Modeling, Analysis and Optimization for the Biodiesel Production Process from Waste Cooking Oil

Walaa Mahmoud Shehata, Ahmad Mohamed Mokhtar

Abstract: The present study proposed a rigorous model using detailed kinetics reaction for the alkali transesterification of waste cooking oil with methanol and Alkali Catalyst (NaOH). Aspen Plus software is used. The results showed that the rigorousness of the model helps in predicting more realism and accurate result. The effect of different parameters on the process like temperature, pressure, residence time, methanol to oil ratio, and catalyst (NaOH) weight percentage were studied. All the studied parameters have significant effect on the process performance except pressure. Optimization of the process also carried out to find the best conditions for maximum profit and maximum production. The optimization results showed that the reaction temperature decreased from 60 to 45 ° C, the reaction time decreased from 60 to 49 minutes, the molar ratio of methanol/oil increased from 6:1 to 7.2:1 mole ratio and the catalytic concentration decreased from 1 to 0.25 wt%.

Keywords: Biodiesel, transesterification, Waste Cooking Oil, Aspen Plus.

I. INTRODUCTION

Biodiesel as an alternative fuel option is a high priority for scientists 'research, even in periods when the price of oil is low, as there are large predictions of the end of the fossil fuel era from non-renewable resources. Alkali transesterification of vegetable oils is the main process used commercially for the biodiesel production, and using waste cooking oil overcomes the issue of high feedstock prices and helps in solving the waste oil treatment process. Biodiesel is considered as a renewable and clean-burning diesel replacement. It can be used in existing diesel engines without any modification as it meets the technical fuel quality and engine performance specifications. It is covered by all major engine manufacturers' warranties, most often in blends of up to 5 percent or 20 percent biodiesel [1].

According to the American Society for Testing and Materials (ASTM), biodiesel is a fuel composed of mono-alkyl esters of long chain fatty acid methyl esters (FAME) derived from vegetable oils or animal fats, designated B100 [2].

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Advantages of biodiesel over petrol-diesel are its renewability and low emission profile of carbon monoxide, sulphur compounds, particulate matter and unburned hydrocarbon [3]. It has relatively higher combustion efficiency and higher cetane number [4, 5]. Also, biodiesel has a higher flash point which makes it safer to transport and handle [6].

Biodiesel is made through a chemical process called transesterification reaction. This transesterification reaction can be alkali-, acid-, or enzyme-catalyzed. It also can take place without the use of a catalyst under the supercritical conditions of the alcohol [7, 8]. However, among all systems of biodiesel production, the alkali-catalyzed process is the most widely used in current commercial biodiesel plants [9]. Vegetable oil is expressed chemically as triglyceride or triacylglycerol. In the transesterification reaction, triglyceride reacts with an alcohol in the presence of a catalyst, to produce alkyl esters and glycerol. Methanol, ethanol and butanol are the recommended alcohols [10], but methanol is the most favorable and commonly used alcohol due to its lower price. The resulting esters are called fatty acid methyl esters (i.e., FAME or biodiesel). Sodium hydroxide and potassium hydroxide are the commonly used alkali catalysts.

Virgin vegetable oils are the main feedstock for biodiesel, but it is reported that the high cost of biodiesel is mainly due to the cost of virgin vegetable oils [6, 11]. Therefore, using a cheaper alternative feedstock is considered a primary solution to lower the production cost. Waste cooking oil (WCO) is the best alternative feedstock as it is estimated to be about half the price of virgin vegetable oil [12]. It also helps to solve the problem of waste oil disposal [13].

For the alkali-catalyzed process, the reaction conditions are a temperature near the boiling point of the alcohol (e.g., 60 °C for methanol) and a 6:1 molar ratio of alcohol to oil [10, 14]. Studies of the kinetics of the alkali-catalyzed system by Noureddini and Zhu [14] and Darnoko and Cheryan [15] showed that approximately 90–98% oil conversion to methyl esters was observed within 90 min.

The presence of water in the system may cause ester saponification in alkaline conditions [16, 17]. Also, the alkaline catalyst is very sensitive to free fatty acid in the biodiesel feedstock. Where free fatty acid can react with the alkaline catalyst to produce soap and water Thus, dehydrated vegetable oil with less than 0.5 wt.% free fatty acids, an anhydrous alkali catalyst and anhydrous alcohol are recommended for commercially viable alkali-catalyzed systems [10, 18].

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As the level of free fatty acids in waste cooking oil is greater than 2 wt.% [19, 20] so, for alkali-catalyzed process, a pretreatment step is required to reduce the free fatty acid content via esterification reaction with methanol in the presence of sulfuric acid catalyst [19].

Presently, a number of biodiesel processes have been developed.

Zhang et al. [21] developed a HYSYS-based process simulation model to assess the technological feasibility of four biodiesel plant configurations (alkali and acid catalyst with both virgin oil and waste oil). All the four models were simulated as conversion reaction according to the data given by Freedman et al.[10] and Noureddini and Zhu [14]. West et al. [22] developed a process flowsheets for the biodiesel production from waste cooking oil using alkali, acid, heterogeneous catalyst and supercritical process. All the models were assumed to be conversion reactions. Marchetti et al. [23] introduced a techno-economic study for a two-stage transesterification process with alkali, acid, heterogeneous catalyst. They found that, the alkali catalyst process was the lowest cost per kilogram of product.

Most previous developed models have lack in the kinetic reaction information and/or unavailability of some components of the oil in simulator databank. They used a single component (Triolein) to represent the vegetable oil and a single fatty acid methyl ester (Methyl Oleate) to represent biodiesel product. Besides, the conversion percent of feedstock is assumed to model the transesterification reaction based on published literatures. Those earlier models provided a useful preliminary description of the biodiesel production process and a preliminary comparison of process parameters and modifications for biodiesel production.

The objective of this study is to develop a rigorous process model for biodiesel production from waste cooking oil using alkali catalyst with a pre-treatment unit using Aspen Plus simulation software. The advantage of the new biodiesel databank available in Aspen properties in Aspen Plus which offers physical properties of triglycerides, diglycerides and monoglycerides, combined with the detailed kinetic data for the reaction from Narvaez et al. [24] has been taken. Also, the update electrolyte components in Aspen Plus helps to behave better when this model is extended and gives more accurate results specially within the separation processes. This new model will have a detailed kinetic model for transesterification, and it can be used to study the effect of different parameters on the process. In addition, the optimization tools are used to find out the best design and operation conditions. Moreover, the quality of biodiesels as measured by properties such as density, kinematic viscosity and cetane number, can be evaluated according to the predicted composition profile of methyl fatty acid esters.

II. DESIGN METHODOLOGY

The biodiesel production process used in this work (Fig. 1) is based on the biodiesel production process developed by Zhang et al. [21] with some modifications as following:

- Using actual composition of oil, and actual kinetic parameters for the reactions as presented in Tables I, II and III.
- Washing towers (Liquid-Liquid extractors) are configured for actual separation instead of component splitter which gave theoretical perfect separation.
- Recycling of the glycerol produced to be used in the pre-treatment washing column.
- Recycling of the unreacted oil to transesterification reactor again.

Process feedstock is waste cooking oil (WCO). It is composed of triglyceride, diglyceride and free fatty acid. The triglyceride is classified as triunsaturated, monosaturated, disaturated and trisaturated triglyceride. On the other hand, diglyceride is presented as 1,3 dipalmitin (PP) [25]. It is assumed that the WCO has 6 wt.%. of free fatty acids (FFA). Using actual composition of virgin palm oil determined by Che Man [26], then a 6 wt.%. of free fatty acid (Oleic Acid) is added. The total composition percent re-normalized to represent the waste cooking oil (WCO) (Table I).

Table I: Composition of waste cooking oil (WCO)

Component	Name	Structure	Mass Fraction
OOO	Triolein (Triunsaturated Triglyceride)	C57H104O6	0.041
OOLI	TAG-OOLI (Triunsaturated Triglyceride)	C57H102O6-5	0.005
PLIO	TAG-PLIO (Monosaturated Triglyceride)	C55H100O6-7	0.091
POO	TAG-POO (Monosaturated Triglyceride)	C55H102O6-6	0.219
OOS	TAG-OOS (Monosaturated Triglyceride)	C57H106O6-4	0.021
MPLI	TAG-MPLI (Disaturated Triglyceride)	C51H94O6-3	0.021
PPLI	TAG-PLIP (Disaturated Triglyceride)	C53H98O6-5	0.087
PPO	TAG-POP (Disaturated Triglyceride)	C53H100O6-5	0.278
POS	TAG-POS (Disaturated Triglyceride)	C55H104O6-3	0.046
MMM	TRIMYRISTIN (Trisaturated Triglyceride)	C45H86O6	0.004
MMP	TAG-MMP (Trisaturated Triglyceride)	C47H90O6-10	0.016
PPP	TRIPALMITIN (Trisaturated Triglyceride)	C51H98O6	0.052
PPS	TAG-PPS (Trisaturated Triglyceride)	C53H102O6-13	0.010

| PP | 1,3 DIPALMITIN (Diglyceride) | C35H68O5-1 | 0.049 |
| FFA | Oleic Acid (Free fatty acids) | C18H34O2 | 0.060 |

The biodiesel production process from waste cooking oil consists of two steps; first step is the pre-treatment process in which the FFA is converted to fatty acid methyl ester according to the esterification reaction presented in Equation 1 using sulfuric acid as catalyst [27].

$$R - COOH \ (oleic \ acid) + CH_3 - OH \ \underset{K_2}{\overset{K_1}{\rightleftarrows}} \ R - COO - CH_3 + H_2O \qquad (1)$$
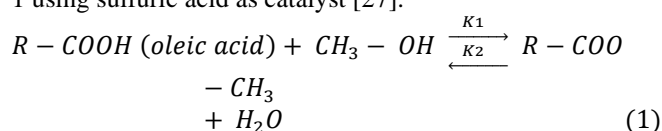
Where R is a linear chain of 11-17 carbon atoms.
In this reaction the free fatty acid feed is esterificated with methanol ($CH_3 - OH$) in presence of acid catalyst (H_2SO_4) to produce fatty acid methyl esters ($R - COO - CH_3$) and water.

Kinetic parameters for the esterification reaction in the pre-treatment step are taken from M. Berrios et al. [27]. The rate of reaction is presented as first order in the forward direction and second order in the reverse direction as presented in Equation 2.

$$r_A = K_1 \ [A] - K_2 \ [B] \ [C] \qquad (2)$$

Where [A] is the concentration of free fatty acid in mg H_2SO_4/g oil which is defined as the acid value; [B] and [C] are concentrations of the fatty acid methyl esters and the water, respectively, that formed during the reaction; K_1 and K_2 are the kinetic constants for the forward and the reverse reaction respectively, can be calculated using Equation 3 and Table II.

$$K_n = a \ . \exp\left[\frac{-\Delta E}{R.T}\right] \qquad (3)$$

Where n is the reaction number; a and $-\Delta E$ are the pre-frequency factor and the activation energy, respectively, calculated as presented in Table II. R is the universal gas constant; T is the reaction temperature.

Table II Kinetic Parameters for the esterification of FFA in the pre-treatment step

	Pre-exponential factor (a)	Activation Energy ($-\Delta E$) kJ/mol
Forward reaction (K_1)	2.869e+06	50.745
Reverse reaction (K_2)	37.068	31.0073

The second step in the biodiesel production process is the transesterification of the other components of the WCO after the pre-treatment process. kinetic parameters for the transesterification reactions are taken from Narvaez et al. [24] with the modification and conversion from Aspentech [25] to add the concentration of catalyst (NaOH) into the kinetics.
The rate of transesterification reaction is presented in following Equation 4 [25]:

$$r = K_n \ exp\left[-\frac{\Delta E}{RT}\right] \prod_{i=1}^{N} C_i^{ai} \ \left[\frac{1}{T} - \frac{1}{T_o}\right] \qquad (4)$$

Where T_o is the reference temperature; N is number of components in the reaction; C_i is concentration of component i ; ai is the stoichiometric coefficient of component i in the reaction equation; E is the activation energy; and R is the universal gas constant. Table III illustrates the different transesterification reactions with pre-exponential factor and the activation energy required for the second step of the biodiesel production process.
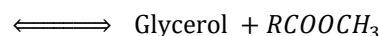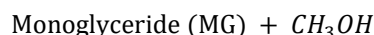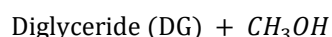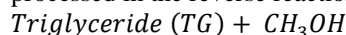
Note that the diglycerides in the feed (WCO) are presented in this work as 1,3- DIPALMITIN (PP). The diglycerides (DG) like 1,3-DIMYRISTIN (MM), 1,3-DIOLEIN (OO), SN-1-PALMITO-3-LINOLEIN (PLI) and SN-1-MYRISTO-3-PALMITIN (MP), in addition to the monoglycerides (MG) like 1-MONOMYRISTIN (1-M), 1-MONOPALMITIN (1-P), 1-MONOSIEARIN (1-S), MONOOLEIN (1-O) and 1-MONOLINOLEIN (1-LI) are formed in the reactions as intermediates.

The biodiesel products are all the methyl esters produced from the reaction as Methyl-Oleate, Methyl-Stearate, Methyl-Linoleate, Methyl-Palmitate and Methyl-Myristate. The catalyst sodium hydroxide used in the reaction is removed at the end of the reaction by adding H_3PO_4 to precipitate Na_3PO_4.

The reactions presented in Table III follow the kinetics presented in Equation 5. Where the biodiesel transesterification reaction consists of three-steps.
The first step is the transesterification of triglyceride into diglyceride, then, the diglyceride reacts with methanol to produce the monoglyceride, after that, the monoglyceride reacts with methanol to produce the methyl esters and the Glycerol.
Note that each reaction of the previous reactions can be processed in the reverse reaction.

$Triglyceride \ (TG) + CH_3OH$

$\Longleftrightarrow Diglyceride \ (DG) + RCOOCH_3$

$Diglyceride \ (DG) + CH_3OH$

$\Longleftrightarrow Monoglyceride \ (MG) + RCOOCH \qquad (5)$

$Monoglyceride \ (MG) + CH_3OH$

$\Longleftrightarrow Glycerol + RCOOCH_3$

The property method used in this work for the biodiesel model is UNIQ-RK which is the UNIQUAC activity model with Redlich-Kwong equation of state with Henry's law. The UNIQUAC model can describe strongly non ideal liquid solutions and liquid-liquid equilibria. The UNIQ-RK property method uses the UNIQUAC activity coefficient model for the liquid phase, the Redlich-Kwong equation of state for the vapor phase, the Rackett model for liquid molar volume and Henry's law for supercritical components. This is suitable for preliminary work. Thermophysical property model parameters of tri-, di-, and mono-glycerides are currently available in the new biodiesel databank in Aspen Plus.

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It includes vapor pressure, heat of vaporization, ideal gas heat of formation, ideal gas heat capacity, liquid heat capacity, liquid molar volume and liquid viscosity. In addition, the required critical temperature (T_C), critical pressure (P_C) and OMEGA for Redlich-Kwong-Soave equation of state (EOS) used to model vapor phase properties are estimated with the Gani group contribution method.

The washing column (C-04) is modeled with the UNIF-DMD property method (Dortmund modified UNIFAC), as the UNIQ-RK methods can't handle the water washing/separation accurately in the presence of H_2SO_4 traces from the previous pre-treatment unit.

Table III: Transesterification reactions in the

Reaction	Pre-exponential factor (a)	Activation Energy ΔE (kcal/mol)	Reaction	Pre-exponential factor (a)	Activation Energy ΔE (kcal/mol)
$OOO + Methanol \xrightarrow{K_3} Methyl-O + OO$	0.02311	13.5	$PLI + Methanol \xrightarrow{K_{51}} Methyl-LI + 1-P$	0.05330	17.4
$OO + Methyl-O \xrightarrow{K_4} OOO + Methanol$	0.001867	10.3	$Methyl-LI + 1-P \xrightarrow{K_{52}} PLI + Methanol$	0.002217	16.2
$OO + Methanol \xrightarrow{K_5} Methyl-O + 1-O$	0.10659	17.4	$PLI + Methanol \xrightarrow{K_{53}} Methyl-P + 1-LI$	0.05330	17.4
$Methyl-O + 1-O \xrightarrow{K_6} OO + Methanol$	0.002217	16.2	$Methyl-P + 1-LI \xrightarrow{K_{54}} Methanol + PLI$	0.002217	16.2
$1-O + Methanol \xrightarrow{K_7} Methyl-O + Glycerol$	0.05754	6.2	$1-LI + Methanol \xrightarrow{K_{55}} Methyl-LI$	0.05754	6.2
$Methyl-O + Glycerol \xrightarrow{K_8} Methanol + 1-O$	0.000267	11.9	$Methyl-LI + Glycerol \xrightarrow{K_{56}} 1-LI$	0.000267	11.9
$MMM + Methanol \xrightarrow{K_9} Methyl-M + MM$	0.02311	13.5	$POO + Methanol \xrightarrow{K_{57}} Methyl-O + PO$	0.01541	13.5
$Methyl-M + MM \xrightarrow{K_{10}} MMM + Methanol$	0.001867	10.3	$Methyl-O + PO \xrightarrow{K_{58}} POO + Methanol$	0.001867	10.3
$MM + Methanol \xrightarrow{K_{11}} Methyl-M + 1-M$	0.10659	17.4	$POO + Methanol \xrightarrow{K_{59}} Methyl-P + OO$	0.00770	13.5
$Methyl-M + 1-M \xrightarrow{K_{12}} MM + Methanol$	0.002217	16.2	$Methyl-P + OO \xrightarrow{K_{60}} Methanol + POO$	0.001867	10.3
$1-M + Methanol \xrightarrow{K_{13}} Methyl-M + Glycerol$	0.05754	6.2	$POS + Methanol \xrightarrow{K_{61}} Methyl-S + PO$	0.00770	13.5
$Methyl-M + Glycerol \xrightarrow{K_{14}} Methanol + 1-M$	0.000267	11.9	$Methyl-S + PO \xrightarrow{K_{62}} Methanol + POS$	0.001867	10.3
$PPP + Methanol \xrightarrow{K_{15}} Methyl-P + PP$	0.02311	13.5	$POS + Methanol \xrightarrow{K_{63}} Methyl-P + OS$	0.00770	13.5
$Methyl-P + PP \xrightarrow{K_{16}} PPP + Methanol$	0.001867	10.3	$Methyl-P + OS \xrightarrow{K_{64}} POS + Methanol$	0.001867	10.3
$PP + Methanol \xrightarrow{K_{17}} Methyl-P + 1-P$	0.10659	17.4	$POS + Methanol \xrightarrow{K_{65}} Methyl-O + PS$	0.00770	13.5
$Methyl-P + 1-P \xrightarrow{K_{18}} Methanol + PP$	0.002217	16.2	$Methyl-O + PS \xrightarrow{K_{66}} POS + Methanol$	0.001867	10.3
$1-P + Methanol \xrightarrow{K_{19}} Methyl-P + Glycerol$	0.05754	6.2	$PLIO + Methanol \xrightarrow{K_{67}} Methyl-O + PLI$	0.00770	13.5
$Methyl-P + Glycerol \xrightarrow{K_{20}} Methanol + 1-P$	0.000267	11.9	$Methyl-O + PLI \xrightarrow{K_{68}} PLIO + Methanol$	0.001867	10.3
$PPS + Methanol \xrightarrow{K_{21}} Methyl-S + PP$	0.00770	13.5	$PLIO + Methanol \xrightarrow{K_{69}} Methyl-P + LIO$	0.00770	13.5
$Methyl-S + PP \xrightarrow{K_{22}} Methanol + PPS$	0.001867	10.3	$Methyl-P + LIO \xrightarrow{K_{70}} PLIO + Methanol$	0.001867	10.3
$PPS + Methanol \xrightarrow{K_{23}} Methyl-P + PS$	0.01541	13.5	$PLIO + Methanol \xrightarrow{K_{71}} Methyl-LI + PO$	0.00770	13.5
$Methyl-P + PS \xrightarrow{K_{24}} Methanol + PPS$	0.001867	10.3	$Methyl-LI + PO \xrightarrow{K_{72}} PLIO + Methanol$	0.001867	10.3
$PS + Methanol \xrightarrow{K_{25}} Methyl-P + 1-S$	0.05330	17.4	$LIO + Methanol \xrightarrow{K_{73}} Methyl-O + 1-LI$	0.05330	17.4
$Methyl-P + 1-S \xrightarrow{K_{26}} Methanol + PS$	0.002217	16.2	$Methyl-O + 1-LII \xrightarrow{K_{74}} LIO + Methanol$	0.002217	16.2
$1-S + Methanol \xrightarrow{K_{27}} Methyl-S + Glycerol$	0.05754	6.2	$LIO + Methanol \xrightarrow{K_{75}} Methyl-LI + 1-O$	0.05330	17.4
$Methyl-S + Glycerol \xrightarrow{K_{28}} Methanol + 1-S$	0.000267	11.9	$Methyl-LI + 1-O \xrightarrow{K_{76}} Methanol + LIO$	0.002217	16.2
$PS + Methanol \xrightarrow{K_{29}} Methyl-S + 1-P$	0.05330	17.4	$OOS + Methanol \xrightarrow{K_{77}} Methyl-S + OO$	0.00770	13.5
$Methyl-S + 1-P \xrightarrow{K_{30}} Methanol + PS$	0.002217	16.2	$Methyl-S + OO \xrightarrow{K_{78}} Methanol + OOS$	0.001867	10.3
$PPO + Methanol \xrightarrow{K_{31}} Methyl-O + PP$	0.00770	13.5	$OOS + Methanol \xrightarrow{K_{79}} Methyl-O + OS$	0.01541	13.5
$Methyl-O + PP \xrightarrow{K_{32}} Methanol + PPO$	0.001867	10.3	$OS + Methyl-O \xrightarrow{K_{80}} OOS + Methanol$	0.001867	10.3
$Methanol + PPO \xrightarrow{K_{33}} Methyl-P + PO$	0.01541	13.5	$OS + Methanol \xrightarrow{K_{81}} Methyl-O + 1-S$	0.05330	17.4
$Methyl-P + PO \xrightarrow{K_{34}} PPO + Methanol$	0.001867	10.3	$Methyl-O + 1-S \xrightarrow{K_{82}} OS + Methanol$	0.002217	16.2
$PO + Methanol \xrightarrow{K_{35}} Methyl-P + 1-O$	0.05330	17.4	$OS + Methanol \xrightarrow{K_{83}} Methyl-S + 1-O$	0.05330	17.4
$Methyl-P + 1-O \xrightarrow{K_{36}} PO + Methanol$	0.002217	16.2	$Methyl-S + 1-O \xrightarrow{K_{84}} Methanol + OS$	0.002217	16.2
$PO + Methanol \xrightarrow{K_{37}} Methyl-O + 1-P$	0.05330	17.4	$OOLI + Methanol \xrightarrow{K_{85}} Methyl-LI + OO$	0.00770	13.5
$Methyl-O + 1-P \xrightarrow{K_{38}} Methanol + PO$	0.002217	16.2	$Methyl-LI + OO \xrightarrow{K_{86}} OOLI + Methanol$	0.001867	10.3
$MMP + Methanol \xrightarrow{K_{39}} Methyl-P + MM$	0.00770	13.5	$OOLI + Methanol \xrightarrow{K_{87}} Methyl-O + LIO$	0.01541	13.5
$Methyl-P + MM \xrightarrow{K_{40}} Methanol + MMP$	0.001867	10.3	$Methyl-O + LIO \xrightarrow{K_{88}} Methanol + OOLI$	0.001867	10.3
$MMP + Methanol \xrightarrow{K_{41}} Methyl-M + MP$	0.01541	13.5	$MPLI + Methanol \xrightarrow{K_{89}} Methyl-LI + MP$	0.00770	13.5
$Methyl-M + MP \xrightarrow{K_{42}} Methanol + MMP$	0.001867	10.3	$Methyl-LI + MP \xrightarrow{K_{90}} MPLI + Methanol$	0.001867	10.3
$MP + Methanol \xrightarrow{K_{43}} Methyl-P + 1-M$	0.05330	17.4	$MPLI + Methanol \xrightarrow{K_{91}} Methyl-M + PLI$	0.00770	13.5
$Methyl-P + 1-M \xrightarrow{K_{44}} Methanol + MP$	0.002217	16.2	$Methyl-M + PLI \xrightarrow{K_{92}} MPLI + Methanol$	0.001867	10.3
$MP + Methanol \xrightarrow{K_{45}} Methyl-M + 1-P$	0.05330	17.4	$MPLI + Methanol \xrightarrow{K_{93}} Methyl-P + MLI$	0.00770	13.5
$Methyl-M + 1-P \xrightarrow{K_{46}} Methanol + MP$	0.002217	16.2	$Methyl-P + MLI \xrightarrow{K_{94}} MPLI + Methanol$	0.001867	10.3
$PPLI + Methanol \xrightarrow{K_{47}} Methyl-LI + PP$	0.00770	13.5	$MLI + Methanol \xrightarrow{K_{95}} Methyl-M + 1-LI$	0.05330	17.4
$Methyl-LI + PP \xrightarrow{K_{48}} Methanol + PPLI$	0.001867	10.3	$Methyl-M + 1-LI \xrightarrow{K_{96}} Methanol + MLI$	0.002217	16.2
$PPLI + Methanol \xrightarrow{K_{49}} Methyl-P + PLI$	0.01541	13.5	$MLI + Methanol \xrightarrow{K_{97}} Methyl-LI + 1-M$	0.05330	17.4
$Methyl-P + PLI \xrightarrow{K_{50}} PPLI + Methanol$	0.001867	10.3	$Methyl-LI + 1-M \xrightarrow{K_{98}} MLI + Methanol$	0.002217	16.2

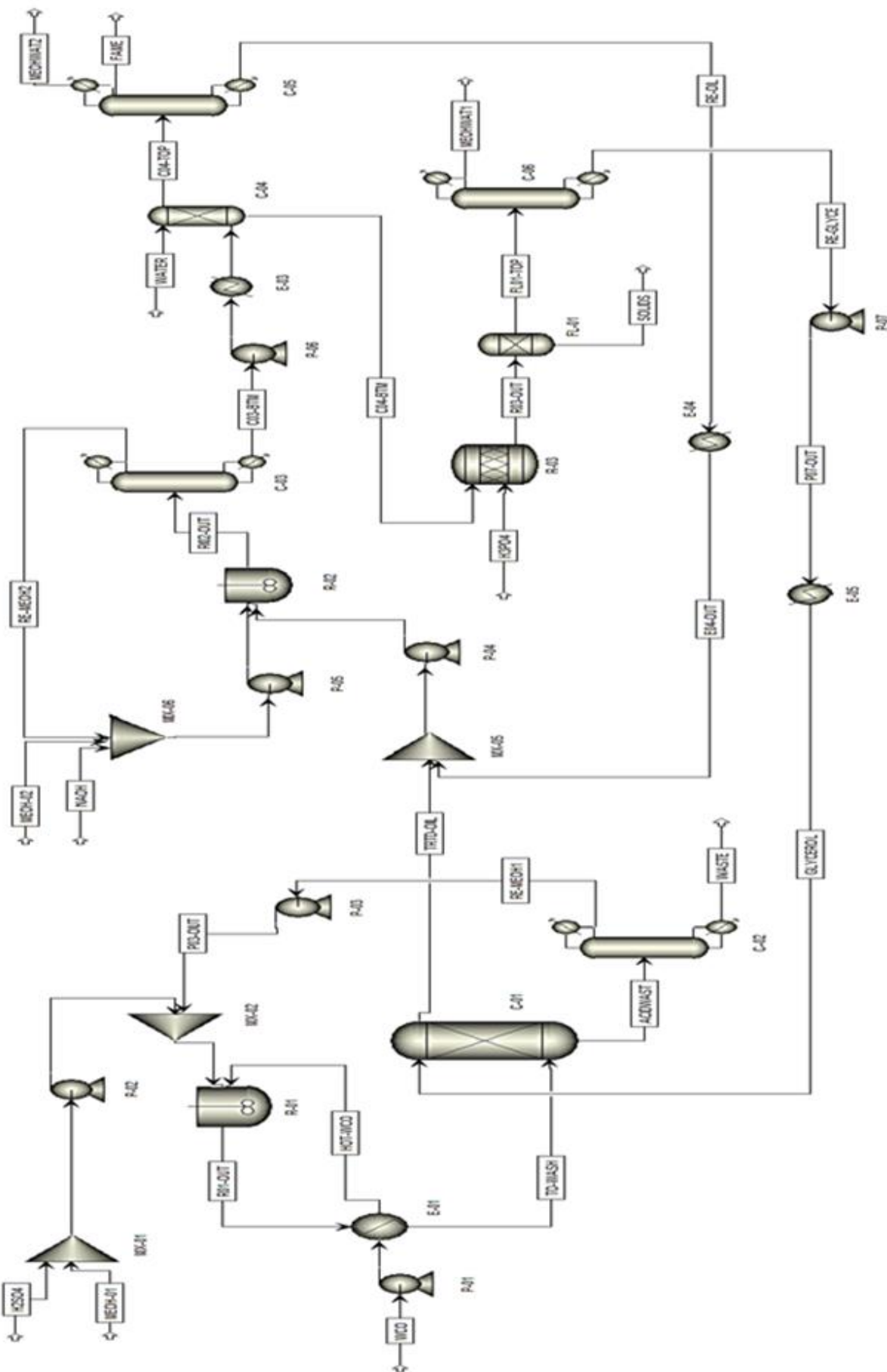Fig. 1. Flow Diagram of the Biodiesel Production Process

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III. PROCESS DESIGN AND SIMULATION

The process consists of two steps, first step is the pre-treatment where the WCO feed esterification with methanol in presence of acid catalyst (H_2SO_4) occurs. The WCO was heated to 60 ºC in heat exchanger (E-01) before entering esterification reactor R-01. The fresh methanol stream is combined with the H_2SO_4 stream and mixed then with the recycled methanol stream (RE-MEOH1). The resulting mixture from MX-02 is pumped into the reactor R-01. In R-01, the reaction was carried out at 60°C, 4 bar, a 6:1 molar ratio of methanol to FFA and 1% sulfuric acid (based on oil). All the free fatty acids in the reactor were converted to methyl esters in 120 min [27].

The resulting water and acid catalyst (H_2SO_4) from R-01 need to be completely removed before proceeding to the alkali-catalyzed transesterification by using glycerin as a liquid entraining agent. Recycled pure glycerin (100%) from glycerin purification column C-06 at 45°C and 4 bar is used in washing the reactor effluent (R01-OUT) in C-01 column. The resulting washed stream TRTD-OIL is consisted only of refined oil and the resulting methyl esters. This stream was sent to downstream transesterification unit. The bottom stream from C-01 composes of unreacted methanol, glycerol, sulfuric acid, water and traces of esters. The methanol in this stream was recovered in C-02. Recovered methanol stream RE-MEOH1 was obtained from the top of C-02 at 28°C and 0.2 bar, with 99% recovery of the total methanol fed to the column, and purity > 99% of methanol. Vacuum distillation was used to keep the temperature under 150°C as FAME and glycerol are susceptible to thermal decomposition above 250ºC and 150ºC respectively [28, 29].

The bottom stream of C-02 (WASTE) composed of glycerol, methanol, sulfuric acid and water, but due to the presence of sulfuric acid, this stream was not reused and is treated as waste.

Step two in the biodiesel production process is the alkali-catalyzed transesterification. The TRTD-OIL stream from pre-treatment step 1 is mixed with the recycle oil stream (RE-OIL) which is heated in the heater E-04. The outlet stream from MIX-05 is pumped into the reactor R-02. The fresh methanol stream (MEOH-02) is combined with the recycled methanol stream (REMOH-02) and the anhydrous sodium hydroxide NAOH in the mixer MX-06. The resulted stream from MX-06 is pumped into R-02. The reaction was carried out at a 6:1 molar ratio of methanol to oil, 1% sodium hydroxide (based on oil), 60 °C and 4 bar. Anhydrous NaOH is used as recommended for commercially viable alkali-catalyzed systems [10, 18]. In R-02, all reactions were performed according to the kinetics of the reactions shown in Table 4 with a residence time of 60 minutes. The reactions convert 99% of the oil to FAME.

The methanol in stream R02-OUT emerged from R-02 was recovered in C-03 tower. The top stream of C-03 with purity of >99.9% of methanol is mixed with fresh methanol to R-02. Vacuum distillation was used to keep the temperature under 150°C as FAME and glycerol are susceptible to thermal decomposition above 250ºC and 150ºC, respectively [28, 29]. The bottom stream of C-03 containing all the FAME from the reactor was pumped by P-06, heated by E-03 then washed in the water washing column C-04 where FAME was completely separated from the glycerol. The content of other compounds, such as vegetable oil, methanol and water in the FAME were all less than 1%. The top product stream from C-04 (C-04-TOP) composed of FAME, water and methanol was forwarded to C-05 to purify the FAME product where water and methanol were removed. A FAME product with 99.3% purity was obtained as a final biodiesel product.

The bottom stream from C-04 (C04-BTM) is proceeded to neutralization reactor R-03 to remove sodium hydroxide by adding pure phosphoric acid (H_3PO_4) with 100% purity. It is assumed that the conversion in R-03 is 100%. The resulting Na_3PO_4 was removed in gravity separator (filter) FL-01. The remaining stream composed mainly of glycerin with little of water, methanol and traces of oil is entered a distillation column C-06 for glycerin purification, where pure glycerin obtained from the bottom and recycled back to the washing tower C-01. The remaining water, methanol and other traces are obtained from the top of column. Table 4 illustrates the simulation results of the biodiesel production process.

IV. RESULT AND DISCUSSION

A. Effect of Reaction Temperature

Keeping all reaction conditions constant and changing only the reaction temperature, the simulation results showed that at the same reaction time, increasing reaction temperature increased reaction conversion (Fig. 2). From Arrhenius, high temperature would push the process to move forward and resulted in more conversion and more products. However, from Fig. 2 and especially with higher residence time, the effect of increasing temperature above 65ºC on conversion is less than 0.2% and would be energy wasting. That's makes temperature an important varying variable for optimization.
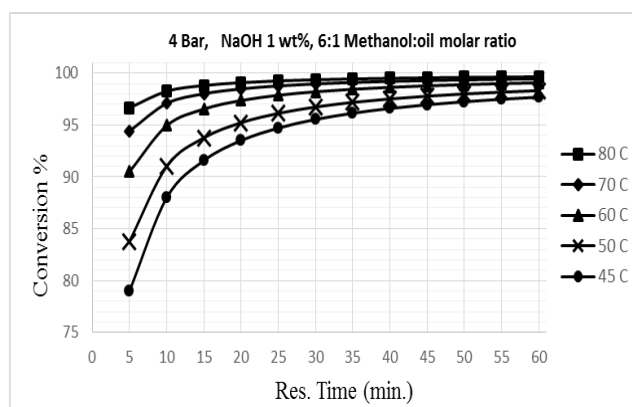

Fig. 1. Effect of reaction temperature on conversion %

Table IV with a residence time of 60 minutes. The reactions convert 99% of the oil to FAME.

Table IV Simulation results of biodiesel production process.

	Units	WCO	MEOH-01	H2SO4	P02-OUT	P03-OUT	MX02-OUT	HOT-WCO
From					P-02	P-03	MX-02	E-01
To		P-01	MX-01	MX-01	MX-02	MX-02	R-01	R-01
Phase		Liquid	Liquid	Liquid	Liquid	Liquid	Liquid	Liquid
Temperature	ºC	25	25	25	25.11	28.55	28.36	50
Pressure	bar	1	1	1	4	4	4	4
Mass Flows	kg/hr	1100	24.24	3.3	27.54	426.56	454.1	1100
Mole Flows	kmol/hr	1.49	0.76	0.03	0.79	13.35	14.14	1.49
	Units	R01-OUT	TO-WASH	ACIDWAST	WASTE	RE-MEOH1	MEOH-02	NAOH
From		R-01	E-01	C-01	C-02	C-02		
To		E-01	C-01	C-02		P-03	MX-06	MX-06
Phase		Liquid	Liquid	Liquid	Liquid	Liquid	Liquid	Liquid
Temperature	ºC	60	45.5	45.84	87.98	28.41	25	25
Pressure	bar	4	4	2	0.3	0.2	1	1
Mass Flows	kg/hr	1554.1	1554.1	563.64	137.09	426.56	114.03	11.03
Mole Flows	kmol/hr	15.63	15.63	14.99	1.64	13.35	3.56	0.28
	Units	RE-MEOH2	P05-OUT	R02-OUT	C03-BTM	E03-OUT	WATER	C04-BTM
From		C-03	P-05	R-02	C-03	E-03		C-04
To		MX-06	R-02	C-03	P-06	C-04	C-04	R-03
Phase		Liquid	Liquid	Liquid	Liquid	Liquid	Liquid	Liquid
Temperature	ºC	28.32	27.39	60	93.76	60	25	60.6
Pressure	bar	0.2	4	4	0.3	1.5	1.1	1.2
Mass Flows	kg/hr	250.52	375.58	1505.81	1255.3	1255.3	50	183.2
Mole Flows	kmol/hr	7.82	11.65	13.61	5.79	5.79	2.78	4.41
	Units	H3PO4	R03-OUT	SOLIDS	FL01-TOP	MEOHWAT1	RE-GLYCE	C04-TOP
From			R-03	FL-01	FL-01	C-06	C-06	C-04
To		R-03	FL-01		C-06		P-07	C-05
Phase		Liquid	Liquid	Liquid	Liquid	Liquid	Liquid	Liquid
Temperature	ºC	20	50	50	50	67.96	261.99	57.68
Pressure	bar	1.1	1.1	1.1	1.1	0.4	0.5	1.1
Mass Flows	kg/hr	45.04	228.24	15.07	213.17	97.89	115.28	1122.1
Mole Flows	kmol/hr	2.09	6.5	0.09	6.41	5.16	1.25	4.16
	Units	RE-OIL	MEOHWAT2	FAME				
From		C-05	C-05	C-05				
To		E-04						
Phase		Liquid	Vapor	Liquid				
Temperature	ºC	291.82	140	140				
Pressure	bar	0.2	0.1	0.1				
Mass Flows	kg/hr	24.5	4.59	1093.01				
Mole Flows	kmol/hr	0.06	0.22	3.88				

B. Effect of reaction Pressure

By changing the reaction pressure while all other variables are constant, as the reaction occurs only in the liquid phase, the simulation showed that at high temperature (75 ºC) lowering the pressure would allow some reactant to be in the vapor phase which reduces the reaction conversion (Fig. 3). A pressure of 4 bar found to be reasonable to keep the reaction in liquid phase for most temperature ranges (Figs. 3 and 4) in the study, and hence the pressure wouldn't be used in the optimization step.
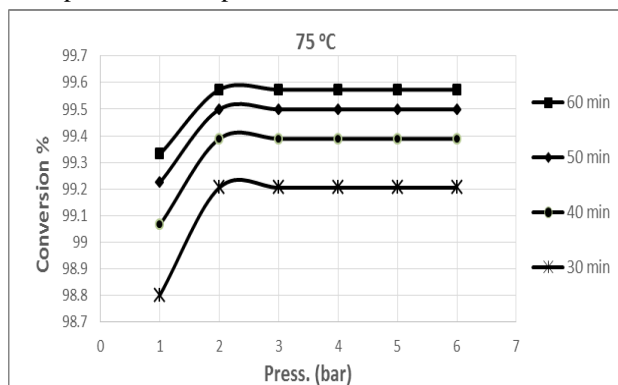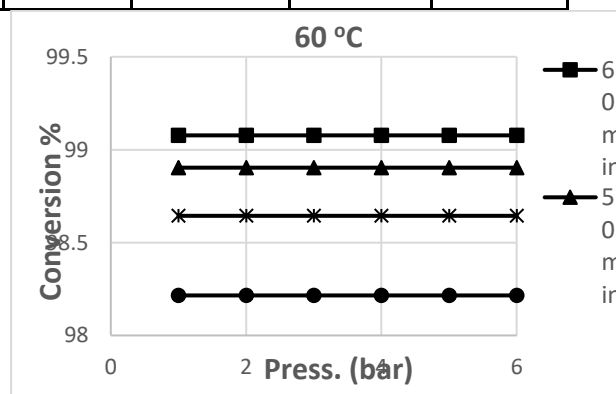

Fig. 3. Effect of Pressure on conversion % at 75 ºC

Fig. 4. Effect of Pressure on conversion % at 60 ºC

C. Effect of reaction time

Also, from Fig. 2 we can see that increasing the reaction time at the same temperature increases the reaction conversion. The curves show clearly that the change of conversion with time is very high in the first 20 – 40 min. where most curves reach the 95% conversion, then any increase in time leads to a slight increase in conversion. Hence the reaction time also will be used as a varying variable in the optimization.

D. Effect of alkali catalyst (Na OH) concentration

Fig. 5 shows that increasing the catalyst concentration increases the reaction conversion till it reaches 99% conversion at 1 wt.%. of NaOH, then the effect of increasing the catalyst didn't show a significant effect. Thus, increasing the concentration above 1% wt. would be meaningless especially at high temperatures.
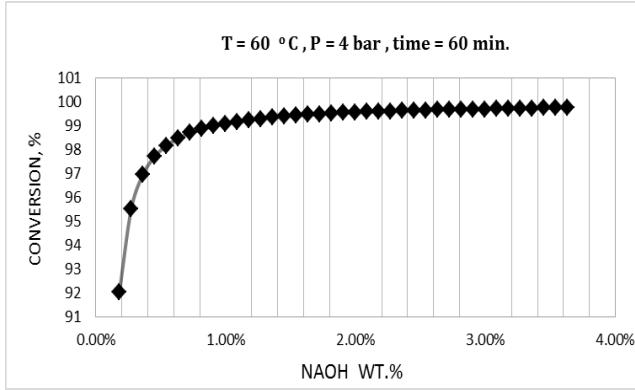

Fig. 5. Effect of catalyst concentration on conversion %

E. Effect of methanol: oil ratio

From Fig. 6, increasing the methanol: oil molar ratio increases the reaction conversion. Also, it is noted that any ratio higher than 6:1 has a little effect on conversion %. That because, increasing ratio would increase the amount of methanol and it would be difficult to recover all unreacted methanol and more energy would be consumed. Moreover, some methanol might be lost from its vaporization.
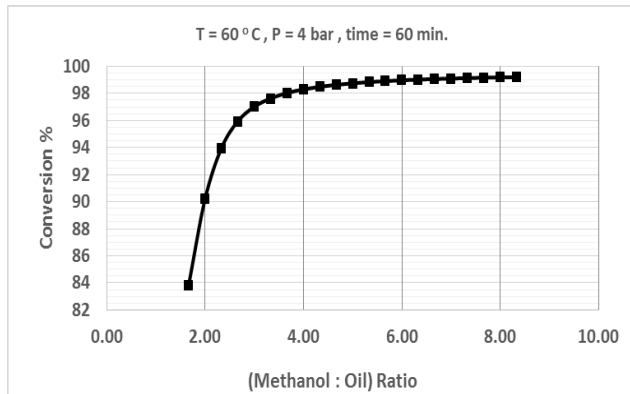

Fig. 6. Effect of methanol: oil ratio

V. PROCESS OPTIMIZATION

Considering the effect of various parameters studied, an optimization model was created for the process to find the optimum values for these parameters. The objective function for optimization is chosen as the maximization of the profit as presented in Equations (6) to (10).

$$Profit = production\ Revenue - operating\ cost \qquad (6)$$

$$production\ Revenue = \text{FAME}_{Prod} \cdot FAME_{Price} \qquad (7)$$

$$operating\ cost = \text{Raw material cost} + \text{Uitilities cost} \qquad (8)$$

$$\text{Raw material cost} = M_{WCO} \cdot P_{WCO} + M_{Meth} \cdot P_{meth} + M_{H_2SO_4} \cdot P_{H_2SO_4} + M_{NaOH} \cdot P_{NaOH} + M_{H_3PO_4} \cdot P_{H_3PO_4} \qquad (9)$$

$$\text{Uitilities cost} = Q_{elect} \cdot C_{elect} + Q_{heating} \cdot C_{heating} + Q_{cooling} \cdot C_{cooling} \qquad (10)$$

Where FAME$_{Prod}$ and FAME$_{Price}$ are the production and the price of the biodiesel produced, respectively; M_{WCO}, M_{Meth}, $M_{H_2SO_4}$, M_{NaOH}, $M_{H_3PO_4}$ are mass flowrate of waste cooking oil, methanol, sulfuric acid, sodium hydroxide and phosphoric acid, respectively; P_{WCO}, P_{meth}, $P_{H_2SO_4}$, P_{NaOH}, $P_{H_3PO_4}$ are the unit cost of waste cooking oil, methanol, sulfuric acid, sodium hydroxide and phosphoric acid, respectively; Q_{elect}, $Q_{heating}$, $Q_{cooling}$ are the energy consumption by using electricity, steam and cooling water, respectively; C_{elect}, $C_{heating}$, $C_{cooling}$ are the unit energy cost of electricity, heating and cooling duties, respectively.

The profit is maximized by varying reaction temperature, reaction time, methanol to oil ratio and the NaOH concentration.

Several constraints are used in the optimization to make the biodiesel production process operate stably and safely. These process constraints are described as follows:

1) The temperature < 103.5 C (the boiling point of methanol @ operating pressure of 4 bar)
2) FAME content of biodiesel > 96.5 % (matching the European Standard for biodiesel EN-14214)

Aspen Plus optimization tool was used and the objective function formula is written in FORTRAN code. The results of the optimization compared to the design values are listed in Table V.

Table V Optimization results for varying variables.

Variable	Initial value	Optimum value
Reaction	60	45
Reaction Time (min)	60	49
NaOH concentration	1	0.25
Methanol : Oil molar	6 : 1	7.2 : 1

Also, the amount of waste streams was reduced as shown in Table VI. The importance of reducing this waste is a low waste disposal fee. Plus, it's environmentally friendly.

Table VI: Optimization results for waste streams.

Waste stream	First value (kg/hr)	Optimization result (kg/hr)
Methanol-water from	5	6
Methanol-water from	98	67
Solid waste from R-03	15	4

The optimum values obtained resulted in about 3% increase in the profit and gave almost the same conversion percent (>99%). In addition, the specifications of the produced biodiesel as measured by physical properties were all combatable with either ASTM or EN standards as illustrated in Table VII.

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Table VII: Major Physical Properties of Biodiesel product

Specification	FAME product	ASTM D6751	EN 14214
Ester content, wt%	98 %	-	Min. 96.5 %
Density at 15°C, kg/m3	878.8	-	860 – 900
Flash Point, °C	155	Min. 130	Min. 120
Cetane No.	62	Min. 47	Min. 51
Kinematic viscosity, 40°C	4.76 mm2/s	1.9–6.0 mm2/s	3.5-5 mm2/s

VI. ECONOMIC STUDY

The process performance of the optimized case and the base case are illustrated in Table VIII. The presented biodiesel production process from waste cooking oil can produce biodiesel with properties similar to diesel fuel produced from crude oil. The process has the advantages of low energy consumption and good economic benefit.

An economic study is presented in this work for the process to demonstrate the initial investment and the payback period (Table VIII). The operation time is assumed 330 days/year.

As presented in Table VIII the optimized model can achieve about 3% increase in the profit with 1 year payback period.

Table VIII: Process performance and economic study of the optimized and the base case.

Items	Price	Price source	Base case ($/yr)	Optimized case ($/yr)
Biodiesel production revenue	1072 $/ton	afdc.energy.gov Neste.com 2019	9842246.4	9858338.2
Waste cooking oil cost	525 $/ton	Average price (2019)	4851000	4851000
Methanol cost	432 $/ton	Methanex.com (2019)	500774.4	490716.02
H_2SO_4 cost	53 $/ton	Echemi.com (2019)	1335.6	1469.16
NaOH cost	650 $/ton	Echemi.com (2019)	60060	17834.418
H_3PO_4 cost	162 $/ton	Echemi.com (2019)	61236	18152.184
Electricity cost	0.0775 $/KW.hr	Egyptian local market at 2019	304.92	324.676
Medium Press. Steam cost	4.476458 $/ton	Egyptian local market at 2019	75742.8	73739.5
Heating Duty cost	4.25 $/GJ	Egyptian local market at 2019	76356	75888.33
Cooling water cost	0.0044 $/m³	Egyptian local market at 2019	10600.8	10303.01
Profit			4204835.9	4318910.9
Added-value tax (20% of the income)				863782.2
Net profit				3455128.7
Equipment cost $				3464300
Payback period (yr)				3464300/3455128.7=1

VII. CONCLUSION

The present work presents a proposed rigorous model using detailed kinetics reaction for the alkali transesterification of waste cooking oil with methanol and alkali catalyst (NaOH). The simulation software used was the Aspen Plus software version 11 with UNIQUAC activity model with Redlich-Kwong Equation of State with Henry's law. Then the effect of different parameters on the process like temperature, pressure, residence time, methanol to oil ratio and catalyst (NaOH) percentage were studied.

Finally, optimization of the process is carried out to find the best conditions for maximum profit and maximum production.

The results showed that, the reaction temperature of 45 ºC, reaction time of 49 min, NaOH concentration of 0.25 wt%, and methanol: oil molar ratio of 7.2:1 were achieved . The optimum values result in about 3% increase in the profit and gave almost the same conversion percent (>99%). Also, the same biodiesel product quantity and quality/specification which was compatible with both ASTM D6751 and EN 14214 is obtained.

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