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Transesterification of Waste Cooking Oil into Biodiesel Using Aspen HYSYS

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ABSTRACT

Increasing uncertainty about global energy production and supply, environmental concerns due to the use of fossil fuels, and the high price of petroleum products are the major reasons to search for alternatives to petrodiesel. Biodiesel fuel has become more attractive because of its environmental benefits, due to the fact that plants and vegetable oils and animal fats are renewable biomass sources. This work presents simulation of an industrial plant for biodiesel production and makes a comparative study of preliminary economic feasibility with a reactive continuous distillation process. The process steady-state simulation was performed using ASPEN/HYSYS 8.0 computer software. Mass and energy balances for each unit, as well as operating conditions, were obtained. The effect of parameters such as molar ratio of methanol to WCO, reflux ratio and reboiler duty on biodiesel mole fraction were investigated.

Keywords: Reactive distillation column, waste cooking oil ;biodiesel, Aspen HYSYS

I. INTRODUCTION

Worldwide interest in biodiesel production has increased dramatically recently due to relentless environmental concerns, step hike in fuels price and increasing demand for fossil fuel consumption. Biodiesel is produced by the transesterification of long chain fatty acids derived from vegetable oils and animal fats with aliphatic alcohols in presence of an appropriate catalyst to form esters of long chain fatty acid (biodiesel) and glycerol (Liu et al., 2012). The use of waste cooking oil instead of virgin oil to produce biodiesel is an effective way to reduce the raw material cost because it is estimated to be about half the price of virgin oil. In addition, using waste cooking oil could also help to solve the problem of waste oil disposal (Supple et al., 1999). It has been known that the transesterification of vegetable oils to fatty acid ester as a biodiesel is an equilibrium-limited reaction. A large excess of alcohol over a stoichiometric ratio is usually employed in conventional reactors to achieve a high degree of the conversion of vegetable oils, thereby requiring the expensive separation of unreacted reactants from the biodiesel product (He et al., 2006). As a consequence, potentially alternative processes to overcome such a difficulty should be explored. When considering the characteristics of the transesterification reaction, the use of reactive distillation, a multifunctional reactor combining chemical reaction and distillation in a single column, is a promising way. Reactive separations are integrated operations that conveniently combine reaction and separation into a single unit allowing the simultaneous production and removal of products, thus improving the productivity and selectivity, reducing energy use, eliminating the need for solvents and leading to intensified, high efficiency systems with green engineering attributes (Malone et al., 2003). The simultaneous separation and reaction inside the column allow the equilibrium-limited reaction to take place more completely and reduce the separation cost of unreacted reactants (Arpornwichanop et al., 2008). Although a number of investigations have been reported on the implementation of a reactive distillation to biodiesel production, most of them focus on the utilization of free fattyacid extracted from vegetable oils as a reactant for an esterification process (Prasertsit et al., 2013). Karacan and Karacan (2015) used oleic acid and methanol as feedstocks to represent canola oil in the simulation. A laboratory-scale continuous-flow Reactive Distillation column system was simulated at optimum conditions by Aspen HYSYS.

Heterogeneous acid and base catalysts have the advantage that separation and regeneration of the catalyst is easy and cheap. Heterogeneous basic catalysts include alkaline–earth metal oxides such as CaO, MgO, SrO, and hydrotalcites. In addition to the economical advantage, the superior catalytic performance of CaO is described in a number of papers reviewing utilization of solid base for the heterogeneous catalytic reaction to produce biodiesel (Yan et al., 2010).

In this study, the process steady-state simulation was performed using ASPEN/HYSYS 8.0 computer software. Biodiesel production from waste cooking oil in the reactive distillation column packed with heteregenous basic CaO catalyst was implemented. The effect of parameters such as feed flow rate, molar ratio of methanol to WCO, reflux ratio and reboiler duty on biodiesel mole fraction and conversion were investigated.

II. METHODS AND MATERIAL

Materials

Waste cooking oil was obtained from local restaurants in Ankara, Turkey. The fatty acid composition of waste cooking oil (see Table 1) was determined by Perkin Elmer Clarus 500 model gas chromatography (GC) using Agilent HP-88 (100 m × 0.25 mm × 0.2 μm) capillary column and Flame Ionization Detector (FID) with helium as the carrier gas. Analysis was performed according to “CoI/T.20/Doc.No.17, 2001” method identified by International Olive Oil Council (IOOC). The oven temperature was programmed at 175 °C for 12 min, and ramped to 225 °C at a rate of 2 °C/min for 12 min.

Table 1 : The chemical and physical properties of WCO

Parameters	Value
FA composition (wt%)	
Palmitic	20.99
Stearic	4.92
Oleic	38.12
Linoleic	29.73
Physical properties	
Water content	0.09%
Acid value	1.09(mg KOH/g oil)
Color	Golden yellow

Kinetics Model

The overall vegetable oil methanolysis reaction could be presented by the following stoichiometric equation,

$$TG + 3ROH \Leftrightarrow 3R'CO_2R + GL \quad (1)$$

where intermediate reaction steps are;

$$TG + ROH \Leftrightarrow R'CO_2R + DG \quad (2)$$

$$DG + ROH \Leftrightarrow R'CO_2R + MG \quad (3)$$

$$MG + ROH \Leftrightarrow R'CO_2R + GL \quad (4)$$

where, TG is triglyceride, DG is diglyceride, MG is monoglyceride and GL is glycerol. Heterogeneously catalyzed methanolysis reaction is very complex because it occurs in a three-phase system consisting of a solid (heterogeneous catalyst) and two immiscible liquid phases (oil and methanol). Also, concurrently with methanolysis, there are some side reactions such as saponification of glycerides and methyl esters and neutralization of free fatty acids by catalyst. Assuming the reaction to be a single step transesterification, the rate law of the transesterification reaction for forward reaction can be expressed by Eq(5).

$$-r_a = -\frac{d[TG]}{dt} = k' \cdot [TG] \cdot [ROH]^3 \quad (5)$$

where [TG] is the concentration of triglycerides and [ROH] that of methanol and k' is the equilibrium rate constant. This overall reaction follows a second order reaction rate law. However, due to the high molar ratio of methanol to oil, the change in methanol concentration could be considered as constant during reaction. This means that by taking methanol in excess, its concentration does not change the reaction order and it behaves as a first order chemical reaction. Hence, the reaction obeys pseudo-first order kinetics. Finally, the rate expression can be written as (Birla et al., 2012),

$$-r_a = -\frac{d[TG]}{dt} = k \cdot [TG] \quad (6)$$

where k is modified rate constant and $k = k' \, [ROH]^3$.

$$k = A_0 \, e^{(-E_a / RT)} \quad (7)$$

The activation energy of transesterification reaction could be calculated by using the Arrhenius equation (Eq(7)). The slope and intercept of the graph between ln k and 1/T gives the values of activation energy and frequency factor. Birla et al used calcined snail shell (CaO) catalyst to produce biodiesel from waste frying oil and investigated the kinetic parameters. The activation energy (E_A) and frequency factor (A_0) for waste frying oil of 79 kJ/mol and 2.98 × 10^{10} min^{-1}, respectively were determined. It was also indicated that the activation energy for the transesterification of waste frying oil was in the range of activation energy obtained for transesterification of soybean oil i.e. 33.6 – 84 kJ/mol (Freedman et al., 1986). .

Thus, Eq(8) was obtained and both of Eq(6) and (8) were used in the simulation and optimization of the reactive packed distillation column by HYSYS 8.0 (Aspen 2012).

i. $$k = 4.97x10^8 \exp\left(-\frac{9,502}{T}\right)$$ ii. (8)

where rate constant (k) and temperature (T) are in $second^{-1}$ and Kelvin units, respectively.

Methods

Figure 1 below shows the flowsheet of the reactive distillation column built and modelled in HYSYS 8.0 environment. The column consists of a condenser, a rectifying section, an WCO feed section, a reaction section, an methanol feed section, a stripping section and a reboiler. The steady state operating parameters used for the HYSYS model formulation and simulation are as shown in Table 2.

In the process, the waste cooking oil and the methanol are fed separately into first stage of reactive packed distillation column at the top. Top product is nearly pure methanol and the bottom product mixture contains methanol, glycerol and biodiesel components. The main column section was divided into two sections of 1.0 m and 0.5 m long. The upper and lower parts were the reaction and the stripping zone, respectively.

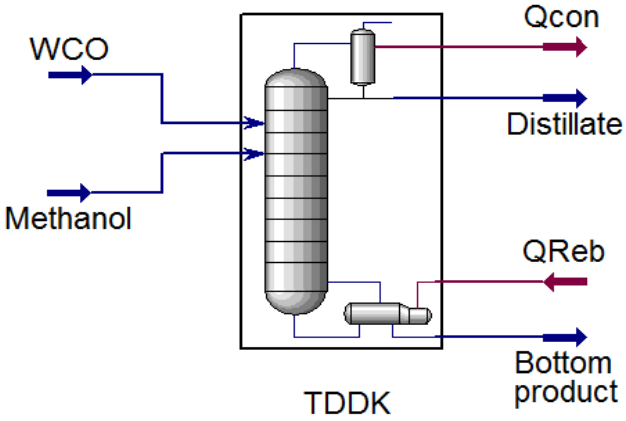

Figure 1: Aspen HYSYS flowsheet of the system

Table 2 : Steady state operating parameters

Parameter	Value
Fluid package	General NRTL
Column stage number	15
Total feed flow (kgmole/hour) (x 10^4)	28
Methanol / WCO mole ratio	6:1
Reflux ratio	6
Reboiler duty (kW)	0.025
Inlet temperature (°C)	40
Waste cooking oil stream	
feed flow (kgmole/hour) (x 10^4)	4.0
mass fraction	
tripalmitin	0.2239
tristearin	0.0525
triolein	0.4065
trilinolein	0.3171
pressure (atm)	1
feed stage	1
Methanol stream	
feed flow (kgmole/hour) (x 10^3)	2.4
pressure (atm)	1
feed stage	1

III. RESULTS AND DISCUSSION

The results obtained used for the Aspen HYSYSV8.0 are determined at the steady state operating parameters. The effects of parameters i.e., molar ratio of methanol to WCO, reflux ratio and reboiler duty on biodiesel mole fraction and conversion are investigated, and optimum operating conditions are determined.

Effect of reboiler duty

Figure 2 shows the effect of reboiler duty on mole fraction of the biodiesel of the column. Table 3 shows the effect of reboiler duty on the percentage of the conversion and the biodiesel mole fraction. While increasing the reboiler duty and reboiler temperature, biodiesel mole fraction increases, but biodiesel conversion was dropped.

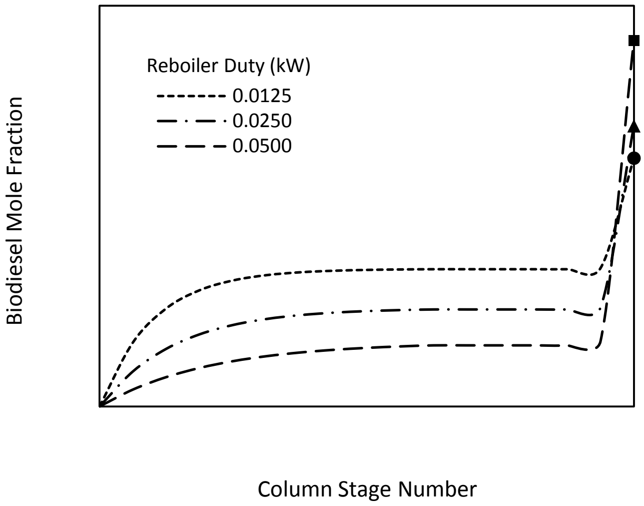

Figure 2 : Column biodiesel mole fraction at different reboiler duty

Table 3: Effect of reboiler duty on the parameters

Reboiler Duty (kW)	Reboiler Temperature ©	Conversion (%)	Biodiesel Mole Fraction (%)
0.0125	88.19	99.72	43.38
0.0250	94.30	98.58	49.03
0.0500	125.6	94.94	63.98

Effect of methanol/WCO mole ratio

Figure 3 shows the effect of mole ratio of methanol to WCO on biodiesel mole fraction and mole fraction alongside the column. Table 4 shows the effect of mole ratio of methanol to WCO on the percentage of the conversion and the biodiesel mole fraction. While increasing the methanol/WCO mole ratio, reboiler temperature, column temperature profile and biodiesel mole fraction decrease but too little increase in biodiesel conversion is obtained.

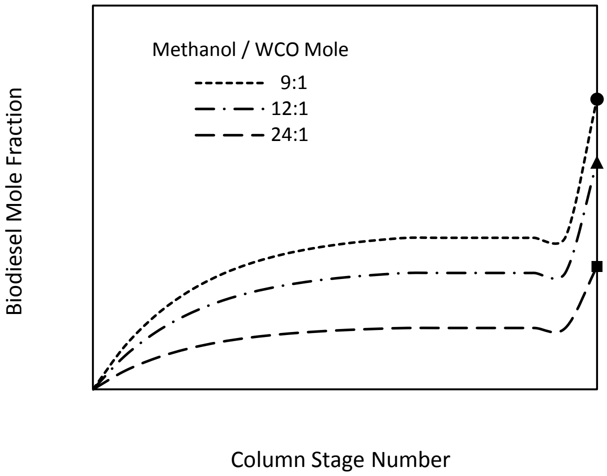

Figure 3 : Biodiesel mole fraction at different methanol/WCO mole

Table 4 : Effect of methanol/WCO mole ratio on the Parameters

Methanol /WCO Mole Ratio	Reboiler Temperature (C)	Conversion (%)	Biodiesel Mole Fraction (%)
9:1	78.43	95.24	30.23
12:1	74.60	95.44	23.68
24:1	69.36	96.41	12.79

Effect of reflux ratio

Figure 4 shows the effect of reflux ratio on biodiesel mole fraction and mole fraction alongside the column. Table 5 shows the effect of reflux ratio on the percentage of the conversion and the biodiesel mole fraction.

Table 5: Effect of reflux ratio on the parameters

Reflux Ratio	Reboiler Temperature (C)	Conversion (%)	Biodiesel Mole Fraction (%)
3:1	217.5	99.86	73.67
6:1	130.8	99.56	66.10
12:1	100.7	99.36	53.91

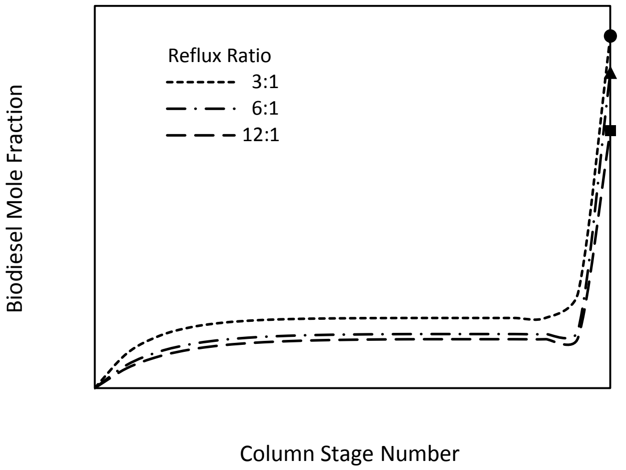

Figure 4 : Column biodiesel mole fraction at different reflux ratio

IV. CONCLUSION

We investigate the use of a reactive distillation for biodiesel production from transesterification of waste cooking and methanol catalyzed by packed heterogenous basic CaO. The effects of parameters i.e., molar ratio of methanol to WCO, reflux ratio and reboiler duty on biodiesel mole fraction and conversion are analyzed.

The results show that increases in reboiler duty and decreases in reflux ratio, total feed flow rate and molar ratio of methanol to WCO enhance the performance of the reactive distillation in terms of the mole fraction of m-oleate in reboiler. On the other hand, decreases in reboiler duty and total feed flow rate improves the performance of the reactive distillation in terms of the conversion of triolein, substantially, at specified conditions of parameters. But, decreases in reflux ratio and molar ratio of methanol to WCO increases the performance in terms of the conversion of triolein, slightly, at specified conditions of parameters.

Because the cost of biodiesel production is highly affected by the price of feedstock and process operating cost, by using waste cooking oil and intensified reactive distillation column packed cheaper heterogenous CaO catalyst can be solution to reduce the biodiesel total cost.

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