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# Simulation of Palm based Fatty Acids Distillation

Awang Bono, Oh Pin Pin and Chin Peng Jiun
Chemical Engineering Programme, School of Engineering and Information Technology,
Universiti Malaysia Sabah, Locked Bag No. 2073, 88999 Kota Kinabalu, Sabah, Malaysia

**Abstract:** Fatty acids have long been recognized for their commercial value in the absence of glycerol. Chemicals derived from fatty acids are widely used in the formulation of detergents, lubricant, surfactants and in pharmaceutical industries. In addition, fatty acids also play a vital role in human metabolism and are widely used as catalyst in some chemical reactions. Commercially produced fatty acids are derived from naturally occurring fats and oils through the process of hydrolysis. Most of these raw materials result in nature as complex mixtures of triglycerides, alcohols and other esters. Alternatively, common edible oils used are sunflower oil, corn oil, soybean oil, palm and palm kernel oil. Crude fatty acids can be obtained from the process of hydrolysis and will be purified through total distillation. Due to fatty acid market demand, the purity requirement of distillated fatty acid products is increasing greatly. Since desired purity of fatty acid is achievable through the most common and most efficient means of fractionation distillation process, study on simulation of fatty acids distillation has a significant contribution to the oleo chemical industry. In this simulation study, the optimization of the tray specification, feed stream pressure and temperature on the purity performance of the fatty acid composition are investigated. In South East Asia, palm tree fruit ripen continuously and can be harvested all year round. Therefore, palm based fatty acids are selected to be used as the feed components. In the present study, binary and multi-component distillations of saturated and unsaturated fatty acids are studied. This simulation model is developed by using HYSYS simulator with suitable thermodynamic package chosen. A shortcut simulation method is built in advanced for preliminary estimations and for determining rigorous operating limits. Eventually, parametric optimization is performed to obtain the optimum operating conditions of the rigorous distillation column.

**Key words:** HYSYS, fractionation distillation, purity of fatty acids, parametric optimization, triglyceride

## INTRODUCTION

Fatty acid is an organic compound consisting of hydrocarbon chain and a terminal carboxyl group. Chain length ranges from one hydrogen atom to nearly 30 carbon atoms. Long chain fatty acids generally have an even number of carbon atoms and unbranched chains predominate over branched chain (Daintith, 2000). Fatty acids can be saturated or unsaturated depend on the type of bonding in aliphatic chain. Examples of saturated fatty acids are palmitic acid, C16:0 and stearic acid, C18:0. While unsaturated fatty acid with single double bond such as oleic acid, C18:1 or two or more double bonds, in which case they are called polyunsaturated fatty acids such as linoleic acid, C18:2. Alternatively, majority of fatty acids are originate from edible oil such as sunflower oil, corn oil, soybean oil, palm oil and palm kernel oil. Fatty acids have long been recognized for their commercial value since it is important in human metabolism and used as catalyst in some chemical reaction. Besides that, fatty acids are used in the fields of detergent, lubricant, surfactants and pharmaceutical industries.

Most commercially fatty acids are derived from naturally occurring fats and oils through process of hydrolysis or fat splitting. There is currently great interest in the use of lipase enzymes as catalysts during hydrolysis in order to produce fatty acids and glycerol from triglycerides which have great potential in the emulsifier market (Kolossvary, 1996). Enzymatic hydrolysis is also occurring in digestive system inside human body. Triglyceride molecules from meal and food taken will be emulsified and then hydrolyzed by pancreatic lipase in duodenum and proximal jejunum (Ros, 2000). Lipases (triacylglycerol acylhydrolases E.C.3.1.1.3) are known well to catalyze hydrolysis of triglycerides to yield diglycerides, monoglycerides and fatty acids (Jurado *et al*., 2006). Unlike traditional chemical processes, the enzymatic hydrolysis of triglycerides is an energy saving process which takes place at ambient temperature and atmospheric pressure as

**Corresponding Author:** Awang Bono, Chemical Engineering Programme, School of Engineering and Information Technology, Universiti Malaysia Sabah, Locked Bag No. 2073, 88999 Kota Kinabalu, Sabah, Malaysia

well as at near neutral pH (Kolossvary, 1996; Jurado *et al*., 2006). In addition, enzymatic hydrolysis of triglyceride process is a cost saving process due to lipase is available at reasonable cost. Besides enzymatic hydrolysis of triglycerides become highly attractive, it is potentially produce heat sensitive fatty acids that would otherwise decompose under the extreme conditions of the chemical process (Jurado *et al*., 2006; Gandhi, 1997; Al-Zuhair *et al*., 2003).

After the fats splitting process, several separation and purification method implemented to purify the fatty acid such as distillation, supercritical fluid extraction, gas chromatography method, high performance liquid chromatography and others. These separation methods are carried out in experimental skill, pilot plant and industrial skill. Desired purity of fatty acid is achievable through the most common and most efficient means of fractionation distillation or rectification process. Distillation is a unit operation that has been around for a long time and continues to be the primary method of separation in processing plant (Kister, 1992) and is the most common form of separation technology used to physically separate a mixture into two or more products that have different boiling points, by preferentially boiling the more volatile components out of the mixture. Rectification is reported to give better separation with higher product purity compared to simple distillation. In cases of the compounds have very high boiling points; the compounds are preferably boiled at lower pressure at which such compounds are boiled instead of at higher temperature. This separation technology is known as vacuum fractionation distillation. For close boiling point mixture, it may require many stages to separate the key components. In order to reduce the number of stages required, vacuum fractionation distillation technique is utilized. In industry, vacuum distillation is preferable for heat-sensitive fatty acids purification.

The objective of this research was to simulate the distillation of palm based fatty acid. Besides that, it is also to obtain the operating conditions of the rigorous distillation column by optimizing the effects of number of trays, feed stream pressure and temperature on the purity performance of the fatty acid composition. In this study, this simulation model is developed by using HYSYS 3.2 simulator with suitable thermodynamic package chosen.

## MATERIALS AND METHODS

The shortcut solution is often being used as the foundation for progressive toward a rigorous solution of the problem. Before proceeding to the multi-component separations, shortcut distillation column is built in advance to estimate the column performance as it relies on certain simplifying assumptions to solve the column equations. Analyzing a distillation problem on the basis of this method is useful for preliminary estimation and for determining practical column operating limits

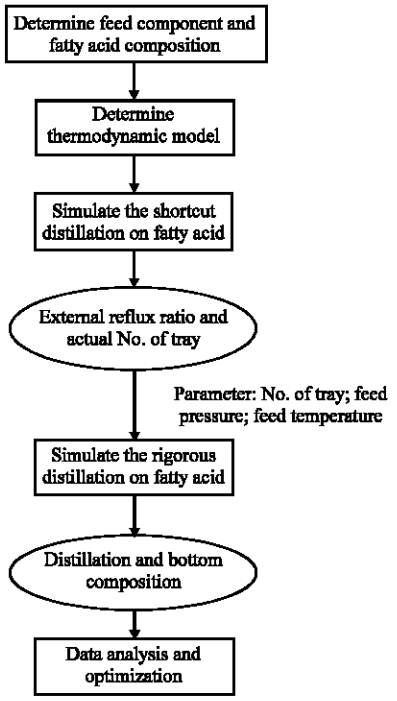


Fig. 1: Overall scheme of simulation process on palm based fatty acid distillation

Table 1: Major fatty acid compositions in palm olein

| | Normal RBD palm olein | | |
|---|---|---|---|
| Parameters | Range | Mean | SD |
| **Fatty acid composition (wt. %)** | | | |
| C16:0 (S1) | 36.8-43.2 | 40.93 | 0.95 |
| C18:0 (S2) | 3.7-4.8 | 4.18 | 0.17 |
| C18:1 (U1) | 39.8-44.6 | 41.51 | 0.84 |
| C18:2 (U2) | 10.4-12.9 | 11.64 | 0.36 |

Source: Siew (2000)

According to Fig. 1, feed compositions and fatty acid compositions are determined at the first stage of the simulation process. In this study, palm based fatty acids are selected to be used as the feed components. By referring to Malaysia Palm Oil Board, major components of refined palm olein fatty acids, such as palmitic acid (C16:0), oleic acid (C18:1), linoleic acid (C18:2) and stearic acid (C18:0), are selected to be used as the main input feed stream to the distillation column. The palm based fatty acid composition is tabulated in Table 1. As shown in Table 2, these major components of palm based fatty acids are categorized into two groups. One group consists

of six binary component mixtures while the other group consists of five multi-component mixtures.

As HYSYS 3.2 is industrially leading simulation software, it is used to simulate the effects of number of trays, feed stream pressure and temperature of fractionation distillation column. Property of mixture could be predicted using the property package available in HYSYS 3.2.

According to Elliott and Lira (1999), for non-polar fluids, equations of state may suffice. On the other hand, for polar fluids, a fitted activity coefficient model is preferred. Palm based fatty acids are non polar component, therefore, equations of state has priority. In the present study, the thermodynamic model called Lee-Kesler-Plocker is used for simulation of palm based fatty acid distillation. Lee-Kesler-Plocker model is the most accurate general method for non-polar substances and mixtures (Hyprotech, 2003).

The feed conditions are tabulated in Table 3. The operating pressure used is under vacuum in order to minimize the risk for chemical decomposition of the fatty acids (Aly and Ashour, 1992).

The shortcut method is used to predict the actual number of stages and reflux ratio for the separation process with appropriate thermodynamic model selected. The column performance and information are further applied in rigorous method simulation. Parametric optimization is performed to obtain optimum operating conditions of the rigorous distillation column in various parameters. For each binary and multi component of palm based fatty acid mixtures, effects of three parameters, i.e., number of tray, feed stream temperature and pressure on the purity performance of distillate and bottoms fatty acid products compositions, are investigated. For a better understanding of the purification performance, for each testing parameter, two separated graphs, distillate product composition versus particular testing parameter and bottom product composition versus testing parameter, are plotted and analyzed.

Table 2: Groups of mixtures of components which are used in the simulation

| Mixture | Binary component | Mixture | Multi-component |
|---|---|---|---|
| 1 | S1-S2 | 7 | S1S2U1 |
| 2 | S1-U1 | 8 | S1S2U2 |
| 3 | S1-U2 | 9 | S1U1U2 |
| 4 | S2-U1 | 10 | S2U1U2 |
| 5 | S2-U2 | 11 | S1S2U1U2 |
| 6 | U1-U2 | | |

Table 3: Default column specifications and feed stream setting

| Components composition (w/w) | Values |
|---|---|
| Palmitic acid | 40.93 |
| Stearic acid | 4.18 |
| Oleic acid | 41.51 |
| Linoleic acid | 11.64 |
| Feed flow rate | 100 kg $h^{-1}$ |
| Liquid fraction | 1 |

## RESULTS AND DISCUSSION

In present study, distillation of four different major palm based fatty acids was simulated by using HYSYS 3.2 simulator. Three parameters such as effects of number of tray, feed stream temperature and pressure on the purity performance of fatty acid composition are investigated. When the mixture of palm based fatty acid was separated, complete separation of the fatty acids was rarely occurred. However, the overhead fraction from the fractionation column consists predominantly of the more volatile component and small amount of less volatile component. While the bottom was lean in more volatile fatty acid but rich in less volatile fatty acid. In market and industry, distillate from distillation was preferred. Therefore, discussion is performed on the distillate composition which obtained from the simulation.

### Binary mixture distillation

**Effect of number of tray:** Distillate composition for binary mixture of palmitic acid and linoleic acid is shown in Fig. 2. When number of tray was 5, 10 and 15, the purity of more volatile component in this mixture which was palmitic acid were 86.76, 91.28 and 93.58%, respectively. As can be seen from Fig. 2, the purity of palmitic acid was optimum when the number of tray increased to 35 trays. Therefore, from the simulation data, it can be concluded that increasing the number of tray will improve the separation. This is due to higher the number of tray, the contacting time between the palm based fatty acid vapor and liquid is increasing. Moreover, according to Halvorsen and Skogestad (2000), high purity separation requires larger number of stages due to large separation factor, S.

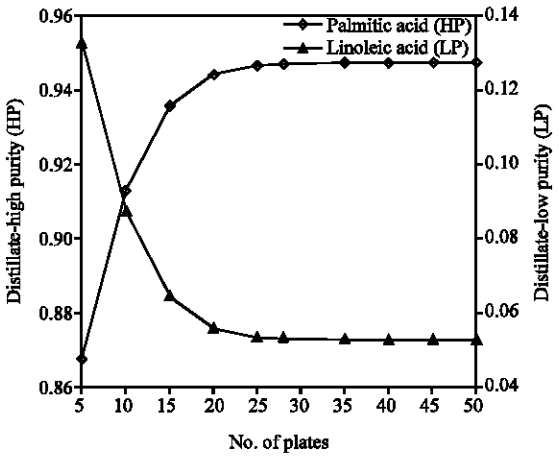


Fig. 2: Effect of number of tray on distillate composition for binary mixture of palmitic acid and linoleic acid

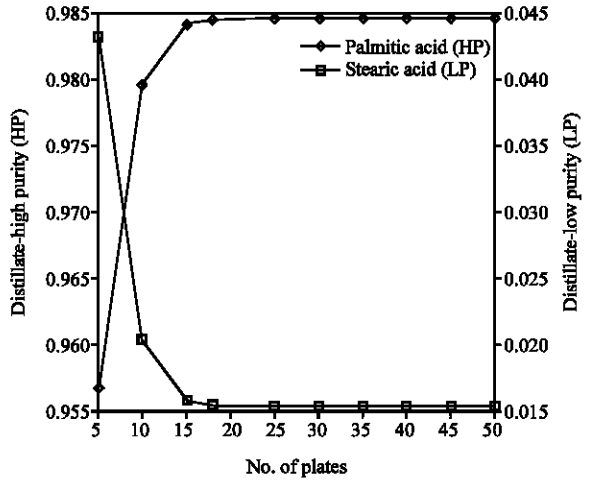


Fig. 3: Effect of number of tray on distillate composition for binary mixture of palmitic acid and stearic acid

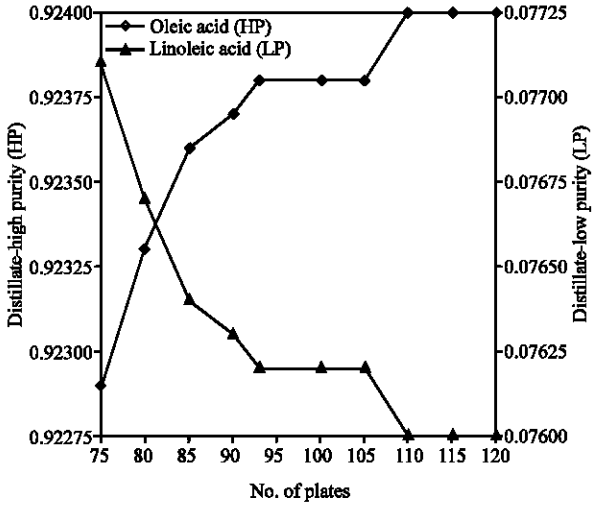


Fig. 4: Effect of number of tray on distillate composition for binary mixture of oleic acid and linoleic acid

For better understanding the relationship between tray number and type of bounding inside fatty acid, comparison on the number of tray needed to achieve the optimum purity for more volatile fatty acid had been studied. Figure 3 shows the distillate composition for binary mixture of palmitic acid and stearic acid, while the purity of oleic acid and linoleic acid against number of tray is shown in Fig. 4. From Fig. 3, at number of tray, 25 and above, palmitic acid achieved optimum composition which was 98.46%. But, purity of oleic acid was at optimum when the number of tray in distillation column was 110 trays. From the results of simulation, the number of tray needed for distillation of both saturated fatty acid

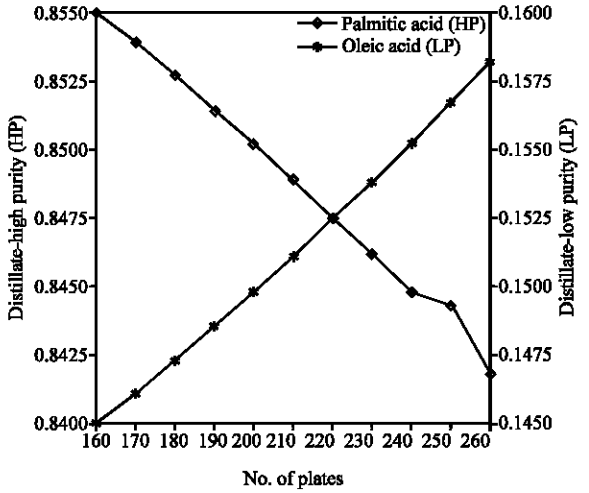


Fig. 5: Effect of feed temperature on distillate composition for binary mixture of palmitic acid and oleic acid

is lower, therefore, it is concluded that saturated fatty acid is easier to be separated compare to unsaturated fatty acid.

Differences in boiling point between components affect the separation efficiency. The normal boiling point of palmitic acid is 351.00°C while it is 375.20°C for stearic acid. For unsaturated fatty acid, oleic acid is 358.85°C and linoleic acid is 353.85°C, respectively. The difference in between boiling point of palmitic acid and stearic acid is 24.2°C but is it only 5°C different for oleic acid and linoleic acid. According to Halvorsen and Skogestad (2000), large relative volatilities imply large differences in boiling points and easy separation. Moreover, close boiling points implies relative volatilities closer to unity.

Besides that, the distillation separation of mono- and di-unsaturated fatty acid with the same carbon number under economical industrial condition, the relative volatilities for the mixture of oleic acid and linoleic acid is 1.156 at pressure of 100 mbar with temperature between 185°C and 230°C. Hence, efficiency of 80-90 theoretical plates is needed for distillation column (Stage, 1984). The study by Stage, 1984 matched with the simulation data in present study, the actual number of tray estimated from shortcut distillation was 93 trays which was near to the 90 theoretical plates.

**Effect of feed temperature:** Figure 5 shows the effect of feed temperature on the distillate composition for binary mixture of palmitic acid and oleic acid. At the feed temperature of 160°C, the purity of palmitic acid was 85.50%. As the feed temperature was increased to 180, 200 and 230°C, the purity of more volatile component, palmitic

acid was 85.27, 85.02 and 84.62%, respectively. At the highest temperature, 260°C, the composition of palmitic acid was 84.18%. Therefore, increasing the feed temperature, decreasing the purity of more volatile component or light key in distillate.

In accordance with thermal stability and oxidation effects for saturated and unsaturated fatty acids, for reason of corrosion, feed temperature above 260°C have to be avoided (Stage, 1984). Moreover, fatty acids are thermally sensitive materials (Al-Zuhair *et al*., 2003). The relative volatility of particular component is temperature dependent. As the relative volatility increase, separation by distillation becomes easier. According to Stage (1984), for mixture with different carbon number, the relative volatility of binary mixture varies within allowable temperature range. The relative volatility for binary mixture of stearic acid and oleic acid vary from 1.3 to 1.2 as feed temperature increased from 140 to 280°C. While for binary mixture of palmitic acid and oleic acid, the relative volatility is also decreased as feed temperature increasing.

Therefore, it can be concluded that higher the feed temperature of binary mixture of palm based fatty acid, lower the relative volatility of that binary mixture, hence, the purity of more volatile component in distillate is decreasing too. Moreover, feed temperature as well as arrangement and quantity of double bond in the fatty acid are responsible for purity and yield of fatty acid distillate (Stage, 1984).

**Effect of feed pressure:** The fatty acid distillate profile for binary mixture of palmitic acid and linoleic acid was shown in Fig. 6. The composition of palmitic acid decreased from 95.18% in mole percent to 94.78% as the feed pressure increased from 50 to 90 mbar. At higher feed pressure of 120 mbar, the purity of palmitic acid became 94.57%. Then, the composition of palmitic acid further decreased to 94.39% when the distillation was carried out at feed pressure of 150 mbar. Therefore, it can be concluded that increasing the feed pressure, decreasing the purity of more volatile component or light key in distillate.

Relative volatility of binary mixture is also pressure dependent. At higher feed pressure, the relative volatility of the system is lower which increases the separation difficulties (Zygula and Dautenhahn, 2000). Therefore, the purity of more volatile component in distillate is decreasing too.

**Multi-component mixture distillation**

**Effect of number of tray:** Figure 7 shows the effect of number of trays required to obtain overhead product with the specified purity at the top of the distillation column for S1S2U1U2 mixture. At the number of trays of 40, overhead

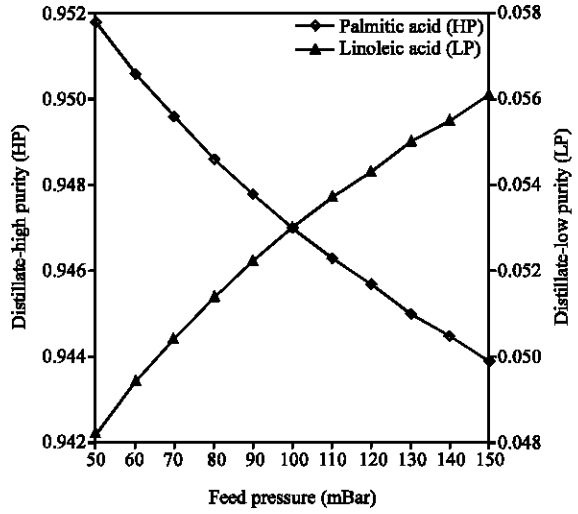


Fig. 6: Effect of feed pressure on distillate composition for binary mixture of palmitic acid and linoleic acid

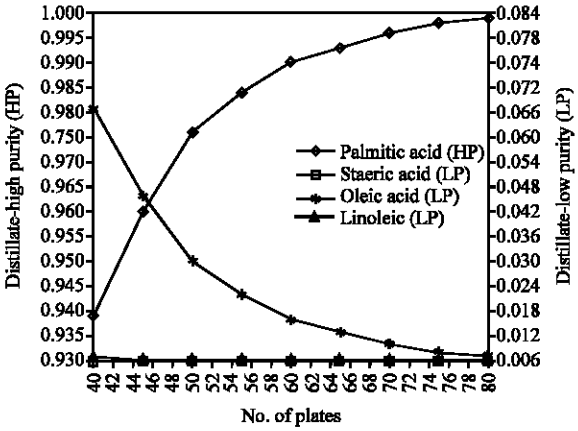


Fig. 7: Distillate composition profile versus number of plates in the column for S1S2U1U2 mixture

product purity of palmitic acid was at the purity level of 99.39% while the oleic acid was at 0.61%, linoleic acid was at 0.01% and stearic acid was at zero of purity level. There is a significant increase in the purity of palmitic acid distillate from 99.39% up to 99.99% at the number of trays of 80. However, there is a significant drop in the purity of oleic acid distillate from 0.61 to 0.01% at the number of trays of 80. For linoleic acid overhead composition profile, it dropped from 0.01 to 0% of purity at the number of trays of 45. For stearic acid overhead composition profile, it showed zero purity level throughout the variation of number of trays simulation.

The tendency of a liquid to evaporate is referred to as its volatility. A more volatile liquid evaporates more readily. Palmitic acid is the most volatile component

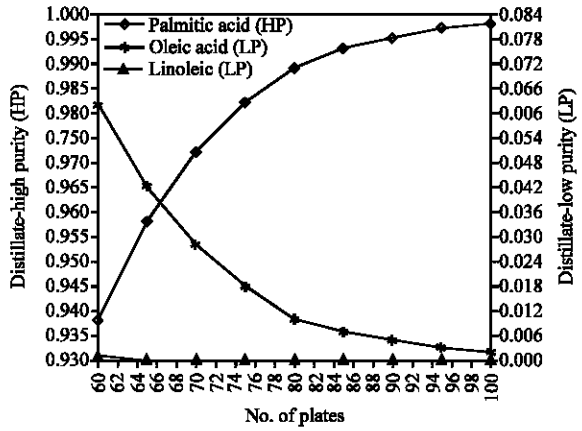


Fig. 8: Distillate composition profile versus number of plates in the column for S1U1U2 mixture

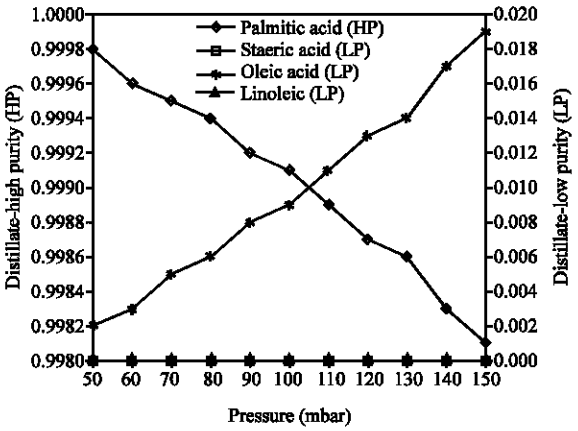


Fig. 9: Distillate composition profile versus feed pressure for S1S2U1U2 mixture

among all the other components. As the number of trays increases, the overhead product composition profile of palmitic acid is shifted through the column resulting in a higher purity composition profile. According to distillation theory, as the number of plates increase, the purity level of more volatile component, palmitic acid, is increasing in the overhead composition profile. On the other hand, the impurity level of less volatile components, such as stearic acid and linoleic acid, is decreasing.

In Fig. 8, it shows the effect of number of trays required to obtain overhead product with the specified purity at the top of the distillation column for S1U1U2 mixture. At the number of trays of 60, overhead product purity of palmitic acid was at the purity level of 99.38% while the oleic acid was at 0.62% and linoleic acid was at 0.01% of purity level. There is a significant increase in the purity of palmitic acid distillate from 99.38% up to 99.98% at the number of trays of 100. However, there is a significant drop in the purity of oleic acid distillate from 0.61 to 0.02% at the number of trays of 100. For linoleic acid overhead composition profile, it dropped from 0.01 to 0 percent of purity at the number of trays of 65. In each simulation stage, the total composition of palmitic acid, oleic acid and linoleic acid are equal to 1 (weight%).

The boiling points of respective components in this S1U1U2 mixture are 351°C (palmitic acid), 353.85°C (linoleic acid) and 358.85°C (oleic acid). As it is a close boiling point mixture, separation becomes difficult because large number of trays is required (Koltmetz *et al*., 2004). As shown in Fig. 8, the more volatile component, palmitic acid, is achieved the level of purity of 99.98% only at the column of 100 plates column. On the other hand, the level of purity of least volatile component, oleic acid, was decreasing steadily to 0.02% from number of trays of 60 to 100.

Comparison between Fig. 7 and 8, relative volatility of mixture S1S2U1U2 is higher than of mixture S1U1U2. As the relative volatility is lower for mixture S1U1U2, it implies that the separation becomes very difficult and large number of plates is required for producing high purity overhead product (Halvorsen and Skogestad, 2000). As shown in both figures, high relative volatility mixture S1S2U1U2 achieved higher purity level in the overhead product than a low relative volatility mixture S1U1U2 with less number of plates set up in the column.

**Effect of feed pressure:** Figure 9 shows the effects of feed pressure to overhead product with the specified purity at the top of the distillation column for S1S2U1U2 mixture. At the operating pressure of 50 mbar, overhead product purity of palmitic acid was at the purity level of 99.98% while the oleic acid was at 0.02%, linoleic acid and stearic acid were at 0% of purity level. There is a significant drop in the purity of palmitic acid distillate from 99.98% to 99.81% at the pressure of 150 mbar. However, there is an increase in the purity of oleic acid distillate from 0.02% to 0.19% at the pressure of 150 mbar. Since the total composition at each stage has to be equal to 1 (weight%), a decrease in the purity level of palmitic acid will increase the purity level of oleic acid. For linoleic and stearic acid overhead composition profiles, it showed zero purity level throughout the variation of the operating pressure.

At a given temperature, substances with higher vapor pressures will vaporize more readily than substances with a lower vapor pressure (Kister, 1992). The lower the normal boiling point of the liquid, the higher the vapors pressure of a liquid at a given temperature and the higher the volatility. This can be seen from Fig. 9, the palmitic acid is achieved a high purity level in the overhead product than oleic acid which is higher normal boiling

point component. At higher operating pressures, the relative volatility of the system is lower which increases the separation difficulty (Zygula and Dautenhahn, 2000). This explains the decreasing trend line of overhead palmitic acid composition profile as shown in Fig. 9. As the total composition at each stage is to be equal to 1 (weight %), a decrease in the purity level of palmitic acid will increase the purity level of oleic acid. This proves the increasing trend line of overhead oleic acid composition profile in Fig. 9.

In the Fig. 9 shown above, the palmitic acid has a higher purity level in the overhead product at lower pressure. This is because lower pressures increase the relative volatilities and high relative volatility mixture will achieve higher purity level in the overhead product. As conclusion from Fig. 9, the separation efficiency can be improved by lowering the pressure of the system.

**Effect of feed temperature:** Figure 10 shows the effects of feed temperature to overhead product with the specified purity at the top of the distillation column for S1S2U1 mixture. By keeping the entire controlled variables constant, the results obtained from the simulation of the effect of feed temperature versus product purity showed as a decreasing trend line for volatile component in Fig. 10.

At the operating pressure of 160°C, overhead product purity of palmitic acid was at the purity level of 99.91% while the oleic acid was at 0.09%, stearic acid was at 0% of purity level. There is slightly dropped in the purity of palmitic acid distillate from 99.91 to 99.90% at the pressure of 260°C. However, there is a slight increase in the purity of oleic acid distillate from 0.09 to 0.10% at the pressure of 260°C. Since, the total composition at each stage has to be equal to 1 (weight%), a decrease in the purity level of palmitic acid will increase the purity level of oleic acid. For stearic acid overhead composition profile, it showed zero purity level along the variation of the operating temperature.

At a given pressure, substances with higher vapor pressures will vaporize more readily than substances with a lower vapor pressure (Kister, 1992). The lower the normal boiling point of the liquid, the higher the vapors pressure of a liquid at a given temperature and the higher the volatility. This can be seen from Fig. 10, the palmitic acid is achieved a high purity level in the overhead product than oleic acid which is higher normal boiling point component.

Relative volatilities are temperature dependant (Kaymak and Luyben, 2008). According to Zygula and Dautenhahn (2000), the relative volatility of the system is lower which increases the separation difficulty. This

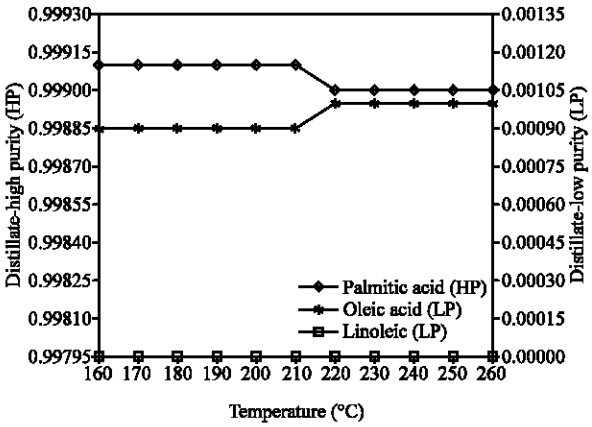


Fig. 10: Distillate composition profile versus feed temperature for S1S2U1 mixture

explains the decreasing trend line of overhead palmitic acid composition profile as shown in Fig. 10. As the total composition at each stage is to be equal to 1 (weight %), a decrease in the purity level of palmitic acid will increase the purity level of oleic acid. This proves the increasing trend line of overhead oleic acid composition profile in Fig. 10.

According to Stage (1984), the relative volatility for the mixture of saturated and unsaturated fatty acids is decreasing as the temperature of the mixture increases. Relative volatilities are temperature dependant (Kaymak and Luyben, 2008). This explains the decreasing trend line of overhead palmitic acid composition profile as shown in Fig. 10 due to the increasing temperature of the mixtures.

## CONCLUSION

Up to the present time, products derived from fatty acids are widely used in the formulation of detergents, lubricant, surfactants, pharmaceutical industry, mineral production and many types of industrial applications. Through the hydrolysis or fat splitting process, commercial fatty acids can be produced from fats and oils. Crude fatty acids will then be purified through a total distillation. The production of palm oil has achieved a very impressive growth over the last ten years and this outstanding growth in production is expected to continue. Therefore, palm based fatty acids are selected to be used as the feed components. In this research, the simulation outcome indicates that the operating parameters, number of stages, feed temperature and feed pressure, are playing a vital significant role in improving the level of purity of overhead product composition. Separation performance of palm based fatty acid enhanced by increasing the number of tray in distillation column. Differences in

between the boiling points of components affect the separation efficiency. Large differences in boiling points imply larger relative volatilities and easy separation. As the feed temperature increased, the mixture relative volatility decreased, thus, the purity of more volatile component in distillate decreased. As increasing in feed pressure, the relative volatility of the system is lower; the purity of more volatile component in distillate is decreasing. In industry, purification of distillated fatty acid achieved around 80%, however, under optimization of operating condition in this simulation study, palm based fatty acids can be successfully distillated from fractionation process and achieved nearly 99% of purity.

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