reported that the high cost of biodiesel is mainly due to the cost of virgin vegetable oil (Krawczyk, 1996; Connemann and Fischer, 1999). For example, in the United States, soybean oil was sold on average for 40 cents/litre in 1999 (Agriculture and Agri-Food Canada, 1999). Therefore, it is not surprising that biodiesel

produced from pure soybean oil costs much more than petroleum-based diesel. Exploring ways to reduce its high cost 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. Waste oil, as a special type of waste, is estimated to cost $0.10/litre (Sittingbourne Analytical laboratory Ltd., 2001). The use of waste cooking oil for biodiesel production will not only reduce the high cost of biodiesel, but also help to solve the problem of waste oil disposal (Wiltsee, 1998).

Most current biodiesel research concentrates on the alkali-catalyzed technology at the batch scale, and no detailed information on continuous processes nor on process simulation and design is available. However, the real process of biodiesel production is not limited only to the transesterification reactor. It includes many process steps from raw material refining to product separation and purification. Hence, evaluating the technological and economic feasibility of a biodiesel plant involves all operating units rather than only one reactor. 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 the alkali-and acid-catalyzed transesterifications and develop different continuous process flowsheets to produce biodiesel from virgin vegetable oil or waste cooking oil. A technical assessment of each process is presented. This is an attempt to explore potential alternatives to current biodiesel production methods, thus contributing to biodiesel commercialization. In a subsequent article, an assessment of the relative economic feasibility of each process is undertaken.

2. Background

2.1 Alkali-catalyzed system

The alkali-catalyzed system has been studied widely and applied industrially, mainly because of its rapid rate of transesterification. Sodium hydroxide, potassium hydroxide or sodium methoxide are the usual alkali catalysts.

Freedman et al. (1984) studied the different variables affecting the yields of fatty acid esters in the alkali-catalyzed system on the laboratory scale. They concluded that the molar ratio of alcohol to oil was of most importance. The recommended conditions for the alkali-catalyzed transesterification were a 6:1 molar ratio of alcohol to soybean oil, 1 wt% sodium hydroxide (based on oil) and a reaction temperature at the boiling point of the alcohol. Moreover, they emphasized that anhydrous alcohol and refined oil containing less than 0.5 wt% free fatty acids were the necessary starting materials. Under these conditions, conversion of oil to esters could reach 95% within one hour. These recommended conditions form the basis of the current process design for the alkali-catalyzed transesterification.

Noureddini and Zhu (1997) carried out a kinetic study of the alkali-catalyzed system using a 6:1 molar ratio of methanol to oil, 0.2 wt% sodium hydroxide and refined soybean oil with less than 0.1 wt% free fatty acids. The effects of temperature and mixing intensity on ester conversion were investigated. When the reaction temperature was 60°C and the mixing intensity N_{Re} (Reynolds Number) was 6200, a 90% conversion of soybean oil to methyl esters was observed within 90 minutes. These data were used for a preliminary estimation of the space time and reaction volume of the alkali-catalyzed transesterification reactor in the present design.

Boocock et al. (1998) suggested the addition of tetrahydrofuran (THF) as a co-solvent to further speed up the alkali-catalyzed reaction by minimizing mass transfer resistance. Ninety-five percent conversion of oil to methyl esters was obtained within 20 minutes when the reaction was carried out at 23°C, using a 6:1 molar ratio of methanol/oil, 1.3 wt% sodium hydroxide and a 5:4 volume ratio of THF/methanol. Because necessary information of the more complex separations involving THF and methanol is not available, this approach was not considered in the process design in this article.

Karaosmanoglu et al. (1996) investigated three different refining methods to purify the biodiesel product from an alkali-catalyzed reaction. One method was to wash the reaction mixture five to seven times with hot distilled water at 50°C, 65°C and 85°C. The second method was to wash the mixture using petroleum ether followed by water washing three times at 20°C. The third method was to neutralize the alkali-catalyst by adding sulfuric acid and then to evaporate the methanol remaining in the ester product.

These authors compared the purity and yield of the biodiesel product from these three methods and concluded that the use of hot water washing at 50°C was the best way to obtain high purity (99%) and yield (86%) of biodiesel product. In the present process design, water washing is used as the principle means to separate the FAME from glycerol, catalyst and most of the methanol. However, some researchers (Hayafuji et al., 1999) found that this water washing is prone to the formation of emulsions, which will affect the yield and purity of the biodiesel product. Thus, in one of the alternative process designs of this study, use of hexane or petroleum ether extraction was suggested instead of water washing.

A commercial, continuous alkali-catalyzed transesterification process to produce methyl ester on the industrial scale using high pressure (90 bar) and high temperature (240°C) was demonstrated by Kreutzer et al. (1984). However, high-energy consumption, a significant increase in equipment costs and process safety issues could make this process prohibitive because of such high pressures and high temperatures. 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 (1999). It was claimed to have successful applications in Europe. In this process, a distillation column was used to separate methanol and glycerol. The methanol was recycled to the transesterification reactor and a multi-stage water washing was employed to purify the biodiesel product. The Marc-IV consulting company (1997) summarized the current typical alkali-catalyzed technology as a sequence of transesterification reaction, methanol removal, separation, neutralization, methyl ester wash and purification. This was the principle used in the design for the alkali-catalyzed processes in this study.

The construction material for the process equipment in the alkali-catalyzed system is also of importance. Freedman et al. (1985) pointed out that the alkali-catalyzed transesterification was less corrosive to process equipment than the acid-catalyzed process. Peterson (1993) studied a batch process to produce biodiesel from rapeseed oil using ethanol (a 4.5:1 molar ratio of ethanol to oil) and potassium hydroxide (0.2 wt%). In his investigation, stainless steel was used as the construction material for the transesterification reactor. However, Davis et al. (2000) stated that carbon steel could be

used as the construction material when the concentration of sodium hydroxide is less than 50% from ambient temperature to 95°C. Since it was not indicated whether this 50% was based on mass or mole, we treated it as a mass percentage in this study. Based on the above discussions, stainless steel was used for the transesterification reactor in the designs for the alkali-catalyzed processes in this study from a conservative standpoint. The construction material of other equipment in the processes was carbon steel. This was discussed in detail later.

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 hydrolysis or saponification under alkali conditions, which consequently yields soaps (Liu 1994; Basu et al., 1996). Also, free fatty acids can react with an alkali catalyst to produce soaps and water. This not only consumes the alkali catalyst, but also causes the formation of emulsions because of the presence of soaps. 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 and an anhydrous alkali catalyst are necessary for commercially viable alkali-catalyzed systems (Freedman et al. 1984; Jeromin et al., 1987). However, this requirement is likely to be a significant limitation when using waste cooking oil as the raw material to reduce biodiesel cost. Usually the level of free fatty acids in waste cooking oil is greater than 2-10 wt% (Lepper et al. 1986; Reed, 1997). Lepper et al. (1986) recommended a pre-treatment step to reduce the free fatty acid content. They demonstrated that in a preliminary esterification stage, an oil phase with a high amount of free fatty acids (30 wt%) could be processed by an acid-catalyzed esterification with an alcohol under mild conditions (< 120°C, 5 bar). p-Toluene sulfonic acid or sulfuric acid were the suggested catalysts. A liquid entraining agent (i.e., glycerine), immiscible with the oil phase, was added to extract other components, such as the acid catalyst and water, from the oil phase. After this 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 pre-treatment step was applied to the alkali-catalyzed process using waste cooking oil in this study.

2.2 Acid-catalyzed system

The acid-catalyzed system is insensitive to free fatty acids in contrast to the sensitivity of the alkali-catalyzed system. Nevertheless, acid-catalyzed transesterification has been largely ignored mainly because of its relatively slow reaction rate. Sulfuric acid is the most commonly used acid catalyst in this process.

Nye et al. (1983) studied the transesterification of used frying oil with various alcohols under acidic conditions. They concluded that, with 0.1% concentrated sulfuric acid and a 3.6:1 molar ratio of methanol to oil, an eighty percent of conversion of oil to methyl esters was achieved at 65°C after 40 hours. After the reaction, hexane at 3 times the reaction volume was added to produce two separate phases: the top ester layer and the bottom glycerine layer. The top layer was washed by sodium bicarbonate and water to obtain high purity methyl esters. The use of hexane to purify the biodiesel product was also proposed in one of the designs of the alternative acid-catalyzed process.

Freedman et al. (1984) investigated the transesterification of soybean oil with butanol, ethanol and methanol using 1 wt% concentrated sulfuric acid (based on oil). They reported that when the molar ratio of alcohol to soybean oil was 30:1 and reaction temperatures were kept near the boiling points of the alcohols, it took 3, 22 and 69 hours respectively to obtain more than 90% oil conversions to butyl, ethyl and methyl esters, respectively. When the reaction was conducted at 65°C for each of three alcohols, similar conversion results were obtained after 69 hours. Thus, they concluded that the reaction temperature rather than the alcohol type was the main factor contributing to the differences in the above conversions. On the other hand, though the use of butanol reduces the reaction time, the viscosity of the resulting butyl esters (e.g., 4.6 mPa.s at 40°C) is higher than that of methyl esters (3.6 mPa.s at 40°C) or ethyl esters (3.9 mPa.s at 40°C) (Schwab et al., 1987).

The kinetics of the acid-catalyzed transesterification with butanol was also investigated by Freedman et al. (1985). At a 30:1 molar ratio of butanol to soybean oil and 1 wt% sulfuric acid, the changes in concentration of each component with reaction time were observed at different temperatures. They found 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 canola oil and methanol rather than soybean oil and butanol were used in this study, the kinetic information given by Freedman et al. (1985) was not taken into consideration.

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 acid-catalyzed transesterification. Each effect was studied independently of the other effects. For example, at 60°C, 3% sulfuric acid and 48 hours, ester conversion was observed with the change of the molar ratio of methanol to soybean oil. They found that higher ester conversions could be obtained at higher molar ratios of alcohol to oil, higher reaction temperatures, higher concentrations of sulfuric acid or longer reaction times. However, possible interaction of these variables was not investigated and optimum conditions for the acid-catalyzed reaction were not recommended.

In the 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. A minimum molar ratio of 50:1 methanol to oil and an acid concentration of 1.5-3.5 mol% (based on the reaction mixture) were used. Such a high portion of methanol was used to ensure the complete conversion of oil to esters in a reasonable reaction time. The reaction was carried out in a 15 L stainless steel reactor equipped with a heating jacket, at a temperature of 70°C, a pressure of 170-180 kPa and an agitation rate of 300 rpm. Under these conditions, nearly 100% conversion was reached within 200 minutes. A first-order kinetics model was proposed and reaction rate constant was calculated. These preliminary results were used in the design for the sizing of the transesterification reactor in the acid-catalyzed processes. Further kinetic investigations are currently underway.

As for the construction material of the process equipment, caution must be taken because of the presence of sulfuric acid. Norden (1973) commented that for sulfuric acid concentrations below 5% or above 85% and temperatures below the boiling point of sulfuric acid solution, stainless steel (type 316) could be used as construction material. Davis et al. (2000) demonstrated that the corrosion rate increases with sulfuric acid concentration. However, when the concentration is greater than 60 wt%, the corrosion

rate decreases with increase in concentration of sulfuric acid. He 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°C and 100°C, stainless steel (type alloy 20) has a good corrosion-resistance for sulfuric acid less than 60 wt% or greater than 80 wt%.

Until now, studies of the acid-catalyzed system are very limited in number. No commercial biodiesel plant to date is reported to use the acid-catalyzed process. Despite its relatively slow reaction rate, the acid-catalyzed process offers benefits with respect to its independence of free fatty acids and the absence of a pre-treatment step. These advantages should be considered, when using waste cooking oil as the raw material to produce biodiesel.

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 real 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.

To set up a process flowsheet and carry out a steady-state simulation, the first step was to define the chemical components and the thermodynamic model to be employed. The system consisted mainly of triglyceride, methanol, methyl ester, glycerol, sulfuric acid (or sodium hydroxide) and water. Information on most of these species is available in the HYSYS™ component library and is not further discussed here. Vegetable oil is a mixture of different triglycerides containing various fatty acids. Among the various types of vegetable oils, canola oil was considered as the raw material in either virgin or waste form in this research because it is the major vegetable oil used in Canada. Lawson (1995) reported that the main fatty acids in the canola oil were oleic (62%), linoleic (22%) and linolenic (10%) acids. Gas chromatography analysis from McBride (1999) showed that 40% of the fatty acids in the canola oil was oleic acid, 31% was linoleic and 13% was linolenic acid. Since oleic acid is the major fatty acid in canola oil, triolein ($C_{57}H_{104}O_6$),

containing three oleic acid chains, was chosen as the representative triglyceride in the HYSYS™ simulation. Triolein is not available in the HYSYS™ component library, so it was defined by using the "Hypothetical Manager" tool for definition of non-library components. The molecular weight of triolein is 884 g/mol. Its normal boiling point and density were defined as 500°C and 900kg/m^3, respectively (Krawczyk, 1996; Goodrum, 1997). Other physical properties, such as critical temperature, pressure and volume, were estimated by HYSYS™. Similarly, the FAME product from canola oil is a mixture of fatty acid methyl esters, such as methyl oleate, methyl linoleate and methyl linolenate. The composition of the resulting esters is determined by the fatty acid composition in the triglyceride. Because triglyceride was represented by triolein in the simulation, 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. Other compounds, such as calcium oxide and calcium sulfate used in the acid-catalyzed system, as well as phosphoric acid and sodium phosphate in the alkali-catalyzed system were also defined using the Hypothetical Manager since they were not available in the HYSYS™ component library.

Due to the presence of methanol and glycerol with high polarity, both NRTL and UNIQUAC thermodynamic/activity models were recommended for liquid phase calculations (Hyprotech Ltd., 2000). However, some interaction parameter coefficients between each pair of components, such as methanol/methyl-oleate and glycerol/methyl-oleate, were not available in the HYSYS™ data library nor from the published literature. Thus, they were estimated using the UNIFAC LLE module in HYSYS™. In addition, both sulfuric acid and sodium hydroxide are strong electrolytes and their behaviour, including their interaction coefficients with other components, cannot be determined accurately. These deficiencies impart a degree of uncertainty to the simulations, which could affect the accuracy of the simulation results.

Once the chemical components and the thermodynamic model were defined, the next step was to develop a process flowsheet by choosing operating units and setting up the input conditions, such as flowrate, composition, temperature, pressure, etc. In order to have an equal basis for comparison, each process was designed for the same plant capacity. This was determined on the basis of availability of waste cooking oil. The quantity of waste cooking oil available in Canada is not known ((S&T)^2 consulting

company, 2001). Therefore, the availability of waste cooking oil was estimated on the basis of information from the United States. Wiltsee (1998) collected and analyzed data on urban waste grease resources in 30 randomly selected metropolitan areas in the United States. He divided urban waste grease into two categories. One was yellow grease feedstock, a valuable commodity to manufacture tallow, animal feed supplements and other products. The other was grease trap waste, which is believed to be useless and enters sewage treatment plants. He concluded that on average, 9 pounds of yellow grease per person were produced annually in the United States. If this statistic is also applicable to Canada, approximately 120,000 tonnes/year of yellow grease are produced in Canada, 45,000 tonnes/year in Ontario, and 4,000 tonnes/year in the Ottawa Region. The same estimation method was also applied by ((S&T)^2, 2001). Thus, in the current process design, a pilot-plant with 8,000 tonnes/year biodiesel was simulated. This is the same capacity as the existing continuous biodiesel plant described by Connemann and Fischer (1999).

The transesterification reactor is the core unit in each process. Because detailed information on the kinetics of the acid-catalyzed system has not been reported, a simple conversion reactor model with 99$^+$% conversion of triglyceride to FAME was used to describe the transesterification reaction for both the acid- and alkali-catalyzed systems. It was assumed that the reactor was a well-mixed, continuous, stirred tank reactor. Accordingly, the space time for the reactor was calculated using Equation 3.1 (Lin et al, 1973; Winterbottom and King, 1999). Reaction volume and reactor volume were obtained in Equations 3.2 and 3.3.

$$\theta = \frac{C_{A0} \bullet x}{-\gamma_A} = \frac{C_{A0} \bullet x}{C_{A0} \bullet e^{-kt} \bullet k} = \frac{x \bullet e^{kt}}{k} \qquad (3.1)$$

where θ = space time, min.,

γ_A = reaction rate of component A, mol/m^3 · min^{-1},

C_{A0} = initial concentration of component A, mol/m^3,

x = fractional conversion of component A at time t,

k = reaction rate constant, min^{-1}.

$$V_r = \theta \bullet Q_0 \qquad (3.2)$$

$$V = \frac{V_r}{f} \tag{3.3}$$

where V_r = reaction volume, m^3,

Q_0 = volume flowrate, m^3/min,

V = reactor volume, m^3,

f = fill factor.

The fill factor f was defined as 0.5 because the system boils easily (Lin et al., 1973). Once V was determined, the size of the reactor including the diameter and height was calculated based on the assumption that the height of the reactor is three times that of its diameter. The theoretical reaction intermediates, such as diglycerides and monoglycerides, were not taken into account in this preliminary estimation.

Multi-stage distillation was used for methanol recovery as well as for purification of both the FAME and glycerine products. In each of these distillation columns, methanol, as the main light component, was distilled from the FAME or glycerol. Although the boiling point of methanol (65°C at 1 atm.) is much lower than that of FAME (>300°C at 1 atm.) or glycerol (300°C at 1 atm.), simulations suggested that the desired purities of biodiesel (ASTM standard >99.6 wt%) and glycerine (>90 wt%) could not be achieved by a simple flash unit. This resulted in the use of distillation. On the other hand, the large difference in their boiling points makes distillation operation easy. For example, simulation results showed that only 5 theoretical stages in the columns were sufficient to yield high quality biodiesel and glycerine. An approximate column sizing method given by Sinnott (1999) was used in this study (see Equation 3.4).

$$D_c = \sqrt{\frac{4\hat{V}_w}{\pi \rho_v \hat{u}_v}} \tag{3.4}$$

where D_C = column diameter, m,

$\hat{V}_w$ = the maximum vapor rate, kg/s,

ρ_v = vapor density, kg/m^3,

$\hat{u}_v$ = the maximum allowable vapor velocity, m/s.

$\hat{u}_v$ was determined by vapor density, liquid density and tray spacing in distillation column. $\hat{V}_w$ was affected by the feed flowrate and reflux ratio. All detailed operating conditions for these columns are presented later.

Because FAME and glycerol are susceptible to thermal decomposition above 250°C and 150°C, respectively (Newman, 1968; Goodrum, 1997), vacuum operation for the FAME and glycerine distillations was necessary to keep the temperature under these temperatures, respectively.

Liquid-liquid extraction was used to simulate the separation of the FAME from the glycerol, methanol and catalyst by water washing. Due to a lack of knowledge concerning the behaviour of electrolytes such as sulfuric acid and sodium hydroxide, their separation was modeled using a component splitter. It was assumed that these electrolytes would remain with most of the glycerol, methanol and water because of their complete miscibility with water (Bam et al., 1995; Connemann and Fischer, 1999). The sizing estimation of the extraction column was given by Sinnott (1999).

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

4. Process design

The four different continuous processes that were designed and simulated are summarized in Table 3.1. Two of them are alkali-catalyzed processes, one using virgin oil (process I) and the other using waste cooking oil (process II). The remaining two (processes III and IV) are acid-catalyzed processes using waste cooking oil as the raw material.

The use of two different thermodynamic/activity models (NRTL and UNIQUAC) led to some differences in the simulation results. For example, in alkali-catalyzed process I, 1006 kg/h FAME as the biodiesel product was achieved at 212°C and 50 kPa when NRTL was employed. In contrast, 1007 kg/h FAME was obtained at 239°C at 20 kPa when UNIQUAC was used. In the following discussion, both results from 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 otherwise specified, in the following process descriptions, each percentage is expressed in mass units and all pieces of equipment are chosen to be horizontal with their sizes described as diameter x height.

Table 3.1 Different processes to produce biodiesel

Process No.	Description	Raw material	Catalyst
Process I	Alkali-catalyzed process	Virgin vegetable oil	Sodium hydroxide
Process II	Alkali-catalyzed process	Waste cooking oil	Sodium hydroxide
Process III	Acid-catalyzed process	Waste cooking oil	Sulfuric acid
Process IV	Acid-catalyzed process using hexane extraction	Waste cooking oil	Sulfuric acid

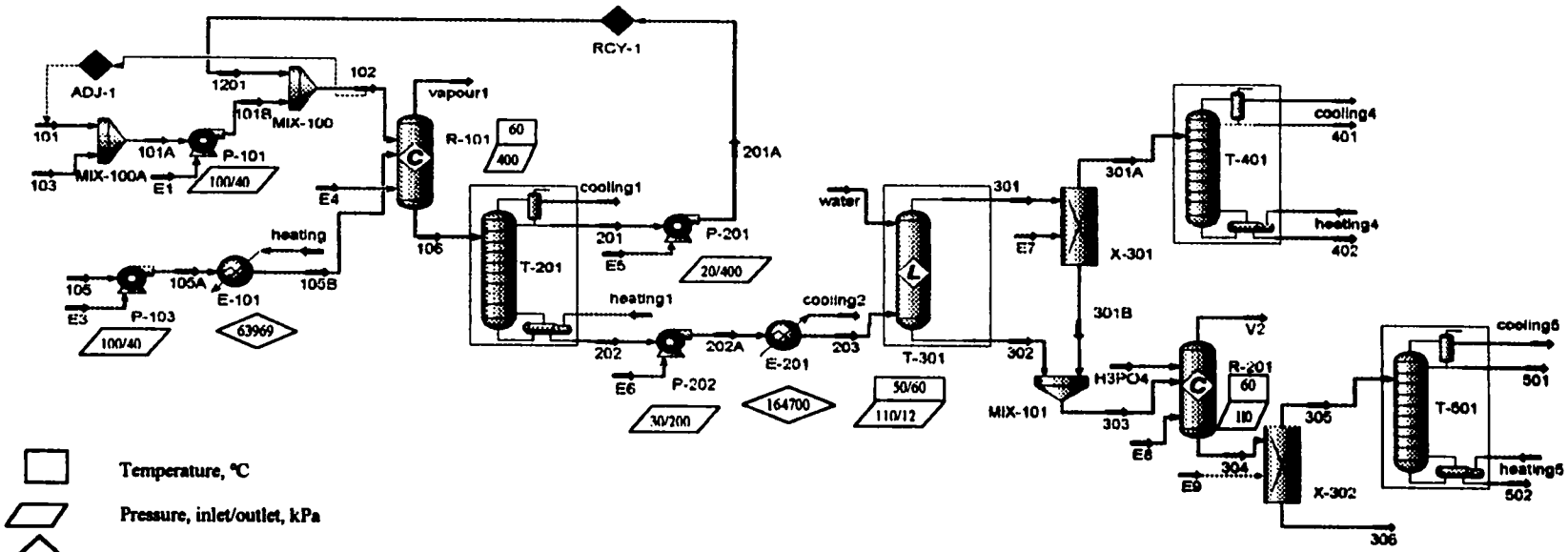
4.1 Alkali-catalyzed process using virgin vegetable oil (process I)

A continuous alkali-catalyzed process flowsheet using virgin oil was first developed. The process flowsheet and stream list are given in Figure 3.2. A detailed process description follows.

Transesterification

The reaction was carried out at a 6:1 molar ratio of methanol to oil, 1% sodium hydroxide (based on oil), 60°C and 400 kPa. 116 kg/h fresh methanol (stream 101), 112 kg/h recycled methanol (stream 1201) and 10 kg/h anhydrous sodium hydroxide (stream 103) were mixed first before being pumped into reactor R-101 by pump P-101. 1000 kg/h virgin vegetable oil (stream 105) were heated to 60°C in exchanger E-101 before entering R-101. In R-101, 99.7% of oil was assumed to be converted to FAME, producing approximately 1003 kg/h FAME and 104 kg/h glycerol in stream 106. There was methanol and some virgin oil remaining in stream 106 because methanol was in excess and 0.3% of oil was unconverted. In brief, a total of 1228 kg/h in stream 106, containing 82% FAME, 8% glycerol, 9% methanol, 0.8% sodium hydroxide and traces of unconverted virgin oil, was introduced to methanol distillation T-201 at 60°C.

Figure 3.2 Alkali-catalyzed process to produce biodiesel from virgin oil



Stream name	102	105B	106	201	202	301A	306	305	401	402	501	502
Temperature (°C)	26.6	60.0	60.0	28.2	124.9	60	60	60	43.9	212.4	56.2	130.4
Pressure (kPa)	400	400	400	20	30	110	110	110	40	50	40	50
Molar flow (kg-mol/h)	7.06	1.13	8.13	3.16	4.97	3.58	0.084	1.99	0.11	3.47	0.42	1.57
Mass flow (kg/h)	228.07	1000.00	1227.92	101.36	1126.56	1009.95	13.73	121.92	3.40	1006.55	9.02	112.90
Liquid volume flow (m^3/h)	0.280	1.111	1.371	0.127	1.244	1.152	0.005	0.101	0.004	1.148	0.010	0.092
Component mass fraction												
Methanol	0.956	0.000	0.088	1.000	0.006	0.003	0.000	0.027	0.941	0.000	0.363	0.000
Triglyceride (oil)	0.000	1.000	0.002	0.000	0.003	0.002	0.000	0.008	0.000	0.002	0.000	0.009
Methyl-oleate (biodiesel)	0.000	0.000	0.817	0.000	0.890	0.993	0.000	0.002	0.000	0.996	0.000	0.002
Glycerol	0.000	0.000	0.085	0.000	0.092	0.000	0.000	0.852	0.000	0.000	0.000	0.920
NaOH	0.044	0.000	0.008	0.000	0.009	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	0.002	0.000	0.112	0.059	0.002	0.637	0.070
H_3PO_4	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	0.995	0.000	0.000	0.000	0.000	0.000

According to data provided by Noureddini and Zhu (1997), the reaction rate constant was $k = 0.0256\ min^{-1}$. The diameter and height of R-101 were computed as 1.8 m and 5.4 m, respectively. Although the concentration of sodium hydroxide was 0.8%, stainless steel was considered as the construction material of R-101. In the future, carbon steel rather than stainless steel may be used to save on equipment costs.

Methanol recovery

In T-201, 5 theoretical stages and a reflux ratio of 2 were used. A good separation was achieved. Stream 201 (101 kg/h) was a pure methanol distillate (100%) and stream 202 (1127 kg/h) contains all of the FAME from the reactor. Ninety four percent of the total methanol in stream 106 was recovered as a distillate in stream 201. The temperature at the top of the column was 28°C at 20 kPa and that at the bottom was 125°C at 30 kPa. Vacuum distillation was used to keep the temperature under 150°C. Pure methanol (stream 1201) was pumped and mixed with the fresh make up methanol (stream 101A) and then charged back into reactor R-101. Bottom stream 202, containing 89% FAME, 9% glycerol, 0.6% methanol, 0.9% sodium hydroxide and traces of unreacted oil, was sent to washing column T-301 after being cooled in exchanger E-201 to 60°C.

At this operating condition, the heat duties of the overhead condenser and bottom reboiler were 0.4 MJ and 0.5 MJ, respectively. The size of this column was calculated to be 0.6 x 10 m. Although most of the methanol was distilled, the concentration of sodium hydroxide in the bottom stream changed little (0.9%). Carbon steel was used as the material of construction of this column and the downstream units.

Water Washing

In water washing column T-301 with 5 theoretical stages, the FAME in stream 203 was completely separated from the glycerol. The simulations indicated that at 60°C and 110 kPa, stream 301A (1010 kg/h) contained 98% FAME and no glycerol. The content of other compounds, such as vegetable oil, methanol and water in stream 301A were all less than 1%. All of the glycerol remains in the bottom stream 303 (127 kg/h), whose composition was 81% glycerol, 7% water, 2% methanol and 8% sodium hydroxide. In total, 11 kg/h water was added to T-301.

The data using the UNIQUAC model were somewhat different from the above results. 144 kg/h water usage was required to separate the FAME from other substances. Thereby, the main composition of stream 301A (1131 kg/h) was 88% FAME, 10% water. The load of T-401 was increased because of the presence of more water in the feed stream, as discussed later. Bottom stream 303 (140 kg/h) contained 74% glycerol, 16% water and 7% sodium hydroxide. However, regardless of which model was used, the simulation results demonstrated that adding the proper amount of water could guarantee a clear separation between the FAME and other substances, such as glycerol, methanol, sodium hydroxide and water. This washing column was 0.8 x 10 m when the NRTL model was used and 1 x 10 m when the UNIQUAC model was employed.

FAME purification

In order to obtain the final biodiesel product adhering to ASTM specifications (more than 99.6%), FAME distillation T-401 was used. Stream 301 from T-301 was forwarded to T-401 to further purify the FAME product. Water and methanol were removed at 5 theoretical stages and a reflux ratio of 6. To keep the bottom temperature under 250°C, the operating pressure had to be 40 kPa at the top and 50 kPa at the bottom. A 99.65% FAME product with 1007 kg/h was obtained in stream 402 at 212°C. Methanol and water were distilled in stream 401 (3.4 kg/h) at 44°C. Detailed compositions of streams 401 and 402 are shown in Figure 3.2.

The energy requirements of the overhead condenser and bottom reboiler were 0.03 MJ and 0.4 MJ, respectively. Superheated medium pressure steam was considered to be the heating medium for the reboiler. The size of this column was 0.5 x 10 m.

When the UNIQUAC model rather than NRTL was employed, the load in T-401 increased. Simulations showed that the heat duties of condenser and reboiler were 0.9 MJ and 1.3 MJ, respectively. The size of T-401 became 0.8 x 10 m (diameter x height). However, the same desired purity of FAME product was obtained in either thermodynamic/activity model.

Alkali removal

At 60°C, stream 302 (121 kg/h) proceeded to neutralization reactor R-201 to remove sodium hydroxide by adding pure phosphoric acid (100%). The resulting Na_3PO_4 was removed in gravity separator X-302. When potassium hydroxide was used as an alkali catalyst, the potassium phosphate may be used as a valuable by-product (e.g. fertilizer). After removing the sodium hydroxide, stream 305 (122 kg/h) contained 85% glycerol, 11% water, 3%methanol and traces of oil. If a glycerine by-product with a higher grade (e.g., 92%) was preferred, this stream would pass to T-501 for further distillation. When the UNIQUAC model was used, the composition of stream 305 was 77% glycerol, 20% water, 2% methanol and traces of oil. This stream had to enter T-501 to obtain 85% or 92% glycerine.

No kinetic model was used in the preliminary sizing of reactor R-201. Instead, it was regarded as a settler (Sinnott, 1999). According to the volume flowrates of stream 303 ($0.1 m^3/h$) and phosphoric acid ($0.005\ m^3/h$), R-201 was estimated to be 0.3 x 1 m (diameter x height).

Glycerine purification

Glycerine purification T-501 was designed with 5 theoretical stages and a reflux ratio of 2. At 56°C and 40 kPa, water and methanol (9 kg/h) were removed in the distillate 501. At the bottom (130°C and 50 kPa), 92% glycerine was obtained at a rate of 113 kg/h as a high quality by-product. The energy requirements of the overhead condenser and bottom reboiler of this column were 0.05MJ and 0.07MJ, respectively, its diameter was 0.5 m, and its height was 10 m.

When the UNIQUAC model was applied, despite some changes in operating conditions (e.g., the temperatures, the heat duties of the condenser and reboiler), the size of the column remained the same.

Waste treatment

The water streams from the top of T-401 (stream 401, 3.4 kg/h) and T-501 (stream 501, 9 kg/h) both contained methanol and water. Their compositions are listed in Figure 3.2. The total amount of methanol in streams 401 and 501 was 6.5 kg/h, which only

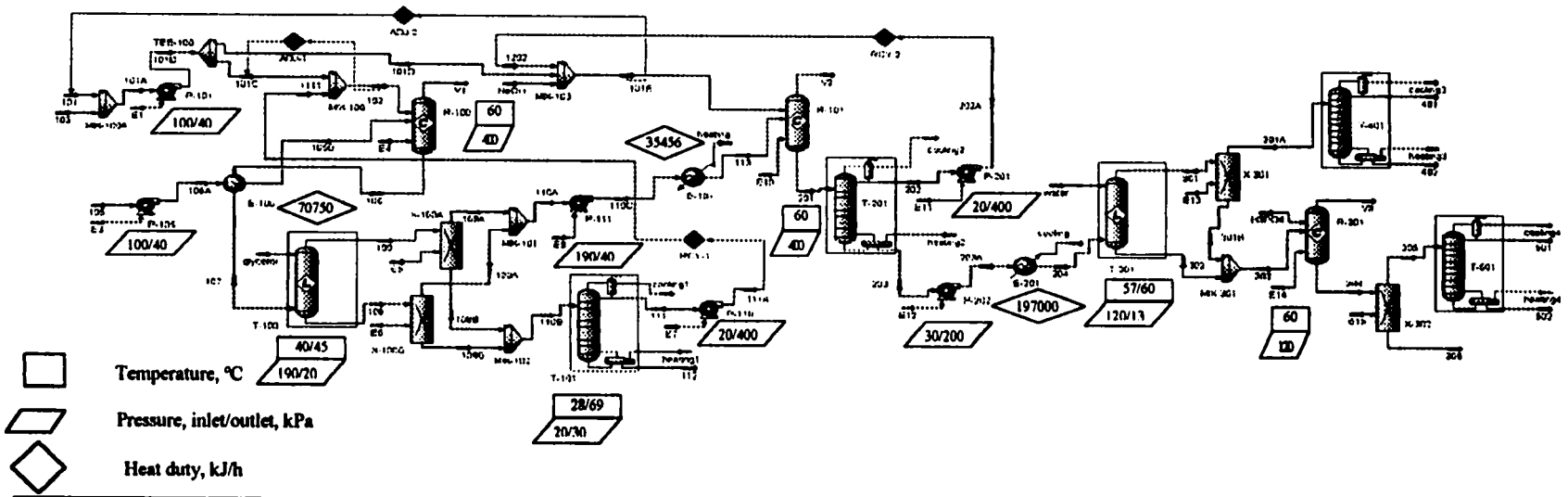
amounted to 3% of the overall methanol entering reactor R-101. These streams were treated as hazardous liquid wastes at present because of their small amounts. However, further consideration on reusing these streams may be necessary in the future, especially when they are of large amounts. For example, stream 401 contained 94% methanol and 6% water. Methanol has a lower boiling point than water but they are all much more volatile than FAME (i.e., bottom product). Thus, adding a side-draw for water removal in distillation column T-401 may be feasible. If the water in stream 401 is completely removed from the methanol, a pure methanol distillate from T-401 can be recycled. Stream 501, containing 36% methanol and 64% water, can be returned to T-301 as a washing solvent instead of fresh water. When UNIQUAC rather than NRTL was used, stream 401 (124 kg/hr) contained 97% water and 3% methanol. However, the total amount of methanol in stream 401 is the same as that using NRTL. In this case, recycling stream 401 together with stream 501 to T-301 may be a reasonable scheme. Recovery of the solid waste stream 306 from X-302 (13.7 kg/h with 99.5% Na_3PO_4) as a possible fertilizer credit could also be considered. These changes offer potential approaches for reducing waste treatment.

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

In order to introduce an environmentally friendly means of lowering the cost of biodiesel, a continuous alkali-catalyzed process flowsheet for biodiesel production from waste cooking oil was developed. The process flowsheet is shown in Figure 3.3, and includes a stream list. The following description of this process concentrates only on the differences from process I (i.e., the addition of a pre-treatment unit including esterification, glycerine washing and methanol recovery).

The amount of free fatty acids in the waste cooking oil was assumed to be 6%. The following conditions were applied to the pre-treatment unit to remove the free fatty acids: reaction at 70°C, a 6:1 molar ratio of methanol to oil, 1% sulfuric acid (based on oil), and a pure glycerine (100%) stream was used as a liquid entraining agent to extract the excess methanol, unreacted acid catalyst and resulting water from the oil phase.

Figure 3.3 Alkali-catalyzed process to produce biodiesel from waste cooking oil



Stream name	102	105B	106	113	201	202	203	301A	305	306	401	402	501	502
Temperature (°C)	28.08	60.00	70.00	60.00	60.00	28.19	131.46	59	60	60	36.38	252.19	66.71	119.80
Pressure (kPa)	400	400	400	400	400	20	30	120	120	120	20	30	40	50
Molar flow (kg-mol/h)	6.60	1.40	8.00	1.39	8.11	2.83	5.29	3.77	4.02	0.092	0.08	3.69	2.24	1.78
Mass flow (kg/h)	218.01	1100.00	1318.01	1092.49	1311.76	90.59	1221.18	1093.46	166.71	15.03	1.80	1091.66	42.45	124.26
Liquid volume flow (m^3/h)	0.266	1.223	1.489	1.216	1.464	0.114	1.350	1.247	0.147	0.006	0.002	1.245	0.044	0.103
Component mass fraction														
Methanol	0.954	0.000	0.152	0.000	0.074	1.000	0.005	0.001	0.029	0.000	0.566	0.000	0.112	0.000
Triglyceride (oil)	0.000	0.940	0.784	0.937	0.008	0.000	0.008	0.003	0.041	0.000	0.000	0.003	0.000	0.054
Methyl-oleate (biodiesel)	0.000	0.000	0.053	0.063	0.830	0.000	0.891	0.995	0.004	0.000	0.000	0.996	0.000	0.006
Glycerol	0.000	0.000	0.000	0.000	0.080	0.000	0.086	0.000	0.634	0.000	0.000	0.000	0.000	0.850
H_2SO_4	0.045	0.000	0.008	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	0.008	0.000	0.009	0.000	0.000	0.000	0.000	0.000	0.000	0.000
H_2O	0.001	0.000	0.003	0.000	0.000	0.000	0.000	0.001	0.293	0.000	0.434	0.000	0.888	0.090
Oleic acid	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
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
Na_3PO_4	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

Esterification

The reaction was carried out at 70°C and 400 kPa. The fresh methanol stream 101 (137 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 (1100 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 assumed to be converted to methyl esters, thereby yielding 1318 kg/h of reaction effluent 106. The main composition of stream 106 was 78% refined oil, 15% methanol, 5% methyl esters, 1% sulfuric acid and traces of water. After being cooled to 45°C, stream 106 was forwarded to a glycerine washing column T-100 to remove the sulfuric acid and water.

Due to lack of information on the kinetics of this reaction, the sizing of R-100 was estimated as a settler (Sinnott, 1999). The diameter and height of the reactor was 0.8 m and 2.4 m, respectively. Stainless steel (type 316) was recommended for the construction material because the concentration of sulfuric acid was 0.8% at 70°C.

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 45°C and 200 kPa, all of the resulting water was removed from oil stream 110A after three- theoretical stages of washing. Stream 110A (1092kg/h) from T-100 only consisted of 94% refined oil and 6% resulting methyl esters and was sent to downstream transesterification unit. On the other hand, stream 110B (336 kg/h) included 60% unreacted methanol, 33% glycerol, 3% sulfuric acid, 3% oil, 1% water and traces of esters. Recovering a portion of the methanol in this stream to reuse it in R-100 was a logical step. This column was 1 x 10 m, respectively. The column was constructed of stainless steel (type 316) because of the presence of 0.8% sulfuric acid at 45°C.

Methanol recovery

In T-101, 5 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 is treated as waste.

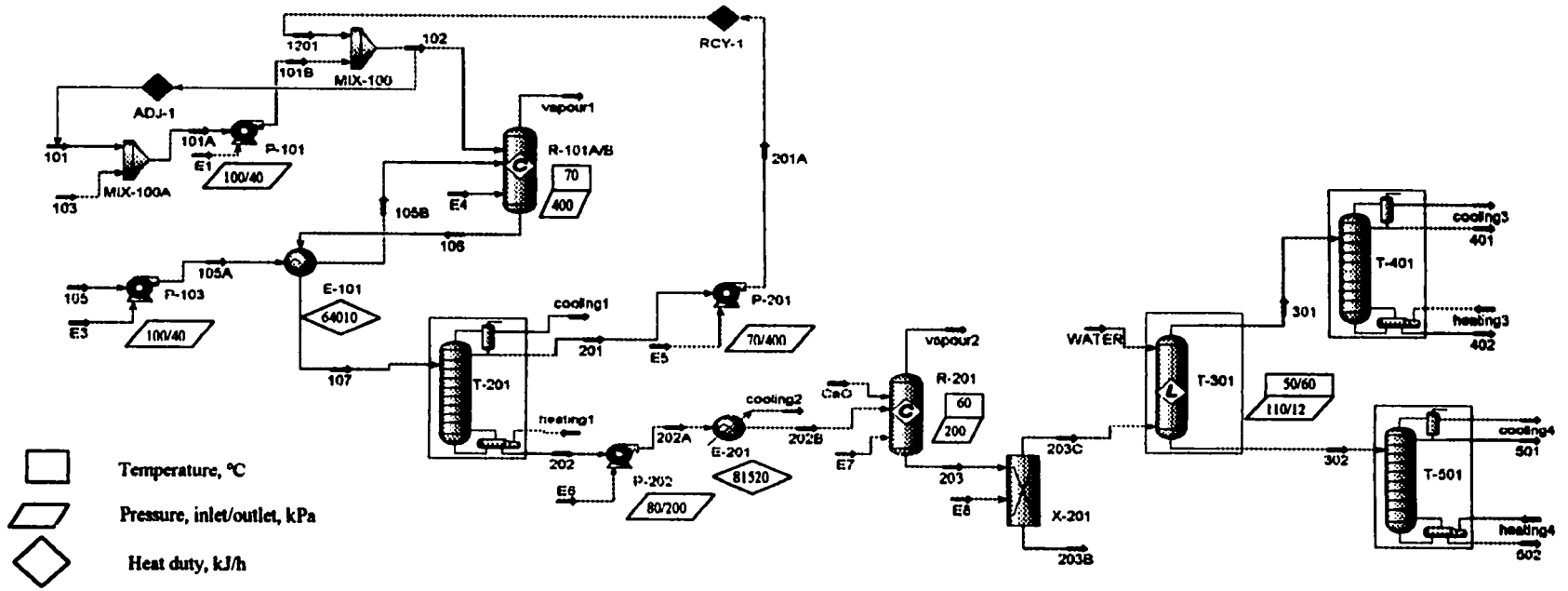
Under these operating conditions, the energy needs of the overhead condenser were the same as that of the bottom, 1.4 MJ. The size of this column was calculated to be 1 x 12 m. When stainless steel (type 316) was used for 7% sulfuric acid at 70°C, the corrosion rate would exceed 0.5 mm/yr. Therefore, stainless steel type alloy 20 was used instead of type 316.

Once the refined oil without free fatty acids is obtained, the downstream units were similar to those in process I using virgin vegetable oil. The operation conditions and specifications of some main streams are presented in Figure 3.3. Compared to process I, despite the decrease in raw material cost by using waste oil, the addition of a pre-treatment unit to reduce the content of free fatty acids in the feedstock oil in process II would incur extra costs.

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

As mentioned earlier, an acid-catalyzed system is insensitive to the free fatty acids in the oil. There is no limit to the amount of free fatty acids that can be present in the acidic system. Consequently, an acid-catalyzed continuous process to produce biodiesel from waste cooking oil 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. Its flowsheet is shown in Figure 3.4, along with a stream list.

Figure 3.4 Acid-catalyzed process to produce biodiesel from waste cooking oil



Stream Name	102	105B	106	201	202	203B	301	302	401	402	501	502
Temperature (°C)	51.21	60.00	70.00	55.36	87.02	60	59.28	60.00	64.30	214.15	47.32	109.82
Pressure (kPa)	400	400	400	70	80	130	110	120	100	110	40	50
Molar flow (kg-mol/h)	59.03	1.13	60.03	50.69	9.33	1.53	3.78	6.56	0.28	3.50	4.44	2.12
Mass flow (kg/h)	1992.41	1000.00	2992.41	1624.33	1368.08	208.03	1014.02	249.73	8.81	1005.21	120.92	128.81
Liquid volume flow (m^3/h)	2.396	1.111	3.485	2.041	1.444	0.070	1.157	0.252	0.011	1.146	0.145	0.107
Component mass fraction												
Methanol	0.925	0.000	0.577	1.000	0.076	0.000	0.010	0.375	0.994	0.001	0.774	0.000
Triglyceride (oil)	0.000	1.000	0.001	0.000	0.001	0.000	0.001	0.005	0.000	0.001	0.000	0.010
Methyl-oleate (biodiesel)	0.000	0.000	0.335	0.000	0.733	0.000	0.988	0.006	0.000	0.997	0.000	0.011
Glycerol	0.000	0.000	0.037	0.000	0.080	0.000	0.000	0.438	0.000	0.000	0.000	0.850
H_2SO_4	0.075	0.000	0.050	0.000	0.110	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	0.002	0.176	0.006	0.002	0.226	0.129
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
$CaSO_4$	0.000	0.000	0.000	0.000	0.000	1.000	0.000	0.000	0.000	0.000	0.000	0.000

Transesterification

On the basis of discussions in Section 2, the reaction conditions were set up at a 50:1 molar ratio of methanol to oil, 15% sulfuric acid (based on waste oil), a reaction temperature of 70°C and a pressure at 400 kPa.

218 kg/h fresh methanol (stream 101), 1774 kg/h recycle methanol (stream 1201) and 150 kg/h sulfuric acid (stream 103) were mixed first and fed to transesterification reactor R-101 by pump P-101. 1000 kg/h waste cooking oil was fed to R-101 after being heated to 60°C in exchanger E-101. In R-101, it was assumed after 200 minutes that 99.8% of the oil was converted to FAME. Altogether, 2992 kg/h effluent (stream 106) was discharged from R-101, containing 58% methanol, 34% methyl oleate (FAME or biodiesel), 4% glycerol, 5% sulfuric acid and traces of unconverted oil.

Based on the descriptions provided by McBride (1999), the reaction rate constant was calculated as 0.0219 min^{-1}. Accordingly, the reactor volume was determined to be 423 m^3. If only one reactor was used, its diameter and height would be 5.6 m and 17m, respectively. Instead, two reactors operated in series were used with a diameter of 2.1 m and a height of 6.3 m (Winterbottom and King, 1999). In the process flowsheet (see Figure 3.4), one reactor with two equipment numbers R-101A/B was used to represent the two reactors operated in series. Stainless steel (type 316) was chosen as the construction material since the concentration of sulfuric acid in R-101 is 5%.

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, 4 theoretical stages, a reflux ratio of 2 and vacuum distillation were selected. Similar to process I, 1624 kg/h pure methanol was obtained in stream 201 at 55°C and 70 kPa, with a 94% methanol recovery rate. Bottom stream 202 (1368 kg/h) was achieved at 87°C and 80 kPa, including 73% methyl oleate, 8% methanol, 8% glycerol, 11% sulfuric acid and traces of oil. It was forwarded to acid removal unit R-201.

The heat duties of both the overhead condenser and bottom reboiler in T-201 were 5.5 MJ. The size of this column was estimated at 1.2 m x 10 m (diameter x height). The presence of over 10% sulfuric acid in the bottom of T-201 required the use of stainless steel (alloy 20) as the construction material.

Vacuum distillation was applied to keep the temperature below 100°C. If the column was operated at normal pressure (e.g., 110/120 kPa), the bottom temperature would be 125°C when the UNIQUAC model was applied. In this case, a nickel alloy, such as C-22 or G-30, would be chosen as the construction material due to the higher sulfuric acid concentration (i.e., 11%) (Davis et al, 2000). This would incur a higher cost of construction material.

Acid removal

In contrast to process I, acid removal was used rather than alkali removal. However, the design principle was the same. 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 formed could be absorbed by the resulting $CaSO_4$. A gravity separator, X-201, was employed to remove the $CaSO_4$. The resulting stream 203C (1246 kg/h) consisted of 80% methyl oleate, 9% glycerol and 8% methanol. It proceeded to water washing column T-301 at 60°C and 130 kPa. Reactor R-201 was sized at 0.5 m x 1.5 m. Stainless steel (alloy 20) was used because of the presence of 11% sulfuric acid.

In terms of equipment sizing and operating conditions, the remaining water washing column (T-301) and purification units (i.e., FAME distillation T-401 and glycerol purification T-501) were similar to those used for process I. For example, 18 kg/h water was applied to T-301 in process III whereas 11 kg/h water was needed in process I. Finally, 99.65% FAME and 92% glycerol could be obtained as biodiesel product and by-product, respectively. Detailed specifications for main streams, such as streams 301, 302, 401, 402, 501 and 502, are shown in Figure 3.4. Because of the removal of sulfuric acid in R-201, the downstream units were made of carbon steel.

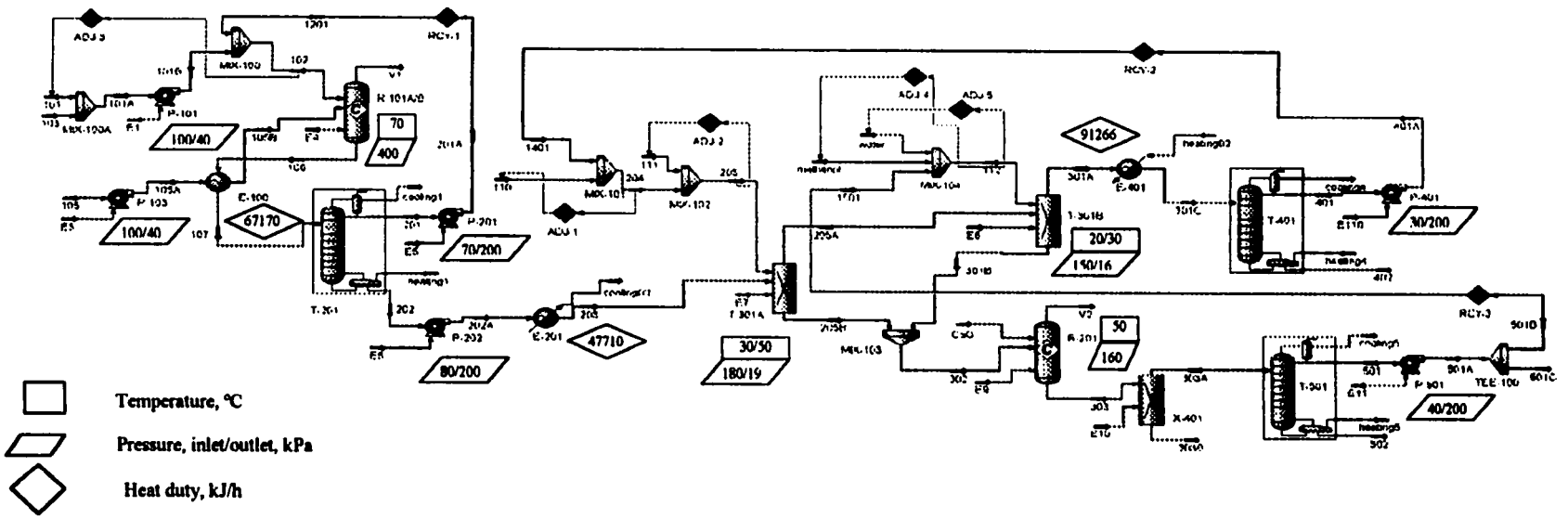
Similar to process I, the use of the UNIQUAC rather than the NRTL model in process III resulted in some differences in the sizing of washing column T-301 and FAME distillation column T-401: T-301 was 1.1 x 10 m and T-401 was 1 x 10m.

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

To avoid the formation of emulsions in water washing, the use of hexane or petroleum ether as a solvent to separate the FAME from other components was proposed as an alternative (see Figure 3.5). 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 the methanol distillation column T-201.

After T-201, the reaction mixture contained methanol, FAME, glycerol, sulfuric acid, unconverted oil and hexane. When a liquid-liquid extraction was used to simulate such a complicated multi-component system, the simulation results exhibited a deviation from previous experimental observations (Nye et. al., 1983; McBride, 1999). This was mainly due to the absence of many interaction parameter coefficients between the components in the HYSYS^{TM} library. Therefore, in the current work, we assumed that a good separation between the FAME/hexane and glycerol/methanol was achieved after the addition of hexane and water. Based on their amount in feed streams 203 and 205, 100% of the hexane and unconverted oil, 99.5% of the FAME, 4% of the methanol, 4% of the water, 2% of the sulfuric acid and 1% of the glycerol, still remained in the upper layer (stream 205A) from T-301A. The lower layer (stream 205B) consisted of glycerol, methanol, sulfuric acid and water. A second washing with methanol/water (T-301B) attempted to remove the water, glycerol and sulfuric acid from the hexane and FAME in stream 205A completely. The separation of the components was determined according to the experimental experience. Component splitters T-301A and T-301B instead of a liquid-liquid extraction were applied to simulate the hexane extraction and methanol/water washing.

Figure 3.5 Acid-catalyzed process using hexane extraction to produce biodiesel from waste cooking oil



Stream name	102	105B	106	201	202	205A	301C	303A	303B	401	402	501	502
Temperature (°C)	60.83	60.00	70.00	55.36	87.02	30	60.00	50.00	50	26.87	222.82	46.5	114.43
Pressure (kPa)	400	400	400	70	80	180	150	160	160	30	40	40	50
Molar flow (kg-mol/h)	59.03	1.13	60.03	50.69	9.33	5.00	4.92	10.71	1.53	1.33	3.59	8.73	1.98
Mass flow (kg/h)	1992.41	1000.00	2992.41	1624.33	1368.08	1168.75	1165.85	373.04	208.13	113.02	1052.83	244.59	128.44
Liquid volume flow (m^3/h)	2.396	1.111	3.485	2.041	1.444	1.371	1.371	0.402	0.070	0.170	1.201	0.296	0.107
Component mass fraction													
Methanol	0.925	0.000	0.577	1.000	0.076	0.004	0.000	0.535	0.000	0.004	0.000	0.816	0.000
Triglyceride (oil)	0.000	1.000	0.001	0.000	0.001	0.002	0.002	0.000	0.000	0.000	0.002	0.000	0.000
Methyl-oleate (biodiesel)	0.000	0.000	0.335	0.000	0.733	0.898	0.900	0.014	0.000	0.000	0.997	0.000	0.041
Glycerol	0.000	0.000	0.037	0.000	0.080	0.001	0.000	0.293	0.000	0.000	0.000	0.000	0.850
H_2SO_4	0.075	0.000	0.050	0.000	0.110	0.002	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	0.001	0.158	0.000	0.002	0.001	0.184	0.109
N-Hexane	0.000	0.000	0.000	0.000	0.000	0.093	0.097	0.000	0.000	0.994	0.001	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
$CaSO_4$	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

From T-201, bottom stream 202 (1420 kg/h) contained 7% methanol (i.e., 0.13 m^3/h). An equal volume of hexane (0.13 m^3/h) and 0.01 m^3/h water (vol. ratio of water to methanol is1:10) were added to T-301A at 60°C and 200 kPa. After hexane extraction in T-301A, stream 205A (1173 kg/h, or 1.37 m^3/h) contained 89% FAME, 10% hexane and traces of methanol, glycerol, water and sulfuric acid. It was forwarded to a second washing unit T-301B. Because of the presence of 11% sulfuric acid, T-301A was made from stainless steel alloy 20. In bottom stream 205B, there was no hexane and only 1.4% FAME remained with 27% methanol, 29% glycerol and 40% sulfuric acid. In T-301B, 0.14 m^3/h methanol-water (80% methanol and 20% water) was added. After T-301B, it was expected that no glycerol and sulfuric acid would remain in the FAME and hexane stream, 301A. The composition of 301A (1164 kg/h) was 90% FAME, 10% hexane with traces of oil, which passed to the downstream FAME distillation column T-401 to remove the hexane. Although only traces of sulfuric acid were possibly present in T-301B, stainless steel (type 316) was employed from a conservative viewpoint. Stream 205B from T-301A was combined with stream 301B from T-301B. At a total flowrate of 496 kg/h, they entered R-201 for sulfuric acid removal by adding calcium oxide. Because most of the methanol and FAME were removed in T-201 and T-301A/B, the concentration of sulfuric acid in R-201 was much higher than that in other equipment pieces. Results showed that 30% sulfuric acid was present in R-201 at 50°C. This required the use of alloy 20 as the construction material of R-201. Regarding the equipment downstream of R-201, the use of carbon steel was reasonable because of the absence of sulfuric acid.

Although component splitters were used in the simulation, the sizing estimation of T-301A and T-301B still used the same methods for liquid-liquid extraction (Sinnott, 1999). Altogether, they were estimated to be 0.8 x 10 m and 0.6 x 10 m in diameter x height, respectively.

FAME distillation

Since 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 5 theoretical stages and a reflux ratio of 5, 113 kg/h

distillate 401 was discharged from the top of T-401 at 27°C and 30 kPa, containing 99.4% hexane, 0.4% methanol and 0.2% water. This stream was recycled and reused in T-301A to reduce the need for fresh solvent (stream 110). At the bottom, stream 402 (1053 kg/h, 223°C and 40 kPa) had a composition of 99.65% FAME with traces of hexane, oil and water. This column was sized as 0.6 x 10 m. The energy requirements of the top condenser and bottom reboiler were 0.2 MJ and 0.6 MJ, respectively.

Glycerine purification

Stream 303A (373 kg/h) from R-201 with 53% methanol, 29% glycerol and 16% water, entered T-501 at 50°C and 160 kPa. After a 5-theoretical-stage distillation with a reflux ratio of 2, 85% glycerine could be obtained as a by-product at a rate of 128 kg/h at 114°C and 50 kPa (stream 502). As for top stream 501 (at 46°C and 40 kPa), it contained 82% methanol and 18% water. Thus, a portion of it (112 kg/h, or 0.14 m^3/h) returned to T-301B as the solvent for the second washing. This column was sized at 0.8 x 10 m (diameter x height). The duties of the condenser and reboiler were the same, 1 MJ. 118 kg/h glycerine with 92% purity could also be achieved in stream 502 under similar operating conditions.

Because of the use of a component splitter, the differences between using the NRTL and UNIQUAC models were not displayed.

The investigation of another alternative acid-catalyzed process using a supported catalyst is underway. The preliminary description is presented in the Appendix A.1 and Figure A.1.

4.5 Process comparison

A technical comparison of the four different processes is summarized in Tables 3.2 and 3.3.

Pre-esterification unit

A pre-treatment was required in the alkali-catalyzed process using waste cooking oil

Table 3.2 Description of operating conditions of main equipment (NRTL)

Main process equipment			Process I	Process II	Process III	Process IV
Pre-treatment unit	R-100	Temp., °C	N/A	70	N/A	N/A
		Pressure, kPa		400		
		Size (D x H), m		0.8 x 2.4		
	T-100	Temp., °C		42/45		
		Pressure, kPa		190/200		
		Size (D x H), m		1 x 10		
	T-101	Temp., °C		28/69		
		Pressure, kPa		20/30		
		Size (D x H), m		1 x 12		
Transesterification	R-101	Temp., °C	60	60	70	70
		Pressure, kPa	400	400	400	400
		Size (D x H), m	1.8 x 5.4	1.8 x 5.4	2.1 x 6.3[a]	2.1 x 6.3[a]
Separation unit	T-201	Temp., °C	28/125	28/130	55/87	55/87
		Pressure, kPa	20/30	20/30	70/80	70/80
		Condenser duty, MJ	0.4	0.3	5.5	5.5
		Reboiler duty, MJ	0.5	0.5	5.5	5.5
		Normal vaporflowrate, kg/h	300	270	4870	4870
		Size (D x H),	0.6 x 10	0.6 x 10	1.2 x 10	1.2 x 10
	T-301	Total flowrate, kg/h	1270	1414	1570	T-301A 1547 / T-301B 1288
		Size (D x H), m	0.8 x 10	1 x 10	1 x 10	T-301A 1 x 10 / T-301B 0.8 x 10
	T-401	Temp., °C	44/212	36/250	64/214	27/223
		Pressure, kPa	40/50	20/30	100/110	30/40
		Condenser duty, MJ	0.03	0.07	0.06	0.2
		Reboiler duty, MJ	0.4	0.6	0.4	0.6
		Normal vapor flowrate, kg/h	73	55	60	680
		Size (D x H), m	0.5 x 10	0.5 x 10	0.5 x 10	0.6 x 10
	T-501	Temp., °C	N/A	67/120	47/110	46/114
		Pressure, kPa		40/50	40/50	40/50
		Condenser duty, MJ		0.3	0.5	1
		Reboiler duty, MJ		0.3	0.5	1
		Normal vapor flowrate, kg/h		127	360	730
		Size (D x H), m		0.5 x 10	0.6 x 10	0.8 x 10

[a] Two reactors with the same size.

Table 3.3 Summary of the number of main process equipment in different processes

Equipment	Process I	Process II	Process III	Process IV
Reactors	2	3	3	3
Columns	4	6	4	5
Exchangers	8	11	8	9
Pumps + gravity separator(s)	8	11	8	8
Total	22	31	23	25
Stainless steel equipment	2	7	9	11

(process II). As shown in Table 3.2, this pre-treatment unit was not necessary in other processes. Virgin oil without free fatty acids was used in process I; processes III and IV were acid-catalyzed processes, which were insensitive to free fatty acids.

The pre-treatment unit included esterification reactor R-100, glycerine washing column T-100 (1 x 10 m) and methanol distillation column T-101 (1 x 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 not small compared to the other columns in all processes (see Table 3.2). This was due to the addition of pure glycerine as a washing solvent in T-100. This would also offset the credit for selling the glycerine by-product from the transesterification unit. In addition, 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, these factors would contribute to an increase in process complexity, equipment costs and operating cost in process II.

Transesterification

Processes III and IV required more and larger reactors than processes I and II. The larger amount of methanol used in processes III and IV also led to an increase of reaction volumes. For example, the flowrate of effluent from R-101 (i.e., stream 106) in processes

I and II was 1228 kg/h but became 2992 kg/h in processes III and IV. Therefore, compared to processes I and II, two larger sized reactors were needed in acid-catalyzed processes III and IV.

Methanol distillation T-201

As for methanol distillation column T-201, its operating loads (i.e., vapour flowrate) in processes III and IV were much higher than those in processes I and II (as shown in Table 3.2). The main reason was because a 50:1 molar ratio of methanol to oil was used in the acid-catalyzed processes whereas only a 6:1 molar ratio was employed in the alkali-catalyzed processes. This resulted in larger column sizes and higher heat duties processes III and IV. T-201 was only 0.6 m in diameter in processes I and II whereas it was 1.2 m in diameter in processes III and IV. Energy requirements in the top condenser and bottom reboiler in processes III and IV were approximately 10 times those in processes I and II. On the other hand, there was only 0.8 wt% methanol in the feed stream of T-201 in processes I and II. Compared to the same stream containing 60 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 of methanol could be recovered with more rigid requirements in the operating conditions. If only 40% of 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 of methanol entering the waste stream (streams 401 and 501) and more fresh make-up methanol (stream 101) would be required. As a result, waste disposal expenses and reactant costs would increase.

Currently, 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. 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 construction material cost of this column in processes III and IV must be higher than that in processes I and II.

Washing column T-301

As presented in Table 3.2, despite the different data resulting from the thermodynamic/activity model, 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, in process IV, two washing columns were required rather than one column in the other processes. In addition, because of the presence of sulfuric acid in T-301A/B in process IV, stainless steel was still used as the construction material whereas carbon steel was sufficient in processes I, II and III.

FAME distillation column T-401

FAME distillation column T-401 had a similar size in processes I, II and III (see Table 3.2). Most of the methanol was removed in T-201 in process III, which results in loads in the downstream units similar to that 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 due to the presence of the hexane. Thus, the size of this column was larger in process IV than in the other processes. In most processes, vacuum distillation was necessary to keep the column temperature below 250°C. In process III, despite the normal operating pressure (100/110 kPa) when the NRTL model was used, vacuum distillation with 40/50 kPa (top/bottom) respectively was required when the UNIQUAC model was employed.

Glycerine purification column T-501

With regard to glycerine purification column T-501, the flowrate of the feed stream to T-501 was 120-170 kg/h in processes I and II. However, the flowrate of the feed stream was 250 kg/h in process III because of the large excess of methanol in the acid-catalyzed process. Although 94% of the total methanol was recovered in T-201, the unrecovered 6% 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

this column was unnecessary in process I when the NRTL model was used, it was needed when the UNIQUAC model was applied.

Overall, if the pre-treatment unit was not taken into consideration, the sizes of the process equipment in alkali-catalyzed processes I and II were smaller than those in acid-catalyzed processes III and IV. The total number of major processing units in each process is summarized in Table 3.3. The lowest number of units was 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 pre-treatment unit. In acid-catalyzed processes III and IV, a lower number of pieces was required compared to process II but the number of those made from stainless steel was increased, especially in process IV. This represented a potential increase in the cost of construction material.

5. Conclusion

At a biodiesel production rate of 8,000 tonnes/year, four continuous alkali- and acid-catalyzed processes (I to IV) using virgin vegetable oil or waste cooking oil as the raw material were designed and simulated. Process flowsheets, as well as detailed operating conditions and major equipment designs for each process were presented. From our 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 process II, it was the most complex process with the greatest number of equipment pieces because of the addition of a pre-treatment unit. Moreover, the amount of waste produced in process II was more than in the other processes. The acid-catalyzed process III using waste cooking oil had less equipment pieces than process II, but more and larger transesterification reactors, as well as a larger methanol distillation column were required. Methanol distillation was found to be a key separation step in process III. Moreover, more pieces of equipment made from stainless steel material were necessary in process III than in processes I and II. Acid-catalyzed process IV had the

same merits and limitations as process III. Furthermore, 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) was recommended. However, if a low cost of raw material was of concern, the acid-catalyzed process using waste cooking oil (process III) proved to be a competitive alternative with a relatively simple process.

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 in this article, an economic evaluation of these processes is needed, especially for processes I and III. Also, 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.

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Chapter 4 PAPER 2

Biodiesel Production from Waste Cooking Oil: 2. Economic Assessment and Sensitivity Analysis

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Abstract

The economic feasibilities of four continuous processes to produce biodiesel, including both alkali- and acid-catalyzed processes, using virgin vegetable oil or waste cooking oil as the raw material were assessed. Results showed that although the alkali-catalyzed process using virgin vegetable oil had the lowest fixed capital cost, the acid-catalyzed process using waste cooking oil was more economically feasible, providing a lower total manufacturing cost, more attractive aftertax rate of return and lower biodiesel break-even price. On the basis of economic calculations, sensitivity analyses for these processes were carried out. Plant capacity and prices of feedstock oils and biodiesel were found to be the most significant factors affecting the economic viability of biodiesel manufacture.

Keywords: Biodiesel; Economic assessment; Aftertax rate of return; Sensitivity analysis

1. Introduction

Exploring new energy resources, such as biodiesel fuel, is of growing importance in recent years. Biodiesel, derived from vegetable oil or animal fat, is recommended for use as a substitute for petroleum-based diesel mainly because biodiesel is a renewable, domestic resource with an environmentally friendly emission profile and is readily biodegradable. The use of biodiesel as a fuel has been widely investigated. Its commercial use as a diesel substitute began in Europe in the late 1980s.

At present, the most common way to produce biodiesel is to transesterify the triglycerides in vegetable oil or animal fat with an alcohol in the presence of an alkali or acid catalyst. Methanol is the commonly used alcohol in this process, due in part to its low cost. The products, fatty acid methyl esters (FAME), are called biodiesel and include glycerine as a by-product. Alkali-catalyzed transesterification has been most frequently used industrially mainly due to its fast reaction rate. Sodium hydroxide or potassium hydroxide is the usual alkali catalyst. In contrast, acid-catalyzed transesterification has gained less attention because it has a relatively slow reaction rate. Nevertheless, it is more insensitive to free fatty acids in feedstock oil than the alkali-catalyzed system. The typical acid catalyst used in the reaction is sulfuric acid.

Compared to petroleum-based diesel, the high cost of biodiesel is the major barrier to its commercialization. It costs about three times that of petroleum-based diesel (Congressional Research Service, 1993; Bender, 1999). It is reported that approximately 70-95% of the total biodiesel production cost arises from the cost of raw material, that is, vegetable oil or animal fat (Krawczyk, 1996; Connemann and Fischer, 1999). Therefore, the use of waste cooking oil should greatly reduce the cost of biodiesel since waste oil is available at a very low or near zero price.

In previous work (Zhang et al., 2002), four different process flowsheets for producing biodiesel from virgin vegetable oil or waste cooking oil by alkali- or acid-catalyzed transesterification were developed. A comparison of these processes was presented in terms of process technology. The results showed that the acid-catalyzed process from waste cooking oil was a competitive alternative to the commonly used alkali-catalyzed process. However, in addition to technological evaluation, economic feasibility is also of

great importance in assessing process viability. Thus, the main objective of this article is to assess these processes on an economic basis. In this way, a better evaluation of the biodiesel production process will be achieved from both the technological and economic points of view. In addition, a sensitivity analysis of each process is presented, in an attempt to identify the major factors affecting the economic viability of biodiesel production.

2. Background

2.1 Economic studies

In previous economic studies of biodiesel production, capital cost, operating cost and biodiesel price were the main economic criteria used. Nelson et al. (1994) evaluated the economic feasibility of a plant with approximately 100,000 tonnes/year biodiesel production. Beef tallow was used as the raw material to react with methanol in the presence of an alkali catalyst. He concluded that the total capital cost was $12 million; the break-even price of biodiesel was $340/tonne. In their study, the prices of methanol, the alkali catalyst and glycerine by-product were $190/tonne, $4400/tonne and $600/tonne, respectively. These prices were similar to the ones used in the current evaluation. However, there was insufficient information on the reaction type, the nature of the separations or the detailed economic calculations.

Noordam and Withers (1996) carried out an economic study on biodiesel production with a plant capacity of approximately 7800 tonnes/year biodiesel. Canola seed was used as the raw material. Thus, the "total biodiesel cost" (i.e., total manufacturing cost) consisted of procurement cost, oil extraction cost, transesterification cost and overhead cost. The procurement cost was 6.45 million dollars, including the cost of canola seed, transport cost, elevator rental cost and storage cost. It accounted for 70% of the total production cost of the plant. The cost of canola seed was $6.14 million, forming the largest part of the procurement cost. The oil extraction cost was approximately $0.51 million, amounting to 5% of the total production cost. In the oil extraction unit, canola meal produced from seed crushing was a valuable by-product, providing a credit of $2.3

million. The transesterification cost was approximately $1.35 million, amounting to 15% of the total production cost. In the transesterification unit, canola oil from the oil extraction unit was transesterified with methanol in the presence of potassium hydroxide to yield biodiesel. The estimated equipment cost for this transesterification facility was $695,656. A glycerine credit was calculated to be $0.9 million at the price of $1260/tonne glycerine. Overall, after subtracting the credits for glycerine and canola meal, the total manufacturing cost was approximately $5.95 million. The break-even price of biodiesel was $763/tonne. With respect to the transesterification unit, aside from a block diagram of the material balance, no detailed description of the process, flowsheet and equipment sizing was available. Moreover, some other expenses were not taken into consideration in their study, such as the costs of supervision, patents and royalties, research and development, etc. As a result, all of these factors make a comparison to our results difficult.

Bender (1999) compared seven biodiesel plants using oilseed (i.e., soybean seed, canola seed, sunflower seed and rapeseed) or animal fats as the raw material. Four of them were continuous processes producing 2 million litres of biodiesel production annually (i.e., 1,760 tonnes/year). One was a batch process with 7.5 million litres of biodiesel capability per year (i.e., 6,600 tonnes/year). The other two were continuous processes using animal fats as the raw material with capacities of 12 million litres/year (10,560 tonnes/year) and 115 million litres/year (0.1 million tonnes/year), respectively. The capital cost for each process was presented. For example, a continuous plant using animal fats with a size of 12 million litres/year biodiesel (10,560 tonnes/year) was estimated to be $3.12 million in capital equipment cost. For crude glycerine with a price of $660/tonne, a credit of $0.72 million was available. For a technical grade glycerine product, a credit of $1.2 million at a price of $1470/tonne was calculated. The break-even price of biodiesel for the plant was calculated to be approximately $0.37/litre (i.e., $420/tonne). Although the operating costs for each process were provided, their definition was not clarified. Scale-dependent expenses, such as maintenance costs, utility cost and waste disposal fees, were also not discussed. When vegetable oil or waste grease was used as the raw material, the break-even price of biodiesel was roughly estimated to be $0.39-0.48/kg.

Overall, there are some limitations in the above economic studies: first, they all lack a detailed description of the process they evaluated and how their economic results were obtained. Secondly, all these studies used either various oilseeds or animal fats as the raw material. To our knowledge, there is no published economic study on the process using virgin vegetable oil or waste cooking oil. In addition, no economic studies on acid-catalyzed processes have been reported to date. Thirdly, the quoted break-even prices for biodiesel in the above studies underestimate the actual commercial cost of biodiesel because plant profit and taxes were excluded. Moreover, different researchers used different economic criteria to assess the biodiesel plant. Total capital cost was presented by Nelson et al. (1994) whereas total biodiesel cost (i.e. total manufacturing cost) was used by Noordam and Withers (1996) to represent the economic performance of the plant. Capital equipment cost was used as an economic evaluation criterion by Bender (1999). In addition, clear definitions of these criteria were not provided. In the present article, the economic criteria are based on fixed capital cost, total manufacturing cost and aftertax rate of return (Ulrich, 1984; Turton et al. 1998), as described in detail later.

2.2 Sensitivity analysis

The economic performance of a biodiesel plant (e.g., total manufacturing cost, the break-even price of biodiesel) can be determined once certain factors are identified, such as plant capacity, process technology, raw material cost, chemical costs, etc. However, the effects of these factors on the economic viability of the plant are also of concern. A sensitivity analysis is a study of measuring the sizes of these effects (i.e., input variable(s)) on the economic feasibility (i.e., output variable (s)) of the biodiesel plant and exploring the significant factors. This will further provide information for optimization of biodiesel production.

Korus et al. (1993) studied batch transesterification at the laboratory scale. Rape oil was transesterified with methanol or ethanol in the presence of potassium hydroxide or sodium methoxide. They concluded that the cost of feedstock oil played a significant role in determining the economic viability of the biodiesel process. Similarly, Nelson et al. (1994) commented that the significant factors affecting the cost of biodiesel were feedstock cost, plant size and glycerine by-product value but no details were given.

A price sensitivity analysis was performed by Noordam and Withers (1996). The variables were restricted to the costs of raw material and by-products (i.e., prices of canola seed, canola meal and glycerine). By varying the value of one variable while keeping the others unchanged, its effect on the break-even price of biodiesel was studied. Since other factors, such as the ones related to process operation, were not considered, the results from such an analysis cannot be generally applied to other biodiesel plants. Noordam and Withers (1996) reported that on average, a $0.01/kg increase in the canola seed cost would increase biodiesel price by $0.03/kg. A $0.11/kg increase in glycerine price would reduce the biodiesel price by $0.01/kg.

Regarding the above sensitivity studies, only a limited number of factors were examined. On the whole, sensitivity analyses of biodiesel processes have not been investigated widely. In particular, there is lack of a quantitative sensitivity analysis on the impact involving a wide range of factors, such as all the possible chemical prices and variables related to operating conditions. Consequently, in this work, sensitivity analyses of the alkali- and acid-catalyzed processes using waste cooking oil as the raw material were performed. The goal is to set up a model describing the relationship between the input variables (i.e., effects) and output variable (i.e., aftertax rate of return as an economic criterion). By evaluating the sizes of parameters in the model, plotting the residual distribution and testing the model adequacy, the physical significance of each effect and the sensitivity of aftertax rate of return to each factor can be identified.

3. Process descriptions

Four different continuous processes to produce biodiesel from virgin oil or waste cooking oil, previously designed and simulated using HYSYS™ (Zhang et al., 2002), were the focus of the economic evaluation in the present investigation. They are summarized in Table 4.1. A brief description of each process is provided below.

Table 4.1 Different processes to produce biodiesel

Process No.	Description	Raw material	Catalyst
Process I	Alkali-catalyzed process	Virgin vegetable oil	Sodium hydroxide
Process II	Alkali-catalyzed process	Waste cooking oil	Sodium hydroxide
Process III	Acid-catalyzed process	Waste cooking oil	Sulfuric acid
Process IV	Acid-catalyzed process using hexane extraction	Waste cooking oil	Sulfuric acid

Process I was an alkali-catalyzed process to produce biodiesel from virgin vegetable oil. Virgin oil, methanol and sodium hydroxide, were fed into transesterification reactor. After the reaction (at 60°C and 400 kPa), an effluent stream containing FAME, glycerol, methanol, unconverted oil and sodium hydroxide, entered a methanol distillation column where most of the methanol was recovered in a distillate stream. The distilled methanol, mixed with a fresh methanol stream, was recycled to the reactor. The methanol column bottom stream passed to a column for water washing to separate the FAME from glycerol, sodium hydroxide and methanol. The FAME, along with some water and methanol, was then forwarded to a distillation column to further remove methanol and water. From the bottom of that column, 99.6^{+} wt% (purity) FAME was obtained. The bottom stream from the water washing column, containing sodium hydroxide, glycerol, methanol and water, entered a neutralization reactor to remove sodium hydroxide by adding phosphoric acid. After the sodium hydroxide was removed, the stream went into a glycerine purification column where the bottom stream yielded an approximately 85 wt% or 92 wt% glycerine as a high quality by-product.

In process II, waste cooking oil was used as the feedstock oil to produce biodiesel in the presence of an alkali catalyst. Due to the sensitivity of the alkali-catalyzed reaction to free fatty acids found in waste oil, an esterification (i.e., pre-treatment) unit was required prior to the transesterification unit to reduce the content of free fatty acid. Unrefined waste cooking oil, methanol and sulfuric acid were fed into the esterification reactor to reduce the free fatty acid content to the required level (<0.5 wt%). The effluent stream from this reactor was sent to a liquid extraction column. By using pure glycerine (100%) as a solvent, the refined cooking oil was separated from the resulting water and sulfuric acid. Then, the refined cooking oil, together with the produced fatty acid esters, entered

the transesterification reactor. The bottom stream from the liquid extraction column contained methanol, glycerol, water and sulfuric acid, and proceeded to a distillation column for methanol recovery. The other parts of this process were the same as those in process I.

Process III was an acid-catalyzed process using waste cooking oil. Two transesterification reactors operated in series were required. Compared to process I, the removal of alkali catalyst was replaced by the removal of acid catalyst in process III, which followed methanol distillation to reduce the construction material costs in the downstream process units. The construction material for the transesterification and neutralization reactors and the methanol distillation column was made of stainless steel because of the presence of sulfuric acid. As for the other units, there was little difference between processes I and III.

In process IV, to avoid the formation of emulsions, hexane was used as an extraction solvent rather than water washing. This acid-catalyzed process produced biodiesel from waste cooking oil. After methanol distillation, an amount of hexane, equal in volume to the amount of methanol in the feed stream, and 10 vol.% of water (based on the methanol amount) were added to an extraction unit, where all the FAME was expected to be extracted by hexane from the glycerol, sulfuric acid and methanol. As a result of further methanol/water washing, no glycerol or sulfuric acid should remain in the FAME and hexane stream. Hexane was recovered by distillation. Other parts of the process were similar to the previous acid-catalyzed process III.

Zhang et al. (2002) concluded that the acid-catalyzed continuous process to produce biodiesel from waste cooking oil was a competitive alternative to the alkali-catalyzed process from a technological viewpoint. The logical next step includes economic studies and sensitivity analyses of these processes.

4. Economic assessment

4.1 Calculations

Before presenting the detailed economic evaluation, some assumptions are described below.

- Each process is based on an 8,000 tonnes/year biodiesel plant capacity. This is the same size as an existing plant in Europe (Connemann and Fischer, 1999) and is consistent with the plant size discussed previously (Zhang et al., 2002). In the following sensitivity analyses, two other levels of plant capacity, one at 4,000 and the other at 12,000 tonnes/year were considered.
- Operating hours for the biodiesel plant were assumed to be 8000 hours/year. The same value was used by Nelson and Schrock (1994).
- Both waste cooking oil and virgin oil, used as the feedstock for biodiesel production, are clean and free of water and any other solid impurities. The prices of the raw material oil include costs associated with impurity removal and transportation.
- In the simulation, the pump efficiency was assumed to be 70%. This was used to determine the pump shaft power. A 90% motor efficiency was used to calculate the electricity usage. Although a spare pump is usually required in a chemical plant design, no spare pumps were taken into account at this stage.
- Superheated low and medium pressure steam were used as the heating media. Cooling water was the cooling medium. Their specifications and prices are listed in Table 4.2.
- All costs shown are in US$. Equipment prices were updated from available mid-1996 values to 2000 values using the Chemical Engineering Plant Index, where I_{2000} = 394 and $I_{1996,MID}$ = 382 (Turton, 1998; Chemical Engineering, 2001).
- All chemical costs including raw materials, catalysts, solvent and products are shown in Table 4.2. These prices were referred in determining the values of some factors in the following economic calculation and sensitivity analyses.

The prices of methanol, glycerine and alkali catalyst in Table 4.2 are consistent with previous studies (Nelson et al., 1994).

The basic conditions and cases for the economic calculation of each process are summarized in Tables 4.3 and 4.4.

Table 4.2 Prices of chemicals and utilities

Chemical		Specification	Price (US$/tonne)[a]	Source
Chemicals	Biodiesel		400-600	National Biodiesel Board
	Calcium oxide		40	http://www.chemconnect.com
	Glycerine	96+%	2420	Chemical Market Reporter, July,2000
		Crude	730	http://pipeline.to/biodiesel
	Hexane	USD	410	http://www.chemconnect.com Nov., 2000
	Methanol	99.85%	180	http://www.methanex.com
			150-180	http://www.chemconnect.com
	Phosphoric acid	Tech.	340	http://www.chemconnect.com Nov., 2000
	Sodium hydroxide	N.F./F.C.	4000	http://www.chemconnect.com Nov., 2000
	Sulfuric acid	98%	60	http://www.chemconnect.com Nov. 2000
	Virgin canola oil		400-600	http://www.epa.gov July, 2001
	Waste cooking oil		100-300	http://www.state.ga.us http://www.outreach.missouri.edu
Utilities	Cooling water	400kPa, 6°C	$0.007/m^3	Turton (1998)[b]
	Electricity		$0.062/kwh	Turton (1998)[b]
	Low pressure steam (superheated)	450kPa, 210°C	6.8	Turton (1998)[b]
	Medium pressure steam (superheated)	1600kPa, 300°C	8	Turton (1998)[b]
Waste treatment	Liquid	Hazardous	150	Turton (1998)[b]
	Solid		37	Turton (1998)[b]

[a] Unless specified, all prices are in US$/tonne.

[b] Based on the price in mid-1996 provided by Turton (1998) and updated to the year 2000.

Table 4.3 Basic conditions for the economic assessment of each process

Control Variables	Values
Plant capacity	8,000 tonnes/year
Oil price	Waste cooking oil: $200/tonne
	Virgin canola oil: $500/tonne
Methanol price	$180/tonne
Glycerine price	85wt%: $750/tonne
	92wt%: $1200/tonne
Thermodynamic model	NRTL or UNIQUAC
Biodiesel price	$600/tonne
Catalyst price	Acid catalyst: $60/tonne
	Alkali catalyst: $4000/tonne
Methanol recovery in T-201	94%
FAME purity	99.65wt%
Hexane price[a]	$410/tonne
Methanol recovery in the pre-treatment unit	94%

[a] Only required for process IV.

Table 4.4 Case description for basic conditions

Case	Description
Case 1	NRTL, 85wt% glycerine
Case 2	UNIQUAC, 85wt% glycerine
Case 3	NRTL, 92wt% glycerine
Case 4	UNIQUAC, 92wt% glycerine

HYSYS™ simulations of each process design (Zhang et al., 2002) provided mass and energy balances and operating conditions of each piece of equipment. This information was the basis for determining the size of the process equipment in the flowsheet. Straightforward, quick and non-iterative calculations (Lin et al, 1973; Sinnott, 1999) were

applied to the equipment sizing, which were discussed previously (Zhang et al. 2002). Results are shown in Table 4.5.

Table 4.5 Main equipment sizes, equipment costs and fixed capital cost in case 1

Type	Description		Process I	Process II	Process III	Process IV
Reactors	Esterification	Size, (D x L, m)	0	0.8 x 2.4	0	0
		Cost, ($ x 10^{-3})		80		
	Transesterification	Size, (D x L, m)	1.8 x 5.4	1.8 x 5.4	2.1 x 6.3	2.1 x 6.3
		Cost, ($ x 10^{-3})	290	290	673[a]	673[a]
	Neutralization	Size, (D x L, m)	0.3 x 1	0.3 x 1	0.5 x 1.5	0.4 x 1.2
		Cost, ($ x 10^{-3})	21	21	38	29
Columns	Methanol distillation	Size, (D x H, m)	0.6 x 10	1 x 12	1.2 x 10	1.2 x 10
				0.6 x 10		
		Cost[b], ($ x 10^{-3})	132	357	358	358
				130		
	Washing column	Size, (D x H, m)	0.8 x 10	1 x 10	1 x 10	1 x 10
				1 x 10		0.8 x 10
		Cost, ($ x 10^{-3})	100	240	109	240
				109		102
	FAME distillation	Size, (D x H, m)	0.5 x 10	0.5 x 10	0.5 x 10	0.6 x 10
		Cost[b], ($ x 10^{-3})	97	98	97	117
	Glycerine distillation	Size, (D x H, m)	N/A	0.5 x 10	0.6 x 10	0.8 x 10
		Cost[b], ($ x 10^{-3})		106	119	151
Heat exchangers, cost ($ x 10^{-3})			4	23	9	13
Pumps, cost ($ x 10^{-3})			45	72	40	50
Others (separator, vacuum system), cost ($ x 10^{-3})			46	57	63	47
Total basic module cost ($ x 10^{-6}), C_{BM0}			0.64	1.23	1.10	1.27
Total bare module cost ($ x 10^{-6}), C_{BM}			0.74	1.58	1.51	1.78
Contingency fee ($ x 10^{-6}), $C_{CF}=0.18C_{BM}$			0.13	0.28	0.27	0.32
Total module cost ($ x 10^{-6}), $C_{TM}=C_{BM}+C_{CF}$			0.87	1.87	1.78	2.10
Auxiliary facility cost ($ x 10^{-6}), $C_{AC}=0.3C_{BM0}$			0.19	0.37	0.33	0.38
Fixed capital cost, C_{FC} ($ x 10^{-6}), $C_{FC}=C_{TM}+C_{AC}$			1.06	2.24	2.11	2.48
Working capital ($ x 10^{-6}), $C_{wc}=0.15C_{FC}$			0.16	0.33	0.32	0.37
Total capital investment ($ x 10^{-6}), $C_{TC}=C_{FC}+C_{WC}$			1.22	2.57	2.43	2.86

[a] Includes two reactors operated in series.

[b] Includes the overhead condenser, recycle pump and bottom reboiler.

In this study, economic assessment refers to the evaluation of fixed capital cost, total manufacturing cost and aftertax rate of return of a biodiesel plant. Fixed capital cost represents the cost of constructing a new plant (also called grass-root capital cost) or modifying an existing plant. The construction of a new biodiesel plant was assumed herein. Generally, fixed capital cost consists of three parts: total bare module capital cost, contingency and fees, and costs associated with auxiliary facilities. Total bare module capital cost is the sum of the cost of each piece of equipment in the process. Contingency and fees is defined as a fraction of the total bare module capital cost (e.g., 18% was used in this study), to cover unforeseen circumstances and contractor fees (Ulrich, 1984; Turton et al., 1998). Expenses of auxiliary facilities include the purchase of land, installation of electrical and water systems, construction of all internal roads, etc. They are usually represented by 30% of the total basic module cost (Ulrich, 1984; Turton et al., 1998). Total capital investment is calculated by adding the fixed capital cost to the working capital cost. The latter is usually a fraction of the fixed capital cost (e.g. 15% was used in this work) (Ulrich, 1984). Detailed calculation procedures for capital cost are listed in Figure A.2 in the Appendix. Calculation results of the fixed capital cost for each process are presented in Table 4.5.

According to the definition of capital cost estimation provided by Turton et al. (1998), the economic estimation in this article is classified as a "study estimate". It is based on the development of a process flowsheet diagram (PFD) and rough sizing of major process equipment. No further information, such as a layout plot, process instrument diagram (PID) or piping and instrumentation requirements, were considered. They stated that this "study estimate" method had a range of expected accuracy from +30% to –20%. Thus, results from such a preliminary evaluation may not accurately reflect the final profitability of a chemical plant but can be used as a tool for the comparison of several process alternatives (Turton et al., 1998).

Total manufacturing cost refers to the cost of the day-to-day operation of a chemical plant and is usually divided into three categories: direct manufacturing costs, indirect manufacturing costs (or fixed manufacturing cost) and general expenses (Ulrich, 1984; Turton et al., 1998). Direct manufacturing costs consist of raw material costs, catalyst and solvent costs, operating labor fees, supervisory and clerical labor fees, utilities (including

waste disposal), maintenance and repairs, operating supplies, laboratory charges, and expenses for patents and royalties. In brief, all charges related to materials and labor belong in this category. In this study, the direct manufacturing costs, raw material cost and utility cost were calculated based on the price of each chemical (see Table 4.2), and their flowrate and usage from the HYSYS™ simulation results (see Zhang et al., 2002). According to Turton et al. (1998), the operating labor fee was obtained from the information of operator requirements for various pieces of process equipment (see Table A.1 in the Appendix). It was assumed that an operator works on average 49 weeks per year and that there are three shifts a day for a continuously running plant. Operator salary was estimated at US$47,850/year (US$24/h). Other expenses, such as supervisory and clerical labor fees, maintenance and repair expenses, operating supplies charges, etc., were calculated individually and multiplied by related factors, as shown in Table 4.6. Indirect manufacturing costs include overhead, packaging, storage, local taxes, insurance and depreciation. All of the items in this category are independent of the production rate in a plant. The last category, general expenses, includes administrative costs, distribution and selling costs, and research and development charges. Similarly, items pertaining to indirect manufacturing costs and general expenses were also computed and multiplied by various constant factors, which are commonly applied to economic assessments and are shown in Table 4.6 (Ulrich, 1984; Turton et al., 1998). Glycerine cost was regarded as a by-product credit.

Aftertax rate of return is used as a general economic performance criterion for preliminary evaluation of a chemical plant and is defined as the percentage of net annual profit after taxes relative to the total capital investment in a plant (Ulrich, 1984). This percentage represents the corporate tax rate, which is usually kept at approximately 50%. Using the estimated total capital and manufacturing costs, the aftertax rate of return is determined using the following equations:

$$A_{NP} = P \times C - A_{TE};$$

$$A_{NNP} = A_{NP} \times (1 - t);$$

$$\mathrm{I} = \frac{(A_{NNP} + A_{BD})}{C_{TC}} \times 100, \text{ when } A_{NNP} \text{ is positive;}$$

Table 4.6 Total manufacturing cost and aftertax rate of return in case 1 ($ x 10^{-6})

			Process I	Process II	Process III	Process IV
Direct manufacturing cost	Oil feedstock		4	1.76	1.6	1.68
	Methanol		0.17	0.2	0.31	0.32
	Catalyst and solvent		0.32	1.41	0.07	0.07
	Operating labor		0.58	1.03	0.82	0.9
	Supervisory and clerical labor, 15% of operating labor		0.09	0.15	0.12	0.13
	Utilities	LP steam	0.02	0.07	0.16	0.17
		MP steam	0.01	0.02	0.01	0.02
		Electricity	0.02	0.02	0.02	0.03
		Cooling water	0.01	0.01	0.02	0.03
	Waste disposal	Liquid	0.004	0.23	0.15	0.14
		Solid	0.004	0.01	0.02	0.02
	Maintenance and repairs, 6% of C_{FC}		0.06	0.13	0.13	0.15
	Operating supplies, 15% of maintenance and repairs		0.01	0.02	0.02	0.02
	Laboratory charges, 15% of operating labors		0.09	0.15	0.12	0.14
	Patents and royalties, 3% of total manufacturing cost		0.20	0.21	0.15	0.15
	Subtotal, A_{DME}		4.86	4.68	2.98	3.20
Indirect manufacturing cost	Overhead, packaging and storage, 60% of the sum of operating labor, supervision and maintenance		0.43	0.79	0.65	0.71
	Local taxes, 1.5% of C_{FC}		0.02	0.03	0.03	0.04
	Insurance, 0.5% of C_{FC}		0.005	0.01	0.01	0.01
	Subtotal, A_{IME}		0.46	0.83	0.69	0.76
	Depreciation, A_{BD}, 10% of C_{FC}		0.11	0.22	0.21	0.25
General expenses	Administrative costs, 25% of overhead		0.11	0.19	0.16	0.18
	Distribution and selling cost, 10% of total manufacturing cost		0.65	0.70	0.47	0.51
	Research and development, 5% of total manufacturing cost		0.33	0.35	0.24	0.26
	Subtotal		1.09	1.24	0.87	0.95
	Total production cost		7.25	7.72	5.49	5.93
	Glycerine credit		0.73	0.74	0.74	0.77
	Total manufacturing cost, A_{TE}		6.52	6.98	4.75	5.16
	Revenue from biodiesel		4.8	5.24	4.8	5.05
	Net annual profit, A_{NP}		-1.72	-1.74	0.05	-0.11
	Income taxes, A_{IT}		-0.86	-0.87	0.025	-0.05
	Net annual profit after taxes, A_{NNP}		-0.86	-0.87	0.025	-0.05
	Aftertax rate of return, I = $[A_{NNP}+A_{BD}]/ C_{TC}$, (%)		-78.97	-42.55	9.74	-10.52

$$I = \frac{(A_{NNP} - A_{BD})}{C_{TC}} \times 100, \text{ when } A_{NNP} \text{ is negative.} \qquad (4.1)$$

where P = biodiesel sale price, $/tonne,

C = biodiesel plant capacity, tonnes/year,

A_{TE} = total manufacturing costs, $,

A_{NP} = net annual profit, $,

t = corporate tax rate, 50% was used in this study,

A_{NNP} = net annual profit after taxes, $,

A_{BD} = depreciation, $,

C_{TC} = total capital investment, $,

I = aftertax rate of return, %

Aftertax rate of return was chosen as the response variable and objective function in the economic assessment and sensitivity analyses.

4.2 Results and discussion

Based on the above procedures, the values of fixed capital cost, total manufacturing cost and aftertax rate of return for each case in each process are given in Figures 4.1 through 4.3. These results show that on the basis of fixed capital cost, total manufacturing cost or aftertax rate of return, the differences between each case (see Table 4.4) appear to be insignificant. Thus, in the following description, only detailed results for case 1 in each process are reported. A summary of economic performance of each process in case 1 is shown in Figure 4.4 and Tables 4.5 through 4.7.

Fixed capital cost

Table 4.5 illustrates that the cost of the transesterification reactor(s) forms a significant part of the capital cost, especially for acid-catalyzed processes III and IV (i.e., above $0.65 million). The costs associated with the transesterification unit amount to 40-50% of the total bare module cost in the acid-catalyzed processes (see Table 4.7). Due to the slower reaction rate of the acid-catalyzed process, more of methanol is required than

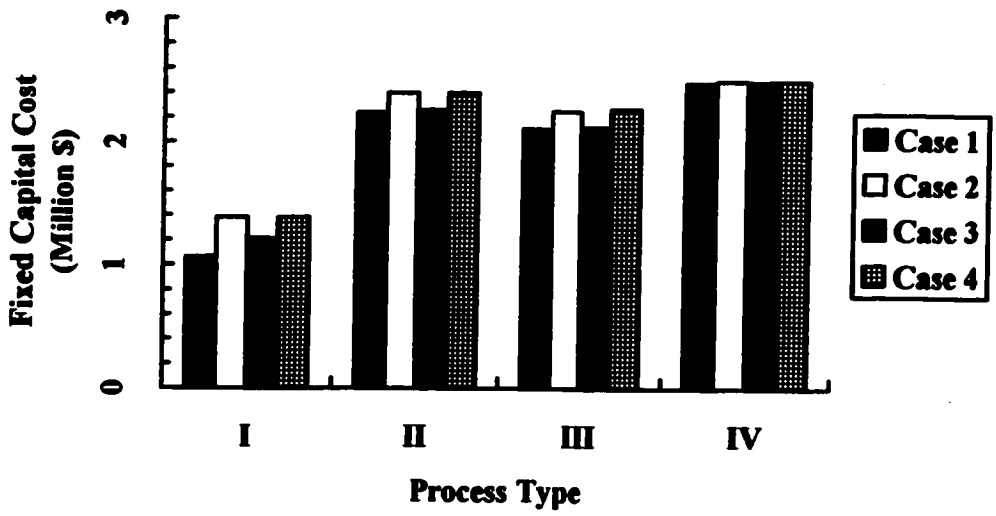


Figure 4.1 A comparison of fixed capital cost for each process

See Table 4.1 for the definition of each process

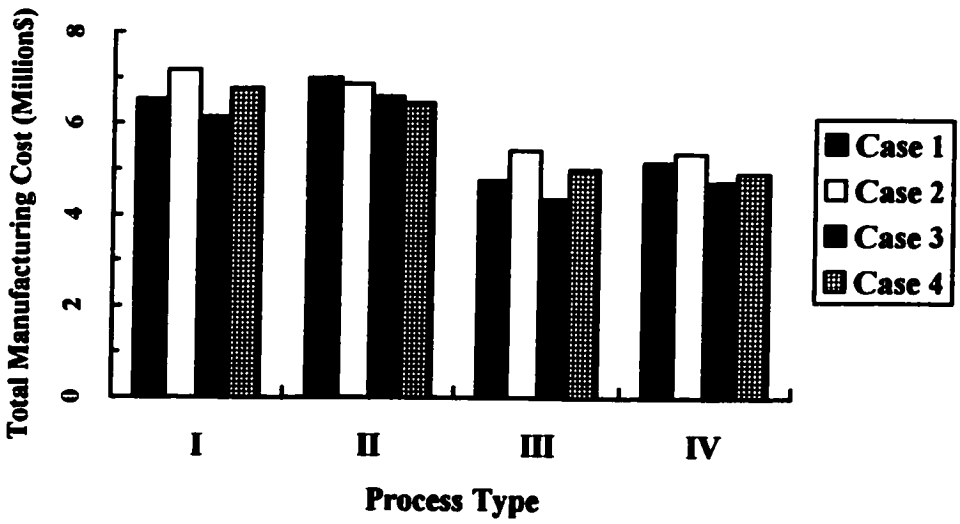


Figure 4.2 A comparison of total manufacturing cost for each process

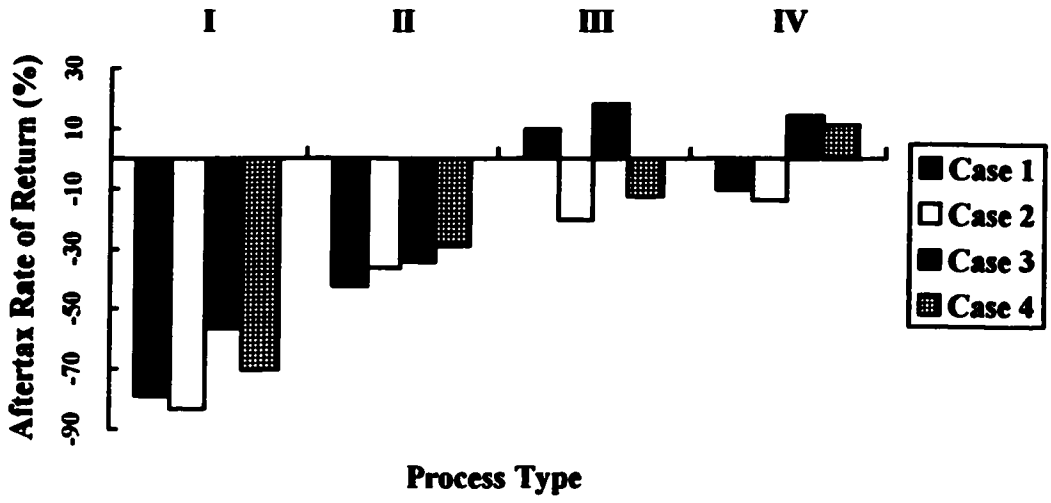


Figure 4.3 A comparison of aftertax rate of return for each process

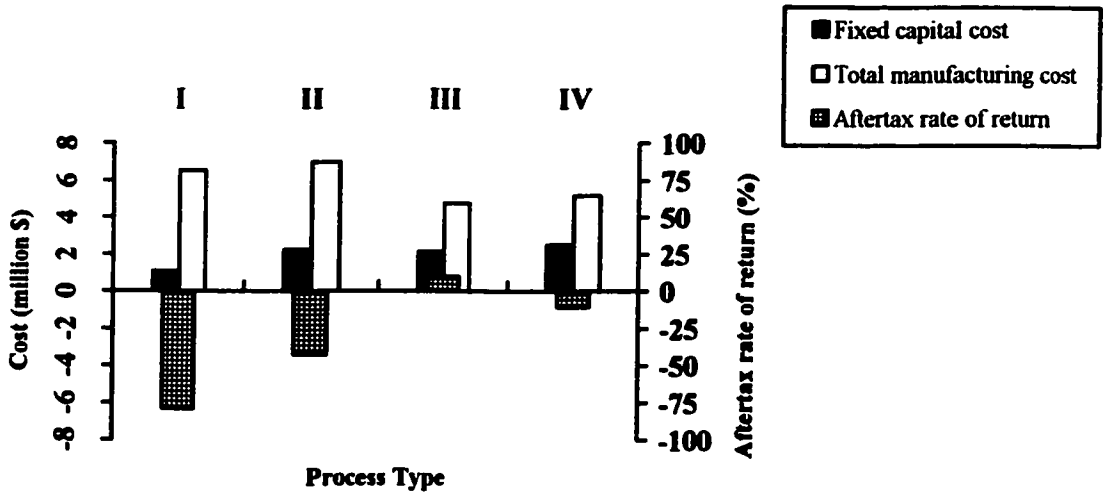


Figure 4.4 Economic performance of different processes in case 1

Table 4.7 Main economic criteria for different processes in case 1

			Process I	Process II	Process III	Process IV
Fixed capital cost	Pre-treatment unit	Cost ($ x 10^{-6})	0	0.76	0	0
		Percentage (%)	0	48	0	0
	Transesterification unit	Cost ($ x 10^{-6})	0.33	0.29	0.72	0.72
		Percentage (%)	46	18	48	40
	Separation unit	Cost ($ x 10^{-6})	0.41	0.53	0.79	1.06
		Percentage (%)	55	34	52	60
	Total bare module cost	Cost (x 10^{-6})	0.74	1.58	1.51	1.78
		Percentage (%)	100	100	100	100
Total manufacturing cost	Direct manufacturing	Cost ($ x 10^{-6})	4.87	4.68	2.98	3.20
		Percentage (%)	75	67	63	62
	Indirect manufacturing	Cost ($ x 10^{-6})	0.46	0.83	0.69	0.76
		Percentage (%)	7	12	15	15
	General expenses	Cost ($ x 10^{-6})	1.09	1.24	0.87	0.95
		Percentage (%)	17	18	18	18
	Depreciation	Cost ($ x 10^{-6})	0.11	0.22	0.21	0.25
		Percentage	1	3	4	5
	Subtotal	Cost ($ x 10^{-6})	6.52	6.98	4.75	5.16
		Percentage	100	100	100	100
Profitability	Net annual profit after taxes ($ x 10^{-6})		-1.72	-1.74	0.05	-0.10
	Aftertax rate of return (%)		-78.97	-42.55	9.74	-10.52
	Break-even price of biodiesel ($/tonne)		814	800	593	612

in the alkali-catalyzed one, which leads to an increased reaction volume. As well, the presence of sulfuric acid requires the construction material of the reactor to be stainless steel. Consequently, the reactor sizes and costs in processes III and IV are much higher than those in processes I and II.

The costs related to the separation units in process IV are much higher than in the other processes (see Table 4.7). This is because the addition of hexane and methanol/water increase the loads in the washing columns, FAME distillation and glycerine purification columns in process IV, which in turn requires larger sizes and higher costs of these units. The cost of the separation units in process III is also high because the presence of sulfuric acid in some units requires stainless steel construction (e.g., the methanol distillation column). In process II, the pre-treatment unit costs more than other units, indicating a large detrimental impact on the fixed capital cost of process II.

Overall, process I, the alkali-catalyzed process using virgin oil as the raw material, has the lowest fixed capital cost. The fast transesterification reaction reduces the size and cost of the reactor. The use of virgin oil with low-levels of free fatty acids removes the need for a pre-treatment unit. The use of less corrosive sodium hydroxide reduces the requirement of stainless steel construction material in some pieces of process equipment. As a result, the fixed capital cost and the total capital investment in process I are much lower than those in the other processes, as shown in Figures 4.1 and 4.4.

As discussed earlier, previous economic studies of biodiesel plants lack descriptions of process equipment sizing. Thus, a detailed comparison of our results with that of others cannot be carried out. According to the results provided by Noordam and Withers (1996), their equipment cost for the transesterification unit with a size of 7,800 tonnes/year biodiesel was estimated to be $0.7 million. If this value is updated to the cost at the year 2000, it is approximated at $0.72 million. The bare module cost in process I with a size of 8,000 tonees/year biodiesel is $0.74 million, which is similar to their value. Compared to $3.12 million capital cost of a 10,000 tonnes/year biodiesel production process from animal fats given by Bender (1999), alkali-catalyzed process II of 8,000

tonnes/year biodiesel from waste cooking oil, has a total capital investment of $2.57 million. Regardless of the difference in the plant capacities, our results appear reasonable.

Total manufacturing cost

Results for the total manufacturing costs are shown in Figure 4.2 and Tables 4.6 and 4.7. It is shown that the direct manufacturing cost amounts to approximately 63-75% of the total manufacturing cost in each process. Therefore, direct manufacturing cost should be the focus of efforts to optimize the total manufacturing cost. Comparison of the direct manufacturing costs for each process shows that processes I and II have higher values than the other two. Accordingly, the total manufacturing costs in alkali-catalyzed processes I and II are higher than those in acid-catalyzed processes III and IV. This is shown in Figure 4.2. For each direct manufacturing cost (see Table 4.6), the cost of feedstock oil comprises up to 50% of the total for acid-catalyzed processes (III and IV). Using virgin oil as the raw material in process I results in approximately 80% of the direct manufacturing cost related to the raw material cost. In process II, despite the fact that the addition of a pre-treatment unit which has increased direct manufacturing costs associated with solvent and operating labor, the raw material cost is approximately 38%. This is still the biggest component of the total direct manufacturing cost. Consequently, raw material costs appear to play the most important role in direct manufacturing costs, which in turn substantially affect the total manufacturing cost.

A comparison of processes I and II shows that they have similar total manufacturing costs. Although process I has the lowest values for equipment costs ($0.87 million) and total capital investment ($1.22 million), the use of virgin vegetable oil greatly increases the raw material cost ($4 million). In contrast, in alkali-catalyzed process II, using waste cooking oil, the raw material cost can be reduced to $1.76 million. However, due to the sensitivity of the alkali-catalyzed process to free fatty acids, a pre-treatment unit has to be added in process II. This pre-treatment unit accounts for approximately 48% of the total bare module cost (see Table 4.7). Moreover, the increased solvent cost in this unit negates the glycerine credit as a by-product (see Table 4.6).

The credit for the glycerine by-product has a significant impact on the net value of the total manufacturing cost. As shown in Table 4.6, the glycerine credit is above $0.7

million at a rate of $0.75/kg for 85 wt% purity in each process. Noordam and Withers (1996) considered $0.9 million as a glycerine credit ($1450/tonne for 96 wt% glycerine). Bender (1999) reported $0.72 million credit for crude glycerine at a price of $660/tonne. Thus, our results are similar to that of both authors. If the glycerine credit is not considered, a rough calculation can be performed as follows: For example, in process II, the fixed capital cost will be reduced by $0.1 million because of the absence of a glycerine purification column and its auxiliary equipment (see Table 4.5). Other costs related to the fixed capital cost, such as maintenance and repairs, local taxes, insurance and depreciation will be reduced by approximately $0.02 million. Therefore, the total production cost will be at least $7.6 million. This will be the same as the total manufacturing cost due to the absence of the glycerine credit. This value is still far higher than the present value of $6.98 million. Moreover, the possible increase in waste disposal fees has not yet been taken into account. In other words, the glycerine credit can lead to a reduction in total production costs by 8% in process II. Using a similar calculation, a reduction of approximately 12% in the total production cost will be achieved in process III.

Noordam and Withers (1996) concluded that the total manufacturing cost for their plant using canola seed was $6.1 million updated to the year 2000. If this value is assumed to cover the same range as the total manufacturing cost in the present study, the total manufacturing cost of process I (i.e., $6.5 million) is similar to their results. This indicates that the use of oilseed as the raw material can lower the raw material cost but will not have much influence on the total manufacturing cost of the plant. Subtracting the canola meal credit, the net cost associated with seed procurement and oil extraction would be $4.61 million in their study. This completely offsets the raw material cost of virgin oil in process I ($4 million). On the other hand, their total manufacturing cost is far higher than the ones in acid-catalyzed processes III and IV of this study.

Aftertax rate of return

From Figure 4.3 and Tables 4.6 and 4.7, process III is shown to have a positive value of net annual profit after taxes, with an aftertax rate of return of approximately 10%. However, for alkali-catalyzed processes I and II and acid-catalyzed process IV, negative

values of net annual profit and aftertax rate of return are observed. As discussed earlier, the absolute values of these numbers are likely to be inaccurate due to uncertainties from the HYSYS™ simulation and the preliminary nature of the economic estimation methods used in this study. However, the relative values or the differences among these results are of important. It is indicated that the acid-catalyzed process to produce biodiesel from waste cooking oil (i.e., process III) is more economical than the other processes.

The break-even prices of biodiesel from all processes are listed in Table 4.7 and range from $593 to $814/tonne. The acid-catalyzed processes III and IV have lower break-even prices than processes I and II. For a similar sized biodiesel plant, Noordam and Withers (1996) estimated the break-even price for biodiesel from canola oilseed at $763/tonne, in good agreement with the range in our results.

5. Sensitivity analysis

After completion of the above economic assessment of the biodiesel production processes, a sensitivity analyses for these processes were conducted to determine the sensitivity of the aftertax rate of return to the different effects (i.e., factors).

The computer modelling results from HYSYS™ can be considered as experiments executed on computer. They are evidently different from traditional physical experiments but have been widely used in recent years. Usually, computer experiments provide an effective alternative to time-consuming or expensive physical experiments. For reaction conditions too difficult or costly to implement in practice, the computer experiment is a powerful tool for predicting system behavior.

Compared to physical experiments, there are two distinct features for computer experiments. First, in physical experiments, replicate data provide important information about the expected values and variances of the process outputs. However, in computer experiments, the output(s) of computer simulations will be deterministic and not subject to random errors. This means that the same result will be obtained each time the computer code is run with the same input values. Therefore, replicate data provide no new information about the system. This implies that the common quantitative lack of fit test cannot be applied to the model obtained from a computer experiment. The other feature involves the manner in which experiments are carried out. In physical

experiments, care has to be taken to use randomization and blocking, so as to spread or minimize the effects of extraneous sources of variability and to obtain unbiased and precise results. However, computer experiments are rarely affected by extraneous factors, such as day-to-day, or computer-to-computer variations. Once the computer code is created and validated, the experimental results are always independent of other disturbances. Sacks et al. (1989) presented a detailed discussion on computer experiments. These two main features of computer experiments determine some special circumstances in the sensitivity analyses. The traditional statistical methods to analyze the effect of each control variable (factor) cannot be applied. Instead, the practical (or physical) significance of each factor can be analyzed with the aid of some "statistical ideas". Herein, Process III, the acid-catalyzed process to produce biodiesel from waste cooking oil, was chosen as an example for demonstrating the detailed procedures. The same procedures were applied to the sensitivity analyses of the other processes.

5.1 Factor description

Aftertax rate of return for the biodiesel plant was used as the performance criterion. It is related to many intermediate outputs, such as the total grass-root capital investment, total manufacturing cost and so forth. Although the quantities of these intermediate outputs were also available in this work, the aftertax rate of return provided the primary basis for the conclusions.

Aside from the chemical prices directly related to the economic calculations, other factors were determined based on the process design and assumptions made in the simulation. For example, NRTL and UNIQUAC were assumed to be the appropriate thermodynamic/activity models for this system. The sizes of their influence on the simulation results, as well as on the aftertax rate of return have to be identified in order to validate this assumption. According to the sequence of process steps in the flowsheet, some design variables were considered, such as the recovery rate of methanol, the purity of FAME product and the purity of glycerine by-product. Overall, in process III, eleven control variables (i.e. control factors) were found to affect the response variable (i.e., aftertax rate of return). They were: plant capacity, the price of waste cooking oil, the price of methanol, the price of glycerine, the thermodynamic/activity model, the price of

biodiesel, the price of sulfuric acid, the methanol recovery in the methanol distillation column, the biodiesel product purity, the oil conversion in the transesterification reactor, and the final by-product glycerine purity.

Among these 11 factors, there are some limitations in setting up the levels of oil conversion and glycerine price. According to ASTM specifications (see Table 4.8), a qualified biodiesel product has at least 99.6 wt% purity. Meanwhile, to achieve a good glycerine credit requires its specification to reach a level of at least 85^{+} wt%. To meet both of these requirements, an overall mass balance calculation was executed and it was found that oil conversion to FAME in the transesterification is required to be 99^{+}%. In addition, the glycerine price greatly depends on the glycerine purity. Hence, at this stage, we arbitrarily set a 99^{+}% oil conversion to FAME for all experimental runs and the purity of glycerine was treated as a block factor. One block (block I) used an 85 wt% glycerine purity, while the other (block II) used a 92 wt% glycerine purity. Each block had different price levels corresponding to the glycerine purity. Therefore, the number of control factors was reduced from 11 to 9, excluding the oil conversion and glycerine purity factors.

Table 4.8 ASTM specification of biodiesel (National biodiesel board, 1999)

Property	ASTM Method	Limits	Units
Flash Point	D93	100.0 (min.)	°C
Water & Sediment	D1796	0.050 (max.)	% vol.
Kinematic Viscosity, 40°C	D445	1.9-6.0	$mm^2/sec.$
Sulfated Ash	D874	0.020 (max.)	% mass
Sulfur	D2622	0.05 (max.)	% mass
Copper Strip Corrosion	D130	No.3 (max.)	
Cetane Number	D613	40 (min.)	
Cloud Point	D2500	By Customer	°C
Carbon Residue, 100% sample	D4530	0.050 (max.)	% mass
Acid Number	D664	0.80 (max.)	mg KOH/gm
Free Glycerin	GC	0.020 (max.)	% mass
Total Glycerin	GC	0.240 (max.)	% mass

5.2 Experimental design

A two-level fractional factorial design is a common screening tool to filter out insignificant variables without losing much important information. In this study, a two-level fractional factorial design with resolution IV was applied. In a resolution IV design, each main effect is at least confounded with one three-factor interaction. Generally, interactions involving more than two factors are of insignificant size and of little interest. As a result, main effects can be identified unambiguously in resolution IV experimental designs. On the other hand, any interactions involving two factors in a resolution IV design are at least confounded with one other two-factor interaction. One special feature in this research is that several factors are chemical prices. In some cases, interactions between two chemical prices or interactions between one chemical price and another unrelated chemical property should be very small or zero (e.g., the interaction between the biodiesel price and sulfuric acid price, the interaction between the methanol price and biodiesel purity). This means that if some effects of such interactions are confounded with another two-factor interaction, the latter one can be easily clarified. This will be further explained in the following example. The description of all factors is listed in Table 4.9.

The setting of the levels of chemical prices was based on some assumptions. Initially, the use of historical pricing values was attempted. However, some prices cover a very large range. For example, according to the Chemical Market Reporter 1997-2001 series, the methanol price fluctuated from approximately $88/tonne to $255/tonne and the 99.7 wt% glycerine price covered a range of approximately $1100-2600/tonne in the past five years. If different price ranges were used, this would create some ambiguities in analyzing the practical significance of these factors. In other words, it would be difficult to clearly determine whether the significance of each chemical price factor is due to the price itself or to its wide price range. To avoid such ambiguities, the price of each chemical was arbitrarily set at the same price range (i.e., $200/tonne) for the sensitivity analyses. Thus, the final results would reflect the practical effect of each factor itself. On the other hand, regardless of the small fluctuation or less than $200/tonne in some

Table 4.9 Descriptions of Control Variables in Process III - Sensitivity Analysis

Control variables	Description	Level	
		-1	1
X_1	Plant capacity	4,000 tonnes/year	12,000 tonnes/year
X_2	Price of waste cooking oil	$100/tonne	$300/tonne
X_3	Methanol price	$80/tonne	$280/tonne
X_4	Glycerine price (85wt%, block I)	$650/tonne	$850/tonne
	Glycerine price (92wt%, block II)	$1100/tonne	$1300/tonne
X_5	Thermodynamic model	NRTL	UNIQUAC
X_6	Biodiesel price	$400/tonne	$600/tonne
X_7	Price of sulfuric acid	$50/tonne	$250/tonne
X_8	Methanol recovery in T-201	90%	98%
X_9	Final FAME (biodiesel) purity	99.6wt%	99.7wt%

chemical prices, the sensitivity of the biodiesel break-even price to the historical impact of the widely changing price of glycerine was also studied, as presented later.

A 2_{IV}^{9-4} fractional factorial experimental design, involving 32 runs for each set of experiments, was used. The four basic generators were $X_2X_3X_4X_5X_6$, $X_1X_3X_4X_5X_7$, $X_1X_2X_4X_5X_8$ and $X_1X_2X_3X_5X_9$. The defining relation and model form used to describe the results follow:

Defining relation:

$$\begin{aligned} I &= X_2X_3X_4X_5X_6 = X_1X_3X_4X_5X_7 = X_1X_2X_4X_5X_8 = X_1X_2X_3X_5X_9 \\ &= X_1X_2X_6X_7 = X_1X_3X_6X_8 = X_1X_4X_6X_9 = X_2X_3X_7X_8 = X_2X_4X_7X_9 = X_3X_4X_8X_9 \\ &= X_4X_5X_6X_7X_8 = X_3X_5X_6X_7X_9 = X_2X_5X_6X_8X_9 = X_1X_5X_7X_8X_9 \\ &= X_1X_2X_3X_4X_6X_7X_8X_9 \end{aligned} \quad (4.2)$$

Model form:

$$E(Y)=L_0+L_1(X_1+...)+L_2(X_2+...)+L_3(X_3+...)+...+L_9(X_9+...)+$$
$$L_{10}(X_1X_2+X_6X_7+...)+L_{11}(X_1X_3+X_6X_8+...)+L_{12}(X_1X_4+X_6X_9+...) \quad (4.3)$$
$$+...+L_{29}(X_5X_8+...)+L_{30}(X_5X_9+...)+L_{31}(X_1X_5X_6+...)$$

where X 's = the coded variables represented by −1 and 1, in which

$X_6=X_2X_3X_4X_5$, $X_7=X_1X_3X_4X_5$, $X_8=X_1X_2X_4X_5$, $X_9=X_1X_2X_3X_5$,

E(Y) = predicted aftertax rate of return,

L 's = the parameter estimates.

The relationship of L's with β's is expressed in Table 4.10: For example, L_1 is an estimate of $(\beta_1+\beta_{267}+\beta_{368}+...)$. β_{267} represents the parameter for the three-factor interaction $X_2X_6X_7$, an alias of X_1. However, as mentioned previously, interactions greater than two-factor are considered to be negligible. Therefore, they are not considered and are not shown in Table 4.10. Thus, L_1 is only regarded as the estimate of β_1.

5.3 Parameter estimates

Once the experimental design was set up, all simulations were performed using HYSYS™. After the response values for different run conditions were obtained (see Table A.2 in the Appendix), the parameter estimates in the polynomial model (Equation 4.3) were derived by the least squares method. Their values are shown in Table 4.10. Due to the fact that these were computer experiments, the interpretation of these estimates was based on their relative magnitudes. Compared to the estimates of L's related to two-factor interactions, the sizes of the estimates of the main effects were relatively large. In particular, L_1, L_2 and L_6 were much larger than other estimates. As explained earlier, L_1, L_2 and L_6 are estimates of β_1, β_2 and β_6, respectively. The sizes of L_1, L_2 and L_6 represent the impacts of factors X_1, X_2 and X_6 on the aftertax rate of return.

With regard to the two-factor interactions, most were small in magnitude. Among them, interactions involving X_1, X_2 or X_6 have relatively larger magnitudes. This is probably due to the influence of X_1, X_2 or X_6 on the response variable. For example, L_{12} is an estimate of $(\beta_{12}+\beta_{67})$. β_{12} is the coefficient for the effect from X_1X_2, the interaction

Table 4.10 Parameter estimates from the 2_{IV}^{9-4} design for process III – sensitivity analysis

Estimates		Values	
		Block I (85wt% glycerine)	Block II (92wt% glycerine)
L_0	β_0	-0.1498	-0.0748
L_1	β_1	0.1976	0.2167
L_2	β_2	-0.1754	-0.1721
L_3	β_3	-0.0373	-0.0361
L_4	β_4	0.0226	0.0210
L_5	β_5	-0.0539	-0.0590
L_6	β_6	0.1479	0.1450
L_7	β_7	-0.008	-0.0076
L_8	β_8	0.0422	0.0409
L_9	β_9	-0.0035	-0.0045
L_{10}	$\beta_{12}+\beta_{67}$	-0.0561	-0.0557
L_{11}	$\beta_{13}+\beta_{68}$	-0.0121	-0.0094
L_{12}	$\beta_{14}+\beta_{69}$	0.0084	0.0109
L_{13}	β_{15}	-0.0266	-0.0243
L_{14}	$\beta_{16}+\beta_{27}+\beta_{38}+\beta_{49}$	0.0583	0.0569
L_{15}	$\beta_{17}+\beta_{26}$	-0.0029	-0.0031
L_{16}	$\beta_{18}+\beta_{36}$	0.0128	0.0168
L_{17}	$\beta_{19}+\beta_{46}$	-0.0026	-0.0032
L_{18}	$\beta_{23}+\beta_{78}$	-0.0022	-0.0032
L_{19}	$\beta_{24}+\beta_{79}$	-0.0037	-0.0091
L_{20}	β_{25}	0.0116	0.0084
L_{21}	$\beta_{28}+\beta_{37}$	-0.0002	-0.0031
L_{22}	$\beta_{29}+\beta_{47}$	0.0003	-0.0023
L_{23}	$\beta_{34}+\beta_{89}$	0.0002	-0.0001
L_{24}	β_{35}	0.0019	0.0008
L_{25}	$\beta_{39}+\beta_{48}$	0.0054	0.0051
L_{26}	β_{45}	-0.0013	-0.0012
L_{27}	β_{56}	-0.0093	-0.0063
L_{28}	β_{57}	0.001	0.0007
L_{29}	β_{58}	0.0029	0.0017
L_{30}	β_{59}	-0.0034	-0.0039
L_{31}	β_{156}	-0.0046	-0.0031

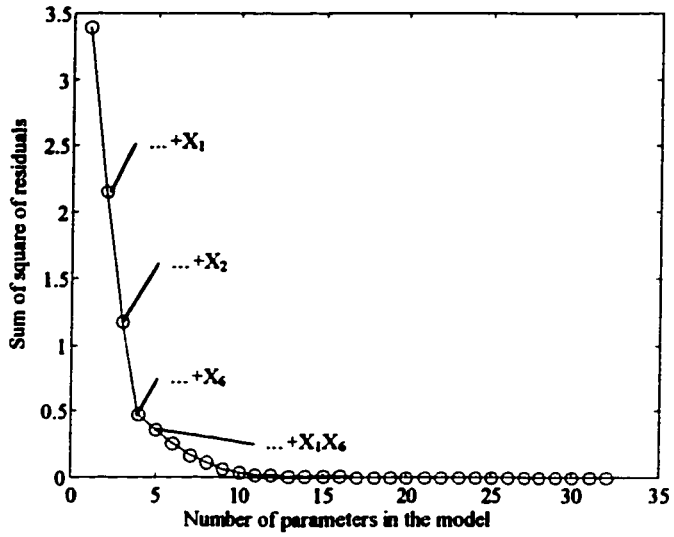
of plant capacity and oil price. β_{67} is the parameter estimate for X_6X_7, the interaction of the price of biodiesel and sulfuric acid. It is often the case that interactions between the prices of biodiesel and sulfuric acid are regarded as zero, as mentioned previously. Hence, the effect from X_6X_7 should be very slight. It is reasonable to conclude that the value of L_{12} mainly represents a contribution from β_{12}. Similarly for L_{16}, it theoretically reflects the combination of effects from β_{16}, β_{27}, β_{38} and β_{49}. β_{27} is a parameter estimate for the effect of X_2X_7, the interaction of oil price and sulfuric acid price. β_{38} represents the effect of X_3X_8, the interaction of methanol price and the methanol recovery rate in the methanol distillation column. β_{49} is an estimate for the effect of X_4X_9, the interaction of glycerine price and purity of the FAME product. All of these sizes are believed to be near zero. Therefore, the value of L_{16} is mainly related to β_{16}. In addition, the three-factor interaction L_{156} is relatively small in size (i.e., -0.0046). Although X_1 and X_6 are relatively large in magnitude, the three-factor interaction of $X_1X_5X_6$ is small and can be ignored. Thus, the previous assumption that interactions involving more than two factors can be neglected appears to be feasible.

5.4 Analysis results

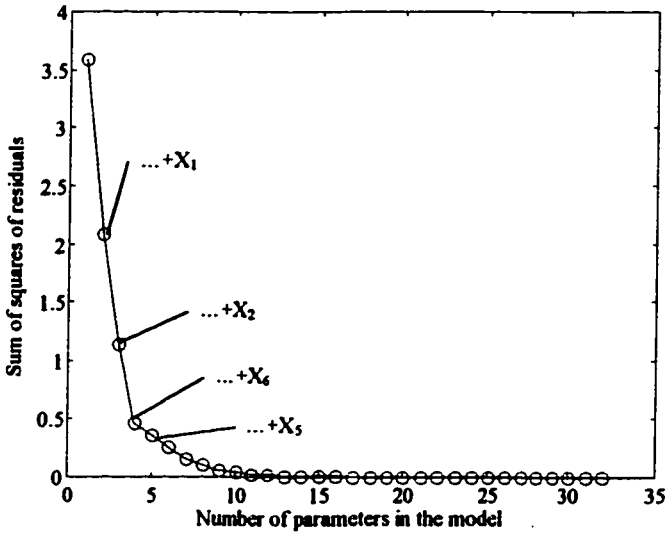
As discussed previously, because there are no random errors associated with parameter estimates obtained from computer experiments, we cannot analyze the statistical significance of each factor. However, the practical significance of each factor can be investigated as follows.

In block I with 85 wt% glycerine, for model $E(Y) = L_0 = -0.1498$, which assumes that none of the factors have an effect on the response variable, the sum of squares of residuals was evaluated and found to be SSR=3.4024. Next, all thirty-one parameter estimates (without L_0) were rearranged in descending order according to their absolute values. The largest estimate was $L_1 = 0.1976$. Then, a second model was generated by adding the L_1X_1 term. The model form was changed to $E(Y) = L_0 + L_1X_1 = -0.1498 + 0.1976X_1$. The sum of squares of residuals for this model was calculated and found to be SSR=2.1525. Each term in order of decreasing magnitude was added and treated in the same manner sequentially. Finally, 32 values of the sums of

squares of residuals corresponding to 32 different models were calculated and plotted in Figure 4.5a.



(a) Block I



(b) Block II

Figures 4.5a and b Description of the sums of squares of residuals for process III

In Figure 4.5a, the change in the sums of squares of residuals with the addition of factors in the model is shown. It shows that the sum of squares of residuals initially decreases sharply as the number of terms in the model is increased. For block I, when factor X_1 was added to the center point, the value of the sum of squares of residuals decreased from 3.4 to 2.2. When X_2 was added, SSR was reduced from 2.2 to 1.2. Then, X_6 was added, SSR decreased to 0.5. After X_6, the magnitude of the decrease was lower. When the number of parameters in the model was more than ten, the sum of squares of residuals reached a very small value and changed little as more were added. A similar analysis was performed for block II with 92wt% (purity) glycerine and the results are shown in Figure 4.5b. Detailed results of the SSR calculation are presented in Table A.3 in the Appendix.

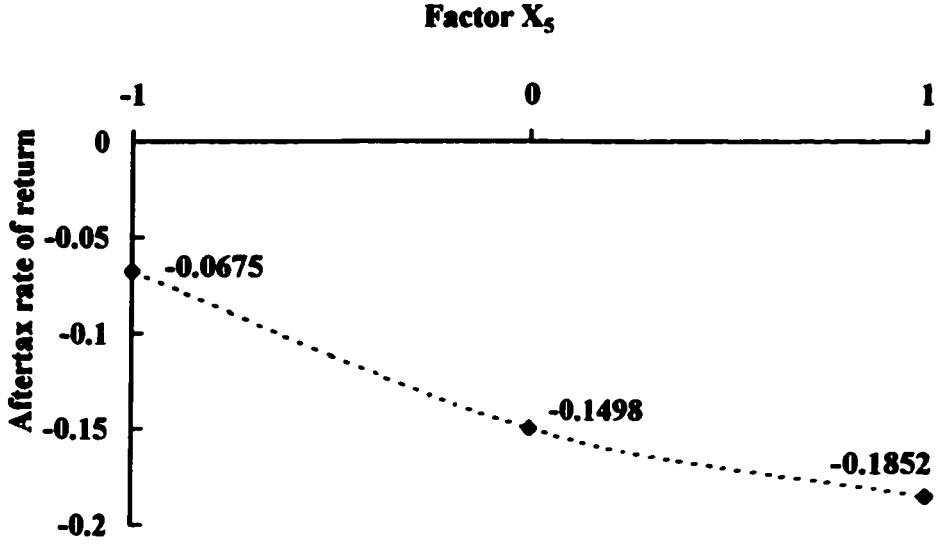
5.5 Model adequacy

Before the practical significance of each factor is determined, the model adequacy has to be checked. First, a test of model curvature was performed. All factors in Table 4.9 were set at the center point of its two levels. Under the conditions of the center point, a process simulation and economic calculation were carried out. The value of aftertax rate of return was determined. Since factor X_5 is not a quantitative variable, four values of the response variable were obtained, corresponding to block I or II and using NRTL or UNIQUAC. By plotting these values of aftertax rate of return along with the predicted value at $E(Y) = L_0 = -0.1498$ or -0.0748, no strong evidence of model curvature was found (see Figures 4.6a and b).

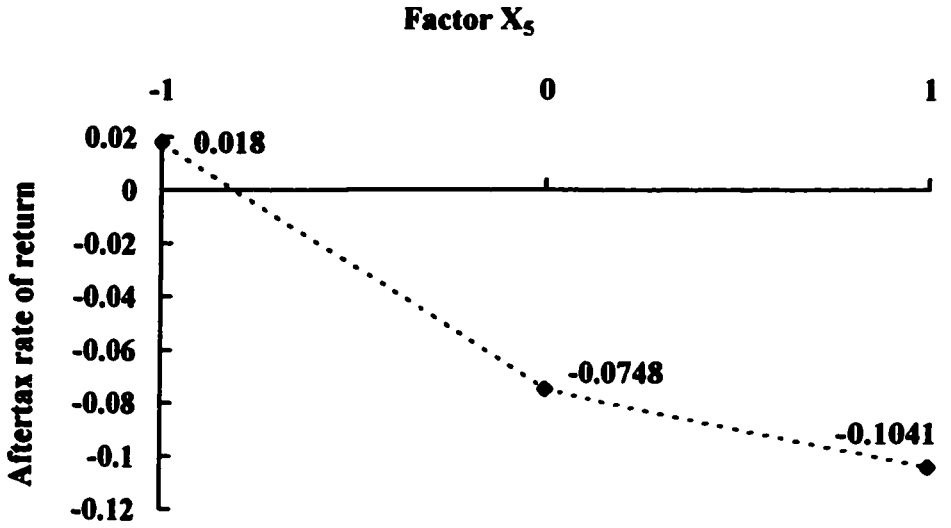
The residual plot is a general measure for testing model lack of fit. For block I (85 wt% purity of glycerine), the following four models were selected and their residual plots shown in Figures 4.7a through d. Residual plots for block II are shown in Figures A.3a through d in the Appendix.

$$\begin{aligned} E(Y) &= L_0 + L_1X_1 + L_2X_2 \\ &= -0.1498 + 0.1976X_1 - 0.1754X_2 \end{aligned} \tag{4.4}$$

$$\begin{aligned} E(Y) &= L_0 + L_1X_1 + L_2X_2 + L_6X_6 + L_{14}X_1X_6 \\ &= -0.1498 + 0.1976X_1 - 0.1754X_2 + 0.1479X_6 + 0.0583X_1X_6 \end{aligned} \tag{4.5}$$

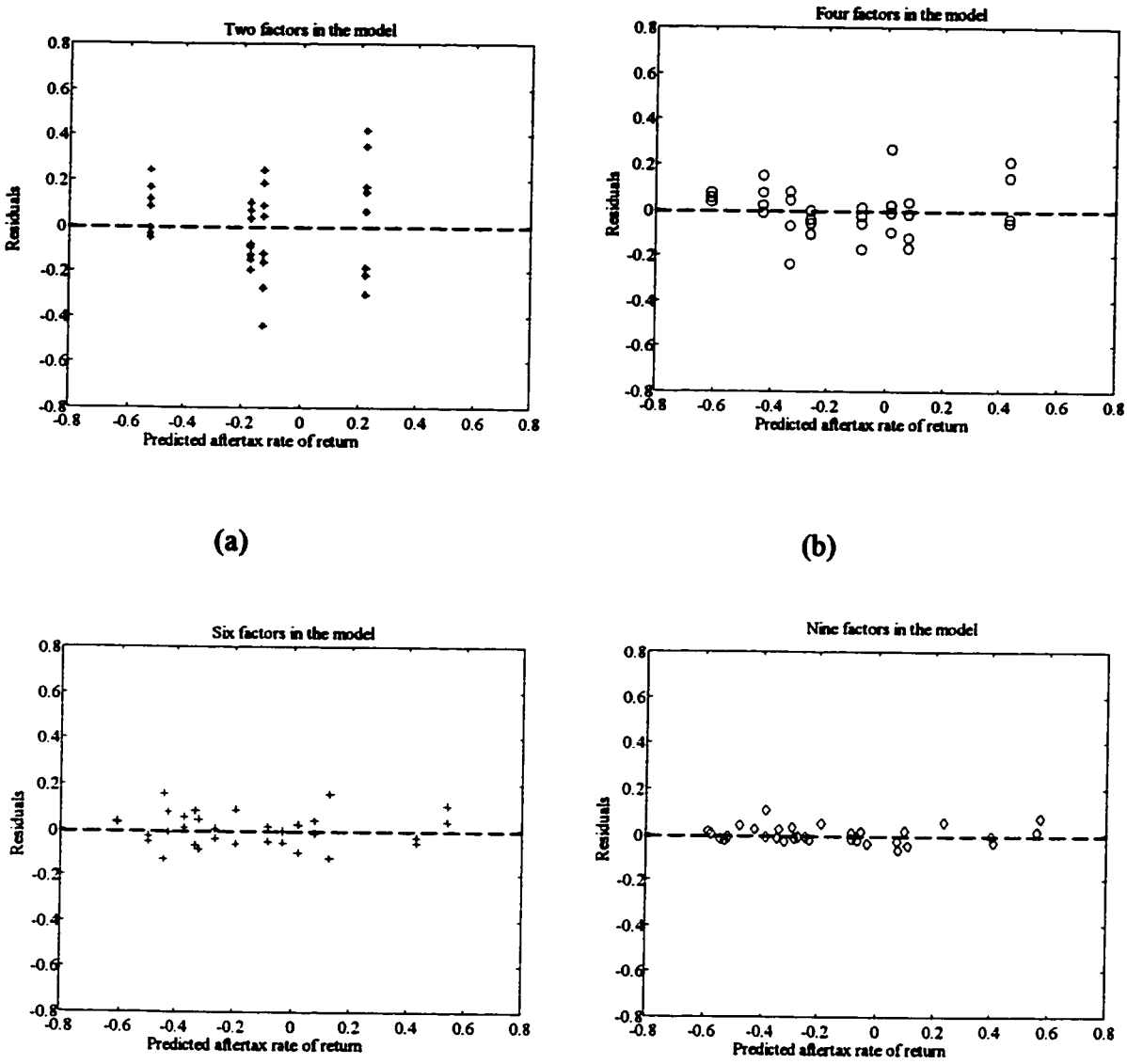


(a) Results of center point simulation (85 wt% glycerine)



(b) Results of center point simulation (92 wt% glycerine)

Figures 4.6a and b Results of center point simulation for process III



Figures 4.7a through d Residual plots for process III (85 wt% glycerine)

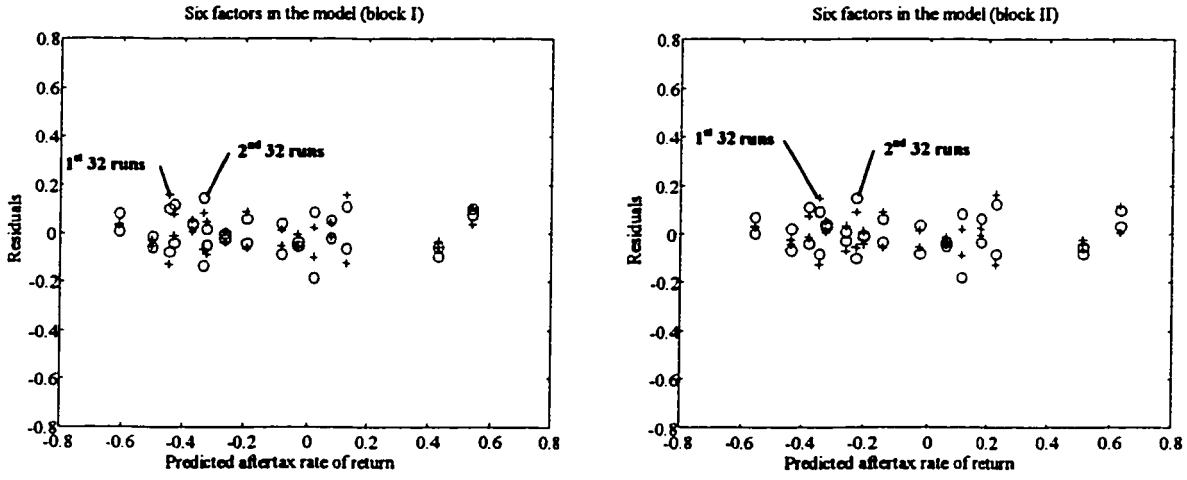
$$
\begin{aligned}
E(Y) &= L_0 + L_1X_1 + L_2X_2 + L_6X_6 + L_{14}X_1X_6 \\
&\quad + L_{10}X_1X_2 + L_5X_5 \\
&= -0.1498 + 0.1976X_1 - 0.1754X_2 + 0.1479X_6 + 0.0583X_1X_6 \\
&\quad - 0.0561X_1X_2 - 0.0539X_5
\end{aligned} \tag{4.6}
$$

$$
\begin{aligned}
E(Y) &= L_0 + L_1X_1 + L_2X_2 + L_6X_6 + L_{14}X_1X_6 \\
&\quad + L_{10}X_1X_2 + L_5X_5 + L_8X_8 + L_3X_3 + L_{13}X_1X_5 \\
&= -0.1498 + 0.1976X_1 - 0.1754X_2 + 0.1479X_6 + 0.0583X_1X_6 \\
&\quad - 0.0561X_1X_2 - 0.0539X_5 + 0.0422X_8 - 0.0373X_3 - 0.0266X_1X_5
\end{aligned} \tag{4.7}
$$

Comparing the distribution of residuals in each plot, two observations arise. First, it is obvious that when the model contained two or four factors, its residual distribution revealed possible trends. This implies the possible absence of some significant effects. However, the residuals tended to be random with an increase in the number of factors involved in the model. When the model contained six factors (Equation 4.6 and Figure 4.7c), the residuals appeared to be distributed randomly about zero. For the model involving nine factors (Equation 4.7 and Figure 4.7d), the residuals exhibited a random distribution. Secondly, the variation in the range of residuals was diminished as the number of factors in the model increased. Similar results were found for block II (92 wt% purity of glycerine). For the model involving nine factors, its residuals fluctuated over a very narrow range. On the whole, these results indicated that there was no evidence of model lack of fit in Equations 4.6 and 4.7. From the factors in Equation 4.6 and the previous analyses (e.g., Figures 4.5a and b and Table 4.10), plant capacity X_1, oil price X_2 and biodiesel price X_6 are believed to have the greatest effect on the response variable. Further investigation confirming the significance of some effects on the response variable is underway (see discussion in Chapter 5).

Because a fractional factorial design was used for the sensitivity analyses in this study, the adequacy of the model obtained was only valid in a fraction of the operating region. A fold-over test was carried out as a cross-validation in order to confirm and strengthen the validity of the model adequacy in another operating region (i.e., "fold-over" region). For example, for block I, the signs for all of the factors in the original experimental design were reversed. Therefore, a new set of experimental runs was

obtained. Based on this new experimental design, HYSYS™ simulations and economic estimations were performed and the value of the aftertax rate of return for each new run was obtained. These values can be regarded as the observed values of the response variable. On the other hand, the simplified and adequate model determined earlier (i.e., Equation 4.6) was used to predict the values of the response variable under the new experimental conditions. Finally, the differences between the observed and predicted values represent new residuals. In Figure 4.8a, plus signs are the original residuals (marked as 1st 32 runs) and circle signs are the new residuals from the fold-over test (marked as 2nd 32 runs). Comparing these two sets of residuals, both display random distributions about zero. Moreover, there are no significant differences between these two sets of residuals. This suggests that there is no evidence for lack of fit for this model in the "fold-over" region. The same analysis was carried out for block II with similar conclusions (see Figure 4.8b). Detailed calculation results are provided in Table A.4 in the Appendix.



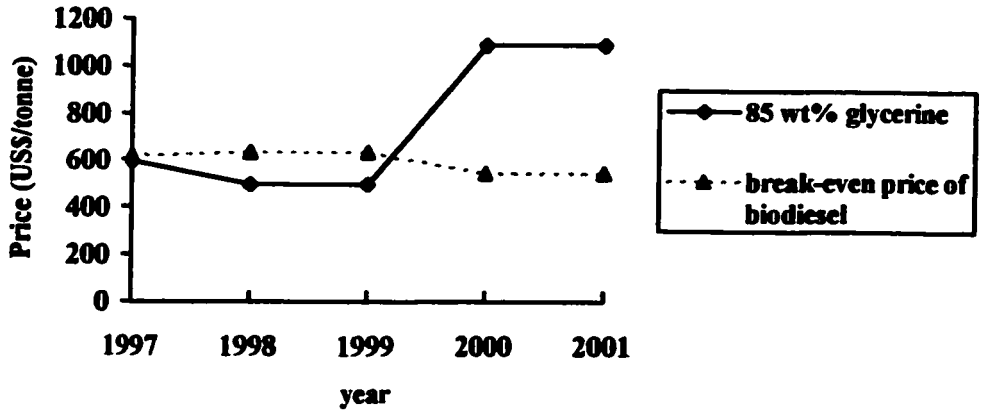
(a) Block I (b) Block II

Figures 4.8a and b Comparison of residuals from original and fold-over experiment designs for process III

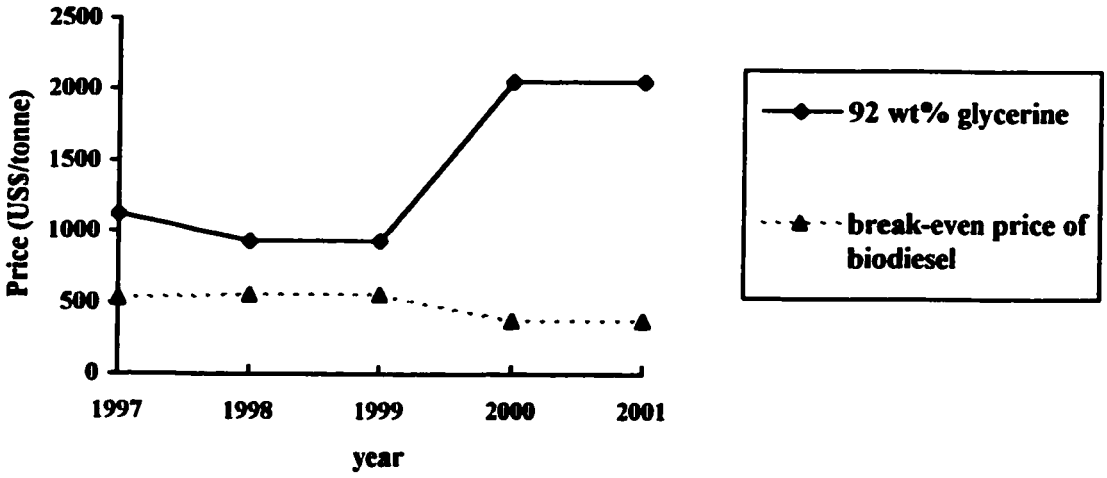
The sensitivity of the break-even price of biodiesel to the prices of waste oil and glycerine at the center point conditions (e.g., 8,000 tonnes/year biodiesel) was studied. The results showed that an increase of $0.01/kg in waste oil price would cause an increase of $0.013/kg in the biodiesel break-even price. On the other hand, a reduction of $0.01/kg in the biodiesel break-even price can be obtained by an increase of $0.07/kg in the price of crude glycerine (85 wt%). These values suggest that the influence of the oil price on the biodiesel price is larger than the influence of the glycerine price. Comparing these values to the results of Noordam and Withers (1996), there is no significant difference. However, the fluctuation of the glycerine price may require additional consideration. Based on the 99^+ wt% glycerine price in the Chemical Market Reporter (1997-2001), 92 wt% glycerine was assumed to have a value of 85% of the price of 99^+ wt% glycerine and 85 wt% glycerine was assumed to have a value of 45% of the price of 92 wt% glycerine (Sonntag, 1991; Bender, 1999). With the fluctuation in the glycerine price, the expected change in the break-even price of biodiesel is shown in Figures 4.9a and b. These results indicate that despite the big fluctuation in glycerine price, biodiesel break-even price shows relatively little variation. In other words, there is no evidence of a strong impact of the price of glycerine on the biodiesel break-even price.

Similar sensitivity analyses were also carried out for processes II and IV. The results showed that apart from some differences in minor effects, plant capacity, oil price and biodiesel price were the main effects in all processes II, III and IV (see Table 4.11).

The approach taken to evaluate sensitivities of the aftertax rate of return to the values of process inputs proved to be efficient and easy to implement. Use of a two-level fractional factorial design of resolution IV provided efficiency in the number of computer simulations required to determine the relative importance of the factors studied. The design provided information about the sensitivity of the aftertax rate of return to changes in each factor individually as well as jointly with other factors (i.e., interaction effects). The orthogonality of this design allowed the impact of various effects on the aftertax rate of return to be evaluated independently of the values of other effects. This independence of effects and the use of plots of the sum of squares of discrepancies between model predictions and simulation results formed the basis for determining which factors had the greatest impact on the economic performance measure (i.e., aftertax rate of return).



(a) Change of break-even price of biodiesel with glycerine price (85 wt% glycerine)



(b) Change of break-even price of biodiesel with glycerine price (92 wt% glycerine)

Figures 4.9a and b Change in the break-even price of biodiesel with glycerine price for process III

Table 4.11 Results of sensitivity analyses for different processes

Process No.[a]	Process Description	Major Effects	Minor Effects
Process II	Alkali-catalyzed process using sodium hydroxide catalyst	Plant capacity X_1, price of waste cooking oil X_2 and biodiesel price X_6	Interaction of X_1X_6, interaction of X_1X_2
Process III	Acid-catalyzed process using sulfuric acid catalyst	Plant capacity X_1, price of waste cooking oil X_2 and biodiesel price X_6	Interaction of X_1X_6, interaction of X_1X_2 and thermodynamic model X_5
Process IV	Acid-catalyzed process using hexane extraction	Plant capacity X_1, price of waste cooking oil X_2 and biodiesel price X_6	Interaction of X_1X_2, methanol recovery X_8 and interaction of X_1X_2

[a] The sensitivity analysis of process I was not carried out

Confirmation of which effects were important was obtained from an examination of residual plots as factors were added to the model. These residual plots also provided an indication of model adequacy. Further validation of the model was obtained by examining residuals obtained from simulation results from a "fold-over" region of the operating region.

6. Conclusions

On the basis of the economic assessment of four continuous alkali- and acid-catalyzed processes using virgin oil or waste cooking oil as the raw material, the following conclusions can be made.

Compared to the other processes, the alkali-catalyzed process using virgin oil (process I) had the lowest total capital investment because of the relatively small sizes and normal construction material (i.e., carbon steel) of most of the process equipment. For a plant size of 8,000 tonnes/year biodiesel, the total capital investment in process I was approximately half of this cost in the other processes. This indicated that process I required the least initial investment when building a biodiesel plant.

Raw material cost accounts for a major portion of the total manufacturing cost. Thus, reduction of the raw material cost should be the first step in optimizing the total

manufacturing cost. Compared to the cost of waste cooking oil, virgin oil costs approximately 2 to 3 times more. This indicated that the use of virgin oil would lead to a substantial increase in total manufacturing cost. As a result, process I had high manufacturing cost. In other words, although process I had the lowest cost requirement for building a biodiesel plant, it had high cost in terms of operating the plant.

When waste oil of low cost was used as the raw material, alkali-catalyzed process II required a pre-treatment unit to reduce the content of free fatty acids. Therefore, the cost associated with this pre-treatment unit, including the extra solvent cost, would balance the credit of using waste oil as the raw material. This led to a reduced economic feasibility for process II. On the other hand, the acid-catalyzed system was insensitive to free fatty acids and no pre-treatment unit was required. Accordingly, the acid-catalyzed process to produce biodiesel from waste cooking oil (process III) had the lowest total manufacturing cost. In brief, process III cost the least in operating a biodiesel plant.

Moreover, glycerine was a valuable by-product, which could add appreciable credit to reduce the total manufacturing cost by approximately 10% for a plant with 8,000 tonnes/year biodiesel capacity.

Finally, according to aftertax rate of return and break-even price of biodiesel, the acid-catalyzed process III had the highest profit (10% for an 8,000 tonnes/year plant), the lowest biodiesel break-even price ($593/tonne for an 8,000 tonnes/year plant) and was economically attractive. Consequently, the acid-catalyzed process using waste cooking oil was an economically competitive alternative to the alkali process for biodiesel production.

Sensitivity analyses of different processes for biodiesel production showed that plant capacity, the price of waste cooking oil and the price of biodiesel significantly affected the economic feasibility of the biodiesel production.

Acknowledgements

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Chapter 5 GENERAL DISCUSSION AND CONCLUSIONS

Aside from the previous description of this work, some discussions related to the catalyst removal in the process design and significance of each effect in the sensitivity analyses are presented in this chapter. In summary, the overall results of the studies are concluded and recommendations for future work are proposed.

5.1 Discussion

Continuous process technologies to produce biodiesel were studied and evaluated in this thesis. Four different process designs were discussed in the first article (Chapter 3). Using HYSYS™ simulation software, process flowsheets, material and energy balances and the sizing of process equipment were developed. In terms of process technology, the four alkali- and acid-catalyzed processes using virgin vegetable oil or waste cooking oil were compared and evaluated. An economic assessment of these processes was performed in the second article (Chapter 4). Fixed capital cost, total manufacturing cost, aftertax rate of return and biodiesel break-even price were calculated for each process. Overall, an assessment involving both technological and economical aspects for these processes was achieved. Furthermore, sensitivity analyses for the alkali- and acid-catalyzed processes using waste cooking oil were carried out. All of these investigations will be of importance in promoting biodiesel production and development.

Catalyst removal

Aside from the main studies described previously, some other issues are worthy of discussion. First, in all of the proposed processes, the acid and alkali catalysts were removed following the methanol recovery or even later. In the acid-catalyzed processes III and IV, the cost associated with construction material of process equipment will be

reduced if sulfuric acid is removed immediately following the transesterification reactor R-101A/B rather than following the methanol distillation column T-201. Due to the absence of corrosive sulfuric acid, the downstream units can be made from carbon steel. However, the presence of a large excess of methanol results in a requirement for a large neutralization reactor. The resulting water from the neutralization reaction can be absorbed by the co-product calcium sulfate. However, it may be difficult to remove all of the water by calcium sulfate because water is completely soluble in methanol and glycerol. Simulation results showed that even 0.5 wt% water remaining in the feed stream to methanol distillation column T-201 could cause a reduction in the methanol recovery rate from 94% to below 80%. Similarly, for the alkali-catalyzed processes I and II, the removal of alkali catalyst by adding phosphoric acid prior to the methanol recovery can reduce the hydrolysis of resulting methyl esters under the alkali condition, as discussed in Chapter 2. However, the production of water cannot be avoided in the neutralization reaction. Even 0.1 wt% water remaining in the feed stream will decrease the methanol recovery in T-201 from 94% to 80%. Again, the saving of construction material cost is attained at the expense of a reduction in methanol recovery or an increase in the amount of fresh methanol make-up.

Confirmation of significant effects

In Chapter 4, the significance of several effects (i.e., factors) on the economic feasibility of the biodiesel process was studied. The following discussion focus on testing the significance of these factors from another point of view.

On the basis of a +30% to -20% uncertainty range for capital cost estimation, it was assumed that the estimation of total capital investment and total manufacturing cost in this study had a similar accuracy range of +25% to -25%. This means that the expected values should lie between 25% higher and 25% lower than the calculated values. On the other hand, these limits can be preliminarily used as a criterion for testing the importance of various factors. Here, case 1 in process III was chosen as an example to show the detailed testing procedures.

Step 1: The calculated values of the aftertax rate of return in 32 experimental runs are regarded as the observed values. From Equation 4.1, the expected value of aftertax rate of return can be depicted as follows:

$$I_I \pm \delta_I = \frac{A_{Pi} \pm \delta_{Pi}}{C_{Ti} \pm \delta_{Ti}} \tag{5.1}$$

where I_i = the calculated value of aftertax rate of return at run i (i =1, 2, 3...32), %,

δ_i = the accuracy range of I_i,

A_{Pi} = the sum of $(A_{NNPi} + A_{BDi})$ at run i, $,

δ_{Pi} = the accuracy range of A_{Pi},

C_{Ti} = the total capital investment at run i, $,

δ_{Ti} = the accuracy range of C_{Ti}.

We assumed that a ± 25% accuracy range applied to the estimation of both capital cost and manufacturing cost, therefore,

$$\pm \delta_{Pi} = \pm 0.25 A_{Pi}$$
$$\pm \delta_{Ti} = \pm 0.25 C_{Ti} \tag{5.2}$$

Equation 5.1 can be simplified as

$$I_I \pm \delta_I = \frac{A_{Pi}(1 \pm 0.25)}{C_{Ti}(1 \pm 0.25)} \tag{5.3}$$

As a rough calculation, when A_{Pi} is positive, the upper limit $(I_i + \delta_i)$ was calculated as $\frac{A_{Pi}(1+0.25)}{C_{Ti}(1-0.25)}$; the lower limit $(I_i - \delta_i)$ was $\frac{A_{Pi}(1-0.25)}{C_{Ti}(1+0.25)}$. On the contrary, when A_{Pi} is negative, $(I_i + \delta_i)$ was set to be $\frac{A_{Pi}(1-0.25)}{C_{Ti}(1+0.25)}$ and $(I_i - \delta_i)$ was $\frac{A_{Pi}(1+0.25)}{C_{Ti}(1-0.25)}$. The upper and lower limits for the observed aftertax rate of return at each experimental run are presented in Table 5.1.

Step 2: By using different models (Equations 4.5 through 4.7), the predicted values of aftertax rate of return for each run were obtained, as shown in Table 5.1. Model A involves four factors (see Equation 4.5). Model B contains six factors (see Equation 4.6) and Model C includes nine factors (see Equation 4.7).

Table 5.1 Values of aftertax rate of return in case 1 for process III

Run	Observed values			Predicted values		
	Upper limit	Aftertax rate of return I_i	Lower limit	Model A (involving 4 factors)	Model B (involving 6 factors)	Model C (involving 9 factors)
1	-0.0459	-0.0764	-0.1274	-0.0824	-0.0846	-0.0317
2	0.9386	0.5631	0.3379	0.4294	0.5394	0.5611
3	-0.3350	-0.5583	-0.9304	-0.6124	-0.5024	-0.5339
4	-0.1533	-0.2555	-0.4258	-0.3338	-0.336	-0.2299
5	-0.1833	-0.3055	-0.5092	-0.2616	-0.2638	-0.2855
6	-0.0001	-0.0002	-0.0003	0.0170	0.127	0.0741
7	-0.2473	-0.4121	-0.6868	-0.4332	-0.3232	-0.4293
8	0.0923	0.0554	0.0332	0.0786	0.0764	0.1079
9	-0.1601	-0.2668	-0.4447	-0.2616	-0.2638	-0.2953
10	0.4639	0.2783	0.1670	0.0170	0.127	0.2331
11	-0.1703	-0.2838	-0.4730	-0.4332	-0.3232	-0.2703
12	0.1839	0.1103	0.0662	0.0786	0.0764	0.0981
13	-0.0871	-0.1451	-0.2419	-0.0824	-0.0846	-0.1907
14	1.0591	0.6355	0.3813	0.4294	0.5394	0.5709
15	-0.3212	-0.5354	-0.8923	-0.6124	-0.5024	-0.5241
16	-0.2421	-0.4035	-0.6724	-0.3338	-0.336	-0.3889
17	-0.2211	-0.3685	-0.6141	-0.2616	-0.3716	-0.3499
18	0.0583	0.0350	0.0210	0.0170	0.0192	0.0721
19	-0.2140	-0.3566	-0.5944	-0.4332	-0.431	-0.3249
20	-0.0566	-0.0943	-0.1572	0.0786	-0.0314	-0.0629
21	-0.1557	-0.2595	-0.4326	-0.0824	-0.1924	-0.2453
22	0.6089	0.3653	0.2192	0.4294	0.4316	0.4099
23	-0.3456	-0.5761	-0.9601	-0.6124	-0.6102	-0.5787
24	-0.3439	-0.5731	-0.9552	-0.3338	-0.4438	-0.5499
25	-0.0666	-0.1109	-0.1849	-0.0824	-0.1924	-0.0863
26	0.6427	0.3856	0.2314	0.4294	0.4316	0.4001
27	-0.3476	-0.5794	-0.9657	-0.6124	-0.6102	-0.5885
28	-0.1736	-0.2893	-0.4821	-0.3338	-0.4438	-0.3909
29	-0.1931	-0.3218	-0.5364	-0.2616	-0.3716	-0.3401
30	-0.0513	-0.0855	-0.1425	0.0170	0.0192	-0.0869
31	-0.2670	-0.4450	-0.7417	-0.4332	-0.431	-0.4839
32	-0.0262	-0.0437	-0.0728	0.0786	-0.0314	-0.0531

Step 3: The predicted values of aftertax rate of return in each run using different models were compared to the observed values.

From Table 5.1, it was found that, with increasing number of factors in the model, the more predicted values fell in the approximate range of plausible expected values for aftertax rate of return. For example, nine of thirty-two predictions of aftertax rate of return marked as shaded cell in Table 5.1 using model A (containing four factors) fell outside the approximate range of plausible expected values. With the model containing six factors (i.e., model B), the number of data points outside the range decreased to seven. For the model containing nine factors (i.e., model C), only four data points were outside the range. This may imply the possible absence of important factors in model A. Therefore, models B or C (containing six or nine factors) were favoured starting points.

5.2 Conclusions

In this thesis, four different process flowsheets to produce biodiesel from virgin vegetable oil or waste cooking oil were developed. A technical comparison of these processes was presented. As a commercial process, the alkali-catalyzed process using virgin vegetable oil (process I) proved to be the simplest process with the least number of processing units with the smallest sizes. Despite this advantage, the cost of virgin oil was too high to make it competitive with petroleum-based diesel. The alkali-catalyzed process using waste cooking oil (process II) had a low raw material cost but was the most complex process. This was mainly due to the sensitivity to free fatty acids in the waste oil required an extra pre-treatment step prior to the transesterification reaction. The acid-catalyzed process using waste cooking oil (process III) required less equipment than process II and also had a low raw material cost. However, compared to process I, the sizes of equipment and the number of processing units required to be made from stainless steel were increased in process III. On the whole, from a technical viewpoint, the acid-catalyzed process using waste cooking oil (process III) proved to be a competitive alternative to the commercial alkali-catalyzed process I.

An economic assessment of the four different processes was also performed. In regard to fixed capital cost or total capital investment, the alkali-catalyzed process using virgin vegetable oil (process I) had the lowest value, which represented the lowest

requirement for initial investment in building a new biodiesel plant. However, regarding total manufacturing cost, processes I and II had high costs and became less attractive. The acid-catalyzed process using waste cooking oil (process III) had the lowest total manufacturing cost.

Raw material cost was found to be the most important component of the total manufacturing cost for biodiesel production. This is also the main reason why alkali-catalyzed process I had high total manufacturing cost. With regard to the alkali-catalyzed process using waste cooking oil (process II), a fatty acid pre-treatment unit resulted in extra costs associated with equipment, solvent and waste disposal, which offset the benefit of the low raw material cost.

Moreover, glycerine was a valuable by-product with an appreciable credit to reduce the total manufacturing cost by 10% for an 8,000 tonnes/year biodiesel plant.

On the basis of the aftertax rate of return and the break-even price of biodiesel, process III had the highest profit (e.g., 10% aftertax rate of return for an 8,000 tonne/year biodiesel plant) and lowest biodiesel break-even price (e.g., $593/tonne for an 8,000 tonnes/year biodiesel plant). Overall, the acid-catalyzed process using waste cooking oil (process III) proved to be more economically attractive than the alkali-catalyzed process using virgin oil or waste oil (processes I and II).

In brief, the acid-catalyzed process to produce biodiesel from waste cooking oil is not only technically feasible but also economically viable. It is a competitive alternative to current alkali-catalyzed process for biodiesel production methods.

The results of the sensitivity analyses for these processes showed that plant capacity, price of feedstock oil and biodiesel cost were the major factors affecting the commercial viability of the biodiesel production.

5.3 Recommendations

Based on the above results and some assumptions we made in the current studies, the following recommendations for the future work are proposed:

- A kinetic study of the acid-catalyzed transesterification reaction using waste cooking oil should be carried out, including model determination, parameter estimation and model verification. This should improve the understanding of

the reaction mechanism and provide more reliable information on the reactor design.

- Investigations on using a supported acid catalyst should be carried out further. In the current work, the use of a supported acid catalyst was studied in preliminary experimental tests. Further studies on selecting an efficient supported catalyst, the reaction mechanism, reaction conditions, and so forth, will be of special interest.
- The use of different characterization techniques, such as on-line infrared (IR) spectroscopy and gel permeation chromatography (GPC) will be tested, to improve the accuracy of analytical data.
- In the current HYSYS™ simulation, some data, such as the critical properties of triglycerides and the interaction parameter coefficients between some components, were estimated because they were not available in either the HYSYS™ data library or from the open literature. For example, in the alternative acid-catalyzed process using hexane as the extraction solvent, component splitters instead of a liquid-liquid extraction model were applied to simulate the process, which acted as a "black box" to avoid the real simulation. In the future, if more reliable information on the interaction parameter coefficients are available, the accuracy of the process simulation will be improved.
- In the real alkali-catalyzed system, soaps are always produced as long as free fatty acids are present in the oil feedstock. In the current work, it was assumed that no soaps were produced in the alkali-catalyzed processes I and II because the behaviour of soaps cannot be simulated precisely. Therefore, in the future, the presence of soaps should be taken into consideration if more information is available.
- The supplementary information on the pre-treatment unit in the alkali-catalyzed process using waste cooking oil can help to improve the reliability of the current results. In particular, other alternative ways to separate the refined oil from the resulting water and acid catalyst should be explored.

- Evaluation of the biodiesel production using oilseed as the raw material may be considered in the assessment of different process designs, which can provide further comparisons with previous studies.

APPENDIX

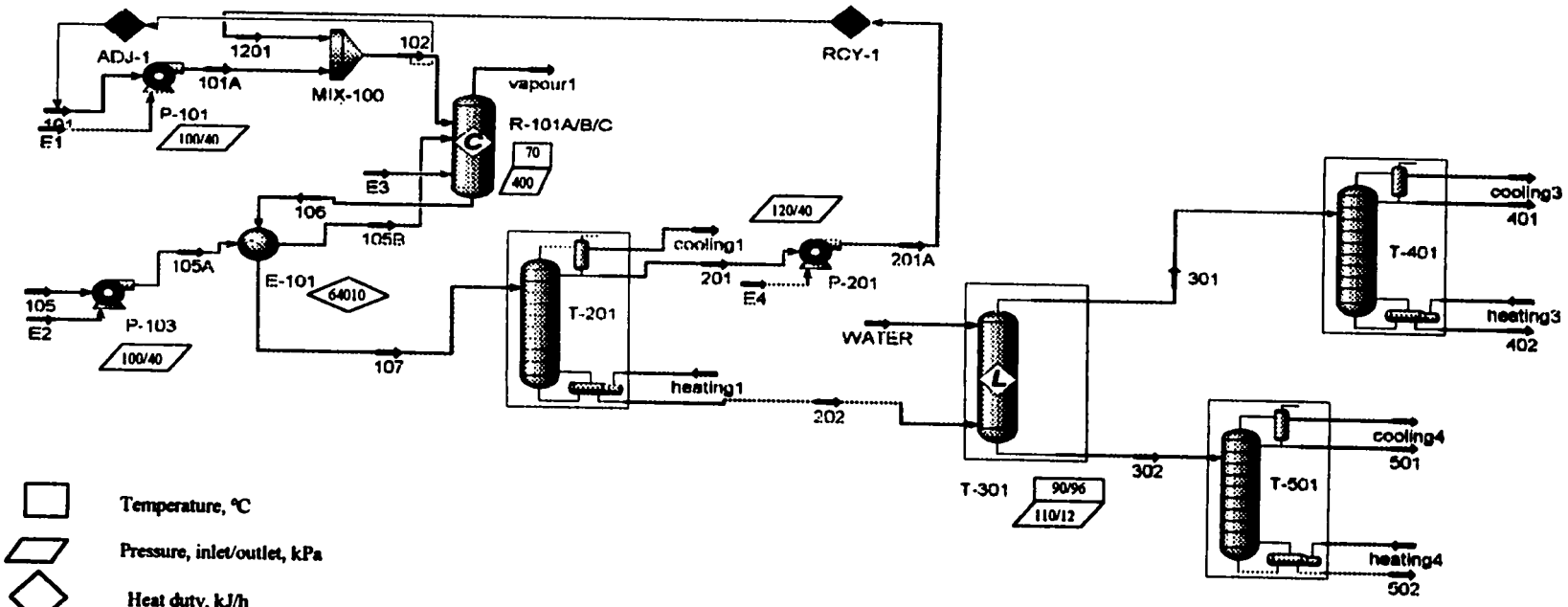
A.1 Acid-catalyzed process with supported catalyst

Due to the presence of sulfuric acid in the acid-catalyzed process, stainless steel material for the transesterification reactors and some separation units must be used. This increases equipment costs. In order to reduce the equipment cost and simplify the downstream separation units, the use of a supported catalyst instead of sulfuric acid to catalyze the transesterification reaction was investigated.

A preliminary test was conducted by using an ion-exchange resin. The resin used was a sulfonated polystrene copolymer with an active RSO_3^- H^+ group. H^+ was the exchangeable ion. The active working density (dry basis) was 455 g/L and the total exchange capacity (dry basis) was 5.1 meq/g. 0.5 mL of waste cooking oil was blended with 5 mL of methanol in a 15 mL tube with a screw cap. 1 g of resin and two small stirring bars were added to the tube. The mixture was heated to 80°C on a magnetic stirring heater. After 4 hours, samples were taken and analyzed by thin layer chromatography (TLC). The results showed that a small amount of oil was converted to FAME under the above conditions. Further work on selecting a proper supported catalyst and optimizing the reaction conditions is currently underway.

A proposed process flowsheet and the equipment list are shown in Figure A.1. By replacing the concentrated sulfuric acid with a supported catalyst, downstream units were not subject to the corrosive acid and the acid removal step became unnecessary. Only the transesterification reactors were constructed of stainless steel in this process. However, depending on the supported catalyst used, regeneration of the catalyst may be required. Therefore, three reactors with the same size as those in the acid-catalyzed process were used. Two of them were operated in series. The third one was used for resin regeneration. Since they were exactly the same, only one reactor was shown in the flowsheet. Of note is that, compared to sulfuric acid, the cost of resin catalyst is much higher; usually $5-

Figure A.1 Acid-catalyzed process with supported catalyst to produce biodiesel from waste cooking oils



Stream Name	102	105B	106	107	201	202	301	302	401	402	501	502
Temperature (°C)	64.03	65.00	70.00	61.70	68.84	95.99	91.10	80.22	64.36	231.31	46.52	117.51
Pressure (kPa)	400	400	400	400	120	130	110	120	100	110	40	50
Molar flow (kg-mol/h)	57.49	1.13	58.57	58.57	50.83	7.74	3.55	6.19	0.09	3.46	4.39	1.80
Mass flow (kg/h)	1842.19	1000.00	2842.19	2842.19	1628.65	1213.54	1004.61	244.96	2.81	1001.80	123.01	121.95
Liquid volume flow (m^3/h)	2.315	1.111	3.407	3.407	2.047	1.360	1.146	0.250	0.004	1.142	0.149	0.101
Component mass fraction												
Methanol	1.000	0.000	0.610	0.610	1.000	0.085	0.004	0.409	0.992	0.000	0.814	0.000
Triglyceride (oil)	0.000	1.000	0.002	0.001	0.000	0.004	0.002	0.014	0.000	0.002	0.000	0.029
Methyl-oleate (biodiesel)	0.000	0.000	0.352	0.352	0.000	0.825	0.994	0.012	0.000	0.997	0.000	0.024
Glycerol	0.000	0.000	0.036	0.036	0.000	0.085	0.000	0.423	0.000	0.000	0.000	0.850
H_2O	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.142	0.008	0.001	0.186	0.097

9/kg depending on the resin properties (REMCO Engineering Company, http://www.remco.com, 1997). Furthermore, the disposal of the resin catalyst would be different from that of common solid wastes.

A.2 Some descriptions of economic evaluation

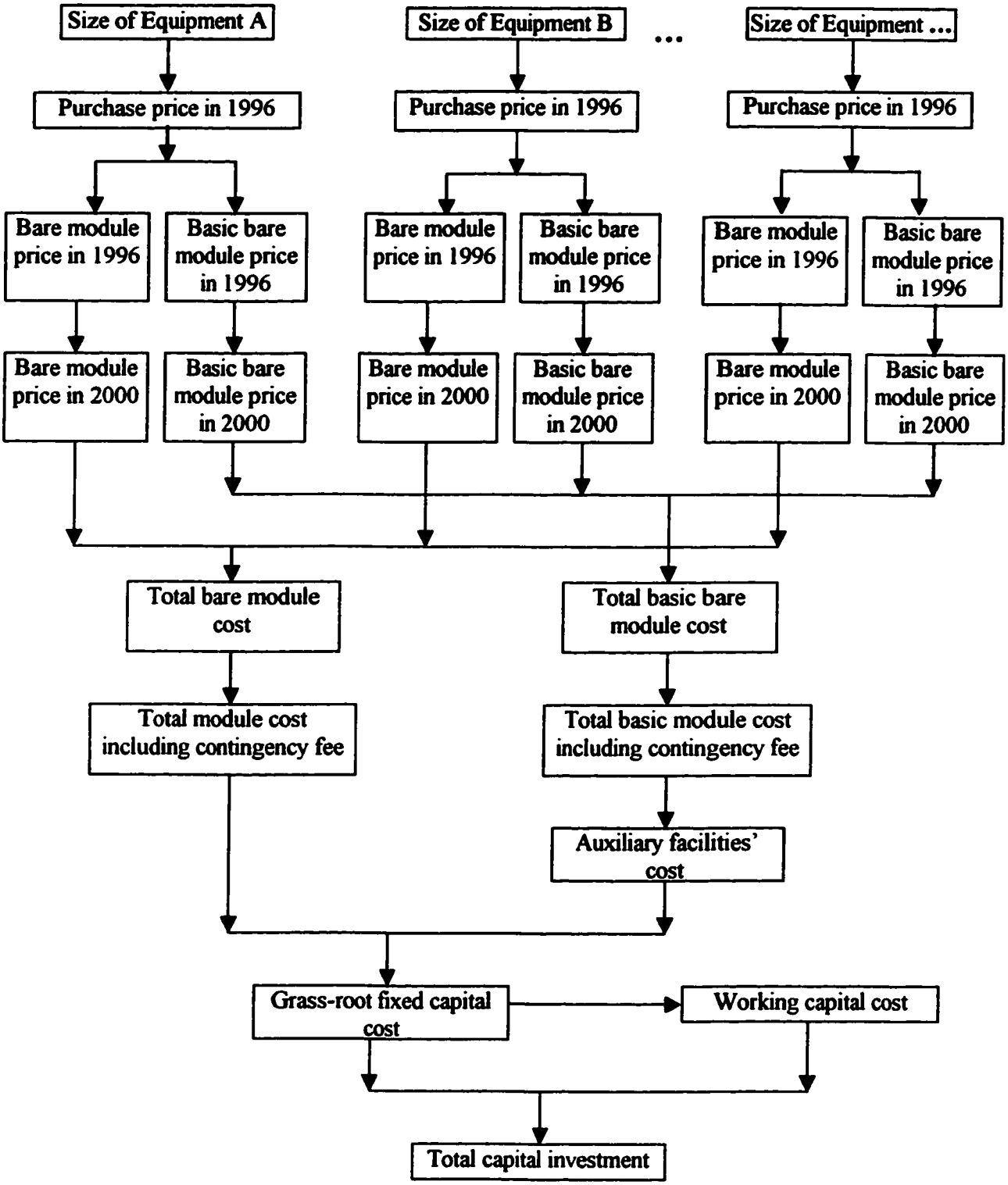
Operator labor cost was calculated on the basis of Table A.1.

Table A.1 Operator requirements for various pieces of process equipment (Ulrich, 1984; Turton et al., 1998)

Process equipment type	Operators per equipment per shift
Heat exchangers	0.1
Vessels	0
Pumps	0
Reactors	0.5
Towers	0.35

Detailed calculating procedures for fixed capital cost and total investment capital are shown in Figure A.2 (Ulrich, 1984; Turton, 1998).

Figure A.2 Detailed procedures of calculating fixed capital cost



A.3 Other results of sensitivity analyses

Experimental design and values of response variable (i.e., aftertax rate of return) at different experimental runs for process III are shown below.

Table A.2 Experimental design and values of response variable for process III

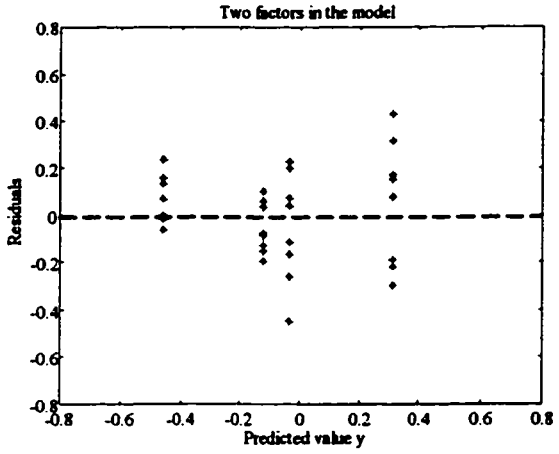
Run	X_1	X_2	X_3	X_4	X_5	X_6	X_7	X_8	X_9	Y (85wt% glycerine)	Y (92wt% glycerine)
1	-1	-1	-1	-1	-1	1	1	1	1	-0.0764	-0.0221
2	1	-1	-1	-1	-1	1	-1	-1	-1	0.5631	0.6225
3	-1	1	-1	-1	-1	-1	1	-1	-1	-0.5583	-0.4652
4	1	1	-1	-1	-1	-1	-1	1	1	-0.2555	-0.1470
5	-1	-1	1	-1	-1	-1	-1	1	-1	-0.3055	-0.2509
6	1	-1	1	-1	-1	-1	1	-1	1	-0.0002	0.0926
7	-1	1	1	-1	-1	1	-1	-1	1	-0.4121	-0.3341
8	1	1	1	-1	-1	1	1	1	-1	0.0554	0.1639
9	-1	-1	-1	1	-1	-1	-1	-1	1	-0.2668	-0.2023
10	1	-1	-1	1	-1	-1	1	1	-1	0.2783	0.3821
11	-1	1	-1	1	-1	1	-1	1	-1	-0.2838	-0.2315
12	1	1	-1	1	-1	1	1	-1	1	0.1103	0.1924
13	-1	-1	1	1	-1	1	1	-1	-1	-0.1451	-0.0895
14	1	-1	1	1	-1	1	-1	1	1	0.6355	0.7349
15	-1	1	1	1	-1	-1	1	1	1	-0.5354	-0.4833
16	1	1	1	1	-1	-1	-1	-1	-1	-0.4035	-0.2904
17	-1	-1	-1	-1	1	-1	-1	-1	-1	-0.3685	-0.3192
18	1	-1	-1	-1	1	-1	1	1	1	0.0350	0.1199
19	-1	1	-1	-1	1	1	-1	1	1	-0.3566	-0.3089
20	1	1	-1	-1	1	1	1	-1	-1	-0.0943	0.0052
21	-1	-1	1	-1	1	1	1	-1	1	-0.2595	-0.2085
22	1	-1	1	-1	1	1	-1	1	-1	0.3653	0.4573
23	-1	1	1	-1	1	-1	1	1	-1	-0.5761	-0.5275
24	1	1	1	-1	1	-1	-1	-1	1	-0.5731	-0.4791
25	-1	-1	-1	1	1	1	1	1	-1	-0.1109	-0.0645
26	1	-1	-1	1	1	1	-1	-1	1	0.3856	0.4754
27	-1	1	-1	1	1	-1	1	-1	1	-0.5794	-0.5304
28	1	1	-1	1	1	-1	-1	1	-1	-0.2893	-0.2014
29	-1	-1	1	1	1	-1	-1	1	1	-0.3218	-0.2762
30	1	-1	1	1	1	-1	1	-1	-1	-0.0855	0.0098
31	-1	1	1	1	1	1	-1	-1	-1	-0.4450	-0.3978
32	1	1	1	1	1	1	1	1	1	-0.0437	0.0376

Regarding to process III, the parameter estimates and the sums of squares of residuals for different runs are listed below.

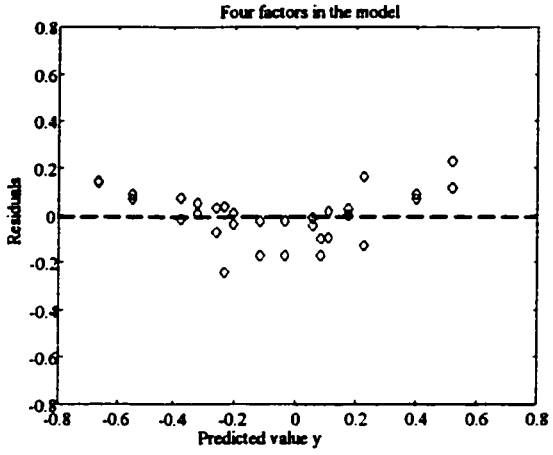
Table A.3 Results of the sums of squares of residuals (SSR) for process III

Block I (85wt% glycerine)			Block II (92wt% glycerine)		
Parameter estimates	Parameter estimates in a descending order (without β_0)	SSR	Parameter estimates	Parameter estimates in a descending order	SSR
-0.1498	-0.1498	3.4024	-0.0748	-0.0748	3.5929
0.1976	0.1976	2.1525	0.2167	0.2167	2.0906
-0.1754	-0.1754	1.1686	-0.1721	-0.1721	1.1430
-0.0373	0.1479	0.4682	-0.0361	0.1450	0.4700
0.0226	0.0583	0.3596	0.0210	-0.0590	0.3587
-0.0539	-0.0561	0.2590	-0.0590	0.0569	0.2551
0.1479	-0.0539	0.1658	0.1450	-0.0557	0.1557
-0.0080	0.0422	0.1088	-0.0076	0.0409	0.1023
0.0422	-0.0373	0.0643	0.0409	-0.0361	0.0605
-0.0035	-0.0266	0.0416	-0.0045	-0.0243	0.0417
-0.0561	0.0226	0.0252	-0.0557	0.0210	0.0276
-0.0121	0.0128	0.0200	-0.0094	0.0168	0.0185
0.0084	-0.0121	0.0153	0.0109	0.0109	0.0148
-0.0266	0.0116	0.0110	-0.0243	-0.0094	0.0119
0.0583	-0.0093	0.0082	0.0569	-0.0091	0.0092
-0.0029	0.0084	0.0060	-0.0031	0.0084	0.0070
0.0128	-0.0080	0.0039	0.0168	-0.0076	0.0052
-0.0026	0.0054	0.0030	-0.0032	-0.0063	0.0039
-0.0022	-0.0046	0.0023	-0.0032	0.0051	0.0031
-0.0037	-0.0037	0.0019	-0.0091	-0.0045	0.0024
0.0116	-0.0035	0.0015	0.0084	-0.0039	0.0020
-0.0002	-0.0034	0.0011	-0.0031	-0.0032	0.0016
0.0003	0.0029	0.0008	-0.0023	-0.0032	0.0013
0.0002	-0.0029	0.0006	-0.0001	-0.0031	0.0010
0.0019	-0.0026	0.0004	0.0008	-0.0031	0.0007
0.0054	-0.0022	0.0002	0.0051	-0.0031	0.0004
-0.0013	0.0019	0.0001	-0.0012	-0.0023	0.0002
-0.0093	-0.0013	0.0000	-0.0063	0.0017	0.0001
0.0010	0.0010	0.0000	0.0007	-0.0012	0.0000
0.0029	0.0003	0.0000	0.0017	0.0008	0.0000
-0.0034	-0.0002	0.0000	-0.0039	0.0007	0.0000
-0.0046	0.0002	0.0000	-0.0031	-0.0001	0.0000

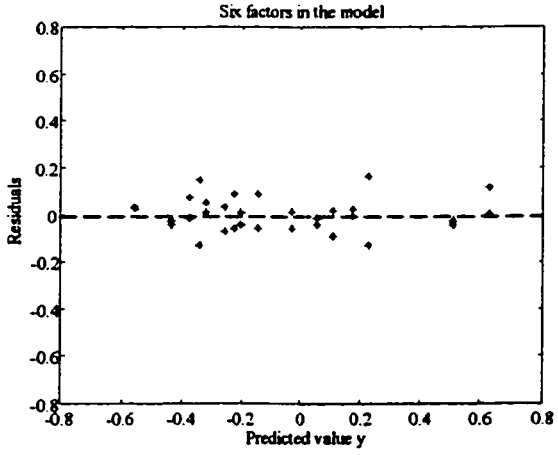
Residual plots using different models for block II (92 wt% glycerine) in process III are described as follows.



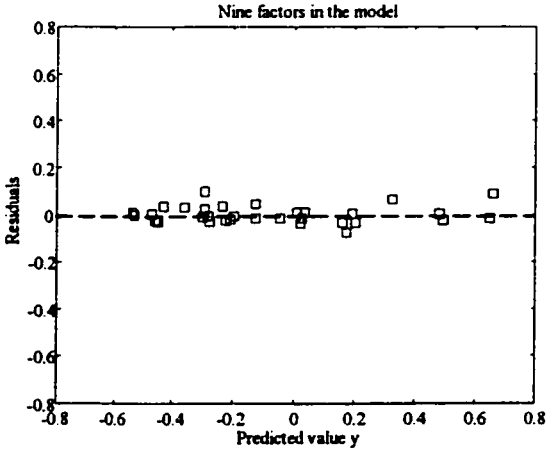
(a)



(b)



(c)



(d)

Figures A.3a through d Residual plots for process III (92 wt% glycerine)

Fold-over experimental design, observed values and predicted values (using Equation 4.6) of response variable (i.e., aftertax rate of return) at different runs for process III are given in Table A.4.

Table A.4 Fold-over experiment design for model adequacy

Run	X_1	X_2	X_3	X_4	X_5	X_6	X_7	X_8	X_9	Y (85wt% glycerine)		Y (92wt% glycerine)	
										Observed	Predicted	Observed	Predicted
1	1	1	1	1	1	-1	-1	-1	-1	-0.5226	-0.4438	-0.4303	-0.3468
2	-1	1	1	1	1	-1	1	1	1	-0.5304	-0.6103	-0.4861	-0.5550
3	1	-1	1	1	1	1	-1	1	1	0.3653	0.4315	0.4478	0.5126
4	-1	-1	1	1	1	1	1	-1	-1	-0.2346	-0.1924	-0.1871	-0.1459
5	1	1	-1	1	1	1	1	-1	1	-0.0719	-0.0313	0.0169	0.0570
6	-1	1	-1	1	1	1	-1	1	-1	-0.3145	-0.4310	-0.2694	-0.3787
7	1	-1	-1	1	1	-1	1	1	-1	0.0995	0.0191	0.1856	0.1088
8	-1	-1	-1	1	1	-1	-1	-1	1	-0.3418	-0.3718	-0.2941	-0.3222
9	1	1	1	-1	1	1	1	1	-1	-0.0879	-0.0313	0.0023	0.0570
10	-1	1	1	-1	1	1	-1	-1	1	-0.4732	-0.4310	-0.4227	-0.3787
11	1	-1	1	-1	1	-1	1	-1	1	-0.1705	0.0191	-0.0776	0.1088
12	-1	-1	1	-1	1	-1	-1	1	-1	-0.3345	-0.3718	-0.2873	-0.3222
13	1	1	-1	-1	1	-1	-1	1	1	-0.3444	-0.4438	-0.2574	-0.3468
14	-1	1	-1	-1	1	-1	1	-1	-1	-0.6059	-0.6103	-0.5543	-0.5550
15	1	-1	-1	-1	1	1	-1	-1	-1	0.3255	0.4315	0.4213	0.5126
16	-1	-1	-1	-1	1	1	1	1	1	-0.1377	-0.1924	-0.0914	-0.1459
17	1	1	1	1	-1	1	1	1	1	0.1252	0.0766	0.2319	0.1750
18	-1	1	1	1	-1	1	-1	-1	-1	-0.3740	-0.3231	-0.2922	-0.2607
19	1	-1	1	1	-1	-1	1	-1	-1	0.0569	0.1270	0.1393	0.2267
20	-1	-1	1	1	-1	-1	-1	1	1	-0.2715	-0.2639	-0.2211	-0.2042
21	1	1	-1	1	-1	-1	-1	1	-1	-0.1929	-0.3359	-0.0852	-0.2289
22	-1	1	-1	1	-1	-1	1	-1	1	-0.5163	-0.5024	-0.4190	-0.4370
23	1	-1	-1	1	-1	1	-1	-1	1	0.6279	0.5394	0.6513	0.6306
24	-1	-1	-1	1	-1	1	1	1	-1	-0.0491	-0.0845	0.0018	-0.0280
25	1	1	1	-1	-1	-1	-1	-1	1	-0.4715	-0.3359	-0.3303	-0.2289
26	-1	1	1	-1	-1	-1	1	1	-1	-0.5602	-0.5024	-0.5070	-0.4370
27	1	-1	1	-1	-1	1	-1	1	-1	0.6060	0.5394	0.7178	0.6306
28	-1	-1	1	-1	-1	1	1	-1	1	-0.1740	-0.0845	-0.1121	-0.0280
29	1	1	-1	-1	-1	1	1	-1	-1	0.0493	0.0766	0.1366	0.1750
30	-1	1	-1	-1	-1	1	-1	1	1	-0.3086	-0.3231	-0.2560	-0.2607
31	1	-1	-1	-1	-1	-1	1	1	1	0.2313	0.1270	0.3427	0.2267
32	-1	-1	-1	-1	-1	-1	-1	-1	-1	-0.2909	-0.2639	-0.2162	-0.2042