Modelling and Optimisation of a Reactive Distillation Process for Biodiesel Production

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Abstract. Reactive distillation is a method that integrates distillation and a chemical reaction into a single entity. The reaction releases heat that automatically drives the separation of the components, which makes the process particularly advantageous for exothermic reactions. The process also offers a novel alternative to liquid-phase chemical reaction processes, in the sense that the separation of products from unconverted reactants enables high conversion, as product removal restores equilibrium and forces the reaction to completion. There are numerous advantages of this method. However, the fusion of chemical activities and separation in the same unit of apparatus has created some difficulties in the process, and chemical engineers are still working on determining the optimal parameters for operating the process effectively. In this article, the authors model and enhance a reactive distillation process that yields biodiesel (methyl propionate) and water as by-products from the esterification of propionic acid and methanol. They accomplished the esterification process by using tests generated with Design Expert and Aspen HYSYS. They optimised the process with MATLAB to maximise the biodiesel yield. The manipulated variables were the reflux ratio and the column's reboiler duty. The results of the optimisation and validation process showed that the best conditions for producing high-purity biodiesel with a mole fraction of 0.8435 were a reflux ratio of 5 and a reboiler duty of 500000 kJ/s, respectively.

Keywords: Reactive distillation; esterification; Aspen HYSYS; Design Expert; MATLAB.

INTRODUCTION

Education encompasses a range of activities aimed at developing technology based on renewable energy sources, which serve as alternatives to the oil economy. This field has garnered increasing attention in recent decades, primarily because it has been discovered that the exhaust from petroleum-based fuels currently in use harms the environment. A practical biofuel derived from animal and plant lipids, for example, has the potential to replace petro-fuels since it is renewable. Biodiesel is one of these green fuels [1].

Biodiesel is a sulphur-free and ecologically friendly alternative diesel fuel that is renewable, biodegradable, and non-toxic. It is composed of fatty acid methyl (or ethyl) esters derived from renewable resources, such as animal fats, vegetable oils, and restaurant grease. The fact that biodiesel doesn't require a significant engine modification is one of its alluring qualities; the engine does not need to be dedicated to biodiesel use [2]. Sulphur level, flash point, aromatic con-

tent, and biodegradability are all advantages of biodiesel fuel over diesel. Additionally, biodiesel reduces the intensity of greenhouse gas emissions, produces fewer pollutants than petroleum diesel, and does not increase the atmosphere's net carbon dioxide concentration [3]. Reactive distillation is a viable method for producing biodiesel.

Reactive distillation is a procedure amplification method that integrates distillation and chemical reaction into a single apparatus. In other words, reactive distillation involves the simultaneous occurrence of a chemical reaction and multicomponent distillation [4]. Merging two process steps into a single unit lowers the ultimate capital cost of the reactive distillation process. This type of integration is also advantageous in terms of lowering pump and other instrumentation costs. The reduction in total energy costs is attributed to the exothermic character of many chemical processes, which are advantageous for supplying heat during simultaneous component separation [5].

Using a reactive distillation process involves, but is not restricted to, dehydration, alkylation, amination, esterification, transesterification, etherification, isomerisation and neutralisation. For instance, author [6] utilised it in an esterification process to produce methyl acetate, and author [7] employed it in a similar process to create ethyl acetate.

Authors [8] developed and refined a reactive distillation method to enhance the synthesis of ethyl acetate, with water as a by-product. Giwa and the author [9] worked on modelling, simulation and optimisation of a reactive distillation process using MINITAB and MATLAB for the production of methanol and butyl acetate from the transesterification reaction between butanol and methyl acetate. Author [5] carried out Modelling, Simulation, and Optimisation of a reactive distillation process for methyl acetate production. Authors [4, 10] worked on modelling, simulation and optimisation of the reactive distillation process for the production of fatty acid methyl ester using Aspen HYSYS. Author [11] carried out the optimisation of a reactive distillation column synthesised for the production of ethylene glycol using a Genetic Algorithm.

It is challenging for an industry to obtain the right purity of a product, such as biodiesel, because there are not enough ideal system parameters. Thus, the goal of this research project is to determine the optimal parameters for producing biodiesel (methyl propionate) through a reactive distillation process. To do this, the fatty acid and alcohol that are appropriate for the biodiesel production process will be identified, the reactive distillation column will be simulated using Aspen HYSYS to determine the steady-state values of the reflux ratio and the reboiler duty, and various runs on Design Expert will be designed using the steady-state values of the reflux ratio and the reboiler duty, applying these mole fractions as the responses on Design Expert to obtain the system model equations, utilising the model equations to estimate the optimal parameters with the help of MATLAB, and entering these runs on Aspen HYSYS to obtain different mole fractions for the top and bottom product of both biodiesel and water [12].

METHOD

Steady-State Model Development. The system's steady-state simulation was run using Aspen HYSYS, following the steps outlined thus.

The researchers selected propionic acid, methanol, methyl propionate, and water from the Aspen HYSYS database. The non-random two-liquid (NRTL) model was chosen as the simulation's Property Package. Since the model effectively describes two liquid phases, NRTL was chosen. Additionally, it can handle any combination of polar and non-polar molecules, even those with very high non-ideality [7].

After selecting the key components and the property pack, the researchers accessed the simulation setting, developed the model, and specified the process conditions. The development of the model involved connecting the two input streams and the two output streams into a distillation column, as illustrated in Figure 1.

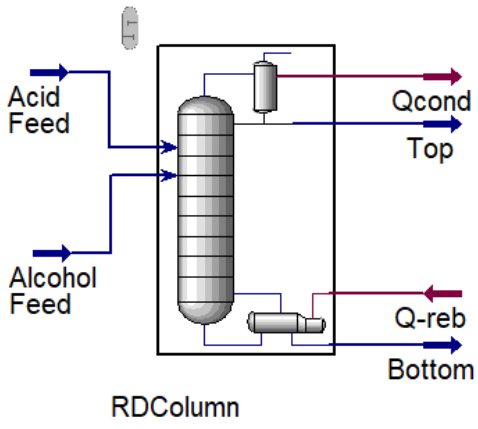

Figure 1 – The reactive distillation process flow sheet for Aspen HYSYS

The researchers picked all the objects from the palette of designs in the simulation environment. After developing the model, the process parameters for the acid and the alcohol input streams were entered as specified in Figures 2 and 3, respectively [13].

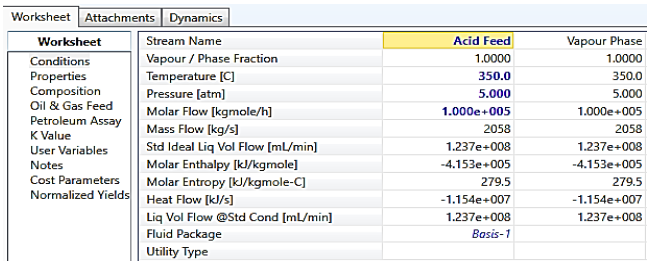

Figure 2 – Inlet conditions for acid Stream

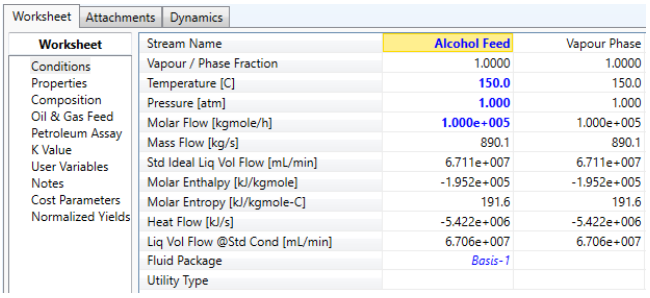

Figure 3 – Inlet conditions for alcohol stream

After specifying the requirements for the input streams, the parameters of the reactive distillation column were established using the information in Table 1.

Table 1 – Process parameters for the reactive distillation column

Parameter	Value/Description
Top inlet stream	Acid feed
Bottom inlet stream	Alcohol feed
Number of stages	30
Calculation type	Equilibrium
Condenser type	Total
Acid feed stage	8
Alcohol feed stage	18
Reaction section	Stages 8 - 18
Reboiler Duty	600000 kJ/s
Reflux ratio	3

Given the use of a reactive distillation column, the researchers added the reaction specified in equation (1) to the column. They achieved this by selecting a response in the Properties environment and choosing an equilibrium reaction from the drop-down menu after clicking 'Add'. They then created the reaction as Rxn-1 and added the components (propionic acid, methanol, methyl propionate, and water) sequentially. As illustrated in Figure 4, they specified the stoichiometric coefficients for both the reactants and the expected products. Finally, they added the reaction to the Fluid Package.

$$CH_3CH_2COOH + CH_3OH \rightarrow CH_3CH_2COOCH_3 + H_2O \qquad (1)$$

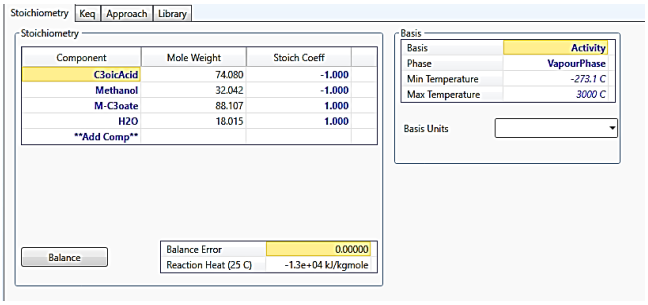

Figure 4 – Reaction specification

When returning to the simulation environment, the researchers opened the reactive distillation column and checked the necessary parameters, as well as the solver, which they configured as a Sparse Continuous solver, to ensure the convergence of the reactive distillation column (Figure 5). The response was made active within the reaction section (Figure 6).

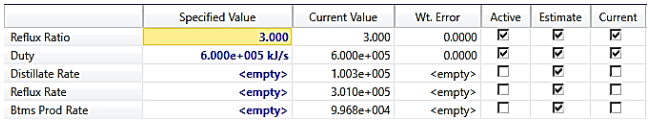

Figure 5 – The column's convergence parameters

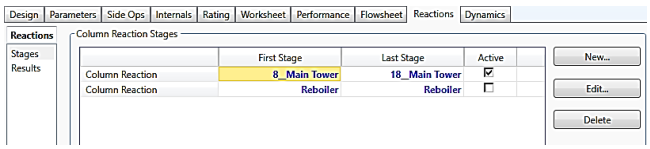

Figure 6 – Column reaction section and active reaction section

Design of Experiments. Following the steady-state simulation conducted in Aspen HYSYS, the Design Expert used the reflux ratio and the reboiler duty as input elements to get the necessary experimental runs. Table 2 provides the ranges for the input parameters, and Table 3 displays the

trial runs generated using the Central Composite design of the Response Surface Methodology in Design Expert [14].

Table 2 – The Input Parameter Ranges

Input Parameter	Minimum	Maximum
Reflux ratio	3.00	5.00
Reboiler duty	200000.00	500000.00

Table 3 – Experimental runs given by the Design Expert

Std	Run	Reflux ratio	Reboiler duty
1	1	3	200000
13	2	4	350000
8	3	4	562132
5	4	2.58579	350000
4	5	5	500000
2	6	5	200000
9	7	4	350000
10	8	4	350000
3	9	3	500000
7	10	4	137868
11	11	4	350000
6	12	5.41421	350000
12	13	4	350000

After conducting the experimental runs, the molecular fractions of the upper and lower products of methyl propionate (biodiesel) and water were obtained and recorded as responses in Design Expert. The researchers examined the outputs from the Design Expert model to produce model equations, using the mole fractions of water and biodiesel as the system's dependent variables.

Optimisation. The model equations obtained from Design Expert were used to formulate the optimisation algorithm for the system, with the assistance of MATLAB's fsolve command. For the optimisation, the reboiler duty and the reflux ratio were the manipulated variables, aimed at maximising the mole fraction of methyl propionate (biodiesel) at the bottom of the distillation column [15].

RESULTS AND DISCUSSION

The steady-state values obtained for both the top and bottom streams are provided in Table 4. The steady-state results indicated that methyl propionate is more concentrated at the top of the column than at the bottom.

Table 4 – Steady-state mole fractions

Component	Top Mole Fraction	Bottom Mole Fraction
Propionic acid	0.0058	0.0449
Methanol	0.0001	0.0507
Methyl propionate	0.6514	0.2968
Water	0.3427	0.6076

After completing the steady-state simulation and achieving the model's convergence, the researchers adjusted the reboiler duty and reflux ratio to produce various runs in Design Expert. They then entered these runs into the Aspen HYSYS simulation to determine the mole fractions of the products for the top and bottom streams, as shown in Table 5. The cubic model displayed in Tables 1 and 2 was created using these mole fractions as the responses in Design-Expert. However, only the coded equation was present in the model instead of an actual equation.

Table 5 – Biodiesel and water mole fractions for the top and the bottom streams

Reflux Ratio	Reboiler Duty	Top		Bottom	
		Biodiesel	Water	Biodiesel	Water
3	200000	0.5465	0.3156	0.2569	0.4338
4	350000	0.6385	0.3597	0.2651	0.4291
4	562132	0.6779	0.3207	0.3013	0.5380
2.58579	350000	0.5654	0.2931	0.2809	0.5638
5	500000	0.6968	0.3018	0.2993	0.4913
5	200000	0.0000	0.0000	0.0000	0.0000
4	350000	0.6386	0.3597	0.2651	0.4291
4	350000	0.6386	0.3597	0.2651	0.4291
3	500000	0.6281	0.3377	0.2871	0.5606
4	137868	0.5942	0.3830	0.2325	0.3425
4	350000	0.6385	0.3597	0.2650	0.4291
5.41421	350000	0.6771	0.3213	0.2779	0.4238
4	350000	0.6386	0.3597	0.2650	0.4290

The results were processed to obtain the model equations given in Equations (2) and (3) for the top biodiesel and water, respectively.

$$TB = -1.85599 + 2.28619R - 4.83432\times10^{-6}Q - \\ -2.82031\times10^{-6}RQ - 0.434041R^2 + 2.64730\times10^{-11}Q^2 + \\ +1.10005\times10^{-6}R^2Q - 7.07823\times10^{-12}RQ^2 \quad (2)$$

$$TW = -1.58232 + 1.62758R - 2.83247\times10^{-6}Q - \\ -1.87317\times10^{-6}RQ - 0.291149R^2 + 1.68682\times10^{-11}Q^2 + \\ +6.8667\times10^{-7}R^2Q - 4.50581\times10^{-12}RQ^2 \quad (3)$$

After analysing the model equations, it was found that each of the overall models was significant, despite some of their elements not being significant.

Table 6 presents the results of optimising the built system using MATLAB's fsolve tool. The objective function was to maximise the top biodiesel mole fraction, while the manipulated variables were the reboiler duty and reflux ratio.

Table 6 – Optimum values

Parameter	Optimum value
Reflux ratio	5
Reboiler duty (kJ/s)	500000
Top methyl propionate	1

The Aspen HYSYS model of the system was then run using the optimal variables, and the results are presented in Table 7. One possible explanation for the discrepancy between the theoretical and practical mole fractions of biodiesel is that the conditions were not as perfect as the theoretical optimisation could have predicted.

Table 7 – Steady-state mole fractions obtained using the optimum values of the parameters

Component	Top Mole Fraction	Bottom Mole Fraction
Propionic acid	0.0001	0.1063
Methanol	0.0018	0.1059
Methyl propionate	0.8435	0.3159
Water	0.1546	0.4719

Using the optimum parameters, plotting the system's temperature profile with Aspen HYSYS (Figure 7) revealed that, as anticipated, the condenser's temperature was lower than that of the reboiler.

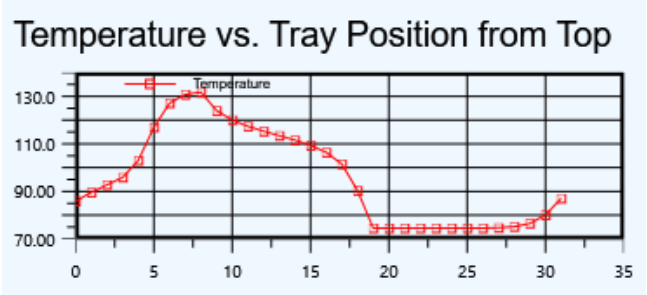

Figure 7 – The Column's temperature profile for reactive distillation

Nevertheless, the simulation showed that the column's reaction region had an extremely high temperature. The esterification reaction occurring in the reaction region was exothermic, which is why the temperature there was so high.

Additionally, Figure 8 provided the system's composition profiles. According to the figure, the intended product had the highest mole fraction in the condenser part of the column, while the mole fraction of propionic acid was highest in the reaction section.

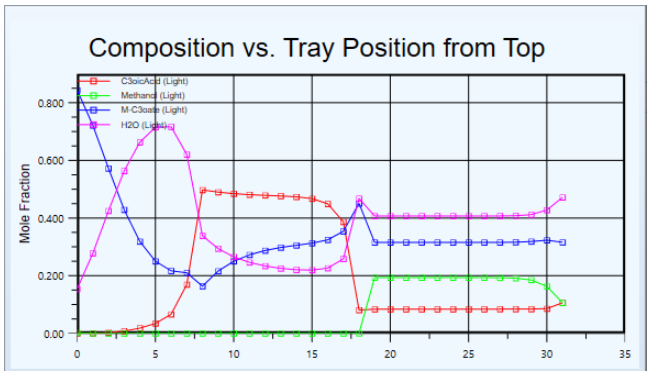

Figure 8 – Profiles of the steady state liquid mole fractions of the system after optimisation

The model was also simulated using MATLAB, and the simulation outcomes were compared with the experimental ones, as shown in Figures 9 and 10 for methyl propionate and water, respectively, in the form of composition profiles.

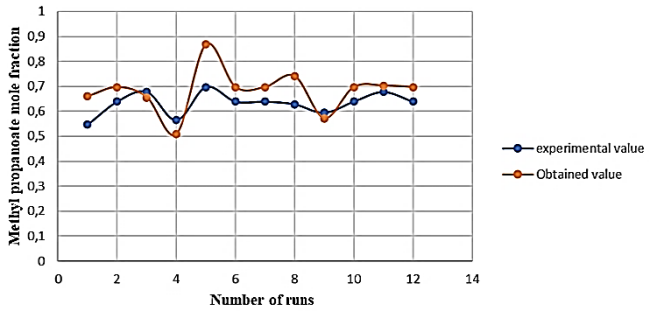

Figure 9 – Comparison of the experimental and the simulated top methyl propionate mole fractions

The researchers also applied the significance criteria (with a significance level of 0.05) and the predicted R^2 value to assess the validity of the developed model equation.

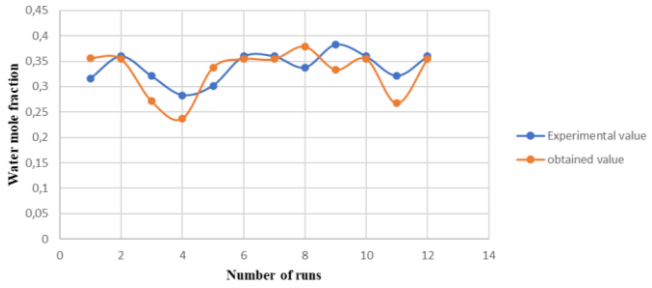

Figure 10 – A comparison between the experimental and the simulated top water mole fractions

It was evident that the profiles were in good agreement based on the figures. The high predicted R^2 value and the importance of the model equations created for the system were both supported by this excellent graphical comparison.

CONCLUSIONS

The outcomes demonstrated that Aspen HYSYS played a crucial role in the successful development of the reactive distillation column for biodiesel production. The expert conducted a trial run to explain how the program could create tests that would be administered appropriately. The mole fraction of unity, derived from the MATLAB-assisted optimisation, demonstrated the MATLAB Optimisation Toolbox's capacity to manage chemical process optimisation. According to the results of the validation of the ideal parameters, a reflux ratio of 5 and a reboiler duty of 500,000 kJ/s can produce a high-purity biodiesel with a mole fraction of 0.8435. Aspen HYSYS is a versatile program that accurately represents the behaviour of complex reactive distillation processes, as demonstrated by the excellent convergence obtained from simulating the Aspen HYSYS model created for the reactive distillation process used in biodiesel manufacture.

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