

Simulation of Reactive Distillation Column for Biodiesel Production at Optimum Conditions

Süleyman Karacan^a, Filiz Karacan^b

^aAnkara University, Engineering Faculty, Department of Chemical Engineering, Tandoğan 06100, Ankara, Turkey.

^bTurkish Atomic Energy Authority, Sarayköy Nuclear Research and Training Centre, Istanbul Road 30 km., 06983 Saray, Ankara, Turkey.

karacan@eng.ankara.edu.tr

Biodiesel is defined as a mixture of fatty acid alkyl esters which are commonly produced from triglycerides and alcohol through transesterification reaction in the presence of alkali catalysts. In this work canola oil and methanol were used in this research as the feedstocks, and potassium hydroxide, potassium methoxide, were used as different formulations of catalysts. A laboratory-scale continuous-flow Reactive Distillation column system was simulated at optimum conditions by Aspen HYSYS. The homogeneous alkali and acid catalyzed was applied to the system. The non-catalytic reaction, where the absence of catalyst simplifies the purification procedures and the products can be easily separated. The critical operating conditions and high consumption of methanol and energy make it uneconomical. Based on the optimization of energy integration and methanol recovery strategies, optimization strategies were assessed for saving energy and recovery methanol.

1. Introduction

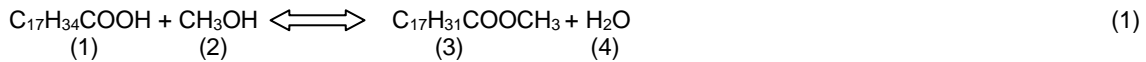
Biodiesel is a clean burning fuel derived from a renewable feedstock such as vegetable oil or animal fat. It is biodegradable, non-inflammable, non-toxic, and produces lesser carbon monoxide, sulphur dioxide, and unburned hydrocarbons than petroleum-based fuel. Biodiesel has become increasingly attractive due to its environmental benefits and to the fact that it is made from renewable resources. The transesterification process can be described as the triglycerides reaction with an alcohol and catalyst to obtain biodiesel glycerol as by-product. The catalytic transesterification of vegetable oils with methanol is an important industrial method used in biodiesel synthesis. Also known as methanolysis, this reaction is well studied and established using acids or alkalis, such as sulfuric acid or sodium hydroxide as catalysts. However, these catalytic systems are less active or completely inactive for long chain alcohols. Usually, industries use sodium or potassium hydroxide or sodium or potassium methoxide as catalyst, since they are relatively cheap and quite active for this reaction (Kralova and Sjoblom, 2010). Most chemical processes involve reaction and separation operations that are typically carried out in different sections of the plant and use different types of equipment, such as continuous stirred-tank reactor, plug-flow reactor, batch reactor and distillation column all operated under a wide variety of conditions. Recent economic and environmental considerations have encouraged the chemical industry to focus on such technologies based on process intensification. Reactive distillation is integrated operations that conveniently combine reaction and distillation 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 (Omota et al., 2003). Many researchers have used alkali catalysts (NaOH, KOH, CH₃-ONa) for production of biodiesel as these catalysts are cheap and readily available (Atapour and Kariminia, 2011). However, the process has some limitations such as high energy consumption which in turn causes a dramatic increase in capital equipment costs and safety issues. In addition, this process is highly sensitive to water and free fatty acid (FFA) content in the feedstock. High water content can change the reaction to saponification, which causes reductions of ester yield, difficult separation of glycerol from methyl ester, increment in viscosity, and the

formation of emulsion. Simasatitkul et al. (2011) proposed the use of RD for biodiesel production by transesterification of soybean oil and methanol, catalyzed by sodium hydroxide. The simulation results showed that a suitable configuration of the RD column consists of only three reactive stages. Methanol and soybean oil should be fed into the column in the first stage. The optimal operating conditions were the molar feed ratio of methanol and oil 4.5:1, molar reflux ratio 3, and reboiler duty $1.6 \times 10^7 \text{ kJ h}^{-1}$.

Martins et al., (2013) worked transesterification of soybean oil for biodiesel production using hydrotalcite as basic catalyst. The reactions of transesterification were carried out at atmospheric pressure and at 64°C (337 K) in a jacketed reactor coupled to a condenser, under magnetic stirring, by varying the molar ratio methanol/oil and the reaction time. Pirola et al., (2014) studied the esterification of FFA in sunflower oil with methanol in a Packed Bed Reactor. Their experimental results permitted to regress the main kinetic parameters using two different models considering an ideal liquid phase behaviour. From the regression results, it could be concluded that the pseudo-homogeneous slightly better to fit the experimental data. This study proposed the use of a reactive distillation for transesterification of soybean oil and methanol catalyzed by potassium hydroxide, potassium methoxide to produce biodiesel. The simulation results showed that a suitable configuration of the reactive distillation column consists of seven reactive stages.

2. Process Description

Here, the esterification of oleic acid (1) with methanol (2) producing methyl oleate (3) and water (4) is given by the following stoichiometric relationship:



The chemical reaction of esterification is considered to be of first order with respect to oleic acid and methanol. The inverse reaction (hydrolysis) is considered to be of first order with respect to methyl oleate and water. These assumptions are the same as those employed by Steinigeweg and Gmehling (Steinigeweg and Gmehling, (2003)) to develop a pseudo-homogeneous reaction rate model dependent on the activity of reagents:

$$r = \frac{1}{m_{cat}} \frac{1}{v_i} \frac{dn_i}{dt} = k_1 a_1 a_2 - k_{-1} a_3 a_4 \quad (2)$$

whereby activities instead of concentrations or mole fractions are used. This leads to a more consistent and accurate description. The constants k_1 and k_{-1} in Eq(2) obey the Arrhenius equation as follows:

$$k_1 = 1.54 * 10^2 \exp\left(\frac{-35027.62 \left(\frac{J}{gmol}\right)}{RT}\right), (L/(g_{cat} \text{ min } gmol)), T(K) \quad (3)$$

$$k_{-1} = 7.323 \exp\left(\frac{-350005.81 \left(\frac{J}{gmol}\right)}{RT}\right), L/(g_{cat} \text{ min } gmol), T(K) \quad (4)$$

HYSYS Modeling Procedure

Figure 1 below shows the flowsheet of the reactive distillation column built and modelled in HYSYS 3.2 environment. The column consists of a condenser, a rectifying section, an oleic acid 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 1.

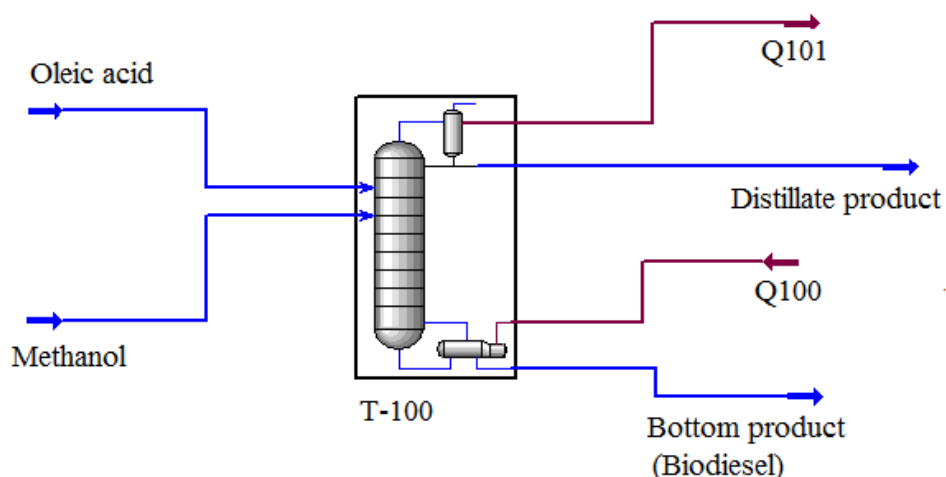


Figure 1: Aspen HYSYS reactive distillation steady state simulation flowsheet

Table 1: Steady state operating parameters of the process

Parameters	Value
Fluid Package	General NRTL
Stage Number	9
Oleic Acid Feed Number	2
Methanol Feed Number	9
Oleic Acid	
Feed Temperature [°C]	300
Pressure [MPa]	35
Molar Flow Rate [kmol/h]	138
Vapor Fraction	0
Methanol	
Feed Temperature [°C]	270
Pressure [MPa]	5
Molar Flow Rate [kmol/h]	2,476
Vapor Fraction	1
Reflux Ratio	2.37
Reboiler Duty [kW]	0.850×10^4
Condenser Pressure [MPa]	7
Reboiler Pressure [MPa]	10

HYSYS Optimization Procedure

After the steady state simulation, the optimization of the plant was carried using the same HYSYS 3.2 process simulator by incorporating an optimizer into the flowsheet (see Figure 2). Three different algorithms were used for the optimization; they are: Fletcher-Reeves, Quasi-Newton and Successive Quadratic Programming (SQP) algorithms. The objective function of the optimization was taken as maximizing the mole fraction of methyl oleate in the bottom stream. The ranges of the adjusted variables used for the optimizations are as shown in Table 2 below.

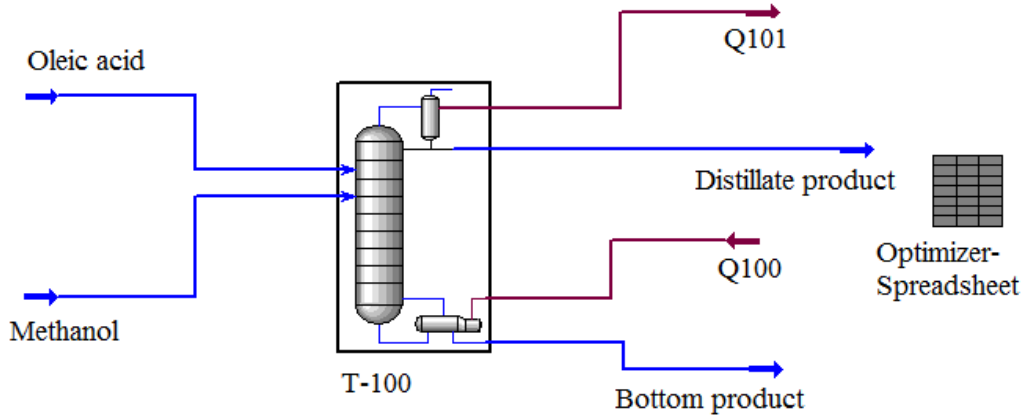


Figure 2: Aspen HYSYS reactive packed distillation optimization flowsheet

Table 2: Parameters used for running the optimization

Parameter	Low Bound	High Bound
Reflux ratio (kmol s ⁻¹ recycled liquid / kmol s ⁻¹ liquid distillate)	0.500	3.739
Reboiler Duty (kW)	5,041	2.016 × 10 ⁴
Condenser Pressure (MPa)	34.54	138.2

After running the HYSYS optimizer, the optimized values of the parameters obtained from one of the algorithms were then used to run the experimental set-up again for validation.

3. Results and Discussion

To simulate and optimize a reactive distillation column for the production of Biodiesel (Methyl oleate) using Aspen HYSYS 3.2 process simulator in this work, the entire column was divided into 9 stage excluding the condenser and the reboiler and its steady state study was carried out by simulating the prototype plant built using the simulator under the conditions of reflux ratio of 2.37, reboiler duty 1.008*10⁴ kW and condenser pressure 7 MPa. The other parameters used for the simulation can be found in Table 1. After the simulation, the temperature and composition profiles obtained are as shown in Figure 3 and Table 3 respectively. As can be seen from the temperature profile shown in Figure 3, the temperature of the stage near the oleic acid feed section was found to be very low.

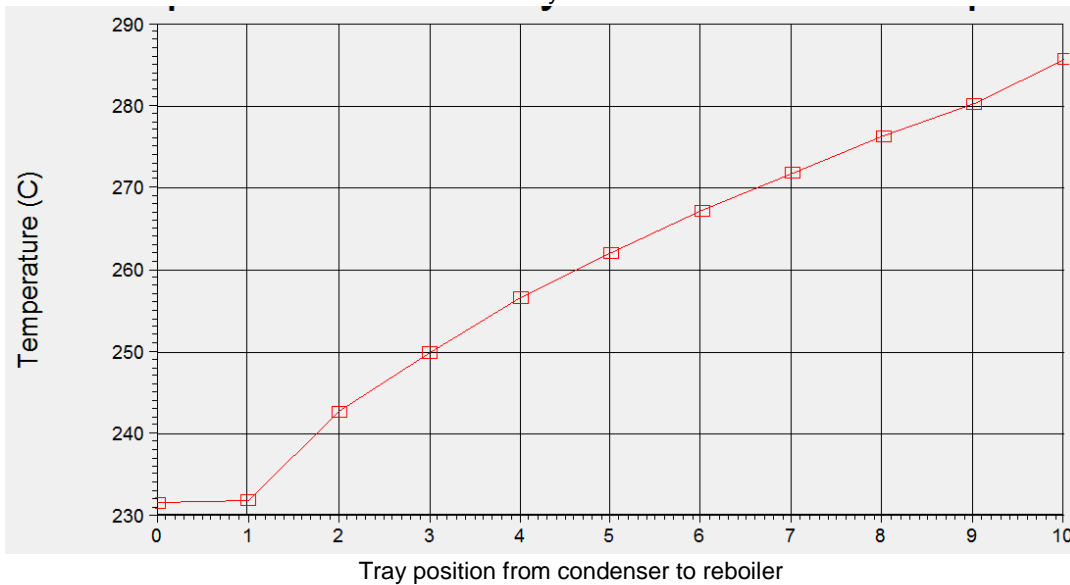


Figure 3: Aspen HYSYS reactive distillation column steady state temperature profile

This was due to the reflux flow effects. The temperature gradient was increased from tray 2 to the reboiler section. From the composition profile (Table 3), Methyl oleate (Biodiesel, the desired product), as expected, was found to have the highest mass fraction of 0.7256 in the bottom section of the column followed by water with a mass fraction value of 0.0042. The mass fractions of the other two components (oleic acid, 0.1207 and methanol, 0.1495), as expected, were found to be very low in the bottom section. This was an indication that effective reaction conversion and separation were achieved in the column.

Table 3: Aspen HYSYS reactive distillation column steady state composition profiles

	OleicAcid (Light Liq)	Methanol (Light Liq)	H2O (Light Liq)	M-Oleate (Light Liq)
Condenser	0.0000	0.9727	0.0273	0.0000
1_Main TS	0.0006	0.9554	0.0440	0.0000
2_Main TS	0.4411	0.5261	0.0328	0.0000
3_Main TS	0.4429	0.5192	0.0373	0.0006
4_Main TS	0.1975	0.5188	0.0406	0.2432
5_Main TS	0.1654	0.5356	0.0326	0.2665
6_Main TS	0.1359	0.5499	0.0258	0.2884
7_Main TS	0.1084	0.5625	0.0200	0.3091
8_Main TS	0.0825	0.5736	0.0148	0.3291
9_Main TS	0.0583	0.5789	0.0100	0.3527
Reboiler	0.1207	0.1495	0.0042	0.7256

Having carried out the steady state simulation of the Aspen HYSYS Reactive Distillation Column, the process was optimised using three different optimization algorithms. The maximization of the mass fraction of methyl oleate in the column bottom section was set as the objective function of each of the optimizations. The results obtained from the optimizations of the process are as shown in Table 4 below.

Table 4: Optimum parameters Value

Parameter	Steady-state	Fletcher-Reeves	Quasi-Newton	SQP
Reflux ratio (kmol s ⁻¹ recycled liquid / kmol s ⁻¹ liquid distillate)	2.37	1.123	1.119	1.05
Reboiler Duty (kW)	1.008 × 10 ⁴	1.006 × 10 ⁴	1.005 × 10 ⁴	1.007 × 10 ⁴
Condenser Pressure (MPa)	7	6.35	6.43	6.55
Objective function	0.7256	0.854	0.852	0.848

It can be observed from the results shown in Table 4 that the increase (due to the maximization) in the mass fraction of methyl oleate in the column bottom section has been obtained. Also, as can be seen from the table, among the three algorithms used for the optimization of the process, Fletcher-Reeves algorithm was found to give the highest mass fraction of methyl oleate in the bottom section of the column by maximizing the objective from the steady state simulation value of 0.7256 to 0.854. Quasi-Newton algorithm yielded a very close value (0.852) of methyl oleate mass fraction to that of the Fletcher-Reeves algorithm. The optimized methyl oleate mass fraction (0.848) gave by SQP algorithm was also found not to be too different beyond acceptance from those of the other two. The differences in the objective functions given by the three algorithms were accounted for by the differences in the optimized operating conditions given by them. For instance, the optimized reflux ratio obtained from the three algorithms can be approximated to one significant figure of 1. The optimized operating conditions of Fletcher-Reeves was used because the value of its objective function was discovered to be close to those of the other two and it had the lowest reboiler duty among the three. Choosing it (Fletcher-Reeves) was considered as an effort to reduce cost. Composition profiles of the optimized case of the process was shown in Table 5. It was noticed that there are changes between the profiles and those of the steady-state simulation shown in Table 3.

Table 5: Aspen HYSYS reactive distillation column optimization composition profiles

	OleicAcid (Hvy Liq)	Methanol (Hvy Liq)	H2O (Hvy Liq)	M-Oleate (Hvy Liq)
Condenser				
1__Main TS	0.0147	0.9536	0.0317	0.0000
2__Main TS	0.3400	0.6377	0.0219	0.0003
3__Main TS	0.3234	0.6462	0.0230	0.0074
4__Main TS	0.1043	0.6435	0.0233	0.2289
5__Main TS	0.0487	0.6627	0.0093	0.2793
6__Main TS	0.0233	0.6694	0.0042	0.3031
7__Main TS	0.0109	0.6732	0.0020	0.3139
8__Main TS	0.0047	0.6768	0.0009	0.3176
9__Main TS	0.0018	0.6602	0.0003	0.3377
Reboiler	0.0046	0.1411	0.0001	0.8541

Aspen HYSYS can be used to represent and simulate the process successfully. The three optimization algorithms investigated were found to produce relatively similar maximized mass fractions of methyl oleate in the bottom section of the column.

References

- Aspen, 2003, HYSYS 3.2 installation guide. Aspen, USA: Aspen Technology.
- Kralova I., Sjoblom J. 2010, Biofuels – renewable energy sources: A review, *J Dispersion Sci. Technol.*, 31, 409–425.
- Omota F., Dimian A.C., Blik A, 2003, Fatty acid esterification by reactive distillation. Part 1: Equilibrium-based design, *Chem. Eng. Sci.*, 58, 3159–3174.
- Atapour M., Kariminia H.R., 2011, Characterization and transesterification of Iranian bitter almond oil for biodiesel production, *Applied , Energy*, 88(7), 2377–2381.
- Simasatitkul L., Siricharnsakunchai P., Patcharavorachot Y., Assabumrungrat S., Arpornwihanop A., 2011, Reactive distillation for biodiesel production from soybean oil. *Korean J. Chem. Eng.*, 28, 649–655.
- Steinigeweg S., Gmehling J., 2003, Esterification of a Fatty Acid by Reactive Distillation. *Ind. Eng. Chem. Res.*, 42, 3612.
- Martins M.I., Pires R..F, Alves M.J., Horib C.E., Reis, M.H.M., Cardoso V.L., 2013, Transesterification of soybean oil for biodiesel production using hydrotalcite as basic catalyst. *Chemical Engineering Transactions*, 32, 817-822.
- Pirola C., Manenti F., Galli F., Bianchi C.L., Boffito D.C, Corbetta M., 2014, Heterogeneously catalyzed free fatty acids esterification in (monophasic liquid)/solid packed bed reactors (PBR). *Chemical Engineering Transactions*, 37, 553-558.