Journal of Chemical Technology and Metallurgy, 49, 5, 2014, 479-486

SIMULATION OF BIODIESEL PRODUCTION BY TRANSESTERIFICATION OF VEGETABLE OILS

Chavdar Chilev, Evgeni Simeonov

University of Chemical Technology and Metallurgy
8 Kl. Ohridski, 1756 Sofia, Bulgaria
E-mail: chavdar_chilev@uctm.edu

Received 10 October 2013
Accepted 04 July 2014

ABSTRACT

This work presents an ChemCAD 6.0 Simulation study for biodiesel production. The simulation illustrates the production of biofuel from pure vegetable oil with an alkaline catalyst. The main areas are transesterification, methanol separation, water washing, FAME purification, catalyst neutralization and glycerol purification. The equipment used includes in particular reactors, distillation and extraction columns and components splitters. As a result of the simulation, the two final target products - biodiesel and glycerol, are obtained with purity 98 % and 99 %, respectively. The suggested technological scheme provides a possibility for recuperation of the heat streams.

Keywords: biodiesel, simulation, ChemCAD 6.0, alkaline catalyst.

INTRODUCTION

Recently, there has been an increase in the use of raw materials and energy. On one hand, the annual increase in the use of diesel leads to a continuous rise in its price but on the other hand, the world faces the threatening problem of exhausting the already limited reserves of fuel. This stimulates science to develop methods and equipment for receiving ecologically clean fuels, produced by renewable resources the so called biofuels. In the first place, it is the replacement of part of the diesel fuels with biodiesel, received by vegetable and animal oils. The use of biodiesel has another strength - the reduction of toxic elements disposal in the atmosphere, hence, a considerable improvement in the social environment for people.he process of manufacturing of biodiesel is well- known. It is carried out as a base catalyzed oil transesterification with low-valent alcohol. For obtaining biodiesel the following raw materials are used: vegetable oil such as sunflower, soya, palm, rape seed, as well as animal fats, as a low-valent alcohol - methanol and as a catalyst - potassium or sodium alkali.

The reaction for receiving biodiesel can be carried out with the help of different catalysts. On industrial scale only chemically homogeneous catalysts have been used so far [1 - 3]. The base-catalyzed reaction is most often used because: it uses low temperature (60^{o}C) and pressure (≈ 1,4 Bar) processing; it achieves high conversion (up to 98 %) with minimum side reactions and low reaction time; conversion to methyl ester is direct with no intermediate steps.

As a result of the production process of biodiesel two products are obtained: biodiesel (methyl ester) and glycerol. The main task is to remove the excess methanol. To meet standards 0.02 % methanol is allowed in the final product [4]. Residual methanol is extremely harmful for the environment, for the health, for the car engines and for the fuel storage [5].

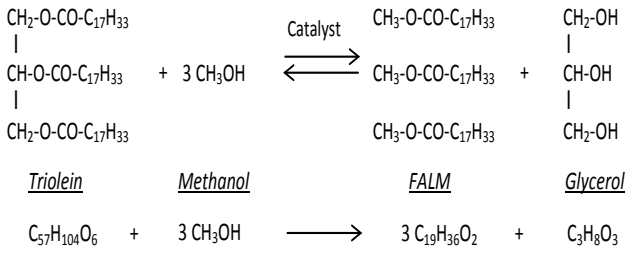
This work illustrates the production of biofuel from pure vegetable oil with an alkaline catalyst. The process

involves a transesterification reaction that requires using an alcohol (usually methanol) and allows producing biofuel and glycerol from oil. It uses mainly simple reactors (for transesterification and catalyst neutralization), scrubbers and splitters to separate heavy components from light ones, and distillation columns to separate products and to purify the biofuel.

Process description

In our case pure vegetable oil as raw material is used. The main constituents of pure vegetable oils are the triglycerides with different chain of its structure. Biofuel can be produced from different type of vegetable oils. The used plant materials determine the type of vegetable oils. There are vegetable oils produced from colza, rapeseed, soya, etc. Taking into consideration its extensive industrial use, in this paper the rapeseed was selected. According to data in the literature the rapeseed contains mainly triolein. This is triglyceride with the same chain ($C_{17}H_{33}$) in its structure.

Biodiesel is produced through a chemical reaction known as transesterification. In transesterification - vegetable oil (triolein) reacts with a primary alcohol (usually methanol) to give basically two products: Fatty Acid Methyl Esters FALM - methyl oleate (biodiesel) and glycerol. When the triglycerides react with alcohol (usually methanol), the three fat acid strings come apart from the glycerol skeleton to settle down on the alcohol, thus producing an oil ester (the biofuel for instance, hereafter noted FAME: Fatty Acid Methyl Esters). Transesterification reaction of triolein can be represented as follows:



The reaction of transesterification is a reversible process. This process proceeds appreciably only by the addition of catalysts. The reaction can be carried out by various forms of catalysts [1], but so far industrially only chemical homogenous catalysts are used on a large scale. The base-catalyzed reaction [1, 4] is most often used because: it uses low temperature (60°C) and pressure (≈ 1,4 Bar) processing; it achieves high conversion (up to 98 %) with minimum side reactions and low reaction time; conversion to methyl ester is direct with no intermediate steps. As a catalyst in our case we use sodium hydroxide.

The process involves reactors, distillation columns, extraction columns, components splitters, heat exchangers and centrifugal pumps. The process flow sheet is given in Fig. 1.

Methanol and sodium hydroxide feed streams are mixed in a mixer (1) and after that their pressure is brought to 400 kPa by a centrifugal pump (4). The pressure of oil feed (stream 1), the methanol recycle stream (40) and the oil recycle stream (26) are also brought to 400 kPa by centrifugal pumps (3, 4 and 5). Five streams are mixed in a mixer (2) and heated to 60°C by a cooler/heater (6). In this heat exchanger these five streams exchange heat with the hot stream of purified biodiesel. Thus, it helps to recuperate the energy of the finished biodiesel. After that the stream 24 constitutes the feed of the transesterification reactor (12).

For modeling the basic reaction of transesterification, the equilibrium type of reactor was chosen. Stoichiometric reactor model is used in ChemCAD simulation when the detail kinetic information of a chemical reaction is not available. Different studies have reported 95 - 98 % conversion for base catalyzed transesterification [6, 7]. In our case 98 % conversion was selected. For explicit the thermodynamic of the system, the Dortmund modified version of UNIFAC model was selected [8 - 10].

After the transesterification, the mixture is brought in a distillation column with total condenser (7), from stream (11) in order to separate the methanol from other components. To increase the inlet feed temperature in distillation column (from 60°C (11) to 95°C (15)) a preheater is used between the reactor and distillation column. The LNG heat exchanger is used to simulate the exchange of heat between multiple hot and cold streams. In our case the total number of hot and cold input streams is tree. The output temperature and heat duty of each stream are calculated. The internal configuration of the exchanger is not considered; therefore, no rating case option is provided. Temperature crossover or the pinch conditions are checked at the outlet conditions. Thus, cold streams 11 and 14 are heated by the hot stream 38

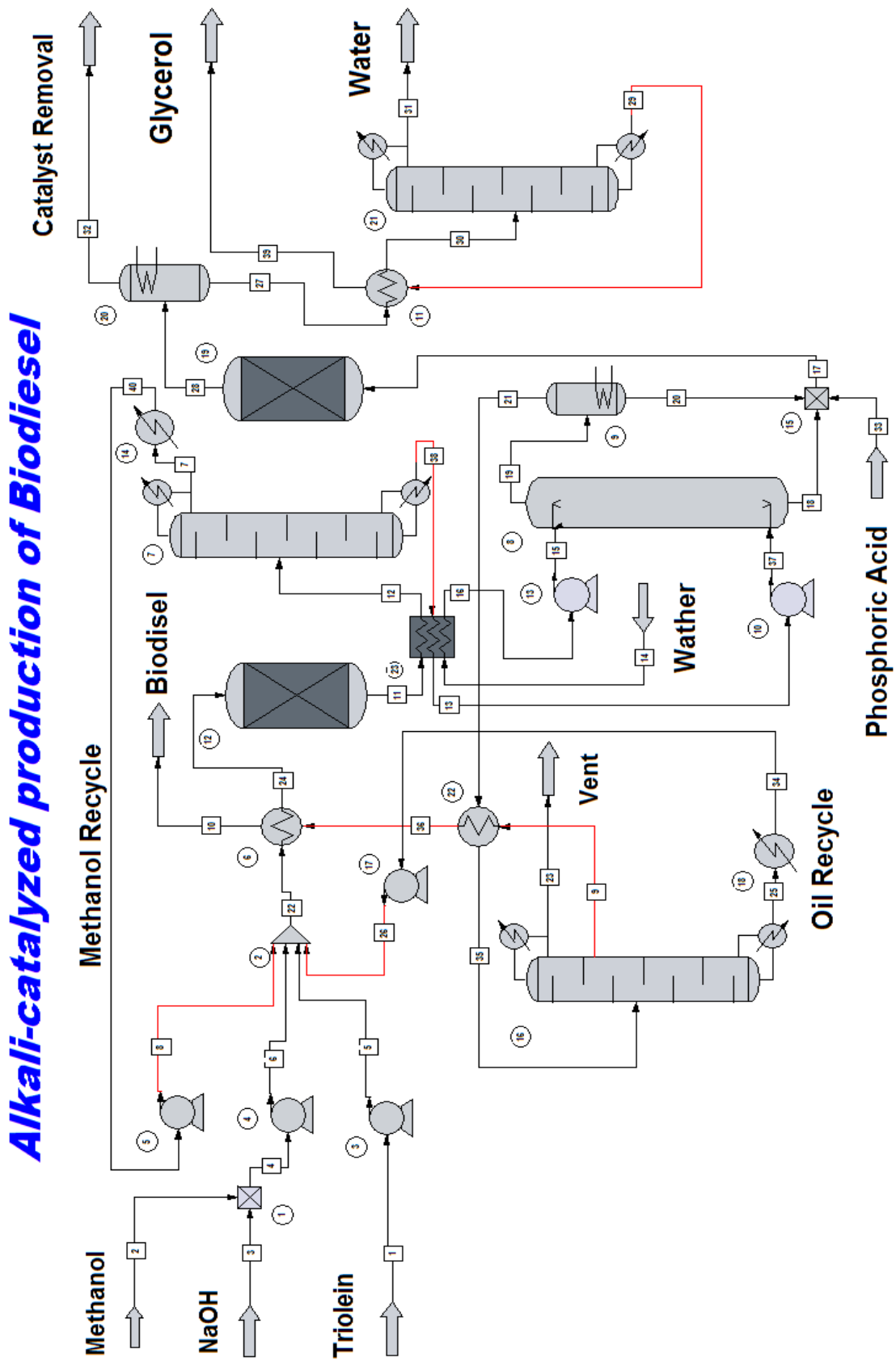


Fig.1. The process flow sheet developed in ChemCAD 6.3.1.

and hot stream 38 is cooled by the streams 11 and 14.

After distillation the distillate containing almost pure methanol is cooled by heat exchanger 14 to 10°C in other to eliminate the vapor fraction (it is necessary for the normal operation of the pump 5). Thus, the stream 40 (it contents only liquid fraction) is recycled at the reactor inlet (stream 24). The residue of the column 7 (stream 38) is cooled to 60°C by LNG heat exchanger (23) and brought to 110 kPa by a centrifugal pump (10).

It is then washed by water in an extraction column (8 from stream 37). The washing separates the biofuel from methanol, glycerol and catalyst. The overhead flow (stream 19) is sent to a gravity splitter (modeled by a component separator 9) that allows recovering NaOH at the bottom (stream 20) from the FAME, oil and a fraction of water and methanol at the head (stream 21).

The FAME, oil, water and methanol recovery ratios in the organic phase of the splitter 9 are preheated by heat exchanger 22 (exchange heat with the hot stream of biodiesel 9) and then separated by a distillation column with partial condenser (16). This additional separation is required to obtain a biofuel purity that meets the ASTM specifications and that has to exceed 99.77 %. The partial condenser facilitates the FAME and water-methanol separation (at the top of the column). It should be noted that vacuum operating conditions are required in order to keep the temperature low enough to avoid the biofuel degradation. The bottom product (25) of distillation column 16 is unreacted oil with purity of 99 % mass. This stream is cooled to 60°C by heat exchanger 18 and formed the oil recycle stream (34 and 26).

The bottom streams (18) of the extraction column (8), the components splitter's (9) bottom streams (20) and the pure phosphoric acid (stream 33) are mixed and then sent to a reactor in order to neutralize NaOH. The following reaction takes place (sodium hydroxide neutralization by phosphoric acid):

As neutralizing agent a phosphoric acid was chosen because the product of reaction Na_3PO_4 can be used as fertilizer in agriculture. The produced Na_3PO_4 is separated from other components in a components splitter (20).

After recovery of Na_3PO_4, (stream 32), the bottom stream 27 contains more than 80 % mass in glycerol. However, glycerol is considered as a secondary product that must have about 92 % purity.

Consequently, an additional separation is required and the bottom stream (29) of the components splitter (20) is preheated by heat exchanger 11 to 90°C and sent to a distillation column with total condenser (21). The glycerol with purity 99.67 % was obtained. In heat exchanger 11 the cold stream 27 is heated by a hot stream of glycerol. Thereby the heat of the hot glycerol is recuperating.

Simulation description

ChemCAD version 6.3.1 is used as the process simulator in this study. The development of the process model for simulations involves defining the chemical components, selecting appropriate thermodynamic models, proper unit operations and operating conditions such as temperature, pressure, and flow rate.

Components taken into account (Table 1) in the simulation are taken from the ChemCAD standard database.

Palm oil is not available in the simulator library. Therefore it is defined using "Hypothetical Manager" function by entering some thermodynamical property of this compound. In this case, the properties used to define palm oil, are listed in Table 2. Biodiesel is simulated as methyl oleate, which is available in the simulator library.

Thermodynamic model

Due to the presence of polar compounds such as methanol and glycerol in the process, the non-random two liquid (NRTL) thermodynamic models [11] are selected for use as the property package for calculation of activity coefficient of the liquid phase in the simulation. Since some binary interaction parameters were not available in the simulation databank, they were estimated using, the Dortmund modified version of UNIFAC model [8 - 10]. Since the UNIFAC decompositions are not available for all the components, such as the triolein and all the inorganic components, the following assumptions were made:

The UNIFAC decomposition of non-organic components is assimilated to water's one (it mainly leads to neglect the pH influence on equilibrium, this approximation is reasonable if we consider the low content in inorganic components that only act as catalysts).

The triolein UNIFAC decomposition is obtained from its chemical structure. The developed chemical formula of triolein is the one that is supplied on the NIST [Nist WebBookhttp://webbook.nist.gov/chemistry] website. The triolein UNIFAC decomposition is given in Table 3.

Table 1. Used components.

Name	Chemical formula	GAS Number	Use in the process
Methyl oleate (FAME)	$C_{19}H_{36}O_2$	112-62-9	Main product
Glycerol	$C_3H_8O_3$	56-81-5	Secondary product
Methanol	CH_3OH	67-56-1	Reactant
Phosphoric Acid	H_3PO_4	7664-38-2	Allows neutralizing NaOH
Sodium Phosphate	Na_3PO_4	7601-54-9	Product coming from NaOH neutralization
OIL	$C_{57}H_{104}O_6$	122-32-7	Raw material, main reactant
Water	H_2O	7732-18-15	Allows separation FAME from other products by scrubbing
Sodium Hydroxide	NaOH	1310-73-2	Alkaline catalyst

Table 2. Physical properties of the oil.

Molecular mass	885.4321
Critical temperature	1366.85 C
Critical pressure	470.0018 kPa
Critical volume	3.090007 m3/kmol
Melting point	5.000007 C
Normal boiling point	846.85 C
IG Gibbs of formation	19459.5 kJ/kg
Acentric factor	1.599314
Solubility parameter	17140.54 (J/m3)**0.5
Dipole moment	1.050002e-029 C.m
Heat of vaporization	326.2352 kJ/kg
Liquid volume constant	153.4908 cc/mol
UNIQUAC area parameter	31.764
UNIQUAC volume parameter	39.17798
Watson factor	13.9026
API gravity	24.22796
Specific gravity 60 F	0.9155723

The process flow sheets are constructed by selecting and connecting proper unit operations such as reactors, liquid-liquid extractor, distillation columns, heat exchangers, pumps, etc. Then, conditions for each unit operation such as temperature, pressure, flow rates and composition of the input and output streams in each stream are specified.

RESULTS AND DISCUSION

Mass and energy balances

In this paper we present only the most relevant stream results. In ChemCAD, mass and energy balances are provided for every stream. Results are also available at the unit operation level. In Table 4 are presented the results of the product streams.

Columns profiles

Composition profiles can be accessed after the simulation in each column configuration window, in the "Profiles" tab. Here, only the liquid-mole fractions are shown for the three columns.

In Fig. 2 are shown the concentration profiles of distillation column 7, intended for separating the methanol

Table 3. The triolein UNIFAC decomposition.

Sub-group	Frequency
CH=CH	3
CH	1
CH_2	44
CH_3	3
CH_2COO	3

Table 4. Product streams specification.

Stream No.	23	24	30	31
Stream name	Vent	Boidisel	Glycerin	Water
Temp C	205.5949	36.7949	75.1915	38.7422
Pres kPa	10	10	50	40
Enth MJ/h	-90.284	-2404.1	-741.14	-250.50
Vapor mole frac.	1	0	0	0
Total kmol/h	0.3384	3.3288	1.1402	0.9277
Total kg/h	20.9332	990	103.7763	20.8133
Total std L m^3/h	0.0236	1.1259	0.0821	0.0231
Total std V m^3/h	7.5843	74.61	25.5552	20.7934
Flowrates in kg/h				
FAME	14.5471	984.1338	0.0018	0.0031
Glycerol	0	0	103.3880	0.0137
Methanol	2.5265	0.0474	0.11612	9.3352
Phosphoric acid	0	0	0	0
TriNa Phosphate	0	0	0	0
Oil	0.0695	5.7914	0	0
Water	3.7202	0.0273	0.2253	11.4613
Sodium hydroxide	0	0	0	0

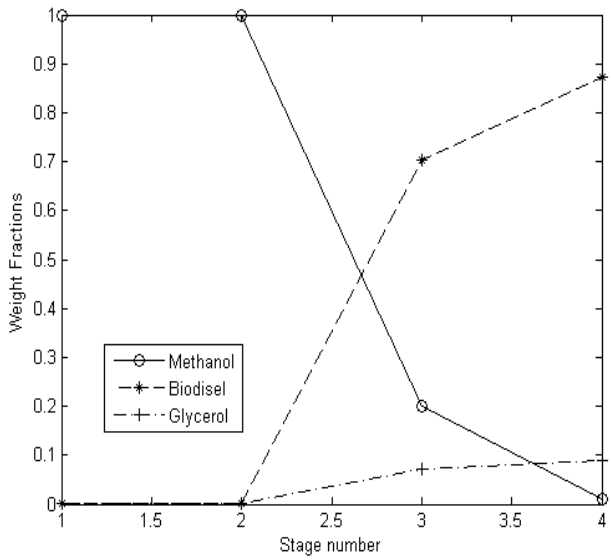


Fig. 2. Liquid mass-fractions profile in the column 7.

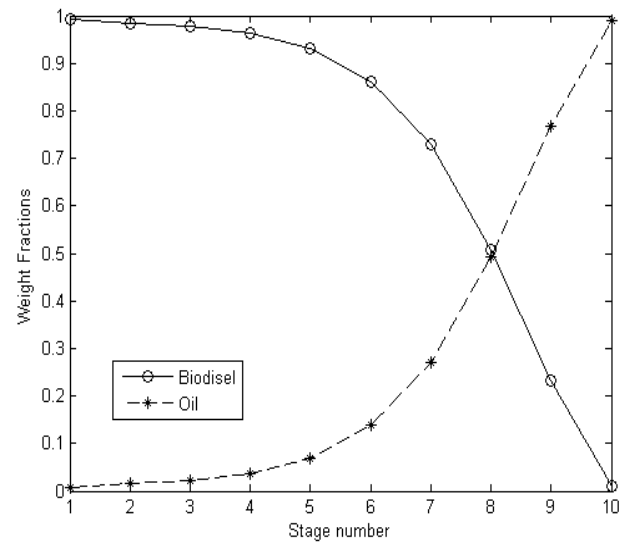


Fig. 3. Liquid mass-fractions profile in the column 18.

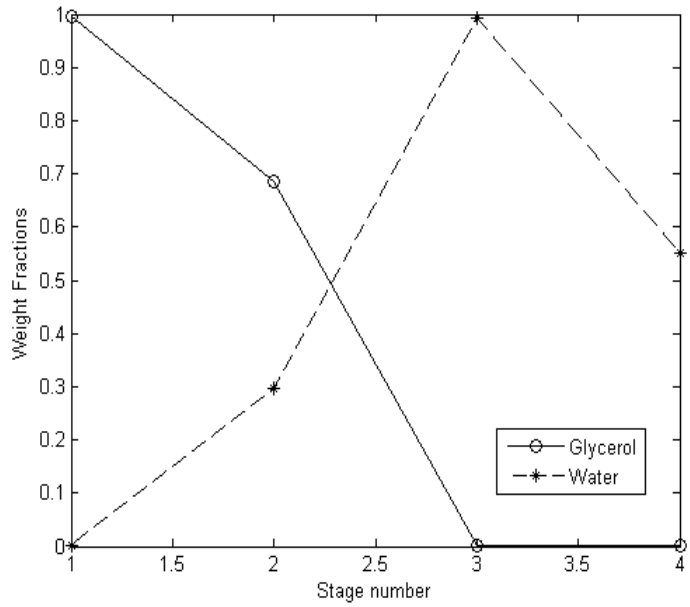


Fig. 4. Liquid mass-fractions profile in the column 21.

from the mixture.

In Fig, 3 is shown the biodiesel concentration change and the unreacted oil in column 18.

The concentration profiles of the completely purified glycerol and water in distillation column 21 are shown in Fig. 4.

CONCLUSIONS

The technological scheme for biodiesel production from purified vegetable oil has been designed using ChemCAD 6.0. The main reaction has been shaped through the alkaline catalysis process. As a result of the simulation of the initial raw materials: 1000 kg/h vegetable oil, 10 sodium alkali, 120 methanol - 900 kg/h biodiesel with purity 99.4 % and secondary product - 103.78 kg/h glycerol with purity 99.63 % mass are obtained. The suggested technological scheme provides a possibility for optimum use of the working environments heat.

Acknowledgements

Part of this work was supported by Project BG-051PO001-3.3.06-0038 funded by OP Human Resources Development 2007-2013 of EU Structural Funds.

Part of this work was supported by Project NIS-UCTM, Development 2014.

REFERENCES

1. P. Ravindra, S. Saralan, R. Abdulla, LCA studies for alkaline and enzyme catalyzed biodiesel production from palm oil, Advances in Biological Chemistry, 2, 2012, 341 - 352.
2. K. Choosak, T. Champorn, P. Pornpote, LCA studies comparing biodiesel synthesized by conventional and supercritical methanol methods, Journal of Cleaner Production, 17, 2009, 143 - 153.
3. L. Brennan, P. Owende, Biofuels from microalgae: A revive of technologies for production, processing and extractions of biofuels and co-products, Renewable & Sustainable Energy Reviws, 14, 2010, 557 - 577.
4. B. Dhar, K. Kirtania, Excess methanol recovery in biodiesel production process using a distillation column: A simulation study, Chemical Engineering Research Bulletin, 13, 2009, 55 - 60.
5. M. Berrios, R. Skelton, Comparison purification methods for biodiesel, Chemical Engineering Journal, 144, 2008, 459 - 465.
6. Y Zhang DDMMK M A Dube, Biodiesel production fromwaste cooking oil: 1. Process design and technological assessment, Biores. Technol., 89, 2003, 1 - 16.
7. A HWest NE, D Posarac, Assessment of four biodiesel productionprocesses using HYSYS Plant, Bioresource Technology, 99, 2008, 6587 - 6601.

8. Gmehling, Lohmann, Jakob, Li, Joh; "A Modified UNIFAC (Dortmund) Model. 3. Revisionand Extension,", Ind.Eng.Chem.Res., 37, 1998, 4876 - 4882.
9. Gmehling, Lohmann, "From UNIFAC to Modified UNIFAC," Ind. Eng. Chem. Res., 40, 2001, 957 - 964.
10. Gmehling, Lohmann, "Modified UNIFAC: ReliableModelfortheDevelopment of Thermal Separation Processes," J. Che. Eng. Jpn., 34, 2001, 43-54.
11. H.Renon, J.M. Prausnitz "LocalCompositions in Thermodynamic Excess Functions for Liquid Mixtures, AIChE J., 14, 1, 1968, 135 - 144.