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# Process analysis of shea butter solvent fractionation using a generic systematic approach

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## ABSTRACT

The application of lipid feedstocks has expanded across different industries as a result of bio-based economies development, consumers and societal requirements. The need for new and better performing lipid-based processes and products has resulted in extensive research within lipid thermodynamic property modelling. In this work, property models for lipid pure compounds and

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3 mixtures are validated by applying them to an industrial process: shea butter solvent fractionation  
4 with acetone. The process modelling, simulation and analysis are performed through a systematic  
5 approach consisting of four steps: (1) process data collection, (2) process modelling, design and  
6 simulation, (3) process performance analysis, (4) process hot-spots identification and retrofit  
7 solutions. The Lipids Database, that includes the required models for pure compounds and  
8 mixtures, is used to perform the modelling and simulation. The analysis of the results shows energy  
9 savings potential, which is achieved through process heat integration and retrofit of separation  
10 units.  
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## 23 **1 INTRODUCTION**

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26 In the context of population growth and climate change, there is a great need to increase the  
27 valorisation of bio-resources in all areas of industrial applications (e.g. food, fuels, etc.). To  
28 maintain competitiveness under current market conditions, R&D initiatives for new feedstock  
29 resources, new products and improved processes have been adopted by the industry in recent years.  
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31 The continuous expansion of the lipid market is a result of increasing utilisation of these types of  
32 feedstocks for the production of food (e.g. specialty fats and oils used in confectionery products),  
33 pharmaceutical products (e.g. vitamin E and other supplements), cosmetics, oleochemicals (e.g.  
34 fatty acids, fatty ester), fuels, and many others.<sup>1,2</sup> The advances within the lipid processing industry  
35 can be achieved through well-established process systems engineering (PSE) methods and tools,  
36 which currently are not extensively applied within this industry. Although oil extraction<sup>3</sup>, oil  
37 refining<sup>4,5</sup> and biodiesel production<sup>6-8</sup> processes, have been rigorously modelled and simulated,  
38 for many other lipid-based processes, including fractionation, a similar detailed investigation has  
39 not yet been performed.  
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3 All PSE methods and tools to be employed for process development requires good knowledge  
4 and understanding of the properties of involved chemicals and their mixtures. Thus, understanding  
5 of thermo-physical properties and phase equilibria of lipid compounds becomes crucial in the  
6 given context. A detailed description of the role that properties may play has been highlighted by  
7 Gani and O'Connell<sup>9</sup>. It is even more important that if new products and processes emerge based  
8 on new lipid feedstocks, models for estimating the properties for the new mixtures, as well as new  
9 lipid compounds, for which no experimental data is available yet, are needed. That is, the  
10 predictive capabilities of the property models need to be verified first. New advances within lipid  
11 phase equilibria modelling have resulted in the availability of new sets of parameters for group  
12 contribution predictive models like UNIFAC (i.e. Original,<sup>2</sup> Linear, Lyngby Modified and  
13 Dortmund Modified<sup>10</sup>) allowing the estimation of properties for a wide range of mixtures for this  
14 class of compounds. The currently available thermodynamic models for pure compounds<sup>4,11,12</sup> and  
15 mixtures<sup>2,10</sup> are included in the Lipids Database, that can be used within different PSE domains<sup>2</sup>.

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33 The current work aims to apply the lipid-based thermodynamic property models covered in the  
34 Lipids Database along with different model-based computer-aided methods and tools for  
35 development and analysis of a lipid process of industrial importance. The methodology used is  
36 systematic and generic while it's the application is highlighted to investigate in detail the  
37 fractionation of shea butter using acetone as a solvent. The work, performed in close collaboration  
38 with Alfa Laval, lead to significant energy savings for solvent recovery reflected very well in the  
39 process operational costs savings analysis. The identified solutions tackle the main drawbacks of  
40 the solvent fractionation process: high energy consumption and high operational costs.

### 51 52 **Lipid fractionation process overview**

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3 Shea butter is one of the five alternative fat sources accepted in chocolate production as per EU  
4 Commission's Directive 2000/36/EC. The two products obtained from the fractionation of shea  
5 butter are shea stearin and shea olein. The particular properties of shea stearin are due to the  
6 presence of high amounts of symmetrical stearic-rich triacylglycerols like 1,3-distearo-2-olein  
7 present in shea butter. Shea stearin is used as a cocoa butter equivalent (CBE) in chocolate products  
8 to enhance the fat profile and stability, to reduce fat blooming and migration, to ensure softness,  
9 gloss and snap properties, which expand the shelf life and improve the quality of the final  
10 product.<sup>13</sup> Shea olein has an extensive application in cosmetic formulations, confectionery and  
11 speciality fat products<sup>14</sup>.

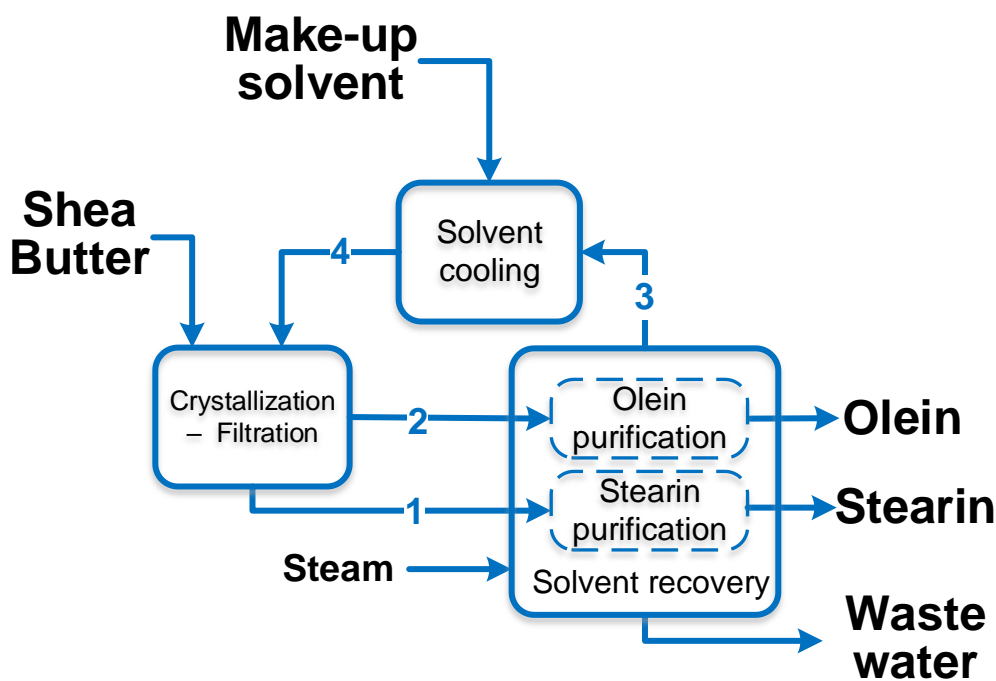
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24 In the lipid processing industry, fractionation refers to the crystallization-based separation,  
25 which can be performed in one or more steps. The process is used to tailor the chemical  
26 composition of the resulting fractions needed for specific applications under controlled  
27 temperature conditions.<sup>15</sup> The main technologies used for fractionation at an industrial scale are  
28 dry fractionation, solvent fractionation and detergent fractionation. Dry fractionation, also known  
29 as simple crystallisation or crystallisation from the melt, is performed by separating the product  
30 directly from the liquid fat mixture by cooling down without adding any other compounds to  
31 facilitate the process and then separate the crystal by centrifugation or filtration. The detergent  
32 fractionation process performs the crystallization from the melt, the same as dry fractionation. To  
33 separate the crystals, an aqueous solution containing a surfactant is used to solubilize the crystals  
34 in the aqueous phase and then separate them by centrifugation. The cost of effluent disposal,  
35 legislative restrictions in certain countries and important advances in dry and solvent fractionation  
36 performance lead to the decline of detergent fractionation process.<sup>16</sup> The solvent fractionation  
37 process consists of performing the crystallization in the presence of a solvent, followed by filtration  
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3 of the crystals to which a washing step can be added. The solvent fractionation is used when the  
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5 desired fractions need a sharp separation from a mixture containing compounds with very close  
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7 melting points and dry fractionation does not achieve the required separation. The main solvents  
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9 used are acetone and hexane, but other solvents, such as alcohol, ketones, or azeotropic mixtures  
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11 are reported in the literature as well.<sup>16</sup> The solvent selection is dependent mainly on the oil  
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13 composition (e.g. presence of polar species such as free fatty acids and diacylglycerols) and less  
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15 on the separation task (e.g. one triglyceride from another triglyceride).<sup>17</sup> Though, there are studies  
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17 showing acetone has a better performance in separating P-O-P (1,3-dipalmito-2-olein) from P-P-  
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19 O (1,2-dipalmito-3-olein) triglycerides, where P-O-P exhibit higher solubility than P-P-O.<sup>18</sup> The  
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21 solvent fractionation has the following advantages: faster crystallization, higher selectivity, more  
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23 material that can be crystallized in one step, and higher separation efficiency of the crystals from  
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25 the mother liquor. Current drawbacks of solvent fractionation are (1) extra safety precautions  
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27 required due to the flammability of used solvents, (2) process energy requirements in terms of  
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29 utility consumption for cooling and heating during crystallization and solvent recovery operation,  
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31 (3) solvent loss.<sup>16</sup> All these have resulted in employing solvent fractionation only for high-value  
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33 products, which can assimilate the extra costs.<sup>19</sup> The shea butter composition, as well as final  
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35 product specifications (i.e. sharp melting point of shea stearin), requires the fractionation to be  
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37 performed only by using a solvent.  
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45 The shea butter solvent fractionation process consists of three parts: (1) crystallization and  
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47 separation of the products, (2) solvent recovery, and (3) solvent cooling, as presented in the  
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49 simplified PFD (process flow diagram) in Figure 1. The first part of the process covers the  
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51 crystallization and the combined filtration and washing operations. The crystallization takes place  
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53 in a stirred vessel, while the filtration and washing are done with a horizontal belt filter operated  
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3 under vacuum. The solvent is recovered through a series of flash units and steam stripping columns  
4 for both products. The objective of the steam stripping columns is to remove solvent traces in the  
5 final products thereby ensuring that the required specifications are achieved. The recovered solvent  
6 is cooled before being recycled back to the process. The low temperatures at which the  
7 crystallization is performed requires the cooling of the solvent with ammonia, in a refrigeration  
8 cycle.  
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17 The paper introduces aspects of process modelling, design and analysis using lipid-based  
18 thermodynamic models and appropriate computer-aided methods and tools for shea butter acetone  
19 fractionation. At the process level, the objective is to reduce the high energy demands, which is  
20 one of the main drawbacks of the solvent-based fractionation processes.  
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50 **Figure 1.** Shea butter acetone fractionation process simplified process flowsheet diagram.

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53 **2 METHOD DESCRIPTION**  
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3 The testing and application of the lipid thermodynamic models are performed through process  
4 design and analysis of shea butter acetone fractionation. The study covers stages two and three of  
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6 the three-stage approach from the synthesis-design-innovation framework presented by Bertran et  
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8 al.<sup>20</sup>. The three stages of the framework are (1) synthesis, (2) design, and (3) innovation. In the  
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10 synthesis stage, stage one, the best processing route for a set of raw materials and products is  
11  
12 selected. Once the processing route is established, the detailed design and process analysis are  
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14 performed. This represents the second stage – design and analysis. Based on the process analysis  
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16 results, more sustainable alternatives are screened within stage three – innovation stage.  
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18 Methodologies for stage one and two are presented in the work of Bertram et al. (2017) and are  
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20 applied in the same work and in the work of Vooradi et al.<sup>21</sup> for an ethanol biorefinery and CO<sub>2</sub>  
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22 utilization case studies. A detailed methodology for the innovation stage, stage three, is presented  
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24 by Garg et al.<sup>22</sup> which applies each of the three stages of the framework to the bio-succinic acid  
25  
26 production. Different stages of the framework, mostly stage one and two were applied to other  
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28 studies presented in the literature (i.e. dimethyl carbonate production from CO<sub>2</sub><sup>23</sup>, waste water  
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30 network<sup>24</sup>, biodiesel biorefinery<sup>25</sup>). For the shea butter solvent fractionation, the processing route  
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32 that results from the synthesis stage, stage one of the synthesis-design-innovation framework, is  
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34 already provided, and it is described in more detail in section 3.1. Together with the process  
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36 requirements, operating conditions, and assumptions, the detailed design and simulation of the  
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38 process are performed, followed by economic and environmental impact analysis. All these steps  
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40 cover stage two, design stage, of the synthesis-design-innovation framework. Further identified  
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42 hot spots are tackled for improvement and new process alternatives are generated and analysed,  
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44 corresponding to stage three of the framework.  
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3 A systematic method consisting of four steps<sup>26</sup> is used to perform the work of stage two (steps  
4 1-2) and stage three (step 4) of the framework. The steps of the method are (1) problem definition  
5 and process data collection, (2) process modelling, design and simulation, (3) process performance  
6 analysis (e.g. energy, economic and environmental analysis), and (4) process hot-spots  
7 identification and retrofit solutions. The work and information flow together with the tools used in  
8 each step of the method are presented in Figure 2.  
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### 10 11 12 13 14 15 16 17 **2.1 Problem definition and data collection**

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19 The problem definition and process data collection step covers the following actions: definition  
20 of the problem to be solved, definition of the process and final product(s) specifications (e.g. feed  
21 composition, solvent ratio, separation factors, impurities content in the final product, etc.),  
22 collection of other support data needed for modelling (e.g. thermodynamic data) from industrial  
23 sources or literature.  
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### 30 31 **2.2 Process modelling, design and simulation**

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33 In the second step of the method, detailed models of the involved unit operations are employed  
34 to perform the design and simulation of the process. Modelling and design follow well-established  
35 methods.<sup>27</sup>  
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### 40 41 **2.3 Process analysis**

42 The results from process modelling, design and simulation are used in this step for the evaluation  
43 of process performance.  
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45 The economic analysis is performed with ECON and gives information on equipment cost, capital  
46 cost, operation cost and economic analysis. The economic model implemented in the software is  
47 based on the economic evaluation presented by Peters et al.<sup>28</sup>  
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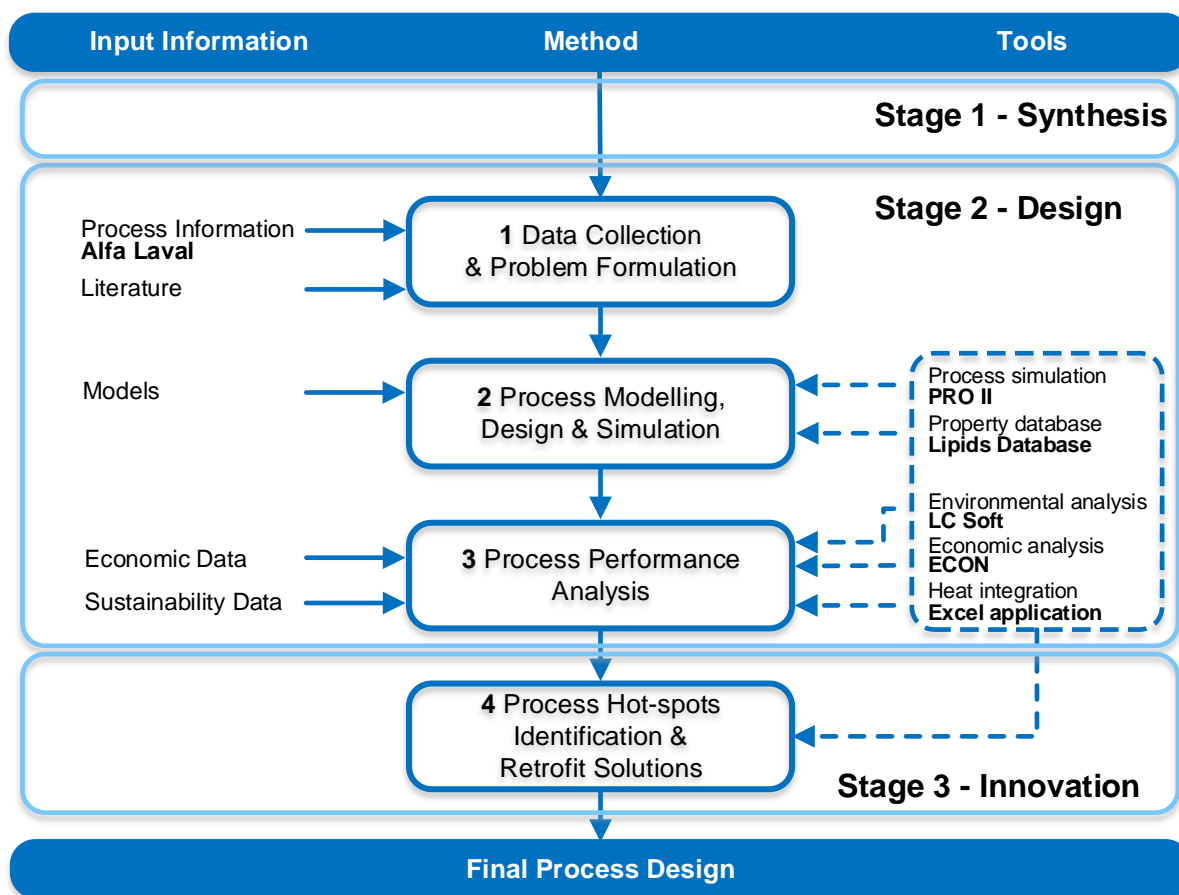
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3 The environmental impact is evaluated with LCSof<sup>29</sup> using the Life Cycle Analysis framework.  
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5 According to the International Standardization Organization (ISO) directive ISO 14040<sup>30</sup>, the LCA  
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7 consists in four steps: (1) goal and scope definition, (2) life cycle inventory (LCI) evaluation, (3)  
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9 life cycle impact assessment (LCIA), and (4) results analysis and interpretation. In the first step  
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11 the boundary of the system is defined (e.g. input streams, products, waste streams, utilities). The  
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13 mass balance and energy balance are used in the second step to calculate the LCI. LCI database  
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15 from LCSof has information from US LCI database<sup>31</sup> and other open sources. The LCI results are  
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17 used in the third step for different environmental impact indicator calculations (e.g.: global  
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19 warming potential (GWP), human toxicity potential indicator (HTPI), etc.). In the final step, the  
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21 results are analysed for identifying possibilities for improvement.  
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26 The results from steps 1-3, stage two of the synthesis-design-innovation framework, represent the  
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28 base case scenario.  
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## 31 **2.4 Process hot-spots identification and retrofit solutions**

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33 In the final step, improved solutions are proposed based on the identified hot-spots from the  
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35 economic and environmental impact analysis of step 3. Candidate solutions that represent new  
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37 process alternatives cover aspects of heat integration, intensification, advanced optimization, or  
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39 other retrofit solutions that match the desired targets for improvement. The economic and  
40  
41 environmental impact performance of the new and improved alternatives are assessed and  
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43 compared with the base case scenario. This step represents stage three, innovation stage, of the  
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45 synthesis-design-innovation framework<sup>20</sup>.  
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**Figure 2.** Generic systematic method used for process design and analysis of shea butter acetone fractionation including the representation of the three-stage approach of synthesis-design-innovation framework from Bertran et al.<sup>20</sup>

### 3 RESULTS AND DISCUSSION

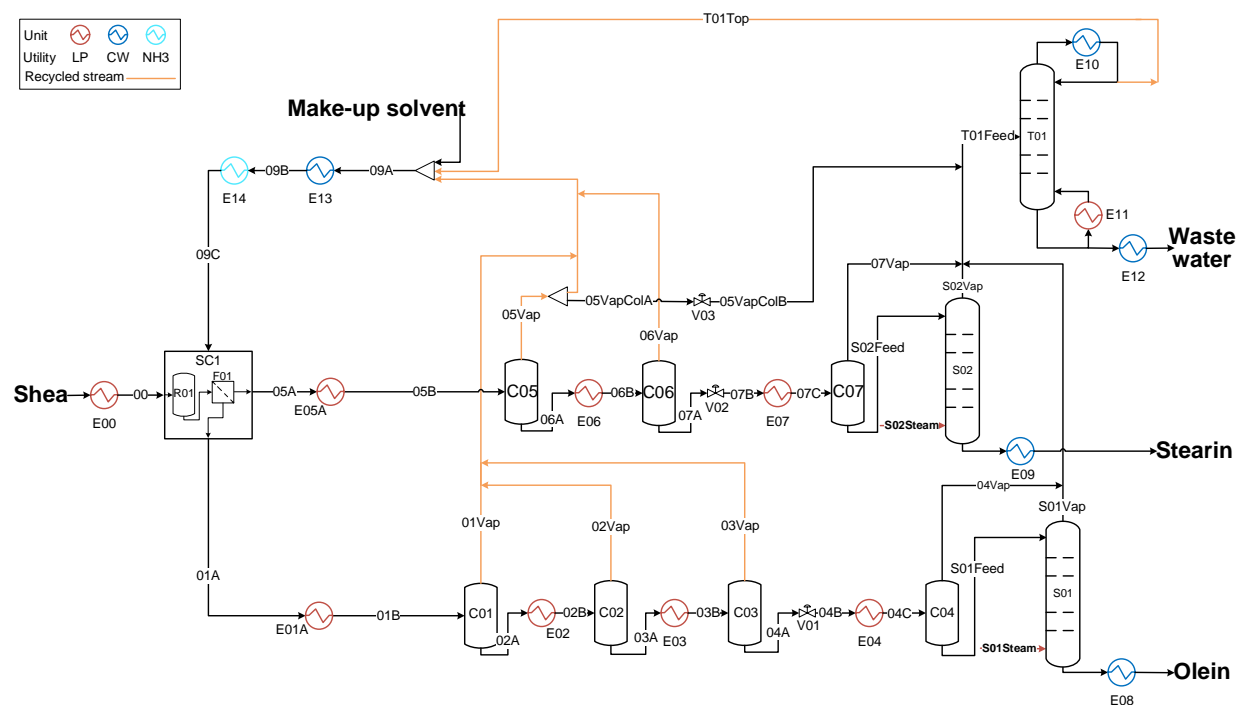
In this section, the details of the method application to shea butter acetone fractionation process are given, highlighting the application of the lipid-based thermodynamic models, as well as the design-innovation methods and tools used. The results obtained in each of the four steps are presented and analysed in detail.

#### 3.1 Problem definition and process data collection

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3 The problem to be solved is to design a process for solvent fractionation for a 2000 kg/h feed of  
4 shea butter. The final product specification should consider the following: <1 mg acetone/kg  
5 product and <0.5% water. The process flowsheet diagram and the main process specifications are  
6 provided by Alfa Laval. The remaining required information is taken from literature or is covered  
7 by using well-established design principles (e.g.: mass and energy balance, thermodynamic  
8 feasibility, cost and environmental impact minimisation, etc.). The process description, including  
9 process parameters and assumptions, is given in the text below. The process and products  
10 specifications are given in Table 1. The detailed stream compositions are presented in the  
11 Supporting Information.  
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24 Shea butter might come with a water content of a maximum 0.5%. In this case, it is assumed that  
25 shea butter is dried before entering the process. The drying process is not considered in the current  
26 analysis. The shea butter is heated at 50 °C in E00 heat exchanger (Figure 3) to melt the crystals  
27 and to erase the thermal history<sup>17</sup>. Next, shea butter is mixed in the crystallizer (R01) with high  
28 purity acetone in a 1:4 ratio. The crystallization process takes place at - 5 °C in a stirred crystallizer.  
29 The two products: Stearin (solid) and Olein (liquid) are separated by filtration (F01) and washed  
30 with acetone. Any impurities in the solvent, as well as water content above 0.5%, can affect the  
31 crystallization process and change the product properties (e.g. narrow melting profile, a melting  
32 point within 32-37 °C interval)<sup>32</sup> thus the need to use a high purity solvent. The solvent selection  
33 has an important impact on the separation process and depends on the quality of the oil (e.g. free  
34 fatty acids content). A polar solvent like acetone has a higher degree of separation for the polar  
35 compounds (e.g. fatty acids, diglycerides) in the liquid fraction (i.e. olein) compared to a non-polar  
36 solvent (e.g. hexane). This results in a solid product (i.e. stearin) with higher TAGs content and  
37 with no need for an extra refining step to remove the free fatty acids or other polar species.<sup>17</sup> The  
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3 presence of several polar compounds in the shea butter (e.g. FAs, DAGs) justifies the selection of  
4 acetone as the solvent to be used. After the fractionation, stream 05A containing the stearin fraction  
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6 is melted in a heat exchanger (E05A) with low pressure (LP) steam. Further, flash units (C05, C06,  
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8 C07) operating under different conditions, as listed in Table 1, aim to maximize the solvent  
9  
10 recovery from each of the two products. The residual acetone is removed from the final product  
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12 by steam stripping (S02). The acetone from the vapour streams of the stripping units (S01 and S02)  
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14 and the flash units C04 and C07 is recovered in the acetone-water distillation column (T01). The  
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16 column working pressure (i.e. 0.2 bar) is selected to maximize acetone recovery in the recycled  
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18 stream (T01Top). The water separated in the bottom product (Waste water) is considered as a  
19  
20 waste stream and its treatment is not taken into account within the process analysis. A significant  
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22 amount of water that is recycled in the process is evaporated in the flash units C01 and C05. To  
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24 avoid the water accumulation in the process, the vapour stream of the C05 unit for stearin  
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26 purification (05Vap) is split into two streams: one stream (05VapColA) is fed in the distillation  
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28 column, while the other is recycled. All the vapour streams from the remaining flash units (C01,  
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30 C02, C03 and C06) are recycled directly into the process. Before the recycle, the acetone is cooled  
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32 at -15 °C. The cooling is performed in a refrigeration cycle with ammonia (NH<sub>3</sub>) which involves  
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34 a single compression stage and is represented in the PFD through the E14 heat exchanger.  
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**Figure 3.** Shea butter acetone fractionation process flowsheet diagram for Base case scenario.

**Table 1.** Process specifications for the Base case scenario.

Name	Parameter	Unit	Value
<b>Stream</b>			
Shea	Flowrate	kg/h	2000
Acetone Make up	Flowrate	wt. ratio	1:4
Stearin	Water content	%	<0.5
Stearin	Acetone content	mg acetone/kg product	<1
Olein	Water content	%	<0.5
Olein	Acetone content	mg acetone/kg product	<1
<b>Unit Operation</b>			
SC1	Crystallization temperature	°C	-5
SC1	Stearin yield	wt. %	47
05A	Acetone composition	wt. fr.	0.5

C01, C02, C03, C05, C06	Pressure	bar	1
C04, C07	Pressure	bar	0.2
C01	Temperature	°C	56.5
C02	Temperature	°C	61.8
C03	Temperature	°C	74.5
C04	Temperature	°C	79.3
C05	Temperature	°C	60.1
C06	Temperature	°C	72.6
C07	Temperature	°C	75.8
SP1	Split fraction (05VapCo1A/05Vap)	wt.fr.	0.15
S01	Acetone recovery in top product (S01Vap)	wt.fr.	0.9999
S02	Acetone recovery in top product (S02Vap)	wt.fr.	0.9999
T01	Pressure	bar	0.2
T01	Acetone recovery in top product (T01Top)	wt. fr.	0.9999
T01	Reflux ratio		2.5
Utility			
LP Steam	Pressure	bar	4
Process steam	Pressure	bar	1
Cooling water	Supply temperature	°C	20
Cooling water	Target temperature	°C	30
Ammonia Cooling	Temperature	°C	-15

### 3.2 Process modelling, design and simulation

The process model is implemented in PRO/II 10.2<sup>33</sup>. The Lipids Database, described in more detail elsewhere<sup>2</sup>, is linked to PRO/II and provides easy access to all the thermo-physical data and models needed for the simulation. This includes primary properties (e.g.: molecular weight, critical



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3 temperature, pressure and volume, melting temperature, formation and fusion enthalpy, Gibbs  
4 enthalpy), secondary properties (e.g.: solubility, specific gravity, compressibility factor, etc.) data  
5 and functional properties (e.g.: vapour pressure, density, viscosity, phase enthalpy) correlations.  
6  
7 The detailed list of properties for pure compounds and mixtures used in the simulation are given  
8 in the Supporting Information. Ideal gas is assumed to describe the vapour phase, while the liquid  
9 phase is modelled with the Original UNIFAC model using the lipid-based parameters<sup>34</sup>. The  
10 missing binary interaction parameters from the lipid-based parameter matrix (i.e. parameters  
11 involving following groups H<sub>2</sub>O, CH<sub>2</sub>CO, OH) are taken from first-order KT-UNIFAC<sup>35</sup>. The  
12 model performance with selected parameters is tested for VLE description of three systems  
13 involved in the mixture for which experimental data is available. The tested systems are acetone -  
14 triolein and acetone - oleic acid at 318.15 K and acetone-water at different pressures. The average  
15 relative deviation for the two lipid systems shows a good agreement between predicted and  
16 experimental data. The results are presented in Table 2. The evaluation of the water-acetone  
17 system, presented in Figure 4, shows good prediction for the data sets at 101 kPa, and slight  
18 deviations for the data set at 20 kPa. This is explained by the quality of the experimental data,  
19 where the overall quality factor<sup>36</sup> is Q=1, Q=0.95 for data at 101 kPa<sup>37,38</sup> and Q=0.23 for data at  
20 20 kPa<sup>39</sup>. The VLE for water-acetone system was modelled also with NRTL using the parameters  
21 implemented in PRO II. Performance similar to UNIFAC model was achieved. More details can  
22 be found in Supporting Information. Examples of model performance for other lipid mixtures can  
23 be found in the work of Perederic et al.<sup>2,34</sup>. The parameter matrix used in the simulation is provided  
24 in Supplementary Information.

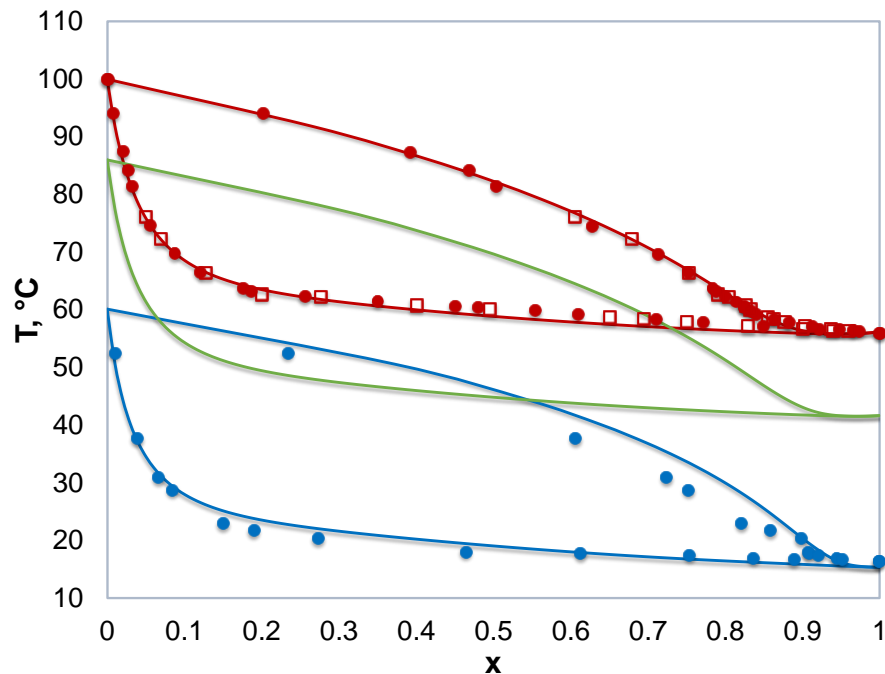
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51 **Table 2.** Original UNIFAC model with lipid-based parameters performance for acetone-lipid  
52 systems.  
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Acetone (1) – Triolein (2) at T=318.15 K <sup>a</sup>				Acetone (1) – Oleic acid (2) at T=318.15 K <sup>a</sup>			
x <sub>1</sub>	P <sub>exp</sub> , kPa	P <sub>calc</sub> , kPa	ARD <sup>b</sup>	x <sub>1</sub>	P <sub>exp</sub> , kPa	P <sub>calc</sub> , kPa	ARD <sup>b</sup>
0.099	6.15	3.68	1.99%	0.031	2.86	1.76	2.10%
0.169	10.60	6.57		0.056	5.16	3.21	
0.241	15.30	9.84	Q <sup>c</sup>	0.082	7.43	4.75	Q <sup>c</sup>
0.318	20.33	13.69	0.476	0.117	10.45	6.85	0.5
0.396	25.54	18.05		0.211	17.96	12.77	
0.523	34.26	26.26		0.309	25.28	19.33	
0.631	41.78	34.55		0.421	33.73	27.29	
0.749	50.05	45.09		0.471	36.58	30.99	
0.811	54.45	51.17		0.598	44.75	40.67	
0.895	60.55	59.51		0.728	52.84	50.62	
0.941	63.89	63.72		0.836	58.98	58.31	
1	68.17			0.947	65.10	64.99	
				1	68.10	68.10	

<sup>a</sup> Data from Eduljee and Boyes<sup>40</sup>

$$b \quad ARD = \frac{1}{N} \sum_{i=1}^N \left| \frac{P_i^{experimental} - P_i^{calculated}}{P_i^{experimental}} \right|, \text{ N data points number, P – pressure, kPa.}$$

<sup>c</sup> Q – quality factor of the datasets evaluated with the algorithm proposed by Kang et al.<sup>36</sup> and implemented in TDE<sup>41</sup>



**Figure 4.** Acetone-water vapor liquid equilibria model prediction and experimental data.

Original UNIFAC with lipid-based parameters and KT UNIFAC parameters prediction: — 101.33

kPa, — 60 kPa, — 20 kPa. Experimental data: • 101.33 kPa<sup>37</sup>, □ 101.33 kPa<sup>38</sup>, • 20 kPa<sup>39</sup>).

The feed composition for shea butter is given by Alfa Laval. The acetone used in the process is assumed to be of high purity. The composition of Shea and Make-up solvent are given in Table 3.

There is a vast literature where various experimental studies for oil and fats crystallization with focus on specific binary or multicomponent systems are conducted, but limited data can be found for shea oils and its products<sup>14,42–44</sup>. Regarding the modelling aspects, several models for solid-liquid equilibria modelling<sup>45–47</sup>, simple crystallization kinetics<sup>48,49</sup> (e.g.: Avrami and Avrami–Erofeev models<sup>50–53</sup>, Gompertz model<sup>54,55</sup>, Foubert model<sup>56</sup>) or crystallization in the presence of a solvent<sup>57</sup> were developed and improved over the years. Each of these models requires a significant amount of experimental data to describe a certain mixture of lipids, many of them requiring

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3 knowledge on the SLE of the binary systems involved in the mixtures. In the Supporting  
4 information we have gathered all the binary SLE data available for the compounds of the shea oil  
5 feed (Shea stream) used in this work, and which cover less than 10% of the total number of binary  
6 systems involved. A systematic approach is used by Hjorth et al.<sup>58,59</sup>, which developed a complex  
7 framework for thermodynamic and crystallization kinetics modelling of triacylglycerides  
8 mixtures. Even though the model is predictive and does not require knowledge of binary SLE of  
9 involved compounds, a set of appropriate experimental is needed to fit the model parameters.  
10 Given the limited available data for the considered mixture, a simple mass balance model (SC1)  
11 is used to describe the crystallization (R01), filtration and washing operations (F01) presented in  
12 Figure 3. The data used for these operations is industrial data provided by Alfa Laval. The  
13 crystallizer duty is estimated from the heat of formation of each compound separated in the stearin  
14 product (stream 05A). The energy balance for the crystallizer is provided in the Supporting  
15 information. The values for the heat of formation were taken from the Lipids Database. The  
16 temperatures in the flash units are selected based on the amount of acetone to be separated from  
17 the mixture and the product temperature limit for degradation, which was determined by the  
18 presence of unsaturated lipid compounds and which should not exceed 110 °C. Selected  
19 specifications are listed in Table 1. The stripping units (S01 and S02) are modelled with six  
20 equilibrium trays. The top pressure is set at 0.2 bar and the set pressure drop is 0.01 bar per tray.  
21 The process steam stream (S01Steam, S02Steam) is fed below the bottom tray and the stream  
22 containing the final product (S01Feed, S02Feed) is fed on the top tray. Acetone recovery in the  
23 top product of the stripping units is set as specification. The pressure in the distillation column  
24 (T01) is set to 0.2 bar. This selection is made by considering the amount of water to be removed  
25 from the process and the behaviour of the acetone-water mixture at different pressures (see Figure  
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4). The system presents a low boiling point azeotrope at pressures higher than atmospheric. The azeotropic point translates into a pinch area at low pressure. The pinch area covers the 0.9 to 1 acetone mole fraction region for atmospheric pressure, it gets smaller with decreasing the pressure and disappears completely at pressures lower than 10 kPa. The column is modelled with 9 trays. The feed tray, tray 9, is selected at minimum reboiler duty using driving force method<sup>60,61</sup>. Acetone recovery (i.e. 0.999 wt. fr.) in top product and reflux ratio (i.e. 2.5) are used as specifications. The column is configured with a total condenser and a Kettle reboiler. For design and sizing purposes, the T01 column was also separately modelled using the NRTL model. For all the other unit operations (e.g. heat exchangers, pumps, valves) rigorous models available in PRO/II are used with appropriate specifications (e.g. cold product temperature, outlet pressure). The utilities required within the simulation are cooling water (CW) ( $T_s=20$  °C,  $T_t= 30$  °C), ammonia cooling ( $\text{NH}_3$ ) and low pressure (LP) steam ( $P=4$  bar). The ammonia refrigeration cycle for ammonia cooling utility is modelled, designed and simulated as well. It consists of two heat exchangers, a compressor, and a valve. The process mass balance for classes of compounds is given in Table 3, while the detailed mass balance for each compound is given in Supplementary Information. The energy balance results are given in Table 4. The design of the equipment is performed following the principles presented by Biegler<sup>62</sup>.

**Table 3.** Mass balance for the Base case of shea butter acetone fractionation process.

Stream	Shea	Make-up solvent	S01Steam	S02Steam	T01Feed	Stearin	Olein	Waste water
Phase	Solid	Liquid	Vapour	Vapour	Vapour	Liquid	Liquid	Liquid
Temperature, °C	25	20	120	120	73.0	50	30	30
Pressure, bar	1	1	2	2	0.2	1	1	1
TAGs, kg/h	1769.8	0	0	0	0	897.6	872.2	0

DAGs, kg/h	20.0	0	0	0	0	9.4	10.6	0
MAGs, kg/h	1.6	0	0	0	0	0.8	0.8	0
FAs, kg/h	200.1	0	0	0	0	28.2	171.9	0
Minors <sup>a</sup> , kg/h	8.5	0	0	0	0	4	4.5	0
Acetone, kg/h	0	0.3	0	0	284.5	0	0	0.3
Water, kg/h	0	0	16.8	13.2	25.5	2.6	3.3	24.3

<sup>a</sup> Minors – tocopherols, sterols and squalene

<sup>b</sup> Flowrates of components smaller than  $10^{-4}$  kg/h are represented in the table with 0.

**Table 4.** Energy balance for the Base case and Alternatives 1-3 of shea butter acetone fractionation process.

Unit Name	Base case		Alternative 1		Alternative 2		Alternative 3	
	Duty, kW	Utility	Duty, kW	Utility	Duty, kW	Utility	Duty, kW	Utility
E00	32.77	LP	32.77	-	32.77	-	32.77	-
E01A	807.83	LP	272.44	-	272.44	-	272.44	-
E01B	-		535.38	LP	22.11	-	22.11	-
E02	461.81	LP	461.81	LP	394.44	-	394.44	-
E03	45.59	LP	45.59	LP	423.54	LP	423.54	LP
E04	16.55	LP	16.55	LP	8.95	CW	8.95	CW
E05A	160.21	LP	65.75	-	65.75	-	65.75	-
E05B	-		94.45	LP	67.27	-	67.27	-
E06	50.68	LP	50.68	LP	100.73	LP	100.73	LP
E07	14.02	LP	14.02	LP	15.92	LP	15.92	LP
E08	28.44	CW	28.44	CW	28.45	CW	46.34	CW
E09	16.83	CW	16.83	CW	16.83	CW	16.83	CW
E10	154.65	NH <sub>3</sub>	154.65	NH <sub>3</sub>	171.36	NH <sub>3</sub>	168.5	NH <sub>3</sub>
E11	88.59	LP	88.59	LP	100.02	LP	118.7	LP
E12	1.21	CW	1.21	CW	1.21	CW	-	-
E13	1236.63	CW	865.67	CW	522.03	CW	522.84	CW

E14	210.83	NH <sub>3</sub>	210.83	NH <sub>3</sub>	210.4	NH <sub>3</sub>	210.4	NH <sub>3</sub>
E15	-		-		-		4.93	NH <sub>3</sub>
E16	-		-		-		5.21	LP
R01	43.45	NH <sub>3</sub>	43.45	NH <sub>3</sub>	43.45	NH <sub>3</sub>	43.45	NH <sub>3</sub>
Total Cold Utility	1692.04	CW, NH <sub>3</sub>	1321.08	CW, NH <sub>3</sub>	1002.68	CW, NH <sub>3</sub>	1022.24	CW, NH <sub>3</sub>
Total Hot Utility	1678.05	LP	1307.07	LP	640.21	LP	664.1	LP

### 3.3 Process performance analysis

The process performance is analysed in terms of energy requirements, environmental impacts and economic performance. The total utility consumption is determined from the energy balance and requires a total of 1.69 MW for cold utilities (cooling water and ammonia cooling) and 1.68 MW for hot utilities (LP steam).

The environmental impact takes into account the effect of the waste stream, Waste water, and the effect of utilities used in the process. The following streams are considered for the analysis: Shea and Make-up solvent streams represented the input materials, Stearin and Olein were considered as product streams, and Waste water is defined as a waste stream. Following utilities and their sources are considered in the environmental impact evaluation: electricity produced from natural gas at a power plant, natural gas combusted in an industrial boiler is used for heating and chilled water is used for cooling. These utilities are taken for the LCSofT default database. The analysis provides results for seven indicators regarding air, soil and water impacts, as well as human toxicity, which are given in Table 5. A significant impact is encountered for the global warming potential indicator, or carbon footprint, which is generated by the process utilities. Acetone traces in the Waste water stream generate most of the impact for photochemical oxidation potential (i.e. 92%) and has an important contribution to HTPe indicator (i.e. 35%), while the impact for remaining categories comes from both the utilities and chemicals.

**Table 5.** Environmental performance for the Base case and Alternatives 1-3 of shea butter acetone fractionation process.

Indicator	Unit	Base case	Alternative 1	Alternative 2	Alternative 3
HTPI	1/LD <sub>50</sub>	$1.78 \cdot 10^{-2}$	$1.80 \cdot 10^{-2}$	$4.00 \cdot 10^{-3}$	$1.10 \cdot 10^{-2}$
HTPE	1/TWA	$5.79 \cdot 10^{-5}$	$5.60 \cdot 10^{-5}$	$1.50 \cdot 10^{-5}$	$3.50 \cdot 10^{-5}$
ATP	1/LC <sub>50</sub>	$3.03 \cdot 10^{-4}$	$2.50 \cdot 10^{-4}$	$1.10 \cdot 10^{-4}$	$1.30 \cdot 10^{-4}$
PCOP	C <sub>2</sub> H <sub>2</sub> eq.	$1.05 \cdot 10^{-1}$	$1.10 \cdot 10^{-1}$	$2.40 \cdot 10^{-2}$	$6.78 \cdot 10^{-2}$
GWP	CO <sub>2</sub> eq	1.82	1.40	1.00	1.00
ODP	CFC-11 eq	$1.65 \cdot 10^{-10}$	$1.30 \cdot 10^{-10}$	$6.30 \cdot 10^{-11}$	$6.50 \cdot 10^{-11}$
AP	H <sup>+</sup> eq	$8.30 \cdot 10^{-2}$	$6.50 \cdot 10^{-2}$	$4.10 \cdot 10^{-2}$	$4.20 \cdot 10^{-2}$

The economic analysis uses the cost index factor<sup>63</sup> which is updated with the latest available value. The plant running time assumed is 288 days per year. The detailed equipment design is taken into account for investment and operating costs. The ammonia refrigeration cycle and the pumps necessary for the process are considered within the economic analysis as well. The drying of shea butter and the treatment of waste stream are not considered in the analysis. The prices of the raw materials, products and utilities, given in Table 6, are selected based on data provided by Alfa Laval, online available data and ECON data. The price for steam and water cooling is given based on energy provided, while the ammonia price is considered per amount and it is used for the cost calculation of the ammonia refrigeration cycle. The design, sizing, economic evaluation and environmental impact of the ammonia refrigeration cycle are taken into consideration in the evaluation and analysis of the results of the base case, as well as, proposed alternatives in step 4 of the method. The results of the economic analysis show a total capital investment of 4.7 M€ with a rate of return (ROR) of 22%. The process break-even point is 1.8 years while the payback period is 3 years. Total operating cost is 21.18 M€/year from which manufacturing cost covers 19.26



M€/year. The cost for utilities is 0.54 M€/year. The raw materials purchase cost accounted for 85% of the total operating costs, and it is similar to other bio-based processes (e.g. bio-diesel production<sup>64,65</sup>). The economic indicators from the analysis are given in Table 7.

**Table 6.** Prices for raw materials, products and utilities used in the economic analysis of Base case and process Alternatives 1-3.

Material	Price	Material	Price
Shea butter	1.3 <sup>a</sup> €/kg	Process water (Steam)	0.2 €/kg
Stearin	3.0 €/kg	CW	0.35 €/GJ
Olein	1.5 €/kg	LP	7 €/GJ
Acetone	2.3 <sup>b</sup> €/kg	Ammonia	0.8 €/kg <sup>c</sup>

<sup>a</sup> Data from CBI Market Intelligence<sup>66</sup>

<sup>b</sup> High purity acetone was considered for the process<sup>67</sup>

<sup>c</sup> Data from Boulamanti and Moya<sup>68</sup>

**Table 7.** Economic performance for the Base case and Alternatives 1-3 of shea butter acetone fractionation process.

Indicator	Base case	Alternative 1	Alternative 2	Alternative 3
Total Capital Investment, M€	4.74	4.82	4.82	4.76
Equipment Purchase Cost, M€	0.59	0.95	0.95	0.94
Total Production Cost, M€/year	21.18	21.14	21.08	21.08
Manufacturing Cost, M€/year	19.26	19.22	19.16	19.18
Raw Materials Cost, M€/year	18.03	18.03	18.03	18.00

### 3.4 Process hot-spots identification and improvement solutions

The analysis of the process performance indicates high utility cost as the main hot-spot of the process with emphasis on the heat exchangers E01, E02 and E14. The improvements can be achieved through process heat integration. More heat integration can be performed if the operating

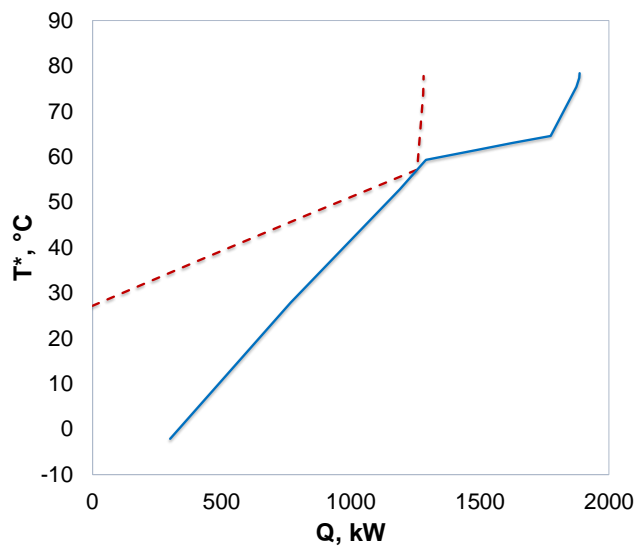
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3 parameters of the flash units are changed. Based on the identified improvement opportunities, two  
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5 process alternatives based on heat integration are developed and analysed: Alternative 1 and  
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7 Alternative 2. A third alternative, Alternative 3, involving a side draw distillation column for Olein  
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9 and solvent separation is investigated as well with the aim to reduce the amount of water that enters  
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11 the process. The set-up and analysis of the three process alternatives are similar to the Base case  
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13 scenario and follows Steps 1-3 of the method. Each of the proposed process alternatives is  
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15 presented individually, highlighting the modifications and comparing the performance with the  
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17 Base case scenario.  
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### 21 **3.4.1 Process Alternative 1**

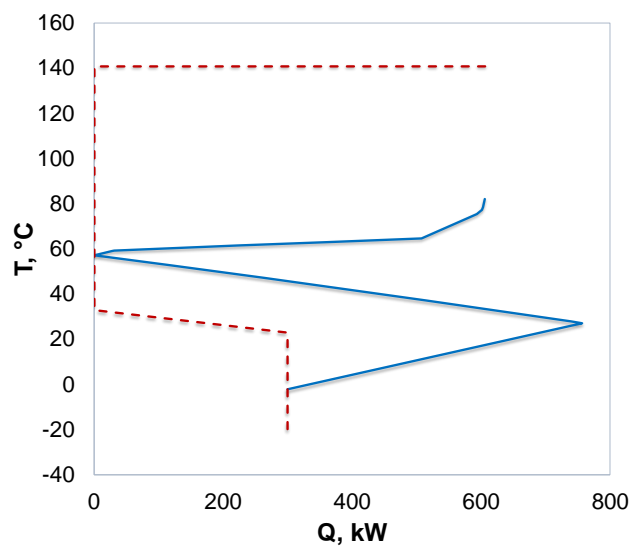
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24 Process Alternative 1 is based on heat integration performed for the Base case scenario. The heat  
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26 integration potential is evaluated through pinch analysis<sup>69,70</sup>. All the cold and hot streams from the  
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28 process are considered within the analysis. The minimum temperature difference selection  
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30 considers capital cost (i.e. heat exchanger price) and operation cost (i.e. utility cost) trade-off. The  
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32 evaluation with ECON of both capital and operation cost is estimated using the same prices and  
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34 cost models used in the economic analysis of the Base case. Several values for minimum  
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36 temperature difference are tested, and the one giving minimum total cost is selected.  
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40 The Base case scenario potential for process-to-process heat recovery for a minimum  
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42 temperature difference of 5.69 °C is 983.4 kW. Under these conditions, the minimum hot utility  
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44 requirement is 673.23 kW and the minimum cold utility requirement is 367.20 kW, as shown by  
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46 the shifted composite curves diagram presented in Figure 5. The pinch point is located at 57.19 °C  
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48 (i.e. 54.34°C for hot streams and 60.04 °C for cold streams). The balance grand composite curve,  
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50 presented in Figure 6, gave the utility placement and satisfied the minimum heat and cold utility  
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52 requirements. No utility pinch point is observed in the grand composite curve.  
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3 For reasons of process control, a sub-problem of the heat integration is considered for Alternative  
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5 1. The heat integration is performed between the acetone recycle stream (i.e stream 09A) which  
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7 needed to be cool down from 60 °C to -15 °C, the two product streams resulted after filtration (i.e.  
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9 stream 01A and 05A which are cold streams), and the oil feed stream (i.e. stream Oil which is a  
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11 cold stream). For this case scenario (i.e. one hot and three cold streams) two heat exchangers are  
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13 added to the initial flowsheet (i.e.E01B, E05B), as presented in Figure 7, while the specifications  
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15 of the heat exchangers already available (i.e. E01A, E05A, E13) are changed. Details of the  
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17 modified and the new heat exchangers energy requirements are given in Table 4. For the proposed  
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19 heat exchanger network (HEN) the recovered heat is 371.0 kW, which represents 37% of the total  
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21 allowed heat recovery for the Base case scenario. The heat integration leads to a 24.5% drop in  
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23 cold utility consumption and 22.1% drop in hot utility consumption, which translates to a 55  
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25 k€/year decrease in the operating cost. In terms of environmental impact, the impact generated by  
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27 the Waste water stream is the same (i.e. the composition of the stream is the same as for the Base  
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29 case scenario), while the impact generated by the utilities dropped leading to a 21% smaller value  
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31 for GWP indicator. The detailed results of the environmental impact are given in Table 5. The  
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33 main economic indicators for Alternative 1 are listed in Table 7, indicating an increase in  
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35 investment cost and a decrease in operating cost compared to the Base case scenario.  
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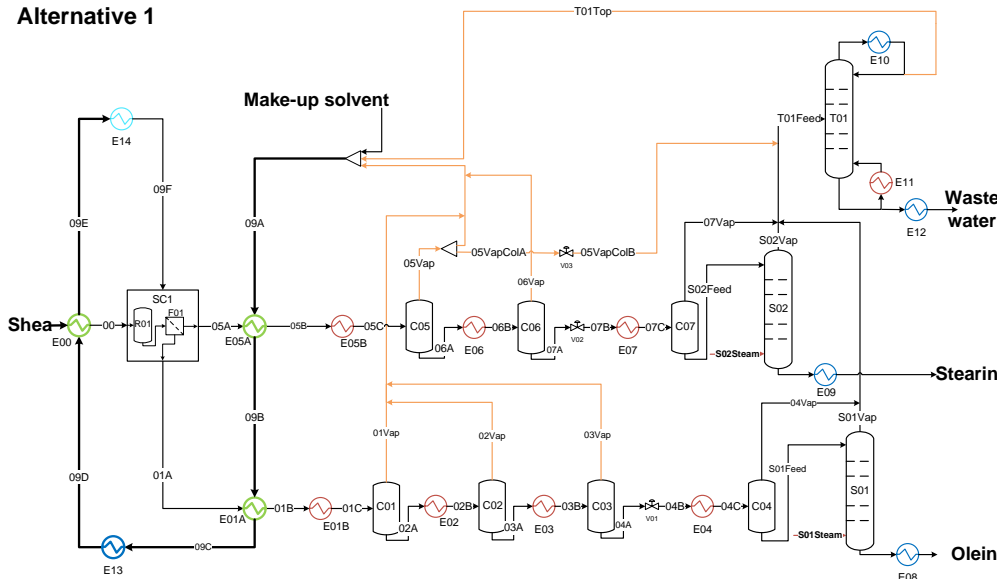


**Figure 5.** Shifted composite curves for the Base case scenario heat integration problem. Cold composite curve ( — ), hot composite curve ( - - - ).

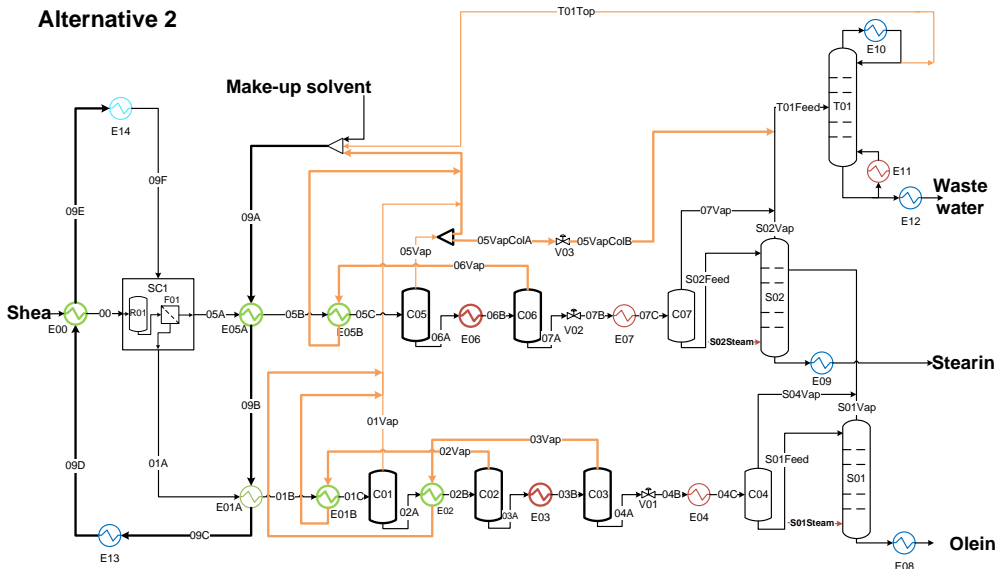


**Figure 6.** Process grand composite curves for the Base case scenario heat integration problem. Process grand composite curve ( — ), utility grand composite curve ( - - - ).

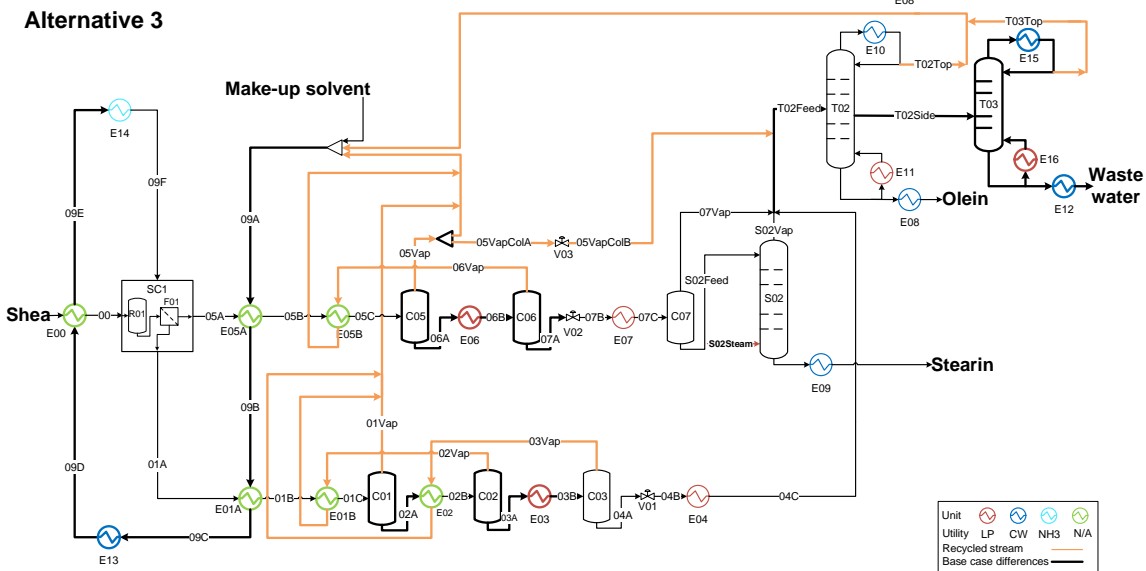
Alternative 1



Alternative 2



Alternative 3



Unit					
Utility	LP	CW	NH3	N/A	
Recycled stream					
Base case differences					

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3 **Figure 7.** Shea butter acetone fractionation process flowsheet diagram for Alternative 1 involving  
4 heat integration of the acetone recycle stream (09A) with the feed stream (Shea) and the two  
5 streams resulted from fractionation (01A, 05A); Alternative 2 involving heat integration of recycle  
6 stream (09A) with feed stream (Shea) and fractionation products (01A, 05A), and integration of  
7 flash vapor product stream (02Vap, 03Vap and 06Vap) with the feed stream (01C, 02A, 05C) of a  
8 previous unit; Alternative 3 involving the heat integration from Alternative 2 and implementation  
9 of side draw column T02 for separation of Olein, acetone recovery (T02Top), and water removal  
10 (Waste water).  
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### 22 **3.4.2 Process Alternative 2**

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24 In Alternative 2 of the process, the flash operating conditions are modified to allow further heat  
25 integration, while the HEN developed in Alternative 1 is implemented with slight modifications  
26 of duty for E013 heat exchanger. The flash specifications are selected such as the separated acetone  
27 vapour stream is able to provide the heat for another flash unit feed (e.g. vapour stream 02Vap  
28 from C02 flash unit heats the feed stream 01C of the C01 flash unit) as it is presented in Figure 7.  
29 The following assumptions are made with respect to the process modifications: the pressure of the  
30 units C04 and C07 is kept at  $P=0.2$  bar, the specifications of strippers feed composition is the same  
31 as the Base case scenario in order to have the same amount of steam entering the process via S01  
32 and S02, and the specifications for the final products are the same. All the new flash specifications  
33 are given in Table 8. The split factor in SP1 splitter is modified to keep the same amount of water  
34 recycled in the process as in the Base case scenario.  
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50 The energy balance for Alternative 2 is given in Table 4. The heat recovered within the process  
51 is 854.8 kW, equivalent 87% of the total heat recovery given by the pinch analysis of the Base  
52 case scenario. The utility requirements decrease by 47% for cold utilities and by 61% for hot utility,  
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corresponding to a 153 k€/year drop in operating costs. The reduced utility consumption has an effect on the environmental impact as well. The GWP indicator value decreases by 43% compared to the Base case scenario and by 30% compared to Alternative 1. Detailed results of the environmental impact of Alternative 2 are given in Table 5.

**Table 8.** Specifications for flash units from process Alternative 2.

Unit	Pressure, bar	Temperature, °C
C01	1	56.25
C02	2	78.55
C03	2.3	107.6
C04	0.2	79.32
C05	1	58.85
C06	2	99.08
C07	0.2	75.77

### 3.4.3 Process Alternative 3

Another alternative of the process, which involves a side-draw column, is investigated. The column aim is to separate the olein product and the solvent. The side draw column (T02) replaces C04 flash and S01 stripping column units, as presented in Figure 7. The design of the column is performed with the driving force method<sup>60</sup> resulting in a column with 15 theoretical trays, feed on tray number 8, and side draw on tray number 11. The side-draw stream, composed of 50% water and 50% acetone, is further separated in a distillation column (T03), where the water is discarded as Waste water and the acetone (T03Top) is recycled. Note that the flowrate of T03 column feed stream is significantly smaller compared to the feed of T01 distillation column. The set-up of T03 distillation column (e.g. operating conditions and specifications) is similar to the distillation column from Base case (T01). The heat integration of the flash units and the other heat exchangers

are implemented as presented in Alternative 2. The mass and energy balance for Alternative 3 are given in Table 9 and Table 4. The results for environmental analysis, and economic analysis, presented in Table 5 and Table 7, indicate performances close to those of Alternative 2: slight improvements for investment costs, a slight increase in operation cost and a slight increase for several environmental impact categories. Better acetone recovery and less process steam have a positive impact also on the raw material purchase cost, slightly lower than Base case scenario, Alternative 1 and Alternative 2, as given in Table 7. The comparison between the three process alternatives to the Base case scenario shows a significant improvement for the proposed process alternatives, with the best performances being achieved for Alternative 2. An overview of the performances of Alternatives 1-3 reported to the Base case scenario is given in Figure 8, where the indicators values from the plot are normalized to the Base case scenario results.

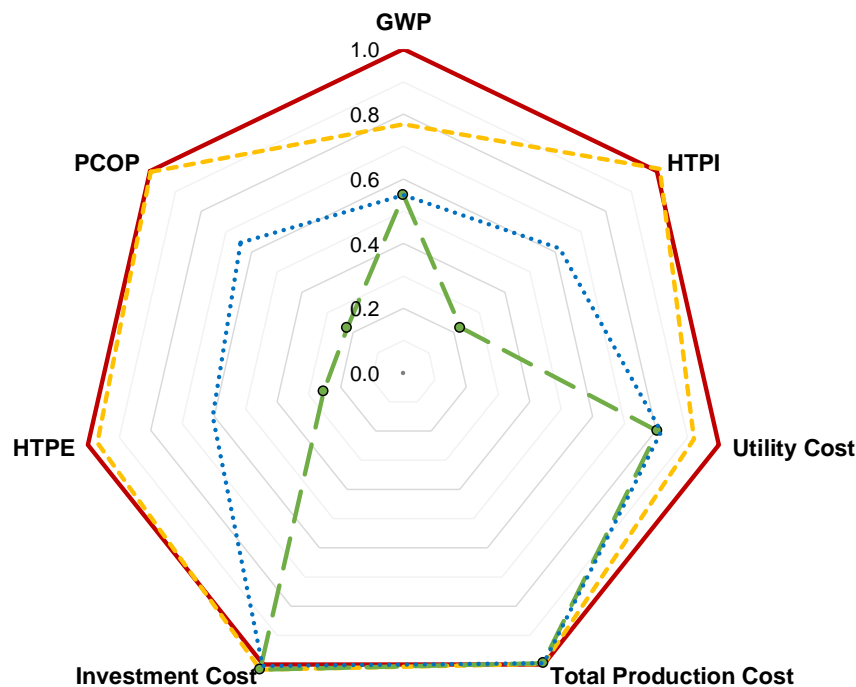
**Table 9.** Mass balance for process Alternative 3 of shea butter acetone fractionation.

Stream	Shea	Make-up solvent	S02Steam	Stearin	Olein	T02Side	Waste Water
Phase	Solid	Liquid	Vapour	Liquid	Liquid	Liquid	Liquid
Temperature, °C	25	20	120	50	30	25	25
Pressure, bar	1	1	2	1	1	0.2	1
TAGs, kg/h	1769.8	0	0	897.6	872.2	0	0
DAGs, kg/h	20	0	0	9.4	10.6	0	0
MAGs, kg/h	1.6	0	0	0.8	0.8	0	0
FAs, kg/h	200.1	0	0	28.2	171.9	0	0
Minors <sup>a</sup> , kg/h	8.5	0	0	4	4.5	0	0
Acetone, kg/h	0	9.3	0	0	0.1	9.2	0.2
Water, kg/h	0	0	13.2	2.6	1.7	9.2	9.2

<sup>a</sup> Minors – tocopherols, sterols and squalene

<sup>b</sup> Flowrates of components smaller than  $10^{-4}$  kg/h are represented in the table with 0.





**Figure 8.** Comparison of proposed process alternatives with respect to the Base case scenario for different economic and environmental impact indicators. Base case (—), Alternative 1 (---), Alternative 2 (---), Alternative 3 (····).

In the presented analysis of the shea butter solvent fractionation process throughout the Base case scenario and three process alternatives, potential improvements that can be brought to the industrial process are proposed. The improvements are focused around heat integration of some of the process streams and can lead to significant cuts in utility costs (e.g. up to 28 %). This could be valuable at the industrial level, since the shea stearin market price is highly dependent on the cocoa butter price, and during low price periods the process can keep good profitability. Moreover, the improvements in energy consumption have a positive impact on the process sustainability, with a reduction in GWP indicator up to 43%. Further improvements in process sustainability can be achieved if renewable resources are used for providing the process utilities (e.g. biofuels, renewable electricity).

## 5 CONCLUSIONS

In the present work, a systematic and generic method for lipid processing is described and exemplified through a case study for shea butter acetone fractionation process. The method involves four steps dedicated to data collection and problem definition, modelling and simulation, process analysis and process improvement, and which cover stage two and three of the synthesis-design-innovation framework<sup>20</sup>. The energy consumption for the solvent recovery, one of the main drawbacks of solvent fractionation processes, is identified in the process analysis step as the main area for improvement. The problem is addressed in step four by applying heat integration concepts and by implementing a side draw column in three process alternatives solutions. The process analysis of the alternatives indicates Alternative 2 as the best solution (i.e. 855 kW energy savings) which lead to lower operating cost and improvements in process sustainability (i.e. 40% lower GWP). The method is suitable to be applied for other lipid fractionation processes, especially the ones involving solvent recovery where significant energy savings can be achieved. Future studies should focus on detailed modelling of the lipid crystallisation process. This could offer a great advantage for the process solvent selection which can be done through a systematic solvent screening approach<sup>71</sup> and which could lead to a lower oil-solvent ratio, and ultimately to lower process energy requirements and environmental impact, making the solvent fractionation process more sustainable and profitable.

The application of the lipid thermodynamic models for both pure compounds and mixtures throughout the study highlights the importance of the availability of these models, of their ability to describe lipid-based industrial processes and the importance of having these models integrated within a database which is easily connected to different computer-aided tools. All these are reflected in the application of the models for the first time to shea butter solvent fractionation for

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3 which important improvements in process performance are achieved. The current available  
4 thermodynamic models, especially the ones describing the phase equilibria, can be further fine-  
5 tuned and expanded to include other lipid systems (once more experimental data are available) to  
6 expand the utilisation of the method and thermodynamic models to other lipid-based processes,  
7 such as oleochemicals production which involve more complex compounds and mixtures (e.g.  
8 fatty dicarboxylic acids, fatty amines, etc.).  
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## 16 ASSOCIATED CONTENT

### 19 Supporting Information

21 The Supporting Information file contains following additional information: pure component  
22 property models used, Original UNIFAC binary interaction parameters matrix used within process  
23 simulations, detailed mass balance for Base case scenario, energy balance for crystallizer, outlet  
24 streams for Base case and Alternative 3, SLE binary data for shea butter compounds, acetone-  
25 water VLE prediction with UNIFAC and NRTL. This information is available free of charge via  
26 the Internet at <http://pubs.acs.org/>  
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## 54 ABBREVIATIONS

1  
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3 ARD Average Relative Deviation; ATP Aquatic Toxicity Potential; CBE Cocoa Butter  
4  
5 Equivalent; CW Cooling Water; DAG Diacylglycerol; FA Fatty Acid; GWP Global Warming  
6  
7 Potential; HEN Heat Exchanger Network; HTPE Human Toxicity Potential by Exposure; HTPI  
8  
9 Human Toxicity Potential by Ingestion; LP Low Pressure steam; MAG Monoacylglycerols; NH<sub>3</sub>  
10  
11 Ammonia cooling; ODP Ozone Depletion Potential; PCOP Photochemical Oxidation Potential;  
12  
13 PFD Process Flowsheet Diagram; PFD Process Flowsheet Diagram; POP 1,3-dipalmito-2-olein  
14  
15 triglyceride; PPO 1,2-dipalmito-3-olein triglyceride; PSE Process Systems Engineering; Q  
16  
17 Quality factor of VLE datasets; ROR Rate of Return; T\* Shifted temperature; TAG  
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19 Triacylglycerol; TS Supply temperature; TT Target Temperature.  
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## 24 REFERENCES

- 25  
26  
27  
28 (1) Cheng, M. H.; Dien, B. S.; Singh, V. Economics of plant oil recovery: A review. *Biocatal.*  
29  
30 *Agric. Biotechnol.* **2019**, 18, 101056.  
31  
32  
33 (2) Perederic, O. A.; Cunico, L. P.; Kalakul, S.; Sarup, B., Woodley, J. M.; Kontogeorgis, G.  
34  
35 M.; Gani, R. Systematic identification method for data analysis and phase equilibria modelling for  
36  
37 lipids systems. *J. Chem. Thermodyn.* **2018**, 121, 153–169.  
38  
39  
40 (3) Martinho, A.; Matos, H. A.; Gani, R.; Sarup, B.; Youngreen, W. Modelling and simulation  
41  
42 of vegetable oil processes. *Food Bioprod. Process.* **2008**, 86, 87–95.  
43  
44  
45 (4) Díaz-Tovar, C. A.; Gani, R.; Sarup, B. Lipid technology: Property prediction and process  
46  
47 design/analysis in the edible oil and biodiesel industries. *Fluid Phase Equilib.* **2011**, 302, 284–293.  
48  
49  
50 (5) Landucci, G.; Pannocchia, G.; Pelagagge, L.; Nicoletta, C. Analysis and simulation of an  
51  
52 industrial vegetable oil refining process. *J. Food Eng.* **2013**, 116, 840–851.  
53  
54  
55  
56  
57  
58  
59  
60

1  
2  
3 (6) Stiefel, S.; Dassori, G. Simulation of Biodiesel Production through Transesterification of  
4 Vegetable Oils. *Ind. Eng. Chem. Res.* **2009**, 48, 1068–1071.  
5  
6

7  
8 (7) Sotoft, L. F.; Rong, B.-G.; Christensen, K. V.; Norddahl, B. Process simulation and  
9 economical evaluation of enzymatic biodiesel production plant. *Bioresour. Technol.* **2010**, 101,  
10 5266–74.  
11  
12  
13

14  
15 (8) Aboelazayem, O.; Gadalla, M.; Saha, B. Design and simulation of an integrated process for  
16 biodiesel production from waste cooking oil using supercritical methanolysis. *Energy* **2018**, 161,  
17 299–307.  
18  
19  
20  
21

22  
23 (9) Gani, R.; O’Connell, J. P. Role of Properties and their Models in Process and Product Design.  
24 In *Computer Aided Property Estimation for Process and Product Design*; Kontogeorgis, G.M.,  
25 Gani, R.; Eds.; Elsevier B.V.: Amsterdam, 2004, 27–41.  
26  
27  
28  
29

30  
31 (10) Damaceno, D. S.; Perederic, O. A.; Ceriani, R.; Kontogeorgis, G. M.; Gani, R. Improvement  
32 of predictive tools for vapor-liquid equilibrium based on group contribution methods applied to  
33 lipid technology. *Fluid Phase Equilib.* **2018b**, 470, 249–258.  
34  
35  
36  
37

38  
39 (11) Cunico, L. P.; Hukkerikar, A. S.; Ceriani, R.; Sarup, B.; Gani, R. Molecular structure-based  
40 methods of property prediction in application to lipids: A review and refinement. *Fluid Phase*  
41 *Equilib.* **2013**, 357, 2–18.  
42  
43  
44  
45

46  
47 (12) Ceriani, R.; Gani, R.; Liu, Y. A. Prediction of vapor pressure and heats of vaporization of  
48 edible oil/fat compounds by group contribution. *Fluid Phase Equilib.* **2013**, 337, 53–59.  
49  
50  
51

52  
53 (13) Smith, K.W. Confectionery Fats. In *Cocoa Butter and Related Compounds*; Garti, N.,  
54 Widlak, N.R.; Eds.; AOCS Press: Urbana, 2012, 475–495.  
55  
56  
57  
58  
59  
60

1  
2  
3 (14) Lovett, P.N. Shea butter: Properties and processing for use in food. In Specialty Oils and  
4 Fats in Food and Nutrition: Properties, Processing and Applications; Talbot G.; Ed.; Elsevier Ltd.:  
5 Amsterdam, 2015, 125-157.  
6  
7

8  
9  
10 (15) Kellens, M.; Gibon, V.; Hendrix, M.; De Greyt, W. Palm oil fractionation. Eur. J. Lipid Sci.  
11 Technol. **2007**, 109, 336–349.  
12  
13

14  
15  
16 (16) Dijkstra, A.J. Modification Processes and Food Uses. In The Lipid Handbook; Gunstone,  
17 F.D., Harwood, J.L., Dijkstra, A.J.; Eds.; CRC Press: Boca Raton, 2007, 263–353.  
18  
19

20  
21 (17) Timms, R.E. Processing methods. In: Confectionery Fats Handbook; Timms R.; Ed.;  
22 Woodhead Publishing: Cambridge, 2012, 105–142.  
23  
24

25  
26  
27 (18) Hashimoto, S.; Nezu, T.; Arakawa, H.; Ito, T.; Maruzeni, S. Preparation of sharp-melting  
28 hard palm midfraction and its use as hard butter in chocolate. JAOCs, J. Am. Oil Chem. Soc. **2001**,  
29 78, 455–460.  
30  
31

32  
33  
34 (19) Salas, J. J.; Bootello, M. A.; Martínez-Force, E.; Garcés, R. Production of stearate-rich  
35 butters by solvent fractionation of high stearic-high oleic sunflower oil. Food Chem. **2011**, 124,  
36 450–458.  
37  
38

39  
40  
41 (20) Bertran, M.-O.; Frauzem, R.; Sanchez-Arcilla, A.-S.; Zhang, L.; Woodley, J. M.; Gani, R.  
42 A generic methodology for processing route synthesis and design based on superstructure  
43 optimization. Comput. Chem. Eng. **2017**, 106, 892–910.  
44  
45

46  
47  
48 (21) Vooradi, R.; Bertran, M.-O.; Frauzem, R.; Anne, S.B.; Gani, R. Sustainable chemical  
49 processing and energy-carbon dioxide management: Review of challenges and opportunities.  
50 Chem Eng Res Des. **2018**, 131, 440-464.  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60

1  
2  
3 (22) Garg, N.; Woodley, J. M.; Gani, R.; Kontogeorgis, G.M. Sustainable solutions by  
4 integrating process synthesis-intensification. *Comput Chem Eng.* **2019**, 26, 499-519.  
5  
6

7  
8 (23) Kongpanna, P.; Pavarajarn, V.; Gani, R.; Assabumrungrat, S. Techno-economic evaluation  
9 of different CO<sub>2</sub>-based processes for dimethyl carbonate production. *Chem Eng Res Des.* **2015**,  
10 93, 496-510.  
11  
12  
13

14  
15 (24) Handani, Z. B.; Quaglia, A.; Gani, R. Synthesis and Design of Integrated Process and Water  
16 Networks; In *Computer Aided Chemical Engineering Vol 37*; Gernaey, K. V.; Huusom, J. K.;  
17 Gani, R.; Eds.; Elsevier B.V.: Amsterdam, 2015, 875-880.  
18  
19  
20  
21

22  
23 (25) Bertran, M.-O.; Orsi, A.; Manenti, F.; Woodley, J. M.; Gani, R. Synthesis of Sustainable  
24 Biofuel Production Processes: A Generic Methodology for Superstructure Optimization and Data  
25 Management. In: Kopanos GM, Liu P, Georgiadis MC, eds. *Advances in Energy Systems*  
26 *Engineering*. Cham, Switzerland: Springer; **2016**, 651-681.  
27  
28  
29  
30  
31

32  
33 (26) Perederic, O. A.; Appel, S.; Sarup, B.; Woodley, J. M.; Kontogeorgis, G. M.; Gani, R.  
34 Design and Analysis of Edible Oil Processes Containing Lipids. *Comput. Aided Chem. Eng.*  
35 **2018a**, 43, 737–742.  
36  
37  
38  
39  
40

41 (27) Seider, W. D.; Lewin, D. R.; Seader, J. D.; Widagdo, S.; Gani, R.; Ng, K. M. *Product and*  
42 *process design principles: synthesis, analysis, and evaluation*, Fourth ed. Wiley, **2016**.  
43  
44  
45  
46

47 (28) Peters, M. S.; Timmerhaus, K. D.; West, R. E. *Plant Design and Economics for Chemical*  
48 *Engineers*. 5th ed; McGraw-Hill Education: Boston, **2004**.  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60

1  
2  
3 (29) Kalakul, S.; Malakul, P.; Siemanond, K.; Gani, R. Integration of life cycle assessment  
4 software with tools for economic and sustainability analyses and process simulation for sustainable  
5 process design. *J Clean Prod.* **2014**, 71, 98-109.  
6  
7

8  
9  
10 (30) de Bruijn, H.; van Duin, R.; Huijbregts, M. A. J. Handbook on Life Cycle Assessment.  
11 Operational Guide to the ISO Standards; Kluwer Academic Publishers: Dordrecht; 2002.  
12  
13

14  
15 (31) National Renewable Energy Laboratory. US EPA LCI Database.  
16  
17 <https://www.nrel.gov/lci/about.html>.  
18  
19

20  
21 (32) Kang, K. K.; Jeon, H.; Kim, I. H.; Kim, B. H. Cocoa butter equivalents prepared by blending  
22 fractionated palm stearin and shea stearin. *Food Sci. Biotechnol.* **2013**, 22, 347–352.  
23  
24

25  
26 (33) AVEVA Group plc. PRO/II TM Process Engineering User Guide. Cambridge, UK; 2018.  
27  
28

29  
30 (34) Perederic, O. A. Systematic computer aided methods and tools for lipid process technology.  
31 Ph.D. Thesis, Technical University of Denmark, December 2018.  
32  
33

34  
35 (35) Kang, J. W.; Abildskov, J.; Gani, R.; Cobas, J. Estimation of mixture properties from first-  
36 and second-order group contributions with the UNIFAC model. *Ind. Eng. Chem. Res.* **2002**, 41,  
37 3260–3273.  
38  
39

40  
41 (36) Kang, J. W.; Diky, V.; Chirico, R. D.; Magee, J. W.; Muzny, C. D.; Abdulagatov, I.;  
42 Kazakov, A. F.; Frenkel, M. Quality Assessment Algorithm for Vapor–Liquid Equilibrium Data.  
43  
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1  
2  
3 (38) Verhoeve, L. A.; Deschepper, H. The vapour-liquid equilibria of the binary, ternary and  
4 quaternary systems formed by acetone, methanol, propan-2-ol, and water. *J. Applid Chem.*  
5  
6 *Biotechnol.* **1973**, 23, 607.  
7

8  
9  
10 (39) Al-Shhaf, T. A. Vapor-Liquid Equilibrium of the Acetone-Water-Salt System. *J. Chem.*  
11  
12 *Eng. Data* **1993**, 38, 522–526.  
13

14  
15 (40) Eduljee, G. H.; Boyes, A. P. Excess Gibbs Energy for eight oleic acid+solvent and triolein-  
16  
17 solvent mixtures at 318.15K. *J Food Process Eng* **1981**, 26, 55–57.  
18  
19

20  
21 (41) Diky, V.; Chirico, R. D.; Muzny, C. D.; Kazakov, A. F.; Kroenlein, K.; Magee, J. W.;  
22  
23 Abdulagatov, I.; Kang, J. W.; Frenkel, M. ThermoData Engine (TDE) software implementation of  
24  
25 the dynamic data evaluation concept. 7. Ternary mixtures. *J. Chem. Inf. Model.* **2012**, 52, 260–76.  
26  
27

28  
29 (42) Zhang, Z.; Ma, X.; Huang, H.; Wang, Y. Shea olein based specialty fats: Preparation,  
30  
31 characterization and potential application. *LWT - Food Sci Technol.* **2017**, 86, 492-500.  
32  
33

34  
35 (43) Ray, J.; Smith, K. W.; Bhaggan, K.; Nagy, Z. K.; Stapley, A. G. F. Crystallization and  
36  
37 polymorphic behavior of shea stearin and the effect of removal of polar components. *Eur. J. Lipid*  
38  
39 *Sci. Technol.* **2013**, 115, 1094-1106.  
40

41  
42 (44) Badu, M.; Awudza, J.; Budd, P.M.; Yeates, S. Determination of Physical Properties and  
43  
44 Crystallization Kinetics of Oil from *Allanblackia* Seeds and Shea Nuts Under Different Thermal  
45  
46 Conditions. *Eur J Lipid Sci Technol.* **2018**, 120(3), 1-9.  
47  
48

49  
50 (45) Wesdorp, L. H.; Van Meeteren, J. A.; De Jong, S.; Giessen, R. V. D.; Overbosch, P.;  
51  
52 Grootsholten, P. A. M.; Struik, M.; Royers, E.; Don, A.; de Loos, Th.; Peters, C.; Gandasmita,  
53  
54

1  
2  
3 I. Liquid-multiple solid phase equilibria in fats: Theory and experiments. In: Fat Crystal Networks.  
4  
5 1st ed.; Marangoni A. G.; Ed.; CRC Press: Boca Raton; 2004, 481-709.  
6  
7

8 (46) Rocha, S. A.; Guirardello, R. An approach to calculate solid–liquid phase equilibrium for  
9  
10 binary mixtures. *Fluid Phase Equilib.* **2009**, 281(1), 12-21.  
11  
12

13 (47) Teles M.; Le Roux, G. A. C.; Gerbaud V. Phase Equilibrium and Optimization Tools:  
14  
15 Application for Enhanced Structured Lipids for Foods. *J Am Oil Chem Soc*, **2011**, 223-233.  
16  
17

18 (48) Foubert, I.; Vanrolleghem, P. A. Modelling of the crystallization kinetics of fats. *Trends*  
19  
20 *Food Sci. Tech.* **2003**, 14, 79-92.  
21  
22

23 (49) Rousset, P. Modeling Crystallization Kinetics of Triacylglycerols. In *Physical Properties of*  
24  
25 *Lipids*; Marangoni A.G.; Narine S. S.; Eds.; CRC Press: Boca Raton; **2002**.  
26  
27

28 (50) Avrami, M. Kinetics of phase change. I: General theory. *J Chem Phys.* **1939**, 7(12), 1103-  
29  
30 1112.  
31  
32

33 (51) Avrami, M. Kinetics of phase change. II Transformation-time relations for random  
34  
35 distribution of nuclei. *J Chem Phys.* **1940**, 8(2), 212-224.  
36  
37

38 (52) Erofeev, B.V. Reactivity of Solids. In *Proc. 4th. Int. Symp. on Reactivity of Solids*, De Boer  
39  
40 J. H., Ed.; Elsevier B.V.: Amsterdam; **1960**, 273-282.  
41  
42

43 (53) Ng, W. Thermal decomposition in the solid state. *Aust J Chem.* **1975**, 28(6), 1169-1178.  
44  
45

46 (54) Zwietering, M. H.; Jongenburger, I.; Rombouts, F. M.; van 't Riet, K. Modeling of the  
47  
48 *Bacterial Growth Curve*. *Appl Environ Microbiol.* **1990**, 56(6), 1875-1881.  
49  
50  
51  
52  
53

1  
2  
3 (55) Kloek, W.; Walstra, P.; van Vliet, T. Crystallization Kinetics of Fully Hydrogenated Palm  
4 Oil in Sunflower Oil Mixtures. *JAOCS, J Am Oil Chem Soc.* **2000**, 77(4), 389-398.

5  
6  
7  
8 (56) Foubert, I.; Vanrolleghem, P. A.; Vanhoutte, B.; Dewettinck, K. Dynamic mathematical  
9 model of the crystallization kinetics of fats. *Food Res Int.* **2002**, 35, 945-956.

10  
11  
12  
13 (57) Schall, J. M.; Mandur, J. S.; Braatz, R. D.; Myerson, A. S. Nucleation and Growth Kinetics  
14 for Combined Cooling and Antisolvent Crystallization in a Mixed-Suspension, Mixed-Product  
15 Removal System: Estimating Solvent Dependency. *Cryst. Growth Des.* **2018**, 18, 1560–1570.

16  
17  
18  
19 (58) Hjorth, J. L.; Miller, R. L.; Woodley, J. M.; Kiil, S. Thermodynamic Modeling of Multi-  
20 phase Solid – Liquid Equilibria in Industrial-Grade Oils and Fats. *J Am Oil Chem Soc* **2015**, 92,  
21 17–28

22  
23  
24 (59) Hjorth, J. L.; Miller, R. L.; Woodley, J. M.; Kiil S. Kinetic modeling of multi-component  
25 crystallization of industrial-grade oils and fats. *Eur J Lipid Sci Technol.* **2015**, 117(7), 1066-1078.

26  
27  
28 (60) Bek-Pedersen, E.; Gani, R. Design and synthesis of distillation systems using a driving-  
29 force-based approach. *Chem Eng Process.* **2004**, 43, 251-262.

30  
31  
32 (61) Lopez-Arenas, T.; Mansouri, S. S.; Sales-Cruz, M.; Gani, R.; Pérez-Cisneros, E. S. A Gibbs  
33 energy-driving force method for the optimal design of non-reactive and reactive distillation  
34 columns. *Comput Chem Eng.* **2019**, 128, 53-68.

35  
36  
37 (62) Biegler, L. T.; Grossmann, I. E.; Westerberg, A.W. *Systematic Methods of Chemical*  
38 *Process Design.* Prentice Hall: New Jersey; **1997**.

39  
40  
41 (63) Plant Cost Index, Chemical Engineering. [www.chemengonline.com/](http://www.chemengonline.com/Assets/File/CEPCI_2002.pdf)  
42 [Assets/File/CEPCI\\_2002.pdf](http://www.chemengonline.com/Assets/File/CEPCI_2002.pdf). Published 2018. Accessed February 15, 2019.

1  
2  
3 (64) Harahap, F.; Silveira, S.; Khatiwada, D. Cost competitiveness of palm oil biodiesel  
4 production in Indonesia. *Energy*. **2019**, 170, 62-72.  
5  
6

7  
8 (65) Budžaki, S.; Miljić, G.; Sundaram, S.; Tišma, M.; Hessel, V. Cost analysis of enzymatic  
9 biodiesel production in small-scaled packed-bed reactors. *Appl Energy*. **2018**, 210, 268-278.  
10  
11  
12

13 (66) CBI Market Intelligence. CBI Product Factsheet: Shea Butter in Europe.; 2015.  
14  
15

16 (67) Chembid. Online search engine for chemicals and services. <https://www.chembid.com/>.  
17  
18  
19 Published 2017. Accessed February 27, 2019  
20  
21

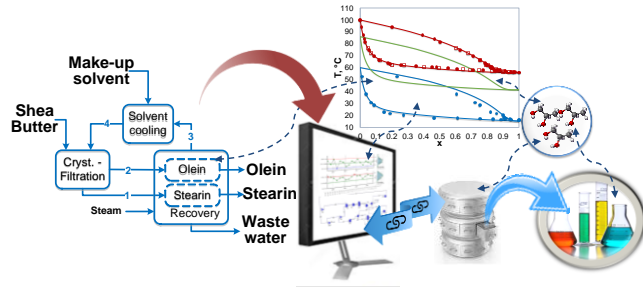
22 (68) Boulamanti, A.; Moya, J. A. Production costs of the chemical industry in the EU and other  
23 countries: Ammonia, methanol and light olefins. *Renew Sustain Energy Rev*. **2017**, 68, 1205-1212.  
24  
25  
26

27 (69) Klemeš, J. J.; Varbanov, P. S.; Wan Alwi, S. R.; Manan, Z.A. Process Integration and  
28 Intesnification. Saving Energy, Water and Resources. Berlin: Walter de Gruyter GmbH; **2014**.  
29  
30  
31

32 (70) Kemp I. C. Pinch Analysis and Process Integration: A User Guide on Process Integration  
33 for the Efficient Use of Energy 2nd ed., Elsevier B.V.: Amsterdam, 2007.  
34  
35  
36

37 (71) Papadakis, E.; Tula, A. K.; Gani R. Solvent selection methodology for pharmaceutical  
38 processes: Solvent swap. *Chem Eng Res Des* **2016**, 115, 443–61.  
39  
40  
41  
42  
43  
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## Abstract TOC Graphic



KEYWORDS: lipid, process design, shea butter, solvent fractionation, process heat integration, process modelling and simulation, lipid processing