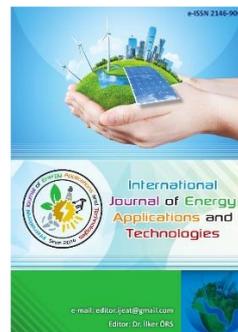




e-ISSN: 2548-060X

## International Journal of Energy Applications and Technologies

journal homepage: [www.dergipark.gov.tr/ijeat](http://www.dergipark.gov.tr/ijeat)

Original Research Article

### Simulation and optimization of reactive packed distillation column for biodiesel production using heterogeneous catalyst

Mehmet Tuncay Çağatay<sup>1</sup>, Süleyman Karacan<sup>2\*</sup><sup>1</sup> National Defence Ministry, General Staff Presidency, Department of Project Development and Management, Kızılay 06420, Ankara, Turkey<sup>2</sup> Ankara University, Engineering Faculty, Department of Chemical Engineering, Tandoğan 06100, Ankara, Turkey

#### ARTICLE INFO

\* Corresponding author  
[karacan@eng.ankara.edu.tr](mailto:karacan@eng.ankara.edu.tr)Received June 28, 2018  
Accepted December 18, 2018Published by Editorial Board  
Members of IJEAT© This article is distributed by  
Turk Journal Park System under  
the CC 4.0 terms and conditions.

doi: 10.31593/ijeat.438001

#### ABSTRACT

It is important to simulate a process to see how its production would be in real time. However, there is a few simulation study in literature on continuous flow-biodiesel production in reactive distillation (RD) column. In this study, simulation and optimization of continuous flow-biodiesel (FAME) production in RD column packed with cheaper heterogeneous basic CaO catalyst by using Aspen HYSYS 3.2 software was investigated to contribute to the literature. In study, low-priced waste cooking oil (WCO) and methanol were fed separately into first stage at top of RD column. In the literature, transesterification was considered as pseudo-first order forward reaction, and activation energy ( $E_a$ ) and frequency factor ( $A_0$ ) for WCO of 79 kJ/mol and  $2.98 \times 10^{10} \text{ min}^{-1}$  were determined, respectively. After discovering composition of WCO by GC, a set pseudo-first order forward reaction based on triglyceride (as tripalmitin, tristearin, triolein and trilinolein) were written to the simulator. The developed model using General NRTL fluid package was simulated to converge by Sparse Continuation Solver. After simulation, optimum conditions were determined by Optimizer tool and Box algorithm. In the optimization, objective function was selected so as to maximize the sum of conversion and mole fraction of m-oleate in bottom product. As a result, optimum values were determined as reflux ratio of 0.1, reboiler duty of 17.9 W, total feed flow rate of  $11.2 \times 10^{-4} \text{ kgmol/hour}$  and methanol/WCO molar ratio of 6.42 for maximum conversion of 99.97% and mole fraction of 70.69%. Consequently, good results were very compatible with literature, thus showing suitability of suggested model, economically feasible biodiesel production and Aspen HYSYS 3.2 capability of handling this process successfully.

**Keywords:** Biodiesel production, Reactive distillation column, Aspen HYSYS

#### 1. Introduction

A number of countries have been looking for alternatives to meet the needs for an environmentally friendly and renewable fuel supply because of the growing demand for fuel and global concern about the effects caused by greenhouse gases. The use of biodiesel is an alternative method for replacing fossil diesel [1]. Biodiesel is produced by the transesterification of long chain fatty acids (FA) derived from vegetable oils and animal fats with aliphatic

alcohols in presence of an appropriate catalyst to form esters of long chain fatty acid (FAME) and glycerol (glycerine) [2]. Transesterification reactions can be catalyzed by an acid, base, or enzymes. Homogeneous and heterogeneous alkali and acid catalysts have been studied [3]. Heterogeneous acid and basic catalysts have the advantage of easy and cheap separation and regeneration process [4]. Heterogeneous basic catalysts include alkaline-earth metal oxides such as CaO, MgO, SrO, and hydrotalcites [5,6]. In addition to its cheaper value and being easily available, CaO has superior catalytic

performance described in a number of papers reviewing catalytic reaction to produce biodiesel [7–10]. Vujjic et al [11] showed that transesterification reaction was considered as pseudo-first order forward reaction based on triglyceride (TG). Birla et al [12] used calcined snail shell (CaO) catalyst to produce biodiesel from waste cooking oil (WCO) and investigated the kinetic parameters. The activation energy ( $E_a$ ) and frequency factor ( $A_0$ ) for WCO of 79 kJ/mol and  $2.98 \times 10^{10} \text{ min}^{-1}$  were determined, respectively. It was also indicated that the activation energy found by Birla et al was in the range of 33.6–84 kJ/mol obtained for transesterification of soybean oil [13].

The most important obstacle to commercial use of biodiesel is production cost and it is not economical compared to petroleum diesel. One of the reason is the use of excessive amounts of equipment and energy to remove high amounts of alcohol for high conversion and the impurities caused by it in the current biodiesel production processes [14]. It was shown that biodiesel production cost by using RD column was lower than those conventional processes [15]. Given low biodiesel production capacity in currently used batch reactor process [16], He and Singh [17] shown that RD has a productive advantage when compared to the conventional batch process. By using RD column, the investment cost could be decreased partly because of occurring the chemical reaction and separation in same equipment, and partly because of with minimum number of equipment by means of reducing pipelines and pumps and the integration of heat [18]. Wang et al. [19] performed the methyl acetate hydrolysis by RD, achieving 10% less energy consumption and 50% increase in production compared to the fixed bed reactor.

The other most important cost effect is raw material's price. In fact, raw material costs account for a major portion of total biodiesel manufacturing cost [20]. As known, vegetable oil is a food commodity and its price is continuously increasing parallel growth of world demand for food [21]. WCO costs are 2-3 times cheaper than vegetable oil, and it has been reported that the use of it could reduce the cost by 60-90% [18, 22]. In recent years, the use of low-cost WCO and animal fats has increased, rather than refined vegetable oils for the economic biodiesel production [23-27].

Before producing biodiesel in plant, it is very necessary that a prototype of its production be setup and simulate using a process simulator like Aspen HYSYS in order to have an idea of how its production will be in real time. Oguz and Celik Tolu [28] published a review for optimization analysis of biodiesel production from vegetable oil by using bio-based CaO as catalyst. When the literature is examined, there are several simulation studies about biodiesel production in batch or continuous flow reactor system with homogenous alkali or acidic catalyst [3, 20, 29, 30]. However, there is a

few study in the literature on the simulation of biodiesel production with RD column. Simasatitkul et al. [31] suggested the use of RD for transesterification of methanol with soybean oil, catalyzed by homogeneous sodium hydroxide. Karacan and Karacan [32] used Aspen HYSYS to simulate RD column using homogeneous potassium hydroxide and potassium methoxide as catalyst in esterification of oleic acid and methanol.

Now that there is a big missing in the literature including simulation and optimization study on continuous flow biodiesel production in RD column with heteroneous catalyst, this study was carried out for the purpose of obtaining biodiesel in continuous flow RD column economically and efficiently, thanks to integrated RD column and raw materials such as inexpensive WCO and heterogenous basic catalyst CaO, which is cheaper, easily recoverable and having superior catalytic performance. To achieve this, simulation and optimization by aspen HYSYS 3.2 were performed and optimum conditions of total feed flow rate, molar ratio of methanol to WCO, reflux ratio and reboiler duty for the maximum biodiesel mole fraction and conversion at outlet stream were determined.

## 2. Methods

### 2.1. Determination the composition of WCO

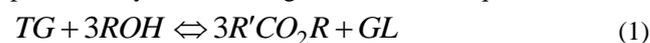
WCO was obtained from local restaurants in Ankara, Turkey. The FA composition of WCO (see Table 1) was determined by Perkin Elmer Clarus 500 model gas chromatography (GC) with Agilent HP-88 (100 m x 0.25 mm x 0.2  $\mu\text{m}$ ) capillary column and Flame Ionization Detector (FID) with helium carrier 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. In addition, the injector and detector temperatures were 250°C and 280°C, respectively.

**Table 1.** The chemical and physical properties of WCO

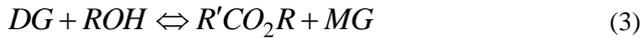
Parameters	Value
FA composition (wt%)	
Palmitic	20.99
Stearic	4.92
Oleic	38.12
Linoleic	29.73
Water content	0.09%
Acid value	1.09 (mg KOH/g oil)
Color	Golden yellow

### 2.2. Kinetics model

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



where intermediate reaction steps are;



where, *TG* is triglyceride, *DG* is diglyceride, *MG* is monoglyceride, *GL* is glycerol, *ROH* is alcohol and *R'CO<sub>2</sub>R* is FAME. Heterogeneously catalyzed methanolysis reaction is very complex because it occurs in a three-phase system consisting of a solid heterogeneous catalyst phase and two immiscible oil and methanol liquid phases. Also, concurrently with methanolysis, there are some side reactions such as saponification of glycerides and methyl esters and neutralization of free FA by catalyst.

While modelling the methanolysis process, it was assumed that the reaction occurred between methoxide ions and glycerides adsorbed on the catalyst surface [33, 34]. Also, methanol mass transfer and adsorption on catalyst active sites, and desorption rate of products from catalyst surface and their mass transfer into liquid reaction mixture did not limit the overall process rate [34]. Besides, assuming the reaction to be a single step transesterification, rate law of the transesterification reaction for forward reaction [11] can be expressed by Eq (5),

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

where *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 effect the reaction order and it behaves as a first order chemical reaction. Hence, the reaction obeys pseudo-first order kinetics. Hence, the reaction obeys pseudo-first order kinetics [35-37]. Finally, the rate expression [12] can be written as,

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

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

### 2.3. Simulation of RD column packed with CaO

According to the designed process (see Fig. 1), WCO and methanol were fed separately into first stage at the top of RD column. The top product was nearly pure methanol and the bottom product mixture contained methanol, glycerol and biodiesel components. The column had a height of 1.5 m and a diameter of 0.05 m except the condenser and the reboiler units. It consisted of a cylindrical condenser having a diameter of 0.05 and height of 0.225 meter. The reboiler was spherical in shape and had a volume of 3 L. The main column

section was divided into two section of 1.0 m and 0.5 m long. The upper and lower parts were the reaction and the stripping zone, respectively.

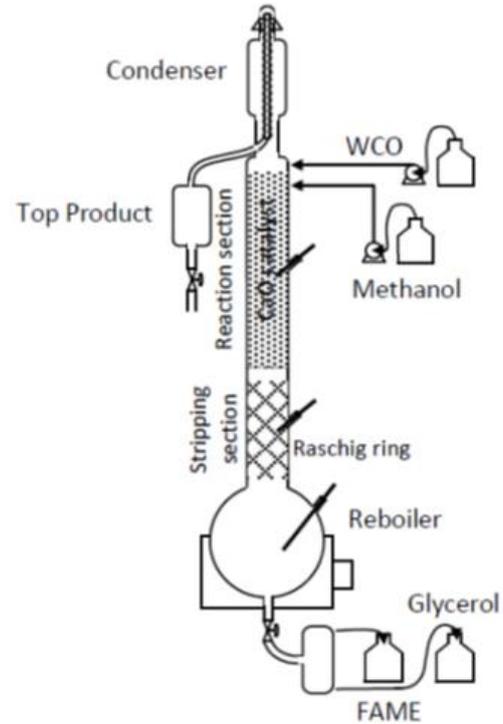


Figure 1. Reactive distillation column packed with CaO catalyst

Table 2. Steady state operating parameters for simulation

Parameter	Value
Fluid package	General NRTL
Column stage number	15
Total feed flow (kgmole/hour) (x 10 <sup>4</sup> )	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 <sup>4</sup> )	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 <sup>3</sup> )	2.4
pressure (atm)	1
feed stage	1

The steady state simulation of the process was performed by using Aspen HYSYS 3.2 computer software. In the simulation, RD column were divided into 15 stages except for the condenser and the reboiler units. Stage 0 and 16 was assigned as condenser and reboiler, respectively. Besides, the reaction mechanism and stripping process was described

between 1-10th stages and 11-15th stages, in turn. The lower 5 stripping stages were packed with raschig rings while the first 10 reaction stage's fillers were chosen as "Flexipac (metal structured) Mellapac 250" supporting cage.

It was necessary to select the main components of WCO for simulation. Zhang et al [20] used triolein and methyl oleate to represent canola oil and FAME. Likewise, Karacan and Karacan [32] used oleic acid and methanol to represent canola oil. In addition, Souza et al [38] used triacylglycerol composition of the cottonseed oil in simulation. In this study, the composition of WCO for simulation was based on triacylglycerol.

In the program, fluid package was chosen as General NRTL model and reaction set option was selected as kinetic type and Sparse Continuation Solver was used to converge. A set with four reaction described by stoichiometric coefficients and pseudo-first order forward reaction Eq (6) based on TG (tripalmitin, tristearin, triolein and trilinolein) were defined only first 10 reaction stages in the simulator. The endothermic [39] methanolysis reaction enthalpies of tripalmitin, tristearin, triolein and trilinolein were calculated and used by HYSYS as 353, 104, 270 and 69.2 kJ/mole, respectively. In addition, the Arrhenius equation Eq (7), with the activation energy ( $E_a$ ) of 79 kJ/mol and frequency factor ( $A_0$ ) of  $2.98 \times 10^{10} \text{ min}^{-1}$  [12], were defined to the simulator. The steady state simulation parameters and conditions were outlined in Table 2. The RD column liquid side mass fractions at steady state simulation were given in Fig. 4.

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

#### 2.4. Aspen HYSYS optimization procedure

After steady state simulation, the optimization process was carried out by incorporating an optimizer into flowsheet (see Fig. 2). The objective function was chosen so as to maximize the sum of mole fraction and conversion of m-oleate in bottom stream. Also, "Box" algorithm was used in the optimization and ranges of the adjusted variables was determined as shown in Table 3.

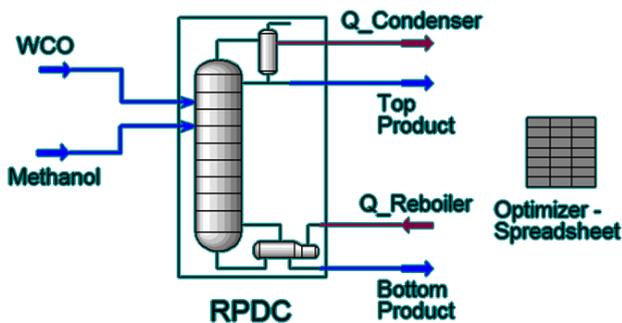


Figure 2 HYSYS optimization flowsheet for RD column

The feed flow of methanol and WCO were changed in range of  $6 \times 10^{-4} - 1.6 \times 10^{-3}$  and  $1.0 \times 10^{-4} - 2.0 \times 10^{-4}$  kgmole/hour,

respectively. Because mole ratio was changed from stoichiometric ratio of 3 to 16 as minimum and maximum, the molar feed flow rates providing the mole ratio condition greater than 6.0 was selected as one condition in the simulator. There was a dual azeotrope between methyl linoleate and glycerol at 229°C. In addition, glycerol and biodiesel components could be decomposed at 150°C and 250°C, respectively [31]. So, the largest temperature of reboiler was chosen as 160 °C as another constraint. Lastly, conversion was specified in the range of 99.00 - 99.99 %.

Table 3. Parameters used for running in the optimization

Parameter	Low Bound	High Bound
Reflux ratio	0.10	10.0
Reboiler duty (W)	8.33	27.8
Total feed flow (kgmole/hour) $\times 10^4$	7.00	18.0
Methanol / WCO mole ratio	3.00	16.0

### 3. Results and Discussion

Aspen HYSYS software had a multi-variable steady-state optimizer. Once our flowsheet was built and converged to a solution, the "Optimizer" was added and used to find the optimum conditions by maximizing the objective function, summing of m-oleate conversion and mole fraction in reboiler. Thus, optimum conditions of reflux ratio, reboiler duty, total feed flow and methanol/WCO mole ratio were determined according to restricted conditions by HYSYS 3.2 "Box" algorithm.

RD column temperature profiles for simulated and optimized conditions were seen in Fig. 3. With regarding to simulation profile, RD column temperature changed from 64.5 to 74.2 °C. On the other hand, RD column temperature profile for optimization changed between 64.5 and 75.9 °C at the first 10 stages. In other words, it was seen an increment in RD column temperature profile for optimization. Reboiler temperature also moved in the direction of augmenting, thus increasing the mole fraction at reboiler, and reached the value of 159.9 °C. As known before, reboiler temperature must have been lower than 160 °C as constraint. The RD column liquid side mass fractions at optimum conditions were given in Fig. 5.

The simulation and optimization mole fraction values for profiles and for bottom liquid product were given in Fig. 4-5 and Table 4, respectively. From first stage to tenth stage of RD column in Fig. 4-5, methanol and WCO amounts decreased due to consumption, and biodiesel and glycerol in stoichiometric ratio were obtained via transesterification reaction. Accordingly, concentrations of reactants reduced and of products increased gradually till 10th stage and remained constant between 11 and 15th stages. At 16th stage, there was a sudden decrease in amount of methanol and increase in amount of biodiesel and glycerol because of heating in the reboiler.

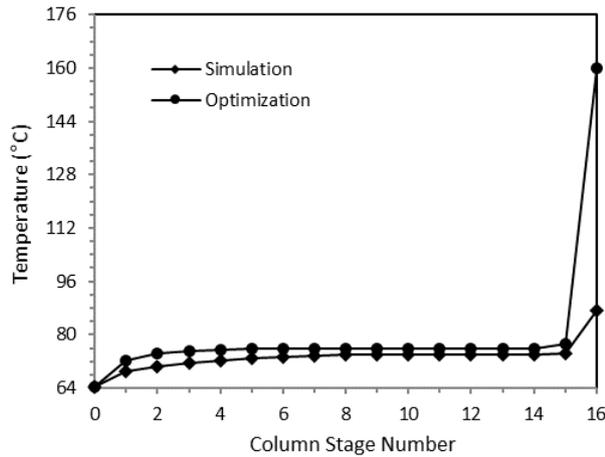


Figure 3. Column temperature profiles at simulated and optimum conditions

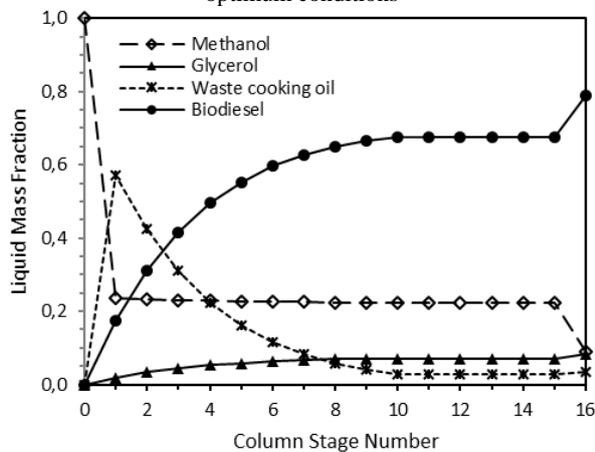


Figure 4. Liquid mass fraction profiles of the column at steady state simulation

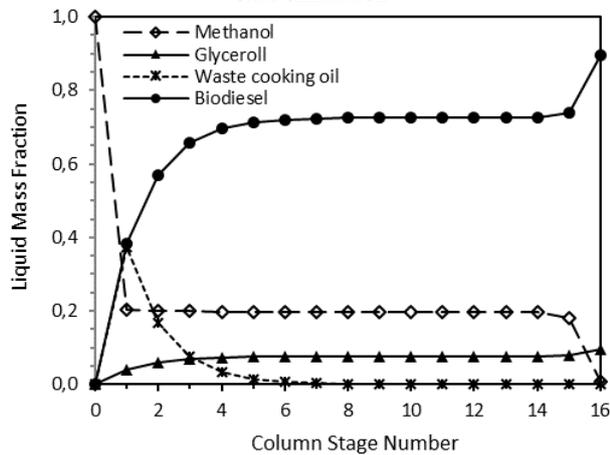


Figure 5. Column liquid mass fraction at optimum conditions

Table 4. Mole fractions of bottom liquid product

Component	Mole Fraction	
	Simulation	Optimization
Methanol	0.4363	0.0574
WCO	0.0061	0.0001
Glycerol	0.1394	0.2356
Biodiesel	0.4182	0.7069

According to Fig. 4-5 and Table 4, it was observed that WCO was consumed nearly wholly and methanol in reboiler

decreased in a great quantity from 43.63% to 5.74% in the optimization. Besides, glycerol and biodiesel products values increased to approximately its maximum value at specified conditions, respectively, depending on stoichiometric mole ratio of 3:1. As a result, the greatest mole fraction of biodiesel and glycerol and the lowest mole fraction of methanol were obtained at specified conditions.

The simulation and optimization values of parameters of laboratory scale reactive CaO-packed distillation column were summarized in Table 5. Accordingly, reflux ratio of 0.1, reboiler duty of 17.9 W, total feed flow of  $11.2 \times 10^{-4}$  kgmole/hour and methanol/WCO mole ratio of 6.42 were obtained. Birla et al [12] obtained the conversion as 99.58% under the optimum conditions i.e. methanol/oil molar ratio of 6.03:1. In comparison with simulation results, reflux ratio, reboiler duty, total feed flow parameters moved in direction of decreasing while maximizing the object function, and methanol/WCO mole ratio value approached to nearly 6:1 value.

Table 5. Simulation and optimization values of the parameters

Parameter	Simulation	Optimization
Reflux ratio	6.00	0.10
Reboiler duty (W)	25.0	17.9
Total feed flow (kgmole/hour) $\times 10^4$	28.0	11.2
Methanol / WCO mole ratio	6.00	6.42

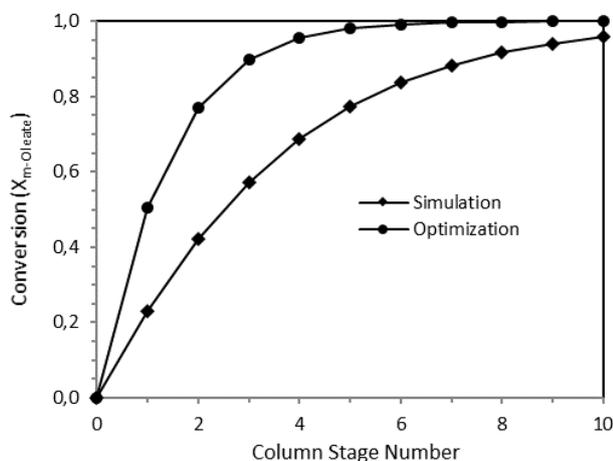
Table 6. Conversion and mole fraction for the simulation and optimization

Parameter	Simulation	Optimization
Reboiler temperature (°C)	87.15	159.9
Biodiesel conversion (%)	95.81	99.97
Biodiesel mole fraction (%)	41.82	70.69

Moreover, as shown in Table 6, mole fraction increased from 41.82% to 70.69%, thus enabling the maximization of target object value. Also, conversion increased from 95.81% to 99.97% as aimed between 99.00-99.99% limit values. As for reboiler temperature, it increased from 87.15 °C to 159.9 °C and it was also lower than 160 °C of reboiler temperature constraint.

After numerous trials with software, it was seen that, it was necessary to increase the reboiler duty and to reduce the reflux ratio, total feed flow rate and molar ratio in order to increase the molar fraction of m-oleate in the reboiler. However, in order to increase the conversion value at the same time under defined conditions, it was seen that the reboiler duty and total feed flow rate should be reduced substantially, and the reflux ratio and the molar ratio should be decreased slightly. So as to increase the performance of the RD column economically, both the mole fraction and the conversion values must be increased simultaneously.

Finally, RD column conversion profiles at simulated and optimized conditions were seen in Fig. 6. In comparison with simulation, in which biodiesel conversion was obtained as 23.2%, 57.2% and 88.4% at 1st, 3rd and 7th stages, respectively, biodiesel conversions at optimized condition were obtained as 50.6%, 89.7% and 99.6% at 1st, 3rd and 7th stages, respectively. Simasatitkul et al [31] proposed that a suitable configuration of RD column with homogenous catalyst should consist of only three reactive stages and performance of RD column was improved slightly when the number of reactive stages were higher than 3. Accordingly, in our study, it was observed that there was a steeper rise in the first three stages, and it gradually reached the final value at the 7th stage. The reason could be that the homogenous basic reaction was much more rapid than the heterogeneous one.



**Figure 6.** Column conversion profiles at simulated and optimum conditions

#### 4. Conclusion

In this study, we simulated and optimized the CaO catalyst packed-RD column in biodiesel production by using WCO (represented as tripalmitin, tristearin, triolein and trilinolein) and methanol, successfully.

Then, optimum conditions were determined for maximum mole fraction and conversion of m-oleate in reboiler. Accordingly, for maximum conversion of 99.97% and mole fraction of 70.69%, optimum conditions were obtained as reflux ratio of 0.1, reboiler duty of 17.9 W, total feed flow as  $11.2 \times 10^{-4}$  kgmole/hour and methanol/WCO mole ratio of 6.42 were obtained. In the literature, conversion values and mole ratios for the methanolysis of WCO in batch reactor by using CaO were obtained as 99.58, 99.0, 94.25, 95.84 % and 6.03:1, 12:1, 12:1, 18:1, respectively [12, 40-42]. In addition, by using; canola oil [43], karanja and jatropha oil [44], and rapeseed oil [45] those were obtained as 99.85, 99.0, 96.5 % and 9:1, 12:1, 12:1, respectively. As well, conversions with using soybean oil were obtained as 95% [5] and 93% [6] at

mole ratio of 12:1. Furthermore, by using WCO, conversions and mole ratios, in turn, of 94% and 25:1 in fixed-bed reactor [46], and of 94.41% and of 6:1 in packed RD column [47] were obtained.

As seen from results, it was understood that our results were very compatible with those. Given good results obtained from simulation and optimization, it was evaluated that FAME could be produced successfully by using packed-RD column. In addition, because biodiesel production cost is highly affected by price of feedstock and process operating cost, total cost could be reduced by employing this method including cheaper and superior catalytic heterogeneous CaO catalyst, inexpensive WCO feedstock and intensified RD column.

Consequently, the simulation and optimization procedure and the model available in this study could be used conveniently in real-time planning phase of plantwide-scaled biodiesel production by using WCO in CaO catalyst packed-RD column.

#### References

- [1] Donato, A.G., Gonçalves, J.A., Peres, J.S., Ramos, A.L.S., Ribeiro de Melo Jr., A.L.D.C.A, Antunes, O.A.C., Furtado, N.C. and Taft, C.A., 2009, "The use of acids, niobium oxide, and zeolite catalysts for esterification reactions", *J. Phys. Org. Chem*, 22, 709–716.
- [2] Srivastava, A. and Prasad, R., 2000, "Triglycerides-based diesel fuels", *Renew. Sustainable Energy Rev.*, 4, 111–133.
- [3] Zhang Y., Dube M.A., McLean D.D. and Kates M., 2003, "Biodiesel production from waste cooking oil: 1. Process design and technological assessment", *Bioresource Technology*, 89, 1-16.
- [4] Sharma, Y.C., Singh, B. and Upadhyay, S.N., 2008, "Advancements in development and characterization of biodiesel A review". *Fuel*, 87, 2355–2373.
- [5] Liu, X., He, H., Wang, Y., Zhu, S. and Piao, X. 2008. Transesterification of soybean oil to biodiesel using CaO as a solid base catalyst. *Fuel*, 87, 216–221.
- [6] Kouzu, M., Kasuno, T., Tajika, M., Sugimoto, Y., Yamanaka, S. and Hidaka, J., 2008, "Calcium oxide as a solid base catalyst for transesterification of soybean oil and its application to biodiesel production", *Fuel*, 87, 2798–2806.
- [7] DiSerio, M., Tesser R., Pengmei, L. and Santacesaria, E. 2008. Heterogeneous catalysts for biodiesel production. *Energy, Fuels*, 22:201–17.
- [8] Zabeti, M., Daud, WMAW and Aroua, MK. 2009. Activity of solid catalysts for biodiesel production: a review. *Fuel Process Technol*, 90:770–7.
- [9] Helwani, Z., Othman, MR., Aziz, N., Kim, J. and Fernando WJN. 2009. Solid heterogeneous catalysts for transesterification of triglycerides with methanol: a review. *Appl Catal A Gen.*, 363:1–10.

- [10] Yan, S., DiMaggio, C., Mohan, S., Kim, M., Salley, S.O. and Ng, K.Y.S. 2010. Advancements in heterogeneous catalysis for biodiesel synthesis. *Top Catal.*, 53:721–36.
- [11] Vujcic, D.J., Comic, D., Zarubica, A., Micic, R. and Boskovi, G., 2010, “ Kinetics of biodiesel synthesis from sunflower oil over CaO heterogeneous catalyst”, *Fuel*, 89,2054–2061.
- [12] Birla A, Singh B, Upadhyay SN and Sharma YC (2012) Kinetics studies of synthesis of biodiesel from waste frying oil using a heterogeneous catalyst derived from snail shell. *Bioresource Technology*, 106, 95–100.
- [13] Freedman, B., Buttefield, R.O. and Pryde, E.H. 1986. Transesterification kinetics of soybean oil. *J.Am.Oil Chem.Soc.*, 63 (10), 1375–80.
- [14] Kulchanat P., Chokchai M., Chakrit T., 2013. Transesterification of palm oil with methanol in a reactive distillation column. *Chemical Engineering and Processing*, 70, 21–26.
- [15] Kapilakarn, K. and Peugtong, A. A. 2007. Comparison of costs of biodiesel production from transesterification. *Int. Energy J.*, 8, 1–6.
- [16] Vogel, A., Mueller-Langer, F. and Kaltschmitt, M. 2008. Analysis and evaluation of technical and economic potentials of BtL-fuels. *Chem. Eng. Technol.*, 31, 755–764.
- [17] He, B.B. and Singh, A.P. 2006. Thompson, J.C. A novel continuous-flow reactor using reactive distillation for biodiesel production. *Am. Soc. Agric. Biol. Eng.*, 49, 107–112.
- [18] Talebian-Kiakalaieh A., 2013. A review on novel processes of biodiesel production from waste cooking oil. *Applied Energy*, 104, 683-710.
- [19] Wang J, Ge X, Wang Z, Jin Y., 2001. Experimental studies on the catalytic distillation for hydrolysis of methyl acetate. *Chem Eng Technol.*, 24 (2), 155–9.
- [20] Zhang, Y., Dubé, M.A., McLean, D.D. and Kates, M. 2008. Biodiesel production from waste cooking oil: 1. Process design and technology assessment. *Bioresour. Technol.*, 99, 1131–1140.
- [21] Festel, G.W. 2008. Biofuels—economic aspects, chemical engineering & technology. *Chem. Eng. Technol.*, 31, 715–720.
- [22] Kulkarni, M.G. and Dalai, A.K. 2006. Waste cooking oil – an economical source for biodiesel: a review. *Ind. Eng. Chem. Res.*, 45, 2901–2913.
- [23] Halim S.F.A., 2009. Continuous biosynthesis of biodiesel from waste cooking palm oil in a packed bed reactor: optimization using response surface methodology (RSM) and mass transfer studies. *Bioresource Technology*, 100, 710–716.
- [24] Jacobson K., Gopinath R., Meher L.C., Dalai A.K., 2008. Solid acid catalyzed biodiesel production from waste cooking oil. *Applied Catalysis B: Environmental*, 85, 86–91.
- [25] Phan A.N., Phan T.M., 2008. Biodiesel production from waste cooking oils. *Fuel*, 87, 3490–3496.
- [26] Wang Y., Pengzhan Liu S.O., Zhang Z., 2007. Preparation of biodiesel from waste cooking oil via two-step catalyzed process. *Energy Conversion and Management*, 48, 184–188.
- [27] Felizardo P., Neiva Correia M.J., Raposo I., Mendes J.F., Berkemeier R., Bordado J.M., 2006. Production of biodiesel from waste frying oils. *Waste Management*, 26, 487–494.
- [28] Oguz H., Celik Tolu M., 2018, “A Review: Optimisation Analysis of Biodiesel Production from Vegetable Oil by Using Biobased CaO as Catalyst”, 7th International Conference on Advanced Technologies (ICAT'18), April 28- May 1 2018, vol 1, 851-855, Antalya Turkey.
- [29] Morais, S., Mata, T.M., Martins, A.A., Pinto, G.A. and Costa C.A.V. 2010. Simulation and life cycle assessment of process design alternatives for biodiesel production from waste vegetable oils. *Journal of Cleaner Production*, 18, 1251-1259.
- [30] Martín, M. and Grossmann I.E. 2012. Simultaneous Optimization and Heat Integration for Biodiesel Production from Cooking Oil and Algae. *Ind. Eng. Chem. Res.*, 51, 7998–8014.
- [31] Simasatitkul, L., Siricharnsakunchai, P., Patcharavorachot, Y., Assabumrungrat, S. and Arpornwichanop, A. 2011. Reactive distillation for biodiesel production from soybean oil. *Korean J. Chem. Eng.*, 28, 649–655.
- [32] Karacan, S. and Karacan, F. 2014. Simulation of Reactive Distillation Column for Biodiesel Production at Optimum Conditions. *Chemical Engineering Transactions*. 39, 1705-1710.
- [33] Hattori, H, Shima, M and Kabashima, H. 2000. Alcoholysis of ester and epoxide catalyzed by solid bases. *Stud Surf Sci Catal*, 130:3507–12.
- [34] Veljkovic', V.B., Stamenkovic', O.S., Todorovic', Z.B., Ladic', M.L. and Skala, D.U. 2009. Kinetics of sunflower oil methanolysis catalyzed by calcium oxide. *Fuel*, 88, 1554–1562.
- [35] Freedman, B., Pryde, C.H. and Mounts, T.L. 1984. Variables affecting the yields of fatty esters from transesterified vegetable oils. *JAOCS*, 61:1638-1643.
- [36] Singh, A.K. and Fernando, S.D. 2007. Reaction kinetics of soybean oil transesterification using heterogeneous metal oxide catalysts. *Chem.Eng.Technol.*, 30 (12), 1716–1720.
- [37] Zhang, L., Sheng, B., Xin, Z., Liu, Q. and Sun, S. 2010. Kinetics of transesterification of palm oil and dimethyl carbonate for biodiesel production at the catalysis of heterogeneous base catalyst. *Bioresour.Technol.*, 101, 8144–8150.
- [38] Souza, T.P.C., Stragevitch, L., Knoechelmann, A., Pacheco, J.G.A. and Silva, J.M.F. 2014. Simulation and preliminary economic assessment of a biodiesel plant and comparison with reactive distillation. *Fuel Processing Technology*, 123, 75–81.
- [39] Hsieh, L.S., Kumar, U. and Wu, J.C.S. 2010. Continuous production of biodiesel in a packed-bed reactor using shell-core structural Ca(C<sub>3</sub>H<sub>7</sub>O<sub>3</sub>)<sub>2</sub>/CaCO<sub>3</sub> catalyst. *Chemical Engineering Journal*, 158, 250–256.

- [40] Kouzu M, Kasuno T, Tajika M, Sugimoto Y, Yamanaka S and Hidaka J (2008) Calcium oxide as a solid base catalyst for transesterification of soybean oil and its application to biodiesel production. *Fuel*, 87, 2798–2806.
- [41] Niju S, Begum KM and Anantharaman N (2014) Enhancement of biodiesel synthesis over highly active CaO derived from natural white bivalve clam shell. *Arabian Journal of Chemistry*.
- [42] Girish N, Niju SP, Begum KM and Anantharaman N (2013) Utilization of a cost effective solid catalyst derived from natural white bivalve clam shell for transesterification of waste frying oil. *Fuel*, 111, 653–658.
- [43] Zhao L, Qiu Z and Stagg-Williams SM (2013) Transesterification of canola oil catalyzed by nanopowder calcium oxide, *Fuel Processing Technology* 114, 154–162.
- [44] Kaur M and Ali A (2011) Lithium ion impregnated calcium oxide as nano catalyst for the biodiesel production from karanja and jatropha oils. *Renewable Energy*, 36, 2866-2871.
- [45] Kouzu M, Hidaka J, Komichi Y, Nakano H and Yamamoto M (2009) A process to transesterify vegetable oil with methanol in the presence of quick lime bit functioning as solid base catalyst. *Fuel*, 88, 1983–1990.
- [46] Buasri A, Ksapabutr B, Panapoy M and Chaiyut N (2012) Biodiesel production from waste cooking palm oil using calcium oxide supported on activated carbon as catalyst in a fixed bed reactor. *Korean J. Chem. Eng.*, 29 (12), 1708-1712.
- [47] Niju S, Begum KM and Anantharaman N (2016) Clam shell catalyst for continuous production of biodiesel. *International Journal of Green Energy*, 13, 1314–1319.