

Simulation Approach to Biodiesel Production from Palm Oil by Conventional and Reactive Distillation Processes

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ABSTRACT

A simulation and design method was proposed for biodiesel production from palm oil. The reactant contained three main fatty acids: palmitic, oleic and linoleic acids. The molecular structure design enabled all parameters to be estimated for the process model and simulation. The biodiesel production simulated both conventional and reactive distillation processes. The purity from the conventional process, catalyzed by sodium hydroxide (homogeneous) and strontium oxide (heterogeneous) was 99.45 and 95.21%, respectively. On the other hand, the purity from reactive distillation with strontium oxide (99.87%) was higher than with sodium hydroxide (99.52%). The steady state result was used for the economic simulation of the equipment design. The total cost of biodiesel production using sodium hydroxide and strontium oxide catalysts in a conventional distillation process was USD 0.6701 L⁻¹ and USD 0.6291 L⁻¹, while for the reactive distillation process, the total cost was USD 0.6302 L⁻¹ and USD 0.6262 L⁻¹, respectively.

Keywords: heterogeneous transesterification, reactive distillation, biodiesel

INTRODUCTION

Biodiesel is an alternative diesel fuel that is produced from vegetable oils and animal fats (Van Gerpen, 2005). There are many methods to produce biodiesel such as esterification, transesterification, pyrolysis, supercritical reaction and lipase-catalyzed for biodiesel production (Marchetti *et al.*, 2007). Transesterification methods can produce biodiesel quality close to that of diesel (Demirbas, 2002). Transesterification is the reaction between vegetable oils or animal fats and alcohol to produce esters and glycerol by using both bases and acids (homogeneous catalyst and heterogeneous catalyst). A homogeneous catalyst

facilitates a fast reaction and high conversion efficiency, but the related saponification always requires a separation stage and releases an amount of waste water (Chopade and Sharma, 1997). A heterogeneous catalyst was the focus of the current study because no separation step is required and a high level of biodiesel purity is produced.

Biodiesel production was studied using four continuous processes under the general categories of the alkali-catalyzed process and the acid-catalyzed process using virgin vegetable oil and waste cooking oil as raw material. The biodiesel process of Zhang *et al.* (2003) can be divided into the transesterification reaction, methanol recovery and separation. In addition, a

washing process would be required if the process used a homogeneous catalyst. The main advantage of using biodiesel is that it is biodegradable, can be used without modifying existing engines and it produces less harmful gas emissions such as sulfur oxide (Knothe *et al.*, 2005; Pahl, 2005). Low operating costs and short downtimes play an important role in successful companies. The simulation of biodiesel consists of many unit operations. Multi-function operations such as reactive distillation will reduce the costs and complexity and thus, may become a more popular alternative. Metal oxides have been used with reactive distillation in experimental work to validate simulation predictions (Kiss *et al.*, 2006, 2008). Heterogeneous catalysis has also influenced the design of the process (Dimian *et al.*, 2010). Therefore, reactive distillation acts as an intensification approach not only to improve the performance but also to reduce the number of units of operation.

This work studied the simulation of conventional and reactive distillation of biodiesel production. The production mainly used homogeneous and heterogeneous transesterification of palm oil.

METHODOLOGY

The simulation procedures involved a selection of chemical components and related details, thermodynamic properties, plant capacity

and suitable units of operation, and sufficient input conditions (flow rate, temperature, pressure and other conditions). Many components such as methanol and glycerol were available from the library of the simulator. Tripalmitic, trioleic and trilinoleic acids are the major components of palm oil while methyl palmitate, methyl oleate and methyl linoleate are the major ones for biodiesel. All of these structures cannot be obtained directly from the library. Therefore, unavailable components such as the mono, di, tri and methyl esters of palmitic, oleic and linoleic acid needed to be simulated using a GaussViewW molecular dynamic simulator (Luyben, 2002). The proposed structures can be optimized by the subprogram GAUSSIAN 03W and are then imported to a separate software package (ASPEN PLUS; to provide the simulation data (Erickson and Hendrick, 1999). Because the methanol and glycerol are highly polar components, a nonrandom, two-liquid (NRTL) thermodynamic/activity model was used to predict the activity coefficients of the components in the liquid phase. The biodiesel simulation was performed based on transesterification from SrO (heterogeneous) and NaOH (homogeneous) catalysts under conventional and reactive distillations. The transesterification reaction with NaOH and SrO as catalysts was studied by Noureddi and Zhu (1997) and Petchtabtim (2005) as shown in Tables 1 and 2, respectively.

Table 1 Energy of activation and reaction rate constant at 50 °C using NaOH (Noureddi and Zhu, 1997).

Reaction	k	Energy of activation (kcal.mol ⁻¹)
TG → DG	4.80×10^7	13.15
DG → TG	5.81×10^5	9.93
DG → MG	2.70×10^{11}	19.86
MG → DG	9.98×10^9	14.64
MG → GL	5.38×10^7	6.42
GL → MG	2.17×10^4	9.59

TG = Triglyceride, DG = Diglyceride, MG = Monoglyceride, GL = Glycerol.

k = Reaction rate constant.

Table 2 Energy of activation and reaction rate constant at 65 °C using SrO (Petchtabtim 2005).

Reaction	k	Energy of activation (kcal.mol ⁻¹)
TG → DG	22.46×10^{10}	16.80
DG → MG	1.79×10^5	7.97
MG → GL	1.13×10^{34}	59.79

TG = Triglyceride, DG = Diglyceride, MG = Monoglyceride, GL = Glycerol.

k = Reaction rate constant.

The reactive distillation used the equilibrium model (Kotora *et al.*, 2005).

RESULTS AND DISCUSSION

Process design

The approach used identified two process simulations in biodiesel production—the conventional and the reactive distillation process. The production by transesterification focuses on the use of a heterogeneous catalyst and a homogeneous catalyst as the product cost of the catalyst is cheap and there is a high rate of conversion. Four continuous processes were simulated. The first and second cases were based on a homogeneous catalyst (NaOH) with conventional and reactive distillation, while the third and fourth cases used a heterogeneous catalyst with conventional and reactive distillation. The transesterification reaction occurred in the first step and the resultant product was then sent to a distillation column to recover the methanol. After that, the bottom products were sent for glycerol separation. Finally, purification by washing with water was performed for the process based on the homogeneous catalyst.

Conventional distillation with homogeneous catalyst

This study was based on the conventional distillation of the homogeneous catalyst recalculated from Zhang *et al.* (2003) and in Figure 1a. There were four feed streams to the process: oil at 1000 kg.h⁻¹, fresh methanol at 120 kg.h⁻¹, sodium hydroxyl at 12 kg.h⁻¹ and water at 900 kg.h⁻¹, which were all at room temperature (25 °C)

except for the fresh water stream (50 °C). The oil, methanol and sodium hydroxyl were pre-heated to 60 °C using a heat exchanger before entering the reaction unit. The rigorous continuous stirred tank reactor model was used as the reaction unit. The reaction was carried out isothermally in the reactor at 1×10^5 Pa and 60 °C within the liquid phase. The effluent from the reactor was sent to the rigorous fractionation model (RadFrac) to recover the excess methanol. The appropriate configuration for fraction unit was 10, and the feed stage was recovery methanol at 28.61 kg.h⁻¹. The bottom product was sent for separation using two decanter models. Glycerol was removed in the first decanter. As sodium hydroxide is more miscible in water than in biodiesel, pure water was mixed into the contaminated biodiesel from the first decanter to remove the sodium hydroxide and then it was sent to the second decanter. The first and the second decanters operated at 50 and 90 °C, respectively. The oil conversion was 99.62% at 99.45% purity of biodiesel.

Reactive distillation with homogeneous catalyst

The reactive distillation process with the homogeneous catalyst of palm oil is shown in Figure 1b. The oil and methanol flow rate were fed at 1,000 kg.h⁻¹ to the eighth tray and at 120 kg.h⁻¹ to the fourth tray. The reactive distillation had 10 stages. The molar reflux ratio was 1 and the boil-up ratio was 0.6 with the pressure column set at 1×10^5 P. The effluent from the bottom reactive distillation comprised methyl ester (1,004.81 kg.h⁻¹), methanol (40.96 kg.h⁻¹), glycerol (114.05 kg.h⁻¹) and sodium hydroxide (12 kg.h⁻¹). These

effluents were sent to the first decanter to separate the glycerol (106.79 kg.h^{-1}) from the methyl ester and other effluents. Then, the methyl ester and other effluents were sent to the washing phase to remove the alkaline catalyst. After washing with water, the purity of the biodiesel was up to 99.87%.

Conventional distillation with heterogeneous catalyst

The conventional distillation process with the heterogeneous catalyst of palm oil is shown in Figure 1c. The flow rate of the oil and methanol were 1,000 and 120 kg.h^{-1} , respectively, at room temperature (25°C). The flow rate of the oil and methanol were heated up to 65°C using a heat exchanger before they were sent to the reaction unit. The reaction unit used the plug flow reactor model with a constant coolant temperature for the presentation of the strontium oxide. The reaction occurred isothermally in the reactor at $1 \times 10^5 \text{ Pa}$ and 65°C . The effluent from the reactor was sent to RadFrac model to recover the excess methanol. The configuration results involved 10 stages with the fifth feed stage where methanol was recovered at 12 kg.h^{-1} . Next, the bottom product went to the separation unit consisting of one decanter model operating at 45°C to separate the glycerol and biodiesel. The oil conversion was 95.90% with a biodiesel purity of 99.64%.

Reactive distillation with heterogeneous catalyst

The reactive distillation process with the heterogeneous catalyst of palm oil is shown in Figure 1d. The reactive distillation involved heterogeneous packs of strontium oxide from the fourth until the eighth stage. This column had 10 stages with a mass fraction reflux ratio of 1, a distillation rate of 21 kg.h^{-1} and a pressure column of $1 \times 10^5 \text{ P}$. The effluent from the bottom was composed of methyl ester ($1,003.57 \text{ kg.h}^{-1}$), methanol (2.08 kg.h^{-1}) and glycerol (108.43 kg.h^{-1}). These effluents were sent to the decanter

to separate the glycerol (108.2 kg.h^{-1}) from the methyl ester ($1,003.36 \text{ kg.h}^{-1}$). The purity of the biodiesel was 99.52% and the oil conversion rate was 99.88%.

The comparison between the homogeneous and heterogeneous catalysts in the reactive distillation processes showed that the heterogeneous reactive distillation could regenerate catalysts more easily than the homogeneous reactive distillation. The homogeneous process needed additional water to wash the alkaline catalyst. The temperature profile of the homogeneous reaction increased slightly and methyl ester was generated as shown in Figure 2 as the temperature profile of the homogeneous reaction increased from the fourth to the fifth stage at 70°C and methyl ester was generated from the fourth to the fifth stage and thereafter the generation of methyl ester decreased. The temperature profile of the heterogeneous reaction increased from the first stage to the third stage where it reached 280°C , then after the third stage, the temperature profile decreased as shown in Figure 3.

The rate of conversion of the homogeneous reactive distillation was lower than the others because a plug flow reactor was used and the resident time was short. On the other hand, the column in the conventional case could purify the biodiesel up to 99.64%. The main streams of all processes are shown in Tables A1–A4 in the Appendix.

Preliminary process design

The Aspen Icarus process evaluation software (ASPEN ICARUS version 2006.5), was used to design the equipment for the biodiesel plant. Table 3 illustrates the production costs including the total project capital cost, total operating cost and total utilities cost. The desired annual rate of return was 20%. The cost production of conventional homogeneous process (total project capital cost, total operating cost and total utilities cost) was the highest; therefore, the

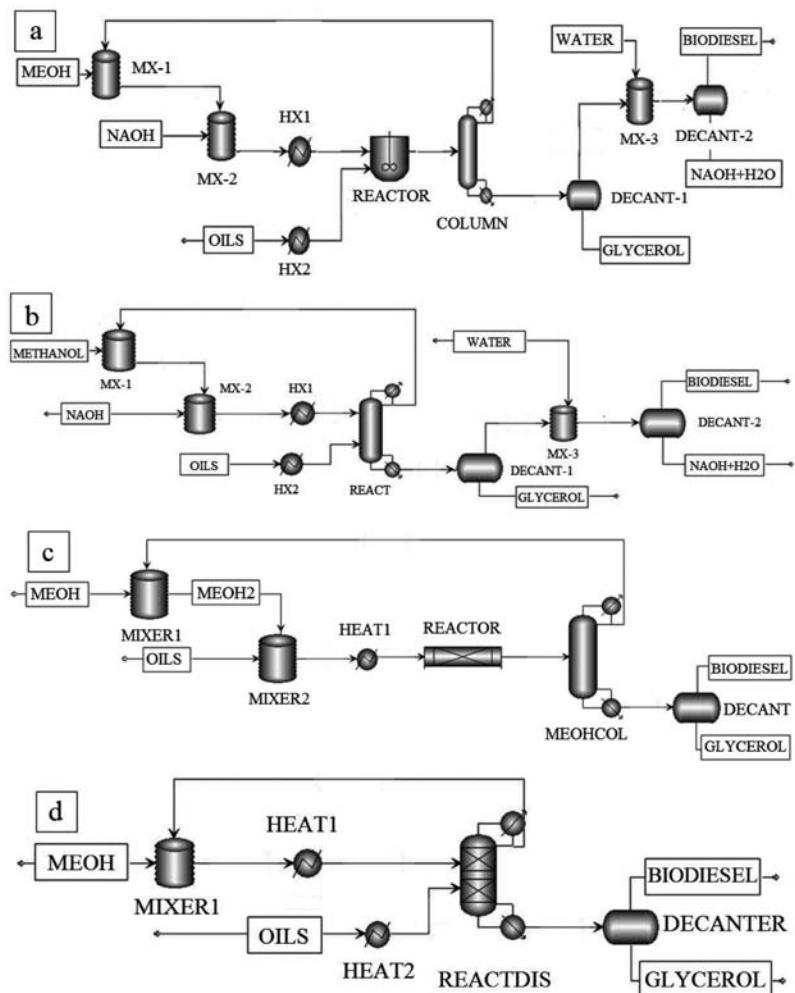


Figure 1 Process flow diagram of biodiesel production: (a) Conventional distillation with homogeneous catalyst; (b) Reactive distillation with homogeneous catalyst; (c) Conventional distillation with heterogeneous catalyst; (d) Reactive distillation with heterogeneous catalyst.

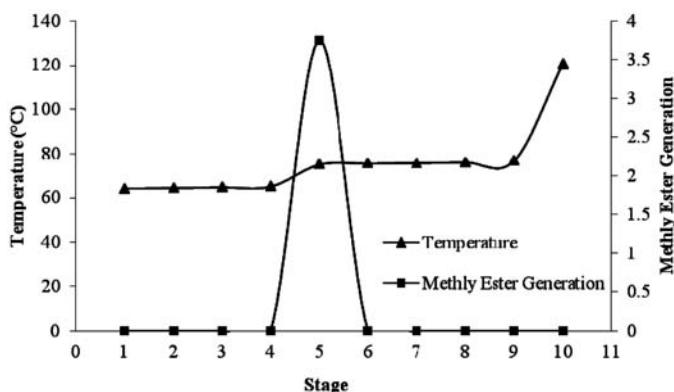


Figure 2 Temperature profile and methyl ester generation during the homogeneous reaction.

cost of biodiesel production per liter from the conventional homogeneous process was higher than the other processes.

The four processes utilized important equipment: continuous stirred tank reactor, plug flow reactor, distillation column, decanter, reactive distillation for homogeneous processing and packed reactive distillation. The Aspen Icarus design specifications for the column,

condenser and reboiler for each process are shown in Tables 4, 5 and 6, respectively. The design columns for the homogeneous (conventional) and heterogeneous (reactive) cases have almost the same configuration (tray type, number of trays, vessel diameter, vessel tangent to tangent height, design gauge pressure, tray spacing, tray thickness, base material thickness, and total weight). The design temperature in the heterogeneous reactive

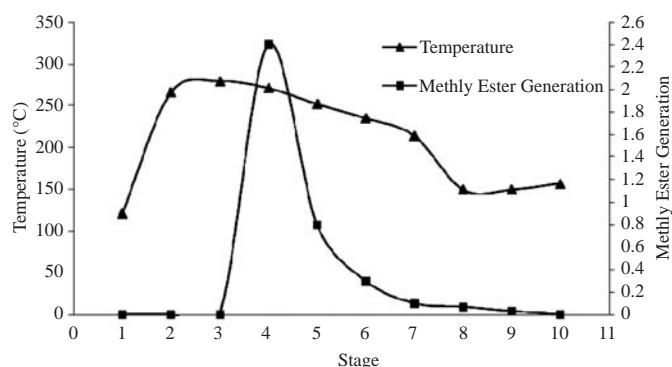


Figure 3 Temperature profile and methyl ester generation during heterogeneous reaction.

Table 3 Comparison of production costs using different processes.

	Conventional homogeneous	Conventional heterogeneous	Reactive homogeneous	Reactive heterogeneous
Total project capital cost (USD million)	3.791	2.712	2.848	2.467
Total annual operating cost (USD million)	1.270	0.8989	0.9020	0.8844
Energy consumption of reactor	–	0.1014	–	–
Water washing	0.02694	–	0.02694	–
Total annual utilities cost (USD thousand)	91.02	54.11	54.99	39.27
Desired annual rate of return (%)	20	20	20	20
Feedstock cost per liter (USD)	0.535	0.535	0.535	0.535
Biodiesel annual production (millions of liters)	10.07	10.13	10.05	10.13
Cost of biodiesel production per liter (USD)	0.6702	0.6291	0.6302	0.6262

case was higher than in the other processes, while in the homogeneous conventional case, the lowest temperature could be maintained. The base material thickness in the homogeneous reactive case was the lowest but total weight was the highest.

From Table 6, the heat transfer area, shell design gauge pressure, shell length, tube design gauge pressure, tube design temperature, tube outside diameter, tube length extended and total weight in all cases were equal. The shell design

temperature and the total weight of heterogeneous conventional were higher than for other process. The shell diameter of heterogeneous reactive was lower than for the other processes.

Table 7 shows the design decanter specifications of the conventional processes using different catalysts. The homogeneous process had two decanters, while the heterogeneous had only one. The liquid volume, vessel diameter, vessel tangent to tangent length and the total weight in both cases were the same.

Table 4 Column detail design using different processes.

	Homogeneous		Heterogeneous	
	Reactive	Conventional	Reactive	Conventional
Tray type	Sieve	Sieve	Sieve	Sieve
Number of trays	13	12	12	12
Vessel diameter (m)	0.610	0.457	0.457	0.457
Vessel tangent to tangent height (m)	11.58	10.97	10.97	10.97
Design temperature (°C)	148.8	142.0	307.1	185.4
Design gauge pressure (Pa)	2.434×10^5	2.434×10^5	2.434×10^5	2.434×10^5
Tray spacing (m)	0.610	0.610	0.610	0.610
Tray thickness (mm)	4.762	4.762	4.762	4.762
Base material thickness (mm)	7.937	9.525	9.525	9.525
Total weight (t)	2.994	2.132	2.132	2.132

Table 5 Condenser detail design using different processes.

	Homogeneous		Heterogeneous	
	Reactive	Conventional	Reactive	Conventional
Liquid volume (L)	1802	1802	1802	1802
Vessel diameter (m)	0.914	0.914	0.914	0.914
Vessel tangent to tangent length (m)	2.743	2.743	2.743	2.743
Design temperature (°C)	148.1	121.1	148.1	121.1
Design gauge pressure (Pa)	0.972×10^5	0.972×10^5	0.972×10^5	0.972×10^5
Vacuum design gauge pressure (Pa)	-1.013×10^5	-1.013×10^5	-1.013×10^5	-1.013×10^5
Base material thickness (mm)	7.937	7.937	7.937	7.937
Total weight (t)	1.225	1.225	1.225	1.225

Table 6 Reboiler detail design using different processes.

	Homogeneous		Heterogeneous	
	Reactive	Conventional	Reactive	Conventional
Heat transfer area (m ²)	1.951	1.951	1.951	1.951
Shell design gauge pressure (Pa)	4.732×10 ⁵	4.732×10 ⁵	4.732×10 ⁵	4.732×10 ⁵
Shell design temperature (°C)	148.8	142.0	184.3	185.4
Shell diameter (m)	0.229	0.152	0.102	0.229
Shell length (m)	3.962	3.962	3.962	3.962
Tube port diameter (m)	0.152	0.102	0.076	0.152
Tube design gauge pressure (Pa)	7.605×10 ⁵	7.605×10 ⁵	7.605×10 ⁵	7.605×10 ⁵
Tube design temperature (°C)	192.1	192.1	192.1	192.1
Tube outside diameter (mm)	25.40	25.40	25.40	25.40
Tube length extended (m)	6.096	6.096	6.096	6.096
Total weight (kg)	417.3	290.3	176.9	453.6

Table 7 Decanter detail design using different processes.

	Homogeneous		Heterogeneous
	Decanter 1	Decanter 2	Decanter
Liquid volume (L)	2402	2402	2402
Vessel diameter (m)	0.914	0.914	0.914
Vessel tangent to tangent length (m)	3.658	3.658	3.658
Total weight (t)	1.179	1.179	1.179

Every configuration needed the same design of condenser, but each with a different design temperature with that for the conventional case being the lowest because there was no reaction in the columns.

CONCLUSION

The simulation and design of biodiesel production was studied under two scenarios using conventional and reactive distillation. These biodiesel processes were based on a transesterification reaction which needed a catalyst to reduce the activation energy. This work focused on two types of catalyst—sodium hydroxide (NaOH) for the homogeneous reaction and strontium oxide (SrO) for the heterogeneous reaction.

The GaussViewW molecular simulator was used to formulate and optimize the structure of tri-di-mono palmitate, tri-di mono olein and tri-di-mono linooleate. The molecular structure was created and imported to estimate the necessary parameters using the Aspen Plus software. The selected thermodynamic property was non-random two-liquid. The purity of the biodiesel from conventional processing with NaOH was 99.45% and with SrO was 95.21%, although the conventional processing with NaOH needed more water in the washing process. The reactive distillation with SrO gave a biodiesel purity of 99.52% while with NaOH, the purity was 99.87%. Reactive distillation could enhance the productivity more than conventional distillation. The Aspen Icarus process evaluation software was used to design the major equipment in the

systems studied. The total annual operating costs of the conventional process with two different catalysts were approximately USD 1,270,000 and 900,000, respectively. The total annual operating costs of the reactive distillation process with the two different catalysts were around USD 900,000 and 880,000.

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LITERATURE CITED

Chopade, S.P. and M.M. Sharma. 1997. Reaction of ethanol and formaldehyde: Use of versatile cation-exchange resins as catalyst in batch reactors and reactive distillation columns. **Reactive & Functional Polymers** 32: 53–64.

Demirbas, A. 2002. Biodiesel fuels from vegetable oils via catalytic and non-catalytic supercritical alcohol transesterifications and other methods: A survey. **Energy Conversion & Management** 44: 2093–2109.

Dimian, A.C., Z.W. Srokol, M.C. Mittelmeijer and G. Rothenberg. 2010. Interrelation of chemistry and process design in biodiesel manufacturing by heterogeneous catalysis. **Top. Catal.** 53: 1197–1201.

Erickson, K.T. and J.L. Hedrick. 1999. **Plantwide Process Control**. Wiley. New York, NY, USA.

Kiss, A.A., A.C. Dimian and G. Rothenberg. 2008. Biodiesel by catalytic reactive distillation powered by metal oxides. **Energy Fuels** 22: 598–604.

Kiss, A.A., F. Omota, A.C. Dimian and G. Rothenberg. 2006. The heterogeneous advantage: Biodiesel by catalytic reactive distillation. **Top. Catal.** 40: 141–150.

Knothe, G., J.H. Van Gerpen and J. Krah. 2005. **The Biodiesel Handbook**. AOCS Press. Champaign, IL, USA. 516 pp.

Kotora, M., Z. Svandova, J. Markos and L. Jelemensky. 2005. Modelling of reactive distillation propylene oxide production. **Petroleum & Coal** 47: 26–8.

Luyben, W. L. 2002. **Plantwide Dynamic Simulators in Chemical Processing and Control**. Marcel Dekker Inc. New York, NY, USA.

Marchetti, J.M., V.U. Miguel and A.F. Errazu. 2007. Possible methods for biodiesel production. **Renewable Energy** 11: 1300–1311.

Noureddini, H. and D. Zhu. 1997. Kinetics of transesterification of soybean oil. **JAOCS**. 74: 1457–1463.

Pahl G. 2005. **Biodiesel: Growing a New Energy Economy**. Chelsea Green Publishers. White River Junction, VT, USA. 368 pp.

Petchtabtim, K. 2005. **Study of Kinetic Rate of Heterogeneous Catalysts for Biodiesel Production**. MSc. Thesis. Kasetsart University. Bangkok, Thailand.

Van Gerpen, J.H. 2005. Biodiesel processing and production, **Fuel Processing Tech.** 86: 1097–1107.

Zhang, Y., M.A. Dub, D.D. McLean and M. Kates. 2003. Biodiesel production from waste cooking oil: 1. Process design and technological assessment. **Bioresource Technology** 89: 1–16.

APPENDIX

Table A1 Main stream of conventional distillation process with homogeneous catalyst.

Mass flow (kg.h ⁻¹)	MEOH	MEOHRE	NAOH	OILS	REACT 1	REACT 2	COLUMN	DECANT 1	WATER	DECANT 2	GLYCERROL	BIODIE	NAOH+H2O
TRIOLEIN	0	0.989	0	413.9	0.989	413.9	2.108	1.119	0	1.117	0.002	1.102	0.015
METHANOL	130	23.39	0	0	153.4	0	40.42	17.04	0	6.637	10.4	0.486	6.151
NAOH	0	0	12	0	12	0	12	12	0	1.754	10.25	0.023	1.731
MET-OLE	0	0	0	0	0	0	413.9	413.9	0	413.3	0.594	413.1	0.157
GLYCEROL	0	0	0	0	0	0	108.1	108.1	0	1.374	106.8	2E-04	1.374
WATER	0	0	0	0	0	0	0	0	900	900	0	0.073	899.9
H2SO4	0	0	0	0	0	0	0	0	0	0	0	0	0
NA2SO4	0	0	0	0	0	0	0	0	0	0	0	0	0
DI-OLEIN	0	0	0	0	0	0	0.795	0.795	0	0.006	0.789	0.004	0.002
MONO-OLE	0	0	0	0	0	0	0.002	0.002	0	0	0.002	0	0
TRI-PALM	0	0.581	0	473.8	0.581	473.8	3.228	2.648	0	2.644	0.003	2.641	0.003
DI-PALM	0	0	0	0	0	0	0.997	0.997	0	0.908	0.089	0.908	0
MONOPALM	0	0	0	0	0	0	0.002	0.002	0	4E-04	0.001	4E-04	0
MET-PALM	0	0	0	0	0	0	472.6	472.6	0	471.6	0.924	471.2	0.414
TRILINO	0	0.047	0	112.3	0.047	112.3	0.148	0.102	0	0.101	2E-04	0.1	0.002
DILINO	0	0	0	0	0	0	0.158	0.158	0	0.136	0.021	0.136	0
MONOLINO	0	0	0	0	0	0	4 × 10 ⁴	4E-04	0	1E-04	3E-04	1E-04	0
METLINO	0	0	0	0	0	0	112.6	112.6	0	112.4	0.176	112.3	0.048
Temperature (°C)	25	78.38	25	25	60	60	60.46	113.2	27	42.59	50.25	320.4	320.1
Pressure (Pa)	3×10 ⁵	1×10 ⁵	3×10 ⁵	3.7×10 ⁵	1×10 ⁵	1×10 ⁵	1.024×10 ⁵	1×10 ⁵	3×10 ⁵	1×10 ⁵	1×10 ⁵	1×10 ⁵	1×10 ⁵

Table A2 Main stream of reactive distillation process with homogeneous catalyst.

Mass flow (kg.h ⁻¹)	MEOH	MEOH RE	NAOH	OIL	REACT 1	REACT 2	DECANT 1	WATER	DECANT 2	GLYCERROL	BIODIE	NAOH+H2O
TRIOLEIN	0	0	0	466.3	0	466.3	0.024	0	0.022	0.001	0.009	0.014
METHANOL	130	148.9	0	0	278.9	0	15.85	0	8.347	7.504	0.511	7.836
NAOH	0	0	12	0	12	0	12	0	8.895	3.105	0.589	8.306
MET-OLE	0	0	0	0	0	0	468.4	0	466	2.337	465.9	0.166
GLYCEROL	0	0	0	0	0	0	109.4	0	4.612	104.7	5E-04	4.611
WATER	0	0	0	0	0	0	0	900	900	0	0.064	899.9
H2SO4	0	0	0	0	0	0	0	0	0	0	0	0
NA2SO4	0	0	0	0	0	0	0	0	0	0	0	0
DI-OLEIN	0	0	0	0	0	0	0.034	0	0.033	9E-04	0.032	4E-04
MONO-OLE	0	0	0	0	0	0	7 × 10 ⁴	0	7E-04	0	7E-04	0
TRIPALM	0	0.007	0	533.7	0.007	533.7	0.028	0	0.028	5E-04	0.015	0.012
DIPALM	0	0	0	0	0	0	0.048	0	0.048	7E-04	0.048	0
MONOPALM	0	0	0	0	0	0	8E-04	0	5E-04	3E-04	5E-04	0
METPALM	0	0	0	0	0	0	536.3	0	533.8	2.472	533.5	0.308
Temperature (°C)	25	64.46	25	25	60	60	121.4	25	33.11	27.26	240.4	240.2
Pressure (Pa)	3×10 ⁵	1×10 ⁵	3×10 ⁵	3.75×10 ⁵	1.048×10 ⁵	1.05×10 ⁵	1×10 ⁵	3×10 ⁵	1×10 ⁵	1×10 ⁵	1×10 ⁵	1×10 ⁵

Table A3 Main stream of conventional distillation process with heterogeneous catalyst.

Mass flow (kg.h ⁻¹)	MEOH	MEOHRE	OILS	REACT	COLUMN	DECANT	DIODIE	GLYCERROL
TRI-PALM	0	0	451.2	451.2	0	0	0	0
DI-PALM	0	0	0	0	0	0	0	0
MONOPALM	0	0	0	0	5 × 10 ⁴	5E-04	0	0
MET-PALM	0	0	0	0	453.5	453.5	453.3	0
TRI-OLE	0	0	432.3	432.3	0	0	0	0
DI-OLE	0	0	0	0	0	0	0	0
MONO-OLE	0	0	0	0	5E-04	5E-04	4E-04	0
MET-OLE	0	0	0	0	434.3	434.3	434.2	0.076
TRI-LINO	0	0	116.5	116.5	0	0	0	0
DI-LINO	0	0	0	0	0	0	0	0
MONOLINO	0	0	0	0	1E-04	1E-04	1E-04	0
MET-LINO	0	0	0	0	117	117	117	0.02
MEOH	120	10	0	130	16.61	6.611	3.288	3.324
GLYCEROL	0	0	0	0	108.6	108.6	0	108.4
Temperature (°C)	25	64.46	25	65	65.6	158	45.49	45.25
Pressure (Pa)	3×10 ⁵	1×10 ⁵	3×10 ⁵	0.32×10 ⁵	1.036×10 ⁵	1×10 ⁵	1×10 ⁵	1×10 ⁵

Table A4 Main stream of reactive distillation process with heterogeneous catalyst.

Mass flow (kg.h ⁻¹)	MEOH	MEOHRE	OILS	REACT 1	REACT 2	DECANT	BIODIE	GLYCEROL
TRI-PALM	0	0.013	451.2	0.013	451.2	2×10^4	2E-04	0
DI-PALM	0	0.061	0	0.061	0	1.25	1.25	0
MONOPALM	0	0	0	0	0	0.001	0.001	3E-04
MET-PALM	0	5.045	0	5.045	0	452.3	452.2	0.117
TRI-OLE	0	0.017	432.3	0.017	432.3	2E-04	2E-04	0
DI-OLE	0	0.002	0	0.002	0	7E-04	7E-04	0
MONOOLE	0	0	0	0	0	0	0	0
MET-OLE	0	2.519	0	2.519	0	434.3	434.2	0.064
TRI-LINO	0	0.004	116.5	0.004	116.5	0	0	0
DI-LINO	0	2E-04	0	2E-04	0	1E-04	1E-04	0
MONOLINO	0	0	0	0	0	0	0	0
MET-LINO	0	0.61	0	0.61	0	117	117	0.018
MEOH	120	2.085	0	122.1	0	6.752	3.315	3.437
GLYCEROL	0	10.64	0	10.64	0	108.4	0.227	108.2
Temperature (°C)	25	120.7	25	65	65	156.9	30.07	30.03
Pressure (Pa)	3×10^5	1×10^5	3×10^5	1.65×10^5	1.3×10^5	2×10^5	1×10^5	1×10^5