# Mechanistic Modelling of a Fatty Acid Distillation Plant: Iterative Approach for Component Lumping and Industrial Validation


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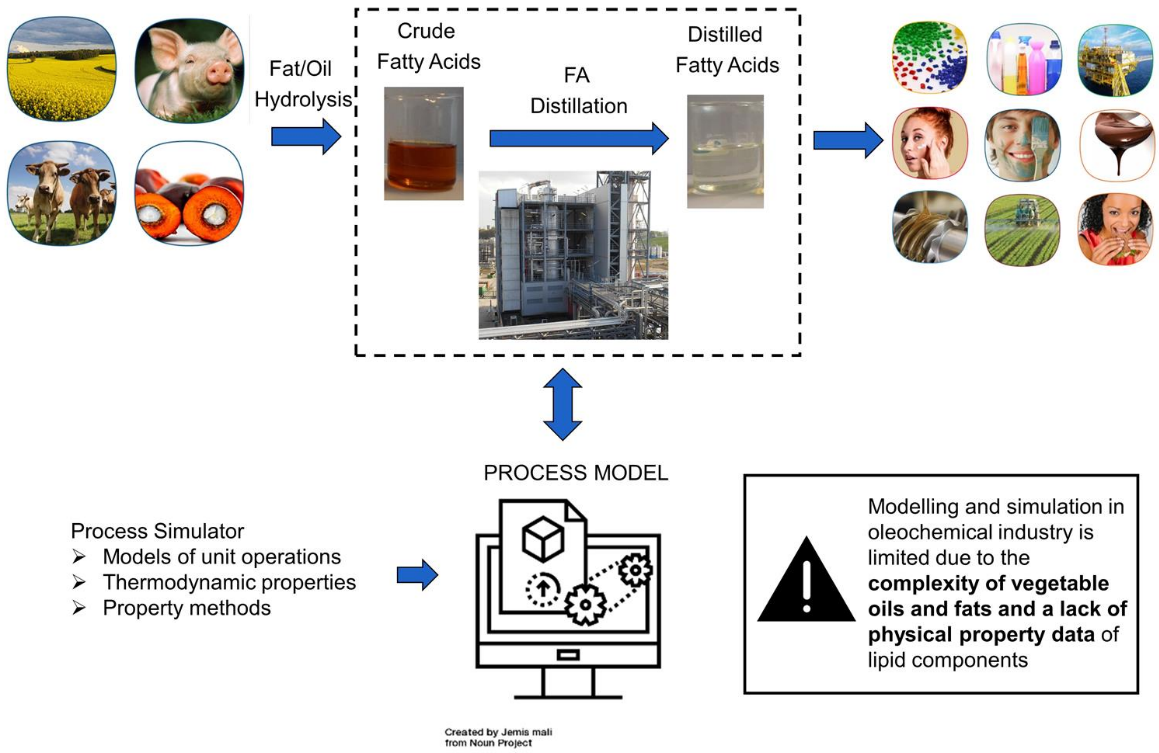
# INTRODUCTION




**Although the oleochemical industry is mature, the use of modelling and simulation within this industry is limited** because of (i) the complexity of vegetable oils and fats, (ii) the lack of predictive models for the physical properties of lipid compounds and (iii) the lack of specific unit operation models. [1] **A specific challenge in fatty acid production is the pronounced feedstock variability.** Operating a continuous process with a variable feed composition and quality poses significant challenges for process control to ensure high yields, low utility costs and excellent product quality. [2] In the petrochemical industry, crude oil feedstocks are successfully modelled as a mixture of pseudocomponents (lumps), where each pseudocomponent is associated with a boiling point range, molecular weight or C-number distribution. [3] **This motivates the development of a lumping approach to simplify the composition of oleochemical feedstocks.**

Lipid components can be divided into two groups, major and minor components, depending on the amount in which they are present. Major components are the fatty acids, with carbon chain lengths between 4 to 26, and the glycerol esters of these fatty acids (mono-, di- and triglycerides). Minor components are non-glyceridic materials such as sterols, tocopherols, phosphatides, terpenes and volatile hydrocarbons like alcohols, ketones and aldehydes. [1, 4]

In this study, a model of an industrial fatty acid distillation plant, operated by Oleon NV in Belgium, is developed in the commercial process simulator Aspen Plus®.  The study has three objectives:

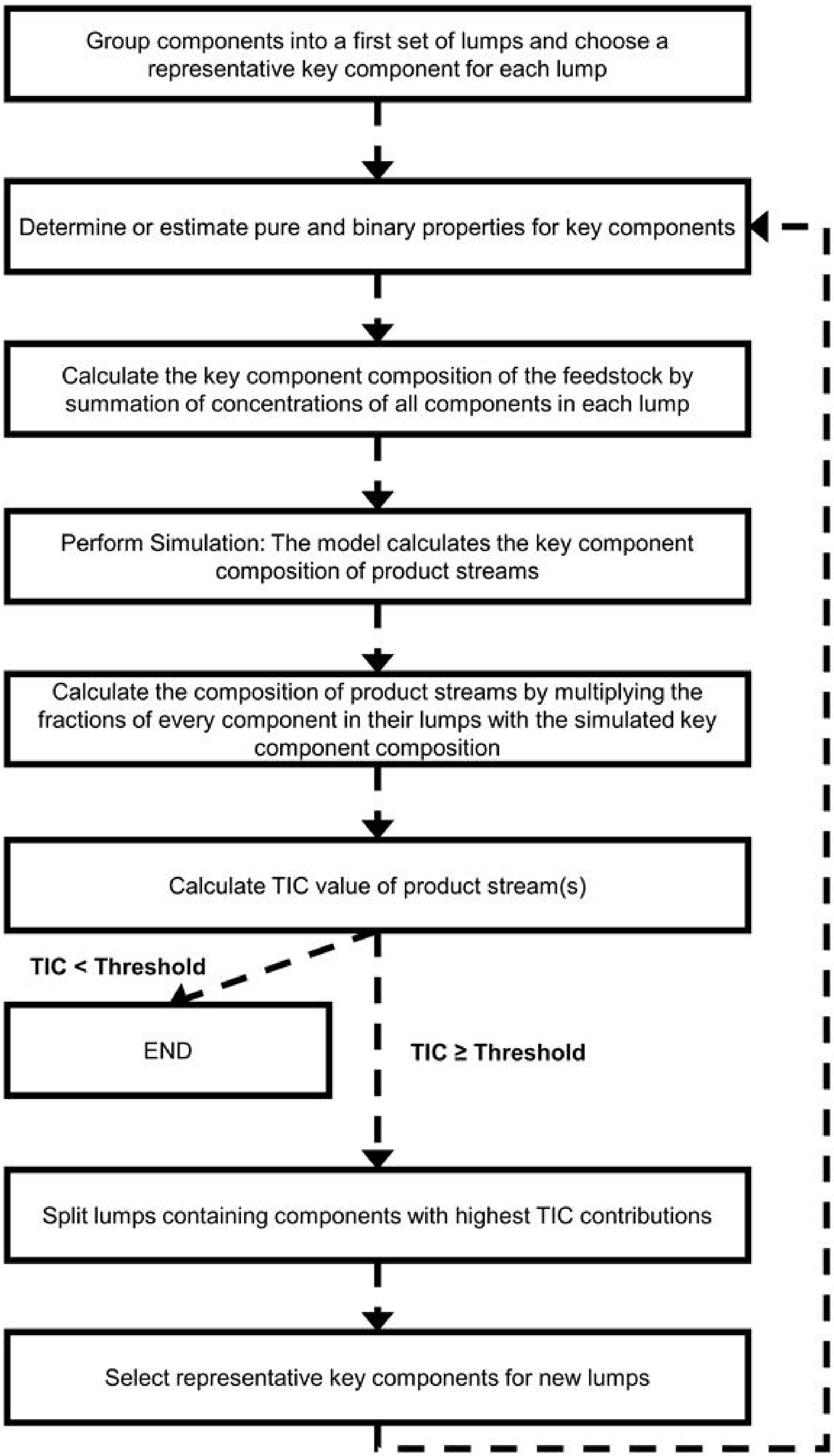
1. **Selection of a thermodynamic property method** towards effectiveness of predicting fatty acid VLE.

2. **Development of an iterative lumping approach** to determine an optimal set of key components for the modelling of oleochemical processes

3. **Demonstrating the applicability of the lumping approach in a case study** by building and validating a comprehensive simulation, using the proper property methods, of an industrial fatty acid distillation plant for optimizing the product yield, purity and heat duty of the process.

# ITERATIVE LUMPING APPROACH FOR KEY COMPONENT SELECTION

One of the key issues in deciding upon the ideal degree of lumping is **determining the point at which further increasing the number of key components no longer enhances the predictive capabilities of the model** [7]. A generic algorithm for an iterative lumping approach is proposed:



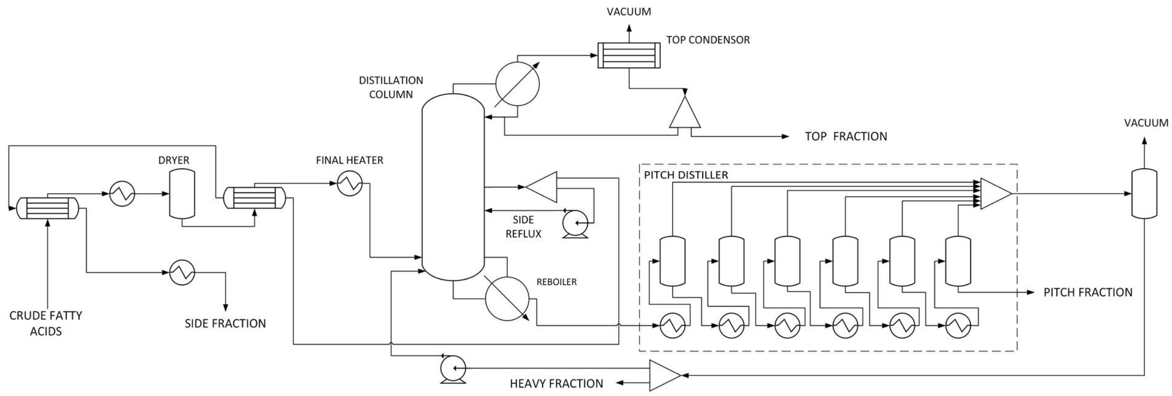
**In the case of lipid feedstocks, a first set of lumps could be: fatty acids, glyceridic components and minor components, each represented by one key component.** The component in every lump with the highest weight fraction can be chosen as key component, however, **also the availability of physical property data for pure components and mixtures should be taken into account when selecting key components to represent each group.** After each iteration, the performance of the model is evaluated by calculating the Theil's inequality coefficient (TIC) for every product stream based on the prediction of the weight fractions (x) of experimental (°) and calculated (m) values. [8]

$$TIC = \frac{\sqrt{\sum_i \left(x_i^o - x_i^m\right)^2}}{\sqrt{\sum_i {x_i^o}^2} + \sqrt{\sum_i {x_i^m}^2}}$$

**In case the model does not properly simulate the behaviour of all components in one lump for a product stream, this lump is split into a new set of lumps**, each represented by a different key component. This methodology is repeated until the TIC value drops below a threshold value, indicating that an acceptable simulation is obtained. Generally, 0.3 is used as a threshold when using the TIC test [9].

# CASE STUDY – DESCRIPTION OF THE INDUSTRIAL FATTY ACID DISTILLATION PLANT

**Fatty acid distillation takes place at temperatures up to 250°C and under vacuum.** There are many types of feedstocks used such as tallow, palm oil, palm fatty acid distillate (PFAD) and canola oil. .




**The crude fatty acids are first preheated, dried and then fed to the bottom of the distillation column.** A top fraction is withdrawn containing lightweight fatty acids and volatile hydrocarbons such as alcohols, ketones and aldehydes. In the middle of the column, in between two packing sections, a side fraction is captured containing the purified C16-C18 fatty acids. **This side fraction is the main and most valuable product.** Also a bottom fraction is withdrawn and fed to a second distillation unit, called pitch distiller, where fatty acids remaining in the bottom fraction are recuperated. The bottom product, which remains after the second distillation, is called pitch and contains mostly glyceridic components and impurities such as sterols.

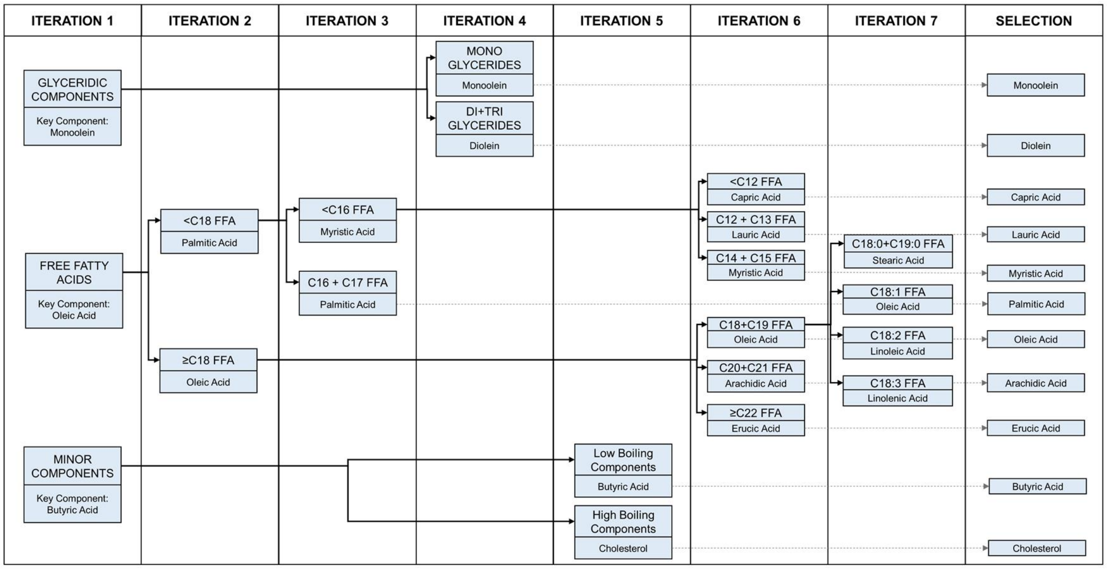
**Important considirations are a high purity, resulting in low colour values and a good stability (storage & heat) of the distilled fatty acids, a high yield, and a reduced heat duty.**

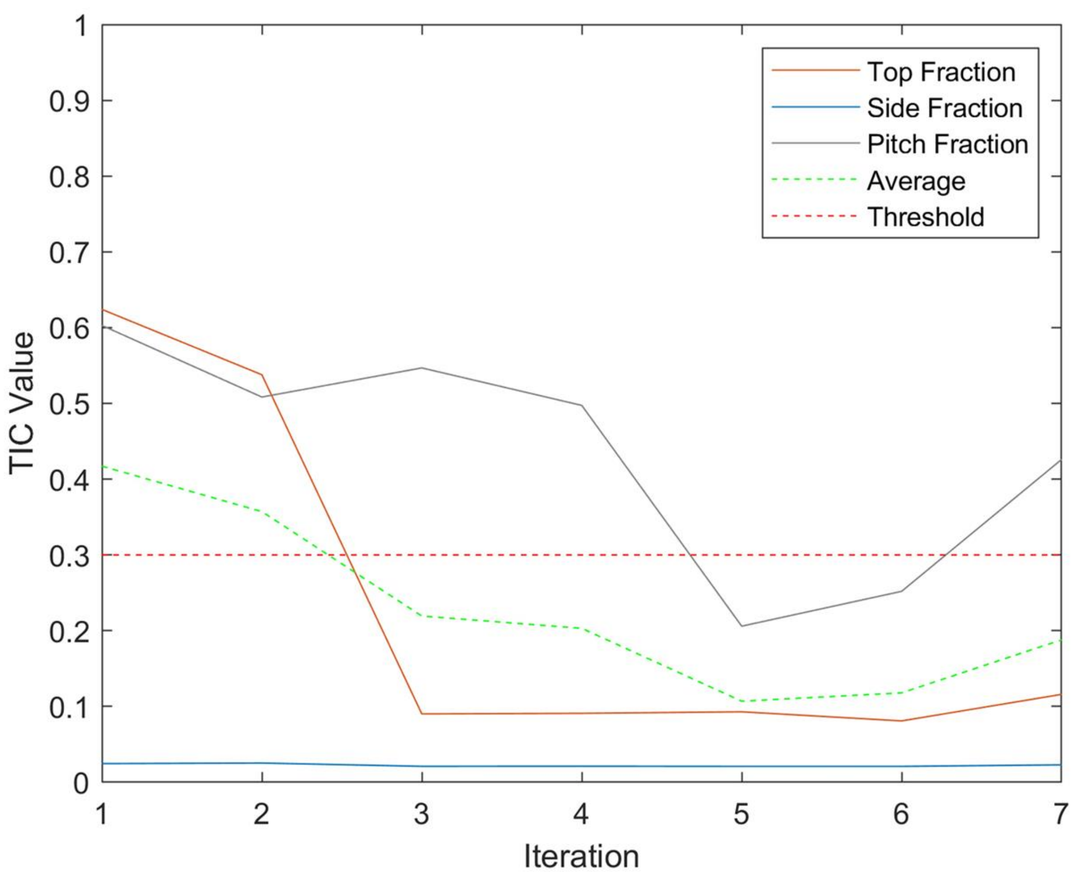
| Indicator | Base Case (tallow) |
|---|---|
| Yield (%) | 93.3 |
| Purity (%) | 99.3 |
| Total Heat Duty (MW) | 2.1 |

In total, samples from 121 industrial campaigns of fatty acid distillation were acquired and analysed, 30 using crude fatty acids from the feedstock tallow, 30 palm, 24 PFAD and 37 canola. **The collected information on feedstock and product composition and process parameters were used for the building and validation of the fatty acid distillation model.** Campaigns with clear process problems, e.g. malfunctioning equipment, were not considered. In addition, samples were taken after the process reached steady state

# CASE STUDY – MODELLING AND OPTIMIZATION

**The iterative lumping approach was applied to fatty acid distillation for the feedstock tallow:**



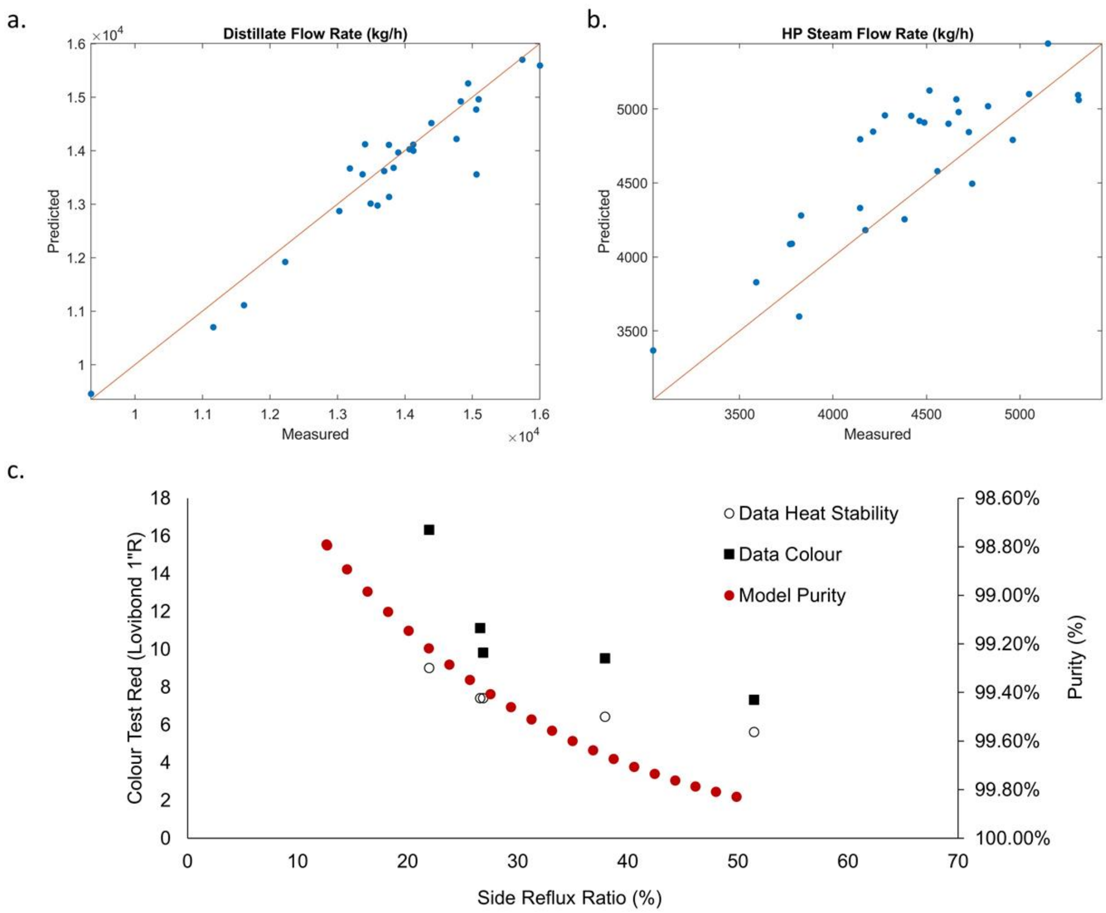

**For the first iteration, three lumps are considered and represented by a key component.** The components with highest wt% in the feedstock are chosen as key component for the lump of free fatty acids (FFA) and glyceridic components, being oleic acid and monoolein. For the lump minor components, butyric acid is chosen as key component due to the availability of physical property data for this pure component and mixtures with FFA. The high TIC value of the top fraction and pitch fraction result in an average TIC above the threshold. In this first iteration, all fatty acids are lumped and represented by a single component. In the top fraction, this results in an overestimation of the fractions of longer chain fatty acids (≥C18) and an underestimation of shorter chain fatty acids (<C18). Therefore, **in the second iteration, the lump of FFA was split into longer fatty acids with**

**equal or more than 18 carbon atoms and shorter fatty acids with less than 18 carbon atoms.** As expected, this resulted in a drop of the TIC value of the top fraction, however, the average TIC value is still above the threshold. Therefore, in a third iteration the lump of shorter chain fatty acids is further split. Based on this model with six lumps, a good prediction of the composition of the side and top fractions can be made, however, the TIC value of the Pitch fraction remains high.

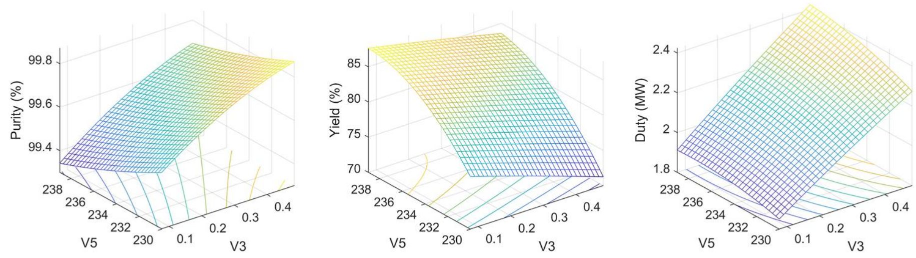
In iteration 4, the lump of glyceridic components is split into monoglycerides, represented and di+triglycerides. The split of this lump resulted in a small decrease of the TIC value of the pitch. In iteration 5, the lump of minor components is split into low- and high boiling impurities. The split of this lump resulted in a major decrease of the TIC values.

In iteration 6 and 7, it was assessed whether further increasing the number of lumps representing the free fatty acids resulted in an enhanced prediction of the composition of the product fractions. However, further splitting based on carbon chain length (iteration 6) only resulted in a small decrease of the TIC values of the top. Taking into account the saturation in iteration 7 even resulted in an increase of the TIC value as less data was available on the properties of these components. **Based on these results, the composition after iteration 6, containing 11 lumps and key components, was used for optimization of the industrial fatty acid distillation for the feedstock tallow.** Results for other feedstocks may be found via the link to the preprint under the presentation.

Parity diagrams for total side flow (kg/h) and steam consumption (kg/h) indicate that **the mechanistic process model adequately reproduces both parameters, showing that the process model can be used to assess the effect of process parameters on yield and total heat duty**. Modelled purity of the side fraction follows a similar trend as the measured fatty acid quality (colour and heat stability). Therefore, **the process model can also be used to investigate the effect of process parameters on the quality of the side fraction by looking at the modelled purity as a proxy for colour quality.**




Working at a lower reboiler temperature (230°C) and with a higher side reflux ratio (0.5) would result in a significant increase of purity, from 99.3 to 99.8%. However, this also results in a significant drop of the yield of the side fraction, from 93 to 71%, and a rise in total heat duty from 2.1 to 2.3 MW. Increasing the side reflux ratio (0.4) while maintaining a higher reboiler outlet temperature (239°C) shows more potential, as the increase in quality remains high, from 99.2 to 99.7%, but the effect on yield is reduced, from 93 to 85%.

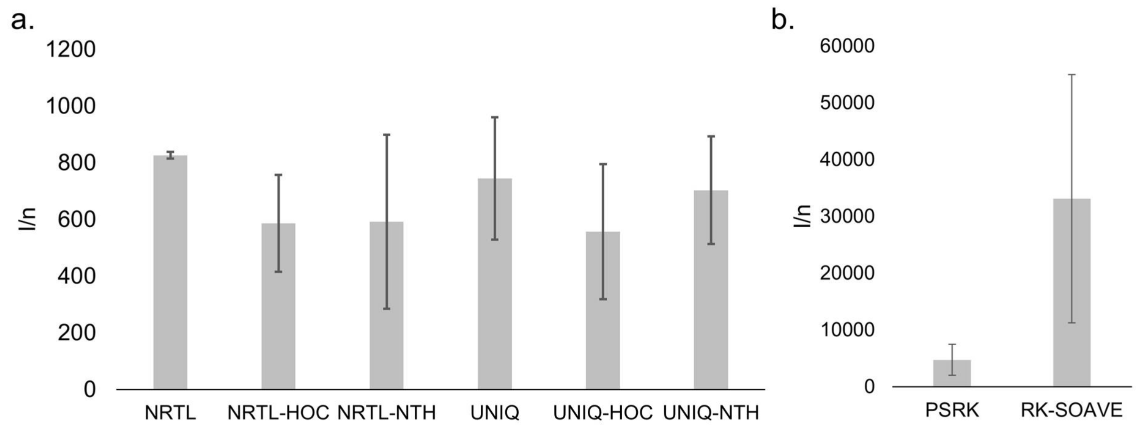



V5 = Reboiler Outlet Temperature
V3 = Side Reflux Ratio

# SELECTION OF PROPERTY METHOD FOR PREDICTING FATTY ACID VLE

**A variance analysis was used to validate the thermodynamic property methods** based on the prediction of the molar fractions in the liquid phase (x), vapour phase (y), temperature (T) and pressure (P). The superscripts ° and M respectively represent experimental values (NIST database) and calculated values. σ is the standard error on the measurement. The property method that minimizes the function I is preferred. However, I needs to be divided by the number of data points (n) in order to compare results from different datasets [5]. Only datasets that passed an area consistency test (tolerance = 10%) were used.

$$\frac{I}{n} = \frac{\sum_{data}\left[\frac{\left(x_i^o - x_i^M\right)^2}{\sigma_{x_i}^2} + \frac{\left(y_i^o - y_i^M\right)^2}{\sigma_{y_i}^2} + \frac{\left(T_i^o - T_i^M\right)^2}{\sigma_T^2} + \frac{\left(P_i^o - P\right)^2}{\sigma_P^2}\right]}{n}$$




The average I/n for both equation of state models are at least one order of magnitude higher compared to the studied activity coefficient models. This shows that PSRK and RK_SOAVE do not properly predict the VLE of fatty acids. For the activity coefficient models, **the best predictions are acquired when NRTL and UNIQUAC are combined with the HOC model**, followed by the combination with NTH and finally the standard property methods with the ideal gas law to describe the vapour phase**.** The better prediction when combining the activity coefficient models with NTH or HOC shows that **the dimerization of fatty acids in the vapour phase is important for VLE calculations of fatty acids**, even though the standard property metFonthods with the ideal gas law are more often used in literature [6]. Based on these results, **UNIQ-HOC was chosen and used to describe VLE in the fatty acid distillation model.**

# PRESENTATION

[VIDEO] https://www.youtube.com/embed/ab4nsQvisZQ?rel=0&fs=1&modestbranding=1&rel=0&showinfo=0

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# CONCLUSIONS

For predicting vapour-liquid equilibria of fatty acids, the best results were acquired using the property method UNIQ-HOC.

**The proposed iterative lumping approach effectively determined a set of key components for fatty acid distillation simulation.** For a tallow-based feedstock, a total of 11 key components resulted in the best predictions of product compositions, with glyceridic components and minor components each represented by 2 key components, and fatty acids by 7. **The need for 7 key components to represent fatty acids shows that lumping all fatty acids should be avoided. Simultaneously, including all fatty acid species in the model is unnecessary and may even lead to worse predictions due to a lack of proper pure and binary component data.** Palm and PFAD based feedstocks could be represented by the same key components as tallow, while for rapeseed-based feedstocks, an additional 3 minor components are required to reach an acceptable prediction of product compositions. In future research, the prediction of fatty acid quality could be further improved by including specific components and side reactions related to colour formation.

Important parameters of fatty acid distillation are side-reflux-ratio, reboiler-outlet-temperature and heat-duty of the pitch-distiller. To increase the purity (99.7%), an increase of side-reflux-ratio (0.4) and reboiler-outlet-temperature (239°C) is recommended. **The model could be used to tackle the challenge of feedstock diversity by model predictive control. In that case, reflux ratio, reboiler outlet temperature and heat duty of the pitch distiller can be changed for compositional variability of the incoming feedstock.** The model could be used to investigate if high quality fatty acids can be produced from lower quality feedstocks, and determine the optimal process parameters to do so

# ABSTRACT

Although the oleochemical industry is mature, the use of modelling and simulation within this industry is limited because of (i) the complexity of vegetable oils and fats, (ii) the lack of predictive models for the physical properties of lipid compounds and (iii) the lack of specific unit operation models.[1] A specific challenge in fatty acid production is the pronounced feedstock variability. Operating a continuous process with a variable feed composition and quality poses significant challenges for process control to ensure high yields, low utility costs and excellent product quality.[2] In the petrochemical industry, crude oil feedstocks are successfully modelled as a mixture of pseudocomponents (lumps), where each pseudocomponent is associated with a boiling point range, molecular weight or C-number distribution.[3] This motivates the development of a lumping approach to simplify the composition of oleochemical feedstocks. Lipid components can be divided into two groups, major and minor components, depending on the amount in which they are present. Major components are the fatty acids, with carbon chain lengths between 4 to 26, and the glycerol esters of these fatty acids (mono-, di- and triglycerides). Minor components are non-glyceridic materials such as sterols, tocopherols, phosphatides, terpenes and volatile hydrocarbons like alcohols, ketones and aldehydes.[1, 4] In fatty acid distillation, a crude fatty acid mixture is purified by separation into a top fraction containing low boiling impurities, a side fraction containing the purified fatty acids and a bottom fraction containing glyceridic components and high boiling impurities

In this study, a model of an industrial fatty acid distillation plant, operated by Oleon NV in Belgium, is developed in the commercial process simulator Aspen Plus®. First, a thermodynamic property method was selected to predict the missing properties of pure components and mixtures.[5] In this study, existing property methods were validated using vapour-liquid equilibrium data of fatty acid mixtures. Secondly, an iterative approach for lumping components was developed and used to determine an optimal set of key components to simplify the feedstock composition. In the first iteration, a simplified composition having only one key component per lump of components is used. In the case of fatty acid distillation, these lumps are fatty acids, glyceridic components and impurities. After simulation, the composition of the acquired product streams are validated with industrial data using Theil's inequality coefficient (TIC). In case the model does not properly simulate the behaviour of all components in one lump, this lump will be split into a new set of lumps, each represented by a different key component. This methodology will be repeated until the TIC value drops below a pre-set threshold, or increases again due to overfitting. This way, the complexity of the required characterization is gradually increased in order to find the characterization with lowest complexity that still delivers an acceptable prediction. The availability of physical property data for pure components and mixtures should be taken into account when selecting key components to represent each group. Finally, a sensitivity analysis followed by an optimization using Response Surface Methodology (RSM) was performed to investigate the effect of independent model parameters, such us reflux ratio, on the yield, product quality and utility cost of fatty acid production.

The results of the property method validation showed that UNIQ-HOC resulted in the best estimation of fatty acid VLE. Using the iterative lumping approach, a total of 10 key components were selected to represent the feedstock, acquiring a TIC below 0.05. Based on the results of the sensitivity analysis, the most important process parameters and their effect on yield, product quality and utility cost were identified.



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