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Investigating the Effects of Operating Parameters of a Reaction Integrated Distillation Process for SAME Production Using Aspen PLUS

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Abstract: ***The effects of some operating parameters of a reaction integrated distillation process used for the production of a biodiesel type have been studied in this research work. The operating parameters considered were reflux ratio and reboiler duty while the biodiesel type produced was stearic acid methyl ester (SAME) that was obtained from the esterification reaction between stearic acid and methanol. The production of the biodiesel was accomplished theoretically with the aid of a process simulator known as Aspen PLUS using RadFrac column that had 32 stages including the condenser and the reboiler and that was divided into three (rectifying, reaction and stripping) sections, excluding the condenser and the reboiler. The reaction was taken to occur in the middle, which was the reaction section of the column as well as in the reboiler. In order to study the effects of the operating parameters, both simulation and sensitivity analysis of the process were carried out using the process simulator. Based on the observations of the simulation and the sensitivity analysis, optimization was carried out also using Aspen PLUS. The results obtained revealed that separate variations of reflux ratio, from 1 to 10, and reboiler duty, from 0.1 to 1 kW, while keeping other simulation parameters constant yielded a bottom product with very high purity SAME at a reflux ratio of 1 and a reboiler duty of 0.1 kW. However, the combination of these values of the operating parameters could not converge when used to run the developed model of the process. Furthermore, using the optimum values of the reflux ratio and the reboiler duty that were estimated to be 2.23 and 0.90 kW, respectively to run the developed process model, SAME mole fraction of 0.9993 was obtained from the bottom product of the column. Therefore, it has been discovered that each of reflux ratio and reboiler duty separately affects the operation of the reaction integrated distillation process, but considering their combined effects simultaneously and optimizing are very necessary in order to achieve very high purity of the desired product.***

Keywords: Stearic acid methyl ester (SAME), modelling and simulation, sensitivity analysis, optimization, Aspen PLUS.

1. Introduction

Biodiesel, as an alternative fuel, is currently receiving attentions both in academics and in industries owing to the limited availability of conventional petroleum diesel as well as environmental concerns. This fuel can be directly used to replace petroleum diesel without modifying diesel engines since their properties such as specific gravity, cetane number, viscosity, cloud point, and flash point, are similar (Simasatitkul *et al.*, 2011; Giwa *et al.*, 2014; Giwa *et al.*, 2015). It is a very good promising alternative to conventional petroleum based diesel fuel. Among its important advantages are that it can be derived from a renewable domestic resource (e.g., waste cooking oil), it reduces carbon dioxide emissions by about 78%, and it is nontoxic and biodegradable. All these benefits have made biodiesel a very good environmental friendly fuel (Wang *et al.*, 2004; Jaya and Ethirajulu, 2011; Giwa *et al.*, 2014; Giwa *et al.*, 2015).

According to Giwa *et al.* (2014), biodiesel with high purity can be produced via esterification reaction of fatty acids with alcohols (methanol or ethanol). Also, Omota *et al.*, (2003) proposed the use of batch reactor for the esterification of fatty acid and alcohol into fatty acid methyl ester (biodiesel). However, the production of biodiesel from the esterification reaction in the conventional batch reactor has been found to possess many problems due to low conversion, heavy capital investments and high energy costs (Gao *et al.*, 2007). In an attempt to resolve these problems, an advanced technology known as "reaction integrated distillation" has been developed (Kusmiyati and Sugiharto, 2010; Giwa *et al.*, 2014; Giwa *et al.*, 2015).

Reaction integrated distillation is a process that combines separation and chemical reaction in a single unit. It is very attractive whenever conversion is limited by reaction equilibrium (Balasubramhanya and Doyle III, 2000; Lai *et al.*, 2007; Giwa and Karacan, 2012e; Giwa and Giwa, 2012; Giwa, 2013). It is sometimes an excellent alternative to conventional flowsheets with different reaction and separation sections (Al-Arfaj and Luyben, 2002; Giwa and Karacan, 2012d). It combines the benefits of equilibrium reaction with distillation to enhance conversion (Giwa and Karacan, 2012a; Giwa and Karacan, 2012c). As in this process, combining reaction and distillation has several advantages that include: a) shift of chemical equilibrium and an increase of reaction conversion by simultaneous reaction and separation of products, b) suppression of side reactions and c) utilization of heat of reaction for mass transfer operation (Giwa and Karacan, 2012b). The utilization of heat of reaction for mass transfer operation, which resulted into low external energy consumption of the process, actually, give rise to reduced investment and operating costs (Giwa, 2012).

Although this (reaction integrated distillation) process for biodiesel production is associated with many benefits, the integration of both chemical reaction and separation in a single unit has made its behaviour complex especially when high boiling materials such as fatty acids are involved. As such, there is a need to handle this process, first, using process simulators like ChemCAD, Aspen HYSYS, Aspen PLUS, and so on so as to gain ideas into how it will perform in real life and provide necessary measures to handle any unusual circumstance.

Based on this, Karacan and Karacan (2014) applied Aspen HYSYS to simulate a reactive distillation process for a fatty acid methyl ester production. In the work, canola oil and methanol were used as feedstocks while potassium hydroxide and potassium methoxide were used as catalysts. Also, Simasatitkul *et al.* (2011) carried out the simulation of a reactive distillation process for a fatty acid methyl ester production from transesterification of soybean oil and methanol, catalyzed by sodium hydroxide, and it was concluded from their work that methanol and soybean oil should be fed into the column at the first stage. Furthermore, Samakpong *et al.* (2012) simulated and optimized a fatty acid methyl ester production using reactive distillation of rubber seed oil, and they discovered that feedstock with high free fatty acids (FFAs) could not undergo transesterification with alkaline catalyst. However, they discovered that the esterification of palmitic acid and methanol to biodiesel could be achieved via reactive distillation with 100% conversion and without feeding excess methanol. They also found that reactive distillation made hydrolysis (reverse of esterification) reaction to be negligible because water was constantly removed from the process. Giwa *et al.* (2014) investigated the performances of some fatty acids used for the production of fatty acid methyl esters in a reactive distillation column with the aid of Aspen HYSYS. The fatty acids considered were oleic acid, which was discovered, according to Kusmiyati and Sugiharto (2010), to give fatty acid methyl ester that had the quality required to be a diesel substitute, and some other ones (stearic acid, linoleic acid and palmitic acid) found to be present in jatropha oil. Methanol was used as the alcohol for the reaction. The results they obtained revealed that palmitic acid had the best performance in fatty acid methyl ester production. Nwambuonwo *et al.* (2015) modelled, simulated and optimized a reactive distillation process used for the production of fatty acid methyl ester (FAME) by considering an esterification reaction between palmitic acid and methanol to give methyl palmitate (FAME) and water (by-product) with the aid of Aspen HYSYS, and they were able to develop a model that could represent the process very well based on the result of the validation that was done. Santander *et al.* (2010) used response surface methodology and Aspen PLUS process simulator to investigate biodiesel production in a reactive distillation using castor oil.

As can be noticed, researches already carried out on the application of Aspen PLUS for biodiesel production are few. Therefore, this work has been carried out to apply Aspen PLUS to a reaction integrated (reactive) distillation process used for SAME (stearic acid methyl ester) production in order to study the effects of reflux ratio and reboiler duty on the purity of the SAME product given by the process. In addition, the optimum values of the operating parameters (reflux ratio and reboiler duty) that could give very high purity of the desired product were estimated, also, with the aid of Aspen PLUS.

2. Methodology

The developed model of the Aspen PLUS (Aspen, 2012) reaction integrated distillation process used, in this work, for the production of SAME from the esterification reaction between stearic acid and methanol (given in Equation 1) is shown in Figure 1. The model comprised two (upper and lower) feed streams. The fatty acid used, which was stearic acid, was passed from the upper feed stream because it was less volatile than the alcohol (methanol) used that was fed through the lower feed stream of the column. Both feeds were introduced into the reaction integrated distillation column at room temperature and pressure. The details of the data used for the development and the simulation of the model are given in Table 1.

$$C_{18}H_{36}O_2 + CH_3OH \leftrightarrow C_{19}H_{38}O_2 + H_2O \quad (1)$$

After the model was developed and simulated using the data given in Table 1, the effects of reflux ratio and reboiler duty on the mole fractions of the components (unreacted stearic acid, unreacted methanol, produced biodiesel and water given as by-product) obtained from the bottom product stream of the column were studied by utilizing the sensitivity analysis section of Model Analysis Tool of Aspen PLUS. Given in Table 2 are the ranges of the values used for the sensitivity analysis.

The combined values of the operating parameters required for the production of high purity biodiesel were later estimated by carrying out the optimization of the process with the aid of the optimization section of the Model Analysis Tool of Aspen PLUS. As implied, the manipulated variables of the optimization were the reflux ratio and the reboiler duty while the objective function was the maximization of the mole fraction of biodiesel (SAME) present in the bottom product of the reaction integrated distillation column. In addition, the lower and the upper bounds of the manipulated variables were set to be the same as those used for the sensitivity studies (see Table 2).

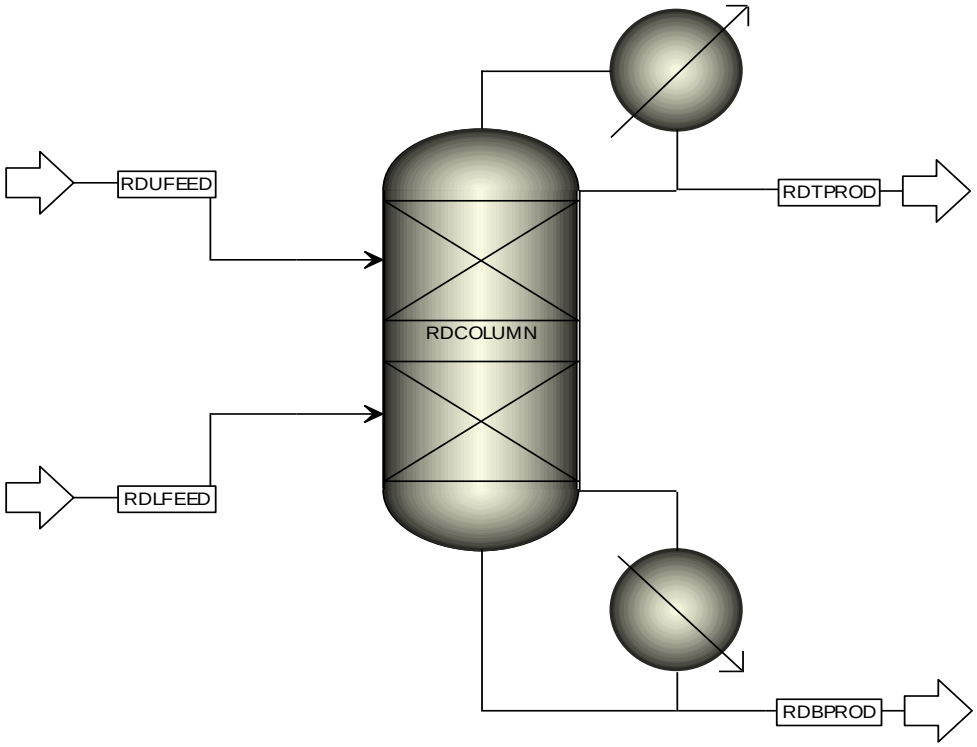

Figure 1: Aspen PLUS reaction integrated distillation column

Table 1: Aspen PLUS reaction integrated distillation process model development parameters

Parameter		**Reactive Distillation Process**
Stearic acid feed (Upper feed)		
	Flow rate (L/min)	0.03
	Temperature (^{o}C)	25
	Pressure (atm)	1
Methanol feed (Lower feed)		
	Flow rate (L/min)	0.01
	Temperature (^{o}C)	25
	Pressure (atm)	1
Property method		Wilson
Reaction		
	Type	Equilibrium
	Reacting phase	Liquid
	K_{eq} basis	Molarity
	K_{eq} computation source	Gibbs energy
Column		
	Type	RadFrac
	Total number of stages	32
	Stearic acid feed stage	11
	Methanol feed stage	20
	Reaction section stages	11-20 and reboiler (stage 32)
	Condenser (stage 1) type	Total
	Reboiler type	Kettle
	Valid phases	Vapour-Liquid
	Reflux ratio	3
	Reboiler duty (kW)	0.7
	Condenser pressure (atm)	1

Table 2: Ranges of operating parameters used for sensitivity analysis

Parameter	Lower limit	Upper limit	Step
Reflux ratio (kgmol/min liquid / kgmol/min distillate)	1	10	0.5
Reboiler duty (kW)	0.1	1	0.1

3. Results and Discussion

The results obtained from the simulation of the Aspen PLUS model developed for the production of stearic acid methyl ester (SAME), which is a biodiesel, were as given in Figure 2. From the figure, it was seen that the reaction conversion was very high because the mole fraction of the reactants (stearic acid and methanol) present and remaining in the stages of the column at the end of the simulation was very low. Also noticed from the results was that water had the highest mole fraction throughout the column except in the condenser (stage 1) and the reboiler (stage 32). In the bottom section of the column, from where the product was collected, the component with the highest mole fraction was found to be SAME (the desired product of the process). This observation made at the reboiler section of the column that SAME had the highest mole fraction there actually indicated that proper separation of the desired product was achieved in the column.

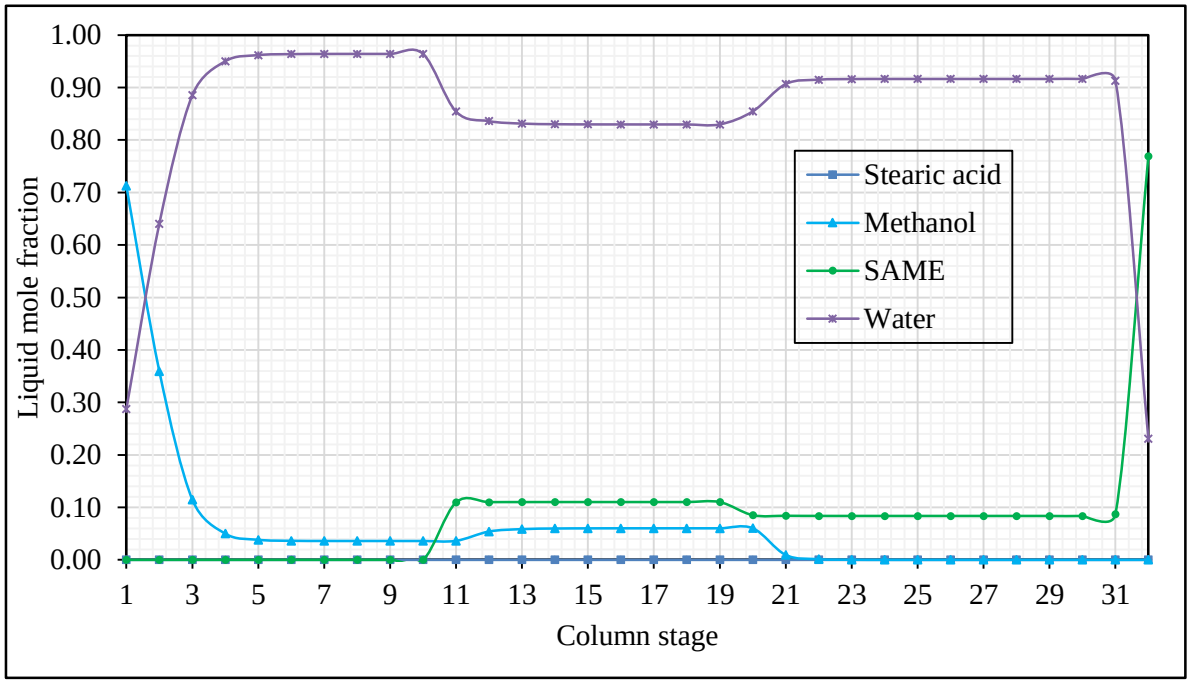

Figure 2: Liquid mole fraction profiles obtained from the simulation of the developed Aspen PLUS model

Figure 3 shows the results obtained when the effect of reflux ratio on the purity of the product obtained from the reaction integrated distillation process was studied. As can be observed from the figure, as the reflux ratio was varied from 1 to 10, while keeping other variables of the model constant at their simulation values given in Table 1, the mole fraction of each of the components present in the bottom product was found to change. According to the result, the highest purity of the desired product (SAME) was achieved when the reflux ratio was 1. At that reflux ratio of 1, the mole fraction of the by-product of the process (water) was found to be negligible, but, thereafter, it increased as the reflux ratio was increased. At the reflux ratio of 5.5 and henceforth, the mole fractions of the two products of the process (SAME and water) were found to be the exactly the same. Also discovered from the results given in Figure 3 was that the mole fraction of stearic acid present in the column after the simulation with each reflux ratio was negligible while that of methanol was also negligible but later increased when the reflux ratio was greater than 5.

Furthermore, the effect of reboiler duty on the composition of the product obtained from the bottom section of the reaction integrated distillation column was also investigated, and the results of the investigation are given in Figure 4. It was observed from the figure that the highest mole fraction of SAME was obtained when the reboiler duty of the column was 1 kW. At that value of the reboiler duty, the mole fraction of the other product of the process (water) was very small. As the reboiler duty was varied from 0.1 to 0.5 kW, the mole fraction of methanol was found to decrease to almost zero, indicating its high consumption in the process, and it remained constant (at almost zero) thereafter up to the maximum reboiler duty of 1 kW that was investigated while that (the mole fraction) of stearic acid was negligible at all the values of the reboiler duty considered. As can be seen from the sensitivity results given in Figures 3 and 4, the highest mole fraction of SAME was achieved at low reflux ratio of 1 and at high reboiler duty of 1 kW considered. However, when the values (a reflux ratio of 1 and a reboiler duty of 1 kW) were used to run the model, it did not converge. This was an indication that the values of each of the operating parameters obtained, separately, that gave high purity biodiesel (SAME) could not be used together to run the plant and get high purity product.

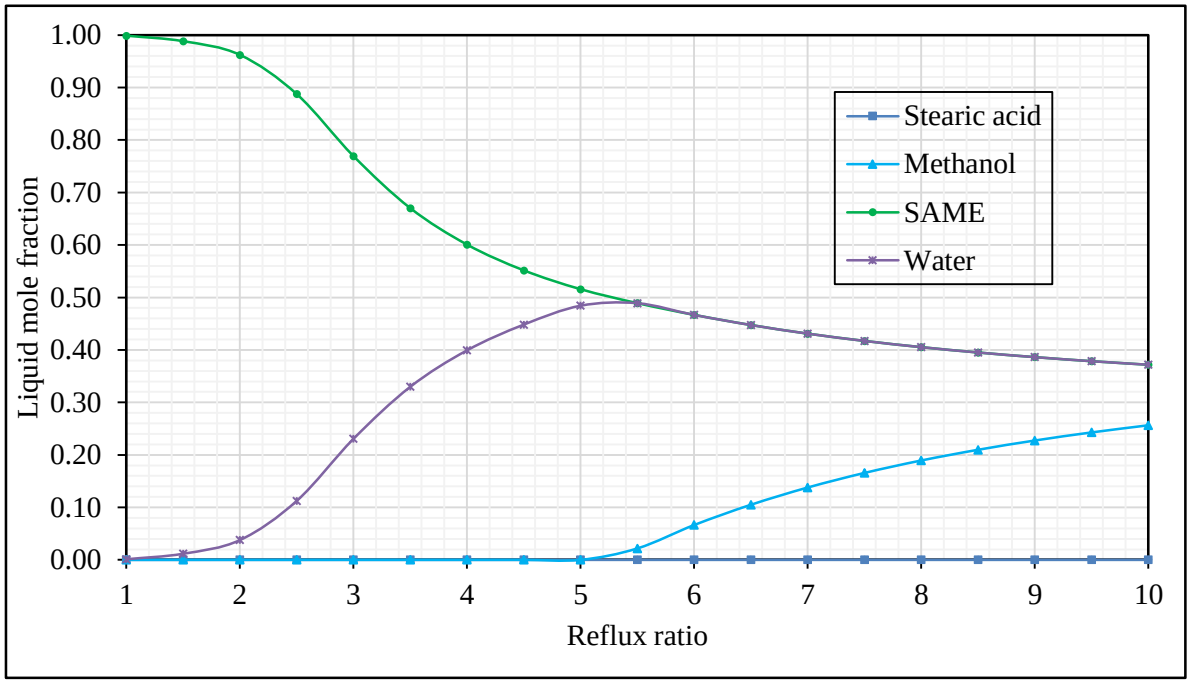

Figure 3: Effect of reflux ratio on the composition of bottom product of the process

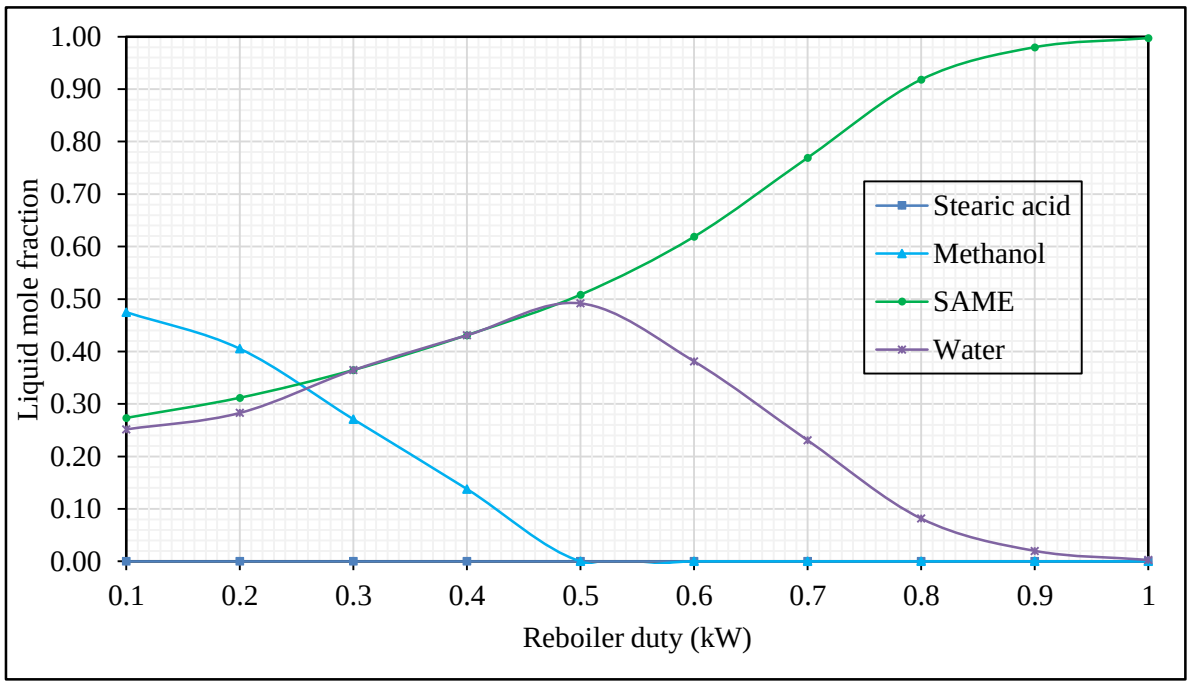

Figure 4: Effect of reboiler duty on the composition of bottom product of the process

Based on this, the interactions of the operating parameters (reflux ratio and reboiler duty) investigated were plotted together, as shown in Figure 5, to estimate their point of intersection, and this point was obtained to be reflux ratio of 5 and a reboiler duty of 0.5 kW. Using these values of the point of intersection to run the developed model of the reaction integrated distillation process, the mole fraction of the biodiesel (SAME) obtained was found to be 0.4062. This value was observed not to be favourable, and, hence, it was deemed necessary to find the best operating parameters that would give a product having high mole fraction of SAME, and the process optimization was, therefore, carried out with the aid of Aspen PLUS.

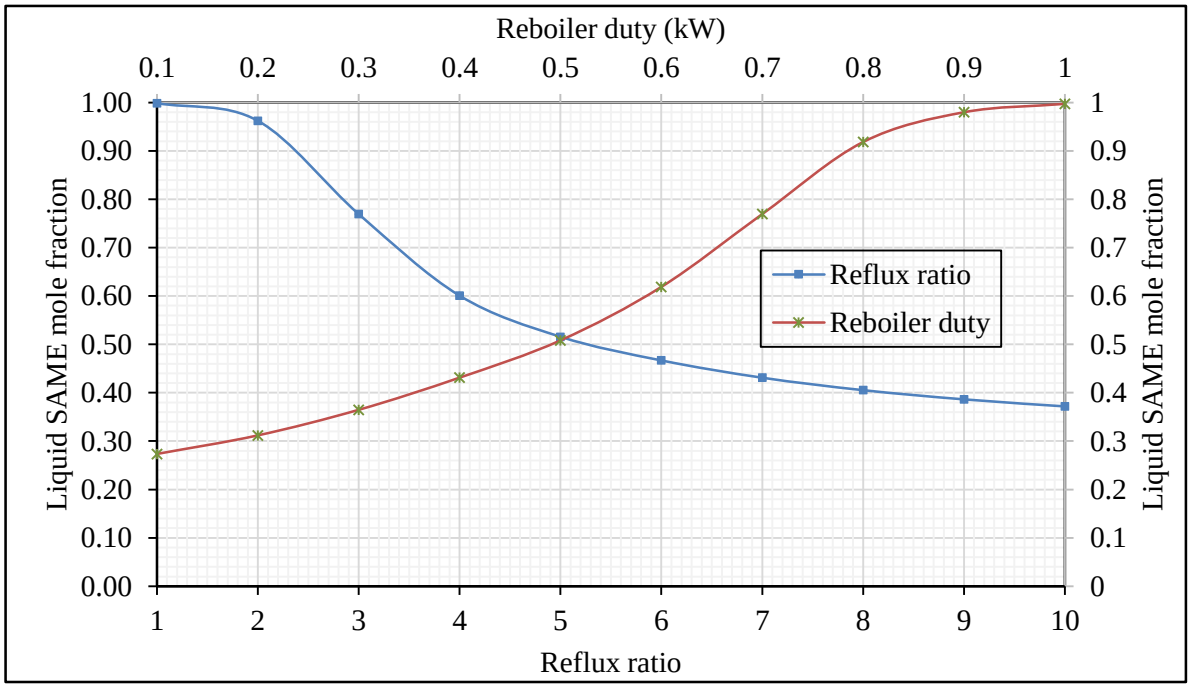

Figure 5: Liquid SAME mole fraction obtained from the separate interactions of the parameters

The results obtained from the optimization carried out in which the maximization of the mole fraction of SAME obtained from the bottom section of the column was taken as the objective function are given in Table 3. According to the table, SAME (the biodiesel produced) having purity as high as a mole fraction of 0.9993 was theoretically obtained as the product when the optimum values of the reflux ratio and the reboiler duty were 2.23 and 0.90 kW, respectively.

Table 3: Optimum parameters of the process

Parameter	Value
Reflux ratio	2.23
Reboiler duty (kW)	0.90
Objective function (Bottom SAME mole fraction)	0.9993

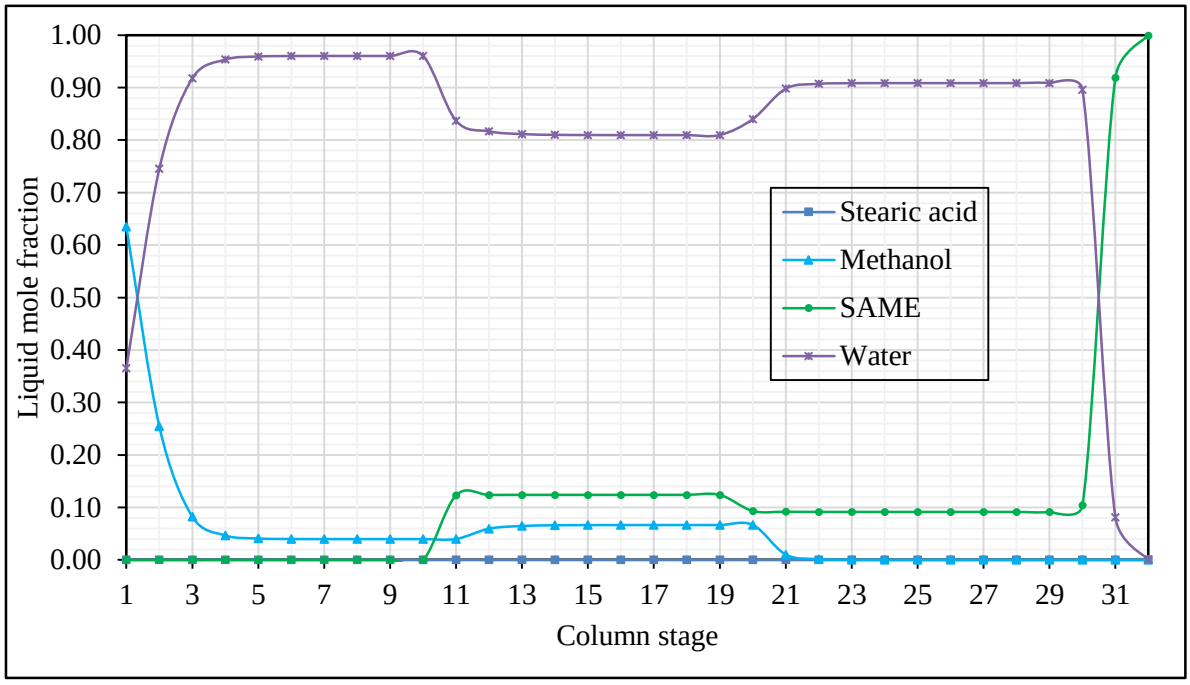

Figure 6: Liquid mole fraction profiles obtained from the optimization of the developed Aspen PLUS model.

In order to validate the values obtained from the optimization carried out, the estimated optimum values of the operating parameters were used to run the developed model of the plant and the results obtained were as given in Figure 6 in terms of the mole fraction profiles of the components present in the column at steady state. The trends of the profiles of the components obtained (Figure 6) were found to be similar to those of the initial simulation carried out (Figure 2) except at the bottom section. Also, in this case, an increment was noticed to occur in the mole fraction of the desired product present in the bottom product of the process collected from the reboiler section.

4. Conclusion

The results obtained from the simulations of the reaction integrated distillation process used for the production of stearic acid methyl ester (SAME) carried out when the reflux ratio was varied from 1 to 10 and the reboiler duty varied from 0.1 to 1 kW revealed that high purity SAME could be obtained at a reflux ratio of 1 and a reboiler duty of 0.1 kW, separately, even though the combination of these values of the operating parameters (reflux ratio and reboiler duty) could not converge when used to run the developed model of the process. Furthermore, using the optimum reflux ratio and reboiler duty estimated to be 2.23 and 0.90 kW, respectively to run the developed Aspen PLUS process model, SAME (a biodiesel) mole fraction of 0.9993 was obtained from the bottom product of the column. Therefore, it has been discovered that each of reflux ratio and reboiler duty separately affects the operation of the reaction integrated distillation process, but in order to obtain high purity of biodiesel, their combined effects should be simultaneously studied and optimized.

5. Acknowledgement

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6. Nomenclature

K_{eq}	Equilibrium constant
RDBPROD	Reaction integrated distillation bottom product
RDCOLUMN	Reaction integrated distillation column
RDLFEED	Reaction integrated distillation lower feed
RDTPROD	Reaction integrated distillation top product
RDUFEED	Reaction integrated distillation upper feed
SAME	Stearic acid methyl ester

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