Empirical Modelling and Optimization of PAME Reactive Distillation Process Using Minitab

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Abstract – The development and optimization of an empirical model of a reactive distillation process producing palmitic acid methyl ester (PAME), with the aid of Minitab, have been carried out in this work. In order to achieve these, Box-Behnken technique of response surface methodology was used to design experiments that were carried out in a prototype plant of the process developed with the aid of Aspen HYSYS using Distillation Column Sub-Flowsheet as the column type and Wilson model as the fluid package. The results obtained from the analysis of the developed full quadratic model revealed that reboiler duty was not having any significant effect on the process as its probability value (P-value) was obtained to be greater than 0.05 that was chosen, based on the confidence level of 95%.This was found to justify the fact that no reaction was occurring in the reboiler section of the column. Based on this, the full quadratic model developed was modified. Although the R-squared value of the full quadratic model was found to be better than that of the modified one, the latter was found to be better in prediction because its predicted R-squared value was discovered to be greater than that of the former. In addition, the optimum values of the factors estimated with the aid of Minitab were found to be valid ones because the measured optimum mole fraction of palmitic acid methyl ester was found be in good agreement with the predicted one given by the Box-Behnken technique of response surface methodology.

Keywords: PAME (palmitic acid methyl ester), reactive distillation, Aspen HYSYS, Minitab, Box-Behnken, response surface methodology.

1 INTRODUCTION

PAME (Palmitic acid methyl ester) is a type of biodiesel that can be produced from a reaction between low palmitic acid content containing oils and methanol via transesterification process using a base catalyst. Also, it can be produced from a reaction between palmitic acid itself and methanol via esterification process using an acid catalyst. However, the commercialization of biodiesel production from the palmitic acid containing oil or from the fatty acid itself still have drawbacks due to high cost of vegetable oil and the purification of the formed biodiesel product.

Generally, biodiesel production can be achieved using a batch reactor (Omota *et al.*, 2003; Giwa and Giwa, 2015). However, that method has been found to possess many problems because of its low conversion, heavy capital investments and high energy costs (Gao *et al.*, 2007; Giwa *et al.*, 2014; Giwa *et al.*, 2015; Giwa and Giwa, 2015). In order to solve this problem, Giwa and Giwa, 2015 decided to use an integrated process known as reactive distillation to produce this biodiesel type in their work.

Recently, integrated reactive separation processes have attracted considerable attentions in both academic research and industrial fields (Völker *et al.*, 2007; Giwa and Giwa, 2015). One of these processes is the one known as reactive distillation, and it is very attractive, particularly when conversion is limited by reaction equilibrium (Giwa and Karacan, 2012a; Giwa and Karacan, 2012d; Giwa and Giwa, 2015).

Actually, this process referred to as reactive distillation is a type that permits the occurrence of both separation and chemical reaction in one unit (Giwa and Karacan, 2012e; Giwa, 2013a; Giwa and Giwa, 2015). It takes the advantages of equilibrium reaction with distillation to enhance conversion, most especially, provided that the desired product is the

most volatile or the least volatile among all the components involved in the process (Taylor and Krishna, 2000; Giwa, 2012; Giwa and Giwa, 2015). Furthermore, this process has a lot of advantages, which include low reduced investment and operating costs as a result of increased yield of a reversible reaction that is due to the separation of the desired product from the reaction mixture (Pérez-Correa *et al.*, 2008; Giwa and Giwa, 2015), high conversion, improved selectivity, low energy consumption, ability to carry out difficult separations and avoidance of azeotropes (Jana and Adari, 2009; Giwa, 2012; Giwa and Giwa, 2012; Giwa and Giwa, 2015).

This process has been applied in a few number of ways in industries for many years, but the last decade has witnessed an increase in both its research and applications (Agreda *et al.*, 1990; Giwa and Giwa, 2015), especially in the area of its modelling, design, and optimization, as it has been a focus of research in chemical process industry and academia (Giwa and Karacan, 2012c).

The traditional 'one-factor at a time' technique used for optimizing a system having more than one input factor is not only time consuming but also often easily misses the alternative effects between the factors involved in the process. Apart from this, this method requires carrying out a number of experiments to determine the optimum levels, which may not be very true. These drawbacks of single-factor-at-a-time optimization can be eliminated by considering all the affecting parameters collectively using a method known as "response surface methodology (RSM)" (Bandaru *et al.*, 2006; Giwa and Giwa, 2012).

Response surface methodology (RSM) is a widely used technique for rational experimental design and process optimization, particularly in the absence of mechanistic information (Box and Draper, 1987; Myers and Montgomery, 1995; Giwa and Giwa, 2012). RSM initiates from Design of Experiments (DoE) to determine the values of the factors to be used for conducting experiments and collecting data. The data are then used to develop an empirical model that relates the process response to the factors. Subsequently, the model facilitates the search for the best process response, which is validated through experiment(s). The above procedure iterates until an optimal process is identified or the limit on experimental resources is reached (Chi *et al.*, 2012; Giwa and Giwa, 2012). RSM has seen diverse applications in almost every area of scientific research and engineering practice, including the development of chemical and biochemical processes (Agatonovic-Kustrin *et al.*, 1998; Baumes *et al.*, 2004; Dutta *et al.*, 2004; Hadjmohammadi and Kamel, 2008; Shao *et al.*, 2007; Tang *et al.*, 2010; Yan *et al.*, 2011a,b; Giwa and Giwa, 2012).

In response surface methodology, when all independent variables (x_1, x_2,. . ., x_k) are measurable, manipulable and continuous in the experiments, with negligible error, the response y can be expressed as

$$y = f(x_1, x_2, \ldots, x_k) + \varepsilon \tag{1}$$

where the form of the true response function f is unknown and perhaps very complicated, and ε is a term that represents other sources of variability not accounted for in f. Usually, ε includes effects such as measurement error on the response, background noise, the effect of other variables and so on. ε is usually treated as a statistical error, it is often assumed to have a normal distribution with mean zero and variance ε^2 (Wang *et al.*, 2012; Giwa and Giwa 2012).

There are different types of techniques available in response surface methodology, viz: central composite, Box-Behnken, D-optimal, and so on. The one applied in this work is Box-Behnken technique.

The Box-Behnken technique is an independent quadratic design in that it does not contain any embedded factorial or fractional factorial design. In this design, the treatment combinations are at the midpoints of edges of the process space and at the centre. These designs are rotatable (or nearly rotatable) and require three (3) levels of each factor (NIST/SEMATECH, 2015).

According to the information gathered from the literature, Giwa and Giwa (2012) applied central composite design of response surface methodology with the aid of Design Expert and Excel Solver to find optimum values that could be used to obtain high mole fractions of n-butyl acetate and methanol at the bottom segment and top segment respectively of a transesterification reaction integrated distillation column. They used a reactive distillation pilot plant developed with Aspen HYSYS process simulator as their experimental setup in which the productions were carried out. The optimum values they obtained were validated by comparing the theoretical value with the one obtained using the optimum values

to carry out an experiment. Similarly, Giwa and Giwa (2013) applied response surface methodology and MATLAB to optimize a reactive distillation process used for the production of isopropyl myristate. They also used an Aspen HYSYS model as their experimental set-up. It was concluded in the work that the obtained optimum values were valid ones. Also, Giwa and Karacan (2012b) used Aspen HYSYS to optimize ethyl acetate reactive packed distillation process and they were able to obtain results from the Aspen HYSYS model of the process that compared well with the experimental ones. Moreover, Giwa (2013b) used the Model Analysis Tools of Aspen PLUS to model, simulate and optimize a reactive distillation process used for the production of methyl acetate from the esterification reaction between methanol and acetic acid. The achievement of the value of the objective function given by the optimization of the process when the estimated optimum values of reflux ratio and reboiler duty were used to run the developed model revealed that the optimum values they obtained from their study were also valid ones.

In this work, the optimization of some of the operating parameters (recycle ratio, feed ratio and reboiler duty) of a reactive distillation process used for the production of palmitic acid methyl ester using Box-Behnken technique of the response surface methodology has been carried out.

2 METHODOLOGY

Experimental Design

This research work was carried out by using Box-Behnken technique of the response surface methodology to design experiments for the production of the palmitic acid methyl ester (PAME) in a reactive distillation column, with the aid of Minitab (MINITAB, 2013). The experiments were designed choosing three (3) centre points. The selected input factors of the production process were reflux ratio, feed ratio and reboiler duty, and their levels used are given in Table 1.

Table 1. Levels of input factors of the experimental design

#	Factor	Low level	High level
1	Reflux ratio	3	5
2	Feed ratio	1	3
3	Reboiler duty (kJ/s)	200000	300000

Also, the output variable of the design was the mole fraction of PAME obtained from the bottom section of the column. Based on the parameters of the Box-Behnken technique of the RSM used, fifteen (15) experiments were designed to be carried out. After designing the experiments, the experimental setup was designed with the aid of Aspen HYSYS in form of a model.

Aspen HYSYS Modelling

The Aspen HYSYS (Aspen, 2012) modelling of the set-up (Figure 1) used to run the statistically designed (with the aid of Minitab using the Box-Behnken technique of the response surface methodology) experiments for the production of palmitic acid methyl ester, was carried out using the version 8.0 of the process simulator.

The column type used for the development of the set-up was Distillation Column Sub-Flowsheet that had two feed streams – upper and lower- and two product streams (top and bottom). The palmitic acid for the process was fed at a temperature and a pressure of 350 ^{o}C and 1 atm, respectively, into the column through the upper feed stream (stage 8 counted from the top) because it was less volatile than methanol, which was fed through the lower feed stream (nineteenth stage counted from the top) at a temperature of 150 ^{o}C and a pressure of 1 atm. In addition, the column had, apart from the condenser and the reboiler, 30 stages. The condenser and the reboiler types used were total and kettle, respectively; the pressure of each of them was 1 atm, and the pressure drop across both of them were the same and had a value of 0 atm. As a result of the reactive distillation occurring in the column used, Sparse Continuation Solver was employed because it was the one that could handle this type of a process. For the entire reactive distillation process, the fluid package used was Wilson model.

The reaction occurring at the reaction (middle) section of the column, which was an equilibrium type, and the equilibrium constant of which was estimated from Gibbs free energy was as given in Equation (2).

$$C_{16}H_{32}O_2 + CH_3OH \leftrightarrow C_{17}H_{34}O_2 + H_2O \quad (2)$$

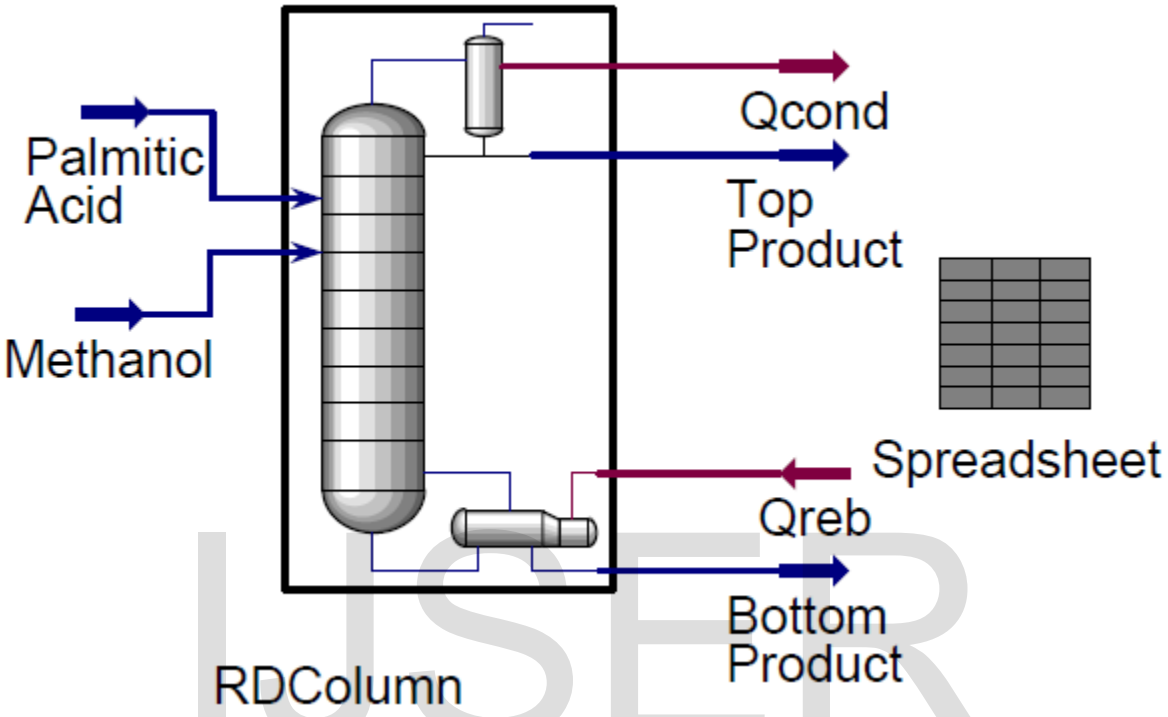

Figure 1. Palmitic acid methyl ester process plant developed with the aid of Aspen HYSYS

After the experimental setup was developed, and the values of the factors obtained from the design carried out using the Box-Behnken technique of the response surface methodology used to run it, the responses obtained were entered into Minitab worksheet for analysis and model development.

Model Development

Using the mole fractions (responses) obtained from the experiments and the input factors used, a selected full quadratic model of the form shown in Equation (3) was developed for the process

$$x_{pame} = b_0 + b_1 RR + b_2 FR + b_3 RD + b_{11}(RR)^2 + b_{22}(FR)^2 + b_{33}(RD)^2 + b_{12}(RR \times FR) + b_{13}(RR \times RD) + b_{23}(FR \times RD) \quad (3)$$

by estimating the model coefficients with confidence level of 95% and without Box-Cox Transformation through the "Analyse Response Surface Design" tool of the program (Minitab). Based on the probability (P-) values of the models and those of the factors obtained, which was an indication of their significance, the model was adequately modified for improvement.

Optimization

The optimization of the response (bottom palmitic acid methyl ester mole fraction) obtained was carried out, with the aid of "Response Optimizer" of Minitab, after the simulation of the developed and modified model equation by setting the goal to "maximize" while the lower and the upper bounds were also appropriately fixed.

3 RESULT AND DISCUSSION

The results obtained when the Box-Behnken technique of response surface methodology was used to design the experiments of this work, with the aid of Minitab, were as given in Table 2. From the table, it can be noticed that the values of the factors given were varied between the two (low and high) levels entered into the Minitab and a centre (midpoint) level for each of the factors. This was found to be in conformity with the theoretical knowledge about the Box-Behnken technique of the response surface methodology. This has thus made it clear that the experiments designed were, actually, Box-Behnken designed ones. It should also be noticed that the standard order given in Table 2 were the normal order of generating the experiments using Box-Behnken technique, but the run order was the one used to carry out the experiments. This was done that way to have ideas concerning the replication of the system.

Table 2. Experimental design factor values generated

Standard order	Run order	Reflux ratio	Feed ratio	Reboiler duty (kJ/s)
14	1	4	2	250000
10	2	4	3	200000
15	3	4	2	250000
3	4	3	3	250000
11	5	4	1	300000
1	6	3	1	250000
12	7	4	3	300000
9	8	4	1	200000
5	9	3	2	200000
2	10	5	1	250000
13	11	4	2	250000
7	12	3	2	300000
8	13	5	2	300000
4	14	5	3	250000
6	15	5	2	200000

Given in Table 3 are the results obtained when the experimental input data designed with Minitab and given in Table 2 were used to run the system that was setup with the aid of Aspen HYSYS. According to the results, the minimum mole fraction of palmitic acid methyl ester obtained from the bottom section of the reactive distillation column was found to be 0.3646 (run 14) while the maximum was 0.8358 (run 6).

Table 3. Mole fractions of palmitic acid methyl ester obtained from the experimental runs

Run order	x_{PAME}
1	0.5477
2	0.3973
3	0.5477
4	0.4634
5	0.7532
6	0.8358
7	0.4006
8	0.7438

9	0.6408
10	0.6861
11	0.5477
12	0.6483
13	0.4973
14	0.3646
15	0.4935

Now, analysing the mole fraction value of the palmitic acid methyl ester obtained together with the values of the factors used to run the experimental set-up for variance, the results of which are given in Table 4, it was discovered that the probability value (P-value) of the model was approximately zero (0), which was very good, but those (P-values) of some of the factors considered were higher than 0.05 that was estimated based on 95 % confidence level. Based on the results obtained, the factors having P-values greater than 0.05 were found to be reboiler duty (RD), square of reboiler duty (RD*RD) and interactions of reboiler duty with reflux ratio (RR*RD) and with feed ratio (FR*RD). It can be seen that all the factors involving the reboiler duty were discovered to have P-values greater than 0.05 and, thus, found to be negligible. This was as a result of the fact the system is a reactive distillation, and, in this case, no reaction was occurring in the reboiler section of the column.

Table 4. Analysis of variance (ANOVA) for the developed full quadratic model

Source		DF	Seq SS	Contribution (%)	Adj SS	Adj MS	F-Value	P-Value
Model		9	0.28342	99.89	0.28342	0.031491	504.71	0
Linear		3	0.280004	98.69	0.280004	0.093335	1495.86	0
	RR	1	0.03737	13.17	0.03737	0.03737	598.92	0
	FR	1	0.242562	85.49	0.242562	0.242562	3887.52	0
	RD	1	0.000072	0.03	0.000072	0.000072	1.16	0.331
Square		3	0.002755	0.97	0.002755	0.000918	14.72	0.006
	RR*RR	1	0.000976	0.34	0.001201	0.001201	19.24	0.007
	FR*FR	1	0.001712	0.6	0.001754	0.001754	28.11	0.003
	RD*RD	1	0.000068	0.02	0.000068	0.000068	1.08	0.346
2-Way Interaction		3	0.000661	0.23	0.000661	0.00022	3.53	0.104
	RR*FR	1	0.000649	0.23	0.000649	0.000649	10.4	0.023
	RR*RD	1	0.000003	0	0.000003	0.000003	0.05	0.827
	FR*RD	1	0.000009	0	0.000009	0.000009	0.15	0.718
Error		5	0.000312	0.11	0.000312	0.000062		
Lack-of-Fit		3	0.000312	0.11	0.000312	0.000104	3.11E+14	0
Pure Error		2	0	0	0	0		
Total		14	0.283732	100				

Despite the high P-values of those terms, they were still included in the model (Equation 4) given by Minitab as the equation relating the mole fraction of palmitic acid methyl ester obtained from the bottom section of the column and the factors affecting the process, even though, looking at the model, the coefficients of those factors having P-values greater than 0.05 were found to be approximately zero (0).

$$x_{pame} = 1.706 - 0.2335\,RR - 0.3047\,FR - 0.0000\,RD + 0.01803\,(RR)^2 + 0.02180\,(FR)^2 + 0.0000\,(RD)^2 + \cdots$$
$$\cdots + 0.01273\,(RR \times FR) - 0.0000\,(RR \times RD) - 0.0000\,(FR \times RD) \quad (4)$$

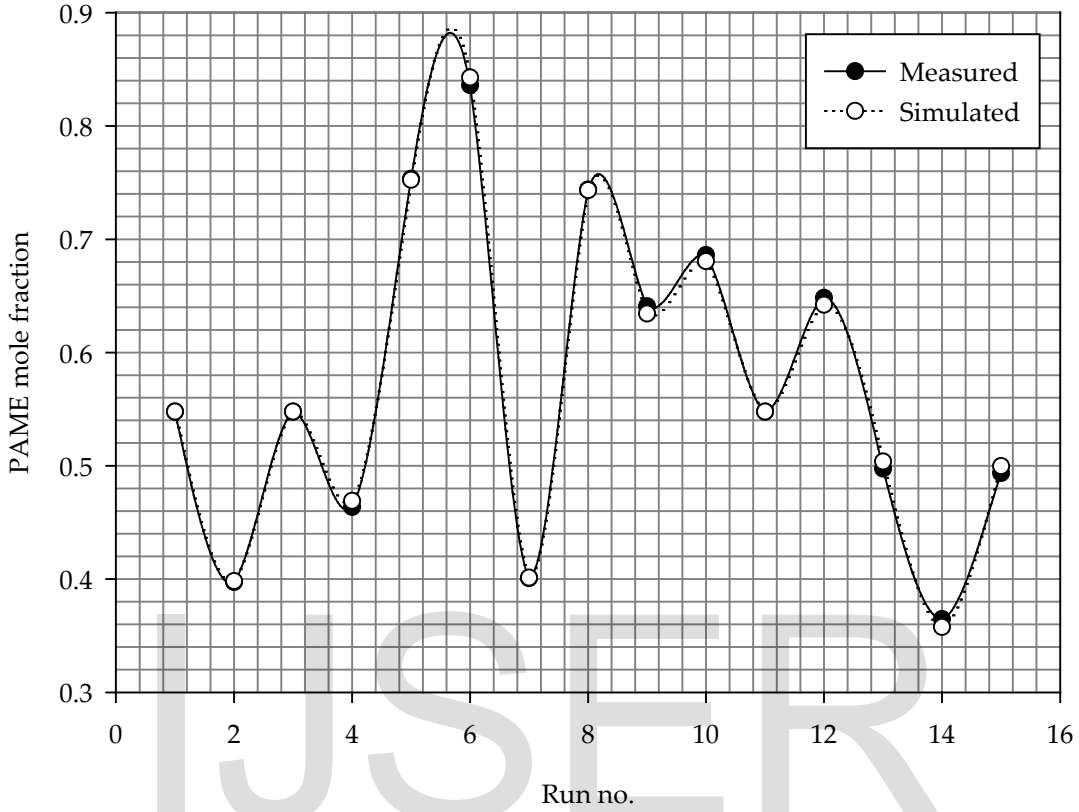

Figure 2. Measured and full quadratic model simulated mole fractions

The high P-values as well as the negligible coefficient values of those factors were found to be an indication of the fact that they (reboiler duty (RD), square of reboiler duty (RD*RD) and interactions of reboiler duty with reflux ratio (RR*RD) and with feed ratio (FR*RD)) were having negligible effects on the process, although, even with the presence of those factors, good correlations were found to exist between the measured and the simulated mole fractions of palmitic acid methyl ester, as can be seen in Figure 2. However, it was deemed necessary to modify the developed model equation so that the factors whose effects were found to be negligible would be removed.

Given in Equation (5) is the modified version of the model of the process obtained, after the factors with negligible effects had been removed. As can be seen from the equation, all the factors present in the model have coefficients that are significant. To avoid any doubt, the results of this modified version of the model were also analysed for variance.

$$x_{pame} = 1.6429 - 0.2354\,RR - 0.3109\,FR + 0.01770\,(RR)^2 + 0.02147\,(FR)^2 + 0.01273\,(RR \times FR) \quad (5)$$

The results of the analysis of variance of the modified quadratic model were as given in Table 5. According to the table, the P-values of the remaining factors, considered to be significant, were found to be less than 0.05 (in fact, some of them were approximately zero). As such, a model whose factors are all significant has been obtained for the system.

Table 5. Analysis of variance (ANOVA) for the modified quadratic model

Source			DF	Seq SS	Contribution (%)	Adj SS	Adj MS	F-Value	P-Value
Model			5	0.283268	99.84	0.283268	0.056654	1098.01	0
	Linear		2	0.279932	98.66	0.279932	0.139966	2712.7	0
		RR	1	0.03737	13.17	0.03737	0.03737	724.27	0
		FR	1	0.242562	85.49	0.242562	0.242562	4701.13	0
	Square		2	0.002688	0.95	0.002688	0.001344	26.05	0
		RR*RR	1	0.000976	0.34	0.001164	0.001164	22.56	0.001
		FR*FR	1	0.001712	0.6	0.001712	0.001712	33.17	0
	2-Way Interaction		1	0.000649	0.23	0.000649	0.000649	12.57	0.006
		RR*FR	1	0.000649	0.23	0.000649	0.000649	12.57	0.006
Error			9	0.000464	0.16	0.000464	0.000052		
	Lack-of-Fit		7	0.000464	0.16	0.000464	0.000066	1.98E+14	0
	Pure Error		2	0	0	0	0		
Total			14	0.283732	100				

Just as it was observed in the case of the full quadratic model, good agreements (see Figure 3) were found to exist between the measured and the modified-model simulated mole fractions of the palmitic acid methyl ester produced and obtained through the bottom section of the column. This was an indication that the modified model obtained was able to represent the measured data very well.

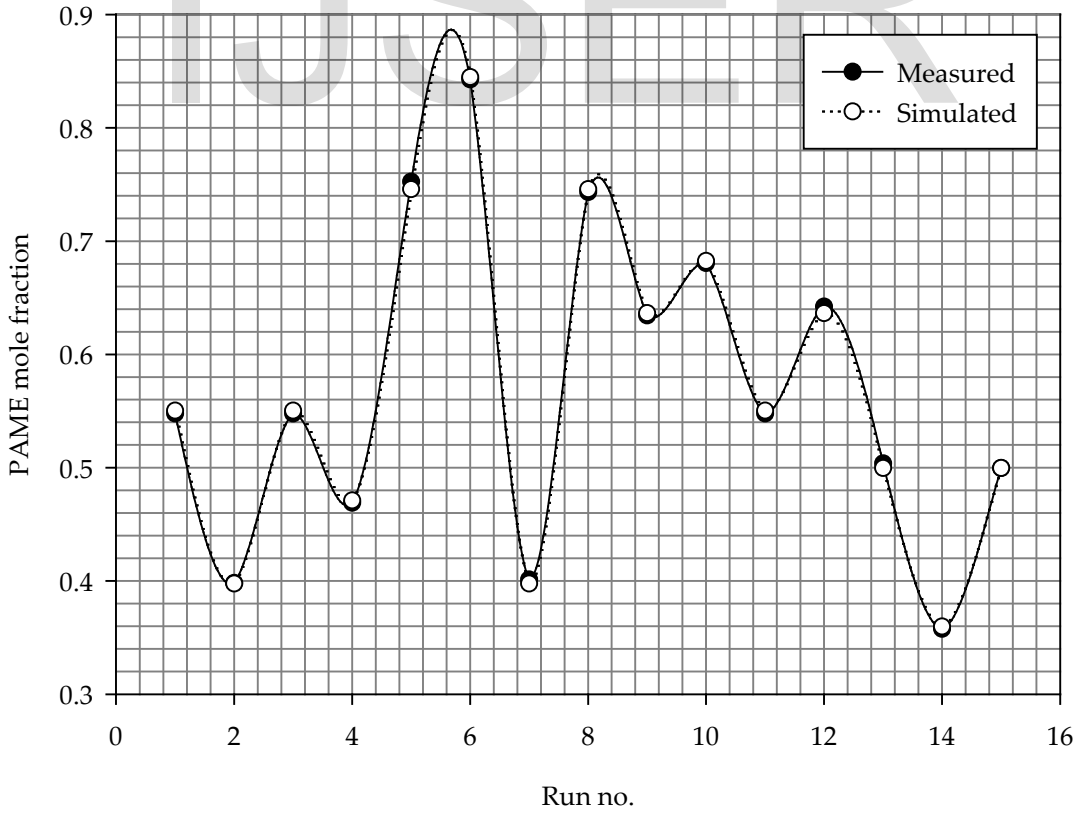

Figure 3. Measured and modified quadratic model simulated mole fractions

The results given in Table 6 show the performances of the developed models in terms of their correlations. According to the table, it was discovered that only the R-squared (a number that indicates how well data fit a statistical model) value of the full quadratic model was better than that of the modified one while the adjusted R-squared (that is, R-squared adjusted for the number of parameters in the model relative to the number of points in the design; a measure of the amount of variation about the mean explained by the model) and the predicted R-squared (a measure of how good the model predicts a response) values of the modified quadratic model were better than those of the full quadratic one.

Table 6. Comparison of the performances of the full and the modified quadratic models

Parameter	Value (%)	
	Full quadratic model	Modified quadratic model
R-squared	99.89	99.84
Adjusted R-squared	99.69	99.75
Predicted R-squared	98.24	99.14

Considering the fact that the prediction capacity of a model is very important because it is one of the important criteria used to determine the usefulness of a model in industries, it has been discovered that the modified quadratic model was better than the full quadratic one developed as its adjusted and predicted R-squared values were found to be greater.

The results obtained from the optimization carried out using the "Response Optimizer" of Minitab with the modified quadratic model of the system revealed that palmitic acid methyl ester having a mole fraction of 0.8447 was theoretically obtainable when the reflux ratio and the feed ratio of the system were 3 and 1, respectively.

Using the results of the optimization carried out with the aid of Minitab to run an experiment in order to validate the theoretical optimization values (a reflux ratio of 3, and a feed ratio of 1) obtained, and making the value of the reboiler duty of the column to be 335000 kJ/s, the value of the mole fraction of palmitic acid methyl ester obtained was found to be 0.8435, and it was observed to be close enough to the theoretical value to say that the theoretical optimization values of the factors obtained using Minitab were valid.

4 CONCLUSION

The results obtained from the analysis of the full quadratic model developed for the reactive distillation process used to produce palmitic acid methyl ester have revealed that reboiler duty was not having any significant effect on the process because no reaction was occurring in that section of the column. Also, even though the R-squared value of the full quadratic model was found to be better than that of the modified one, the latter was found to be better than the former in prediction because its predicted R-squared value was discovered to be higher. In addition, the optimum values estimated with the aid of Minitab were found to be valid ones because the optimum mole fraction of palmitic acid methyl ester measured was very close to the theoretical one given by Minitab.

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NOMENCLATURE

Adj MS	Adjusted mean of squares
Adj SS	Adjusted sum of squares
Adj	Adjusted
Bottom	Bottom product
DF	Degrees of Freedom

FR	Feed ratio
Pred	Predicted
P-Value	Probability value
Q_{cond}	Condenser heat duty, kJ/s
Q_{reb}	Reboiler heat duty, kJ/s
R	Reflux ratio of the column
RD	Reboiler duty, kJ/s
RR	Reflux ratio
Seq SS	Sequential sums of squares
Top	Top product
x_{PAME}	Mole fraction of biodiesel obtained from the bottom section of the column

REFERENCES

(1) Agatonovic-Kustrin, S., Zecevic, M., Zivanovic, L. and Tucker, I.G. 1998. Application of Neural Networks for Response Surface Modeling in HPLC Optimization. Analytica Chimica Acta, 364(1-3), 256-273.

(2) Agreda, V.H., Partin, L.R. and W.H. Heise. 1990. High Purity Methyl Acetate via Reactive Distillation. Chemical Engineering Progress, 86(2), 40-46.

(3) Aspen. 2012. Aspen HYSYS V8.0 (27.0.0.38). Aspen Technology, USA.

(4) Bandaru, V.V.R., Somalanka, S. R., Mendu, D.R., Madicherla, N.R. and Chityala, A. 2006. Optimization of Fermentation Conditions for the Production of Ethanol from Sago Starch by Co-Immobilized Amyloglucosidase and Cells of *Zymomonas mobilis* Using Response Surface Methodology. Enzyme and Microbial Technology, 38, 209-214.

(5) Baumes, L., Farrusseng, D., Lengliz, M. and Mirodatos, C. 2004. Using Artificial Neural Networks to Boost High-Throughput Discovery in Heterogeneous Catalysis. QSAR & Combinatorial Science, 29, 767-778.

(6) Box, G.E.P. and Draper, N.R. 1987. Empirical Model Building and Response Surfaces, Wiley.

(7) Chi, G., Hu, S., Yang, Y. and Chen, T. 2012. Response Surface Methodology with Prediction Uncertainty: A Multi-Objective Optimisation Approach. Chemical Engineering Research and Design, 90, 1235-1244.

(8) Dutta, J.R., Dutta, P.K. and Banerjee, R. 2004. Optimization of Culture Parameters for Extracellular Protease Production from a Newly Isolated *Pseudomonas* sp. Using Response Surface and Artificial Neural Network Models. Process Biochemistry, 39(12), 2193-2198.

(9) Gao, J., Zhao, X.M., Zhou, L.V. and Huang, Z.H. 2007. Investigation of Ethyl Lactate Reactive Distillation Process. Institution of Chemical Engineers, 85, 525-526.

(10) Giwa, A. 2012. Steady-State Modeling of n-Butyl Acetate Transesterification Process Using Aspen PLUS: Conventional versus Integrated. ARPN Journal of Engineering and Applied Sciences, 7(12), 1555-1564.

(11) Giwa, A. 2013a. Sensitivity Analysis of ETBE Production Process Using Aspen PLUS. International Journal of Advanced Scientific and Technical Research, 3(1), 293-303.

(12) Giwa, A. 2013b. Methyl Acetate Reactive Distillation Process Modeling, Simulation and Optimization Using Aspen Plus. ARPN Journal of Engineering and Applied Sciences, 8(5), 386-392.

(13) Giwa, A. and Giwa, S.O. 2012. Optimization of Transesterification Reaction Integrated Distillation Column Using Design Expert and Excel Solver. International Journal of Advanced Scientific and Technical Research, 2(6), 423-435.

(14) Giwa, A. and Giwa, S.O. 2013. Isopropyl Myristate Production Process Optimization Using Response Surface Methodology and MATLAB. International Journal of Engineering Research & Technology, 2(1), 853-862.

(15) Giwa, A. and Giwa, S.O. 2015. Cascade-Forward Neural Network Modelling of a Biodiesel Reactive Distillation Process. International Journal of Scientific & Engineering Research, 6(5), 837-849.

(16) Giwa, A. and Karacan, S. 2012a. Modeling and Simulation of a Reactive Packed Distillation Column Using Delayed Neural Networks. Chaotic Modeling and Simulation, 2(1), 101-108.

(17) Giwa, A. and Karacan, S. 2012b. Simulation and Optimization of Ethyl Acetate Reactive Packed Distillation Process Using Aspen Hysys. The Online Journal of Science and Technology, 2(2), 57-63.
(18) Giwa, A. and Karacan, S. 2012c. Development of Dynamic Models for a Reactive Packed Distillation Column. International Journal of Engineering, 6(3), 118-128.
(19) Giwa, A. and Karacan, S. 2012d. Decoupling Model Predictive Control of a Reactive Packed Distillation Column. International Journal of Advances in Science and Technology, 4(6), 39-51.
(20) Giwa, A. and Karacan, S. 2012e. Decoupling PID Control of a Reactive Packed Distillation Column. International Journal of Engineering Research & Technology, 1(6), 1924-1933.
(21) Giwa, A., Bello, A. and Giwa, S.O. 2014. Performance Analyses of Fatty Acids in Reactive Distillation Process for Biodiesel Production. International Journal of Scientific & Engineering Research, 5(12), 529-540.
(22) Giwa, A., Bello, A. and Giwa, S.O. 2015. Artificial Neural Network Modeling of a Reactive Distillation Process for Biodiesel Production. International Journal of Scientific & Engineering Research, 6(1), 1175- 1191.
(23) Hadjmohammadi, M. and Kamel, K. 2008. Response Surface Methodology and Support Vector Machine for the Optimization of Separation in Linear Gradient Elution. Journal of Separation Science, 31, 3864-3870.
(24) Jana, A.K., and Adari, P.V.R.K. 2009. Nonlinear State Estimation and Control of a Batch Reactive Distillation. Chemical Engineering Journal, 150, 516-526.
(25) MINITAB. 2013. Minitab 17.1.0. Minitab Inc. USA.
(26) Myers, R.H. and Montgomery, D.C. 1995. Response Surface Methodology, Wiley, 1995.
(27) NIST/SEMATECH. e-Handbook of Statistical Methods, http://www.itl.nist.gov/div898/handbook/, 10/06/2015.
(28) Omota, F., Dimian, A.C. and Bliek, A. 2003. Fatty Acid Esterification by Reactive Distillation: Part 2- Kinetics-Based Design for Sulphated Zirconia Catalysts. Chemical Engineering Science, 58, 3175-3176.
(29) Pérez-Correa, S., González, P. and Alvarez, J. 2008. On-Line Optimizing Control for a Class of Batch Reactive Distillation Columns. Proceedings of the 17th World Congress of the International Federation of Automatic Control, Seoul, Korea, 3263-3268.
(30) Shao, P., Jiang, S.T. and Ying, Y.J. 2007.Optimization of Molecular Distillation for Recovery of Tocopherol from Rapeseed Oil Deodorizer Distillate Using Response Surface and Artificial Neural Network Models. Food and Bioproducts Processing, 85, 85-92.
(31) Tang, Q., Lau, Y., Hu, S., Yan, W., Yang, Y. and Chen, T. 2010. Response Surface Methodology Using Gaussian Processes: Towards Optimizing the *trans*-Stilbene Epoxidation over Co^{2+}–NaX Catalysts, Chemical Engineering Journal, 156, 423-431.
(32) Taylor R. and Krishna R. 2000. Modelling Reactive Distillation, Review. Chemical Engineering Science, 55, 5183-5229.
(33) Völker, M., Sonntag, C. and Engell, S. 2007. Control of Integrated Processes: A Case Study on Reactive Distillation in a Medium-Scale Pilot Plant. Control Engineering Practice, 15, 863-881.
(34) Wang, X., Song, X., Jiang, M., Li, P., Hu, Y., Wang, K. and Liu, H. 2012.Modeling and Optimization of Laser Transmission Joining Process between PET and 316L Stainless Steel Using Response Surface Methodology. Optics & Laser Technology, 44, 656-663.
(35) Yan, W., Chen, Y., Yang, Y. and Chen, T. 2011a. Development of High Performance Catalysts for CO Oxidation Using Data-Based Modeling. Catalysis Today, 174, 127-134.
(36) Yan, W., Hu, S., Yang, Y., Gao, F. and Chen, T. 2011b. Bayesian Migration of Gaussian Process Regression for Rapid Process Modeling and Optimization. Chemical Engineering Journal, 166, 1095–1103.