Characterization of Cocoa butter saturated with supercritical CO₂:
Experimental set-up and Modelling

Pedro Santos a,b; Luís Padrela a; Brice Calvignac b; Elisabeth Rodier b; Henrique A. Matos a

a DEQB, Departamento de Engenharia Química e Biológica, Instituto Superior Técnico, Lisboa, Portugal
b Chemical Engineering Laboratory for Particle Solids, École des Mines d’Albi-Carmaux, F810193 Albi, France

Abstract
The main objective of this work was to study and to characterize cocoa butter and the binary system cocoa butter/supercritical carbon dioxide (SC-CO₂). In this way, it was measured the density and the solubility of the heavy phase in equilibrium at high pressures at 40 and 50ºC, as the density and compressibility of cocoa butter.

The density measurements were done through an autoclave with a sapphire window that can be under high pressures and an apparatus to measure the density, which bases in oscillating U-tube principle. The solubility was measured using a synthetic method, through a cell with variable volume. At last, the compressibility measurements were done using a porosimeter of mercury.

The obtained results were modelled in function of pressure. For the density and compressibility of the binary system (cocoa butter/SC-CO₂) and of cocoa butter it was used the Tait Equation and the Modified Tait Equation. The solubility was modelled by the Peng-Robinson Equation of State with two mixing rules: Van der Waals (vdW) and Panagiotopoulos-Reid (P&R). For the solubility calculations of the cocoa butter model-compound was considered the triglyceride 1-palmitoyl-2-oleoyl-3-stearoylglycerol (POS) since it is the major triglyceride of cocoa butter.

The thermo physical properties of the cocoa butter were predicted by four estimation methods: Ambrose, Joback, Constantinou-Gani and Fedors.

Key words: Cocoa Butter; Supercritical Carbon Dioxide (SC-CO₂), Density, Solubility, Compressibility, Tait Equations, Modified Tait Equations, Peng-Robinson Equation of State, Properties estimation methods.

1. Introduction
Cocoa butter is a vegetable fat, characterized by a complex structure that contains different types of triglycerides. This compound is very used in food industry, more specifically in the manufacturing of chocolate, which is the responsible of a good taste of chocolate.

In the development of chemical processes that involves supercritical fluids, it is very important to know solubility data or phase equilibria data (thermodynamic behaviour). The main application of supercritical fluids is extraction (SCFE), but recently this kind of fluids started to be applied as solvents in micronisation processes, as the process for the production and fractionation of fine particles from gas saturated (PGSS), Crystallisation from supercritical fluids; Rapid expansion of supercritical solutions (RESS); and fast antisolvent recrystallisation. In this line, the possible application of micronisation processes in cocoa butter with supercritical carbon dioxide in food, cosmetic and pharmaceutical industries took to many studies and investigations in order to know well the binary system.

Despite, the novelty of micronisation processes, SCFE still to be the main application of the supercritical fluids. This kind of extraction can be found, especially, in food industry, where it is used to extract resin, aromas, fats, oils, etc.

Beyond of this, there is a new process of extraction of cocoa butter from the cocoa beans, which is gas assisted mechanical expression (GAME). This process is a mechanical process (pressing) helped by supercritical carbon dioxide (SC-CO₂). In this process the high solubility of SC-CO₂ allows to increase the yield of cocoa butter.[4]

The supercritical fluids properties, such as good solvent power due to a density near of liquids, low viscosity near the one of gas, low surface tension and diffusivities and mass transfer near to the gases, makes this kind of fluids subjects of many investigations. Carbon dioxide is the most used supercritical fluid because of many advantages, like low price. It is to expect that in several years the knowledge of supercritical fluids will increase a lot.

Objectives
In the present work the objective is to study and to characterize the binary system cocoa butter/SC-CO₂. Therefore, it was measured the density and the solubility of the heavy phase in equilibrium at high pressures at 40 and 50ºC, as the density and compressibility of cocoa butter. For the measurements of density it was used an autoclave with a saphira window that can be under high pressures and an apparatus to measure the density,
which bases in oscillating U-tube principle. The solubility was measured with a synthetic method, through a cell with variable volume. At last, for measure the compressibility it was used a porosimeter of mercury.

The last step of the work was to model the experimental data in function of pressure. For the density and compressibility of the binary system (cocoa butter/SC-CO\textsubscript{2}) and of cocoa butter it was used the Tait Equation and the Modified Tait Equation. For the solubility, it was used the Peng-Robinson Equation of State with two mixing rules: Van der Waals (vdW) and Panagopoulos-Reid (P&R). For the solubility calculations of the cocoa butter model-compound was considered the triglyceride 1-palmitoyl-2-oleoyl-3stearoylglycerol (POS) since it is the major triglyceride of cocoa butter.

The thermo physical properties of the cocoa butter were predicted by the following estimation methods: Ambrose, Joback, Constatinou-Gani and Fedors methods.

2. Measures and modelling of the properties of the binary cocoa butter/SC-CO\textsubscript{2}

2.1. Density measurements

2.1.1. Material
The cocoa butter used was acquired from Gerkens Cacao (Wormer, The Netherlands). The Liquid CO\textsubscript{2} was acquired from Air Liquid SA, France with the purity 99,995%.

2.1.2. Experimental Setup
In the figure 1 it is presented the scheme of the diagram of the experimental device.

2.1.3. Experimental Procedure

- **Density measurements of the mixture Cocoa Butter/CO\textsubscript{2}**

Along the experience, the densities of samples of CO\textsubscript{2}-saturated cocoa butter were measured by the densimeter 11.

2.1.4. Results and Analysis

2.1.4.1. Density of cocoa butter

Figure 14 presents the density of pure cocoa butter, at different relative pressures, at 40\degree C and 50\degree C.

Comparing the density at the two temperatures, it is visible that the density decreases
with the temperature. In all range of pressures, the density at 40ºC is higher than 50ºC.

Figure 2: The density of pure cocoa butter at different pressures at 40 and 50ºC.

In figure 14, it is possible to observe that the cocoa butter density increases linearly with the increase of pressure, as it was expected. This behaviour was expected because with the increase of pressure the quantity of material in the same volume increases, therefore the density obviously increases. The slope of the correlations obtained have a similar value (same order of magnitude), which means that the increase of pressure makes the same effect for the two temperatures.

The regression lines for both temperatures have a good correlation coefficient ($R^2$), which shows the linear behaviour of the density with the pressure. However, the third point (100 bar) at both temperatures shows a high error, compared with the other points. This fact can be due to an error in the calibration at this pressure due to the proximity of the critical point of carbon dioxide.

2.1.4.2. Density of CO$_2$-saturated cocoa butter

The figure below presents the results of the density of CO$_2$/saturated cocoa butter as function of pressure.

Figure 3: The density of CO$_2$-saturated cocoa butter at different pressures at 40 and 50ºC.

In figure 3, it is shown the behaviour of the mixture CO$_2$-cocoa butter. As it is possible to observe, at both temperatures the density seems to increase linearly with the pressure, as it was seen for cocoa butter (figure 2). Beyond this, the behaviour of the density in function of pressure at both temperatures follow the same behaviour, as it proved by the same slope of the linear regression. Through this, it is possible to conclude that the increase of density just depends on the increase of CO$_2$ pressure. However, the density at 40ºC is higher in all range of pressures, like in the case of pure cocoa butter.

Analyzing the influence of CO$_2$ pressure in the density increase, it is evidenced that the magnitude of the density increase is small, proved by the small slope of the linear regression (0.0001).

However, this behaviour was already been observed for triglycerides in previous studies with cocoa butter [4] and corn oil [24]. Venter et al. [4] also observed this behaviour in soybean oil, coconut oil, palm kernel oil, castor oil, linseed oil, olive oil and palm oil.

The correlation coefficients present high values, especially in the case of 50ºC ($R^2$=0.9946). The mixture at 40ºC shows some points which are a little far from the regression line (higher errors), more specifically the points at 0, 125 and 250 bars. To add to this, it seems that the last four points are very well aligning in one different direction of the first three points. This behaviour can be attributed to difference of the properties of CO$_2$ near to the critical point and at higher pressures (CO$_2$ properties changes more gradually).

2.1.4.3. Comparison of cocoa butter density and CO$_2$-saturated cocoa butter density

In order to analyse the influence of the CO$_2$ in the density of the mixture CO$_2$-saturated cocoa butter it is present in figure 5 the density of the pure cocoa butter and the mixture at 50ºC.

Figure 4: The density of CO$_2$-saturated cocoa butter and pure cocoa butter at 50ºC.

In figure 5 is possible to observe the influence of CO$_2$ in the density of the studied mixture. The density of the mixture is higher in all range of pressures; however the difference between the densities isn’t constant. This difference increases with the increase of pressure. This fact is justified by the increase of solubility of CO$_2$ in cocoa butter with the increase of pressure. This fact was observed during the experimental procedure, when the liquid volume of the heavy phase increased with the increase of pressure. Through this, it is possible to conclude that the increase of CO$_2$ quantity in the mixture increases the density.

This behaviour was also observed in corn oil [24] and it was considered by the author as surprising because for all the pressures and temperatures the density of CO$_2$ is lower the density of cocoa butter. However, the density doesn’t depend only of the density of the compounds present in a mixture. Therefore, it is also related with the volume expansion and with the arrangement of the molecules of CO$_2$ in the middle of the triglycerides of cocoa butter.

As it was already referred, during the experimental procedure there was a volume expansion of the heavy phase but this expansion...
wasn’t much high. Venter et al. [4] was observed the same behaviour, which means that probably exist high volumes between the triglycerides (high molecules with long chains of carbons – cocoa butter review). Consequently, the CO₂ are placed in this free volume leading to a low volume expansion. Adding to this, the arrangement of the molecules in the mixture also influences the volume expansion, as the density. In way of conclusion, in the same volume there would be more molecules due to replacing free volumes by the molecules of CO₂ that obviously increase the density.

2.1.4.4. Comparison of experimental data with bibliographic data

The next figure will present the experimental data obtained in this work and data from bibliography [4] in order to compare the different results.

Figure 5: The density of CO₂-saturated cocoa butter of the present work and from bibliography [4].

The density values of the bibliography reference [4] at 40ºC increase linearly with the pressure for pressures above 50 bar. This behaviour was also verified for corn oil [24]. These behaviours are probably due to the proximity of the critical region of carbon dioxide (T_C=31.1ºC and P_C=73.8 bar), which is characterized by a high instability.

In the case of experimental data obtained in this work, this behaviour isn’t so evident. However, as it has already been discussed above, it seems that the last four points aren’t well align with the first three points (figure 3), which is possibly justified by the same reason, proximity of critical point of carbon dioxide. At 50ºC this behaviour wasn’t verified, probably due to the fact of being farther away of the critical point. Beyond this, in Venter and all [4], it was verified the same behaviour for high temperatures (80 and 100ºC) – linearly increase of density with the increase of pressure, in all range of pressures.

Analyzing the experimental values and comparing with the data of Venter and all [4], it is clear that the density values of the bibliography reference are higher than the values obtained during the experimental procedure. With the exception of the first point (at 0 bar), where the difference is minimal, all the other points has an average difference of 1.7%, which is a small error. Despite the fact of the supplier of cocoa butter for both experiences had been the same (Gerkens Cacao), the difference between the values could be justified by a possible difference in a composition of the cocoa butter because the composition of cocoa butter depends on the origin of the cocoa beans. A possible difference in the composition would influence the solubility of CO₂ in cocoa butter, influencing by this way the results. Other fact that should be mentioned is that it isn’t known the precision of the results of bibliography data [4], or how the measurements were done. In the experimental work, all the measurements were done after achieving the equilibrium. The criteria used to guarantee that equilibrium had already been achieved were to keep sure that the pressure, temperature and density values don’t vary. Beyond this, all the measurements were made at least three times, in order to minimize possible errors.

2.1.5. Modelling of density and compressibility with Tait and Modified Tait Equation

2.1.5.1 Tait Equation

The Tait Equation, is known by representing very well the compressibility data of solids at high pressures. For liquids, this equation fits the experimental measurements over a more limited pressure range. However, the Tait Equation (under the form of equation (I)) will be tested for the solid and liquid cocoa butter and for the mixture of CO₂-saturated cocoa butter.

\[
\frac{PV_0}{v_0 - v} = \frac{\pi}{A} + \frac{P}{A}
\]  

The Tait equation under the form of equation (I) is a linear pressure equation, which represents the inverse of compressibility in function of pressure. For that it is required the specific volume, which is the inverse of the density. In this way, with density data is possible to determine the compressibility.

- Cocoa Butter at 40 and 50ºC

Figure 21 shows the fit of the experimental results of liquid cocoa butter at 40 and 50ºC with the Tait Equation.

Figure 6: The fit of the experimental of cocoa butter results at 40 and 50ºC with Tait Equation
Analyzing the figure 7, it is clear that Tait equation doesn’t fit the results obtained, revealing a small regression coefficient at both temperatures. The highest error was verified at 100 bar, as expected (highest deviations in figure 2).

According to Dymond and Malhotra [13], the Tait Equation represents well the compressibility at high pressures. Adding to this, the last three points are aligning in the same direction. In this way, the next figure presents the modelling of the last three points.

![Figure 7: The fit of the last three experimental points of cocoa butter results at 40 and 50ºC with Tait Equation](image)

Figure 7: The fit of the last three experimental points of cocoa butter results at 40 and 50ºC with Tait Equation

Figure 8 shows that, considering only the last three points, the Tait equation fits in a reasonable way the experimental results. However, the trends verified at 40 and 50ºC are different. According to the figure 8, the compressibility at 40ºC increases with the increase of pressure, and at 50ºC decrease with the increase of pressure. However, it was expected to verify that the compressibility decreases with the increase of pressure at both temperatures, as it was verified at 50ºC.

The compressibility is a material capacity to compress. Therefore, with the increase of pressure (compression), this capacity decreases because the free volumes between the molecules decrease. In this way, it was expected to obtain in a figure 8 (where the inverse of compressibility is represented) two correlations with positive slopes.

The highest deviations were obtained at 100 bar. These deviations were already observed in figure 14, and they can be justified by an error in the calibration at this pressure due to the proximity of carbon dioxide. 

- **CO₂-saturated cocoa butter**

In the next figure it is presented the inverse of compressibility as function of pressure of CO₂-saturated cocoa butter.

![Figure 8: The fit of the experimental of CO₂-saturated cocoa butter results at 40 and 50ºC with Tait Equation](image)

Figure 8: The fit of the experimental of CO₂-saturated cocoa butter results at 40 and 50ºC with Tait Equation

Through the figure 9 it is possible to observe that the Tait Equation fits well the experimental data at 40ºC, with a high regression coefficient. However, analyzing in deep way, it is possible to verify that the highest errors are at 80 and 100 bar at 50ºC and 80 bar at 40ºC. These high errors can be justified by the same reason already referred (error in the calibration due to the proximity of CO₂ critical point). At 40ºC, the density was measured at high pressure (120 bar), more distant from the CO₂ critical point. In this way, next figure shows the representation of the inverse of compressibility as function of pressure of CO₂-saturated cocoa butter for pressures above 100 bar.

![Figure 9: The fit of the experimental of CO₂-saturated cocoa butter results at 40 and 50ºC with Tait Equation for pressures above 100 bar](image)

Figure 9: The fit of the experimental of CO₂-saturated cocoa butter results at 40 and 50ºC with Tait Equation for pressures above 100 bar

For pressures above 100 bar, the Tait equation fits well the experimental results, with high regression coefficients for both pressures. Through the last figures, it is possible to conclude that If there wasn’t that deviation at 80 and 100 bar, the Tait equation would have fitted better all the experimental results.

The figures 9 and 10 shows that the compressibility decreases with the increase of pressure at both temperatures, as expected. However, according to figure 10, the decrease of compressibility is sharper at lower temperatures (sharper slope).
2.1.5.2. The Modified Tait Equation

The Modified Tait equation (equation (2)) is an equation used to modeling the density or specific volume as a function of pressure for liquids or liquid mixtures at high pressures. Therefore, this equation was used to modeling the density of cocoa butter and CO₂-cocoa butter saturated at 40 and 50°C, at high pressures.

\[
\frac{\rho - \rho_0}{\rho} = C \log \left( \frac{B + p}{B + p_0} \right) \tag{2}
\]

The parameters \( B \) and \( C \) were determined trough the minimization of the absolute average deviation equation (equation (3) – AAD) using the Solver function of Excel. The minimization of the equation (3) was achieved by the variation of the parameters of modified Tait Equation.

\[
AAD = \frac{1}{N} \sum \frac{\left( \frac{\rho - \rho_0}{\rho} \right)_{\text{calculated}} - \left( \frac{\rho - \rho_0}{\rho} \right)_{\text{measured}}}{\left( \frac{\rho - \rho_0}{\rho} \right)_{\text{measured}}} \tag{3}
\]

Where, \( N \) is the number of points, \( \rho_0 \) and \( \rho \) the density at atmospheric and high pressure, \( \left( \frac{\rho - \rho_0}{\rho} \right)_{\text{calculated}} \) is the calculation of the expression using the Modified Tait equation and \( \left( \frac{\rho - \rho_0}{\rho} \right)_{\text{measured}} \) is the calculation of the expression using the experimental data.

- Cocoa Butter

The following figures show the representation of \( \left( \frac{\rho - \rho_0}{\rho} \right) \) measured and calculated in function of \( \log(B + p) \) at 40 and 50°C.

As it is possible to see in the figures 11 and 12, the modified Tait equation fitted in a reasonable way the experimental results. The second point (100 bar) presents the highest error.

- CO₂-saturated cocoa butter

The modified Tait equation was also applied to the mixture CO₂-saturated cocoa butter. In the next table it is presented the values of the parameter and their errors.

In the next figures are presented the representation of \( \left( \frac{\rho - \rho_0}{\rho} \right) \) measured and calculated in function of \( \log(B + p) \) at 40 and 50°C.
Through the figures 13 and 14, it is possible to conclude that the modified Tait equation is a good tool to model the density in function of pressure (low errors).

Table 1 present a resume of the AAD (Equation (3)) of Modified Tait Equation and Tait Equation, in order to compare both Equations.

Analyzing the table 1, it is evident that the AAD of Modified and Tait Equation (considering all the experimental points) are very similar. These results are in agreement with Hayward [13], which considered that the Modified Tait Equation didn’t have advantageous over the Tait Equation, referring that it didn’t fit the experimental data so well.

The AAD obtained for cocoa butter are higher than the values obtained for CO₂-saturated cocoa butter. These high AAD values are due to the density measurements at 100 bar, where high errors were obtained. The AAD of the Modified Tait equation without the experimental point at 100 bar decrease to 4%.

The Tait equation presents small AAD values for pressures above 100 bar, especially for cocoa butter. However, through this it isn’t possible to conclude if the Tait equation fits well the experimental data for pressures above 100 bar or if the Tait equation didn’t fit well the experimental results in all range of pressure due to a possible error in calibration.

The Tait Equation and the Modified Tait Equation revealed to be good tools for the modelling of density and compressibility of CO₂-saturated cocoa butter in all range of pressure. For cocoa butter, high errors were obtained at 100 bar. However, both equations are empirical and don’t have physical meaning, which complicate the evaluation of the parameters and of the equations.

<table>
<thead>
<tr>
<th>Compound/Mixture</th>
<th>T (ºC)</th>
<th>AAD of Modified Tait Equation (%)</th>
<th>AAD of Tait Equation (%)</th>
<th>AAD of Tait Equation (%) – pressures above 100 bar</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cocoa Butter</td>
<td>40</td>
<td>11.4</td>
<td>9.4</td>
<td>1.1</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>11.4</td>
<td>11.8</td>
<td>0.9</td>
</tr>
<tr>
<td>CO₂-Saturated Cocoa Butter</td>
<td>40</td>
<td>2.7</td>
<td>2.7</td>
<td>1.5</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>4.6</td>
<td>4.5</td>
<td>0.9</td>
</tr>
</tbody>
</table>

2.2. Solubility measurements

2.2.1. Material

The cocoa butter used was acquired from Gerkens Cacao (Wormer, The Netherlands). The Liquid CO₂ was acquired from Air Liquid SA, Portugal with the purity 99.995%.

2.2.2. Experimental Setup

In the figure 8 it is presented the scheme of the diagram of the experimental device. This apparatus is a development of the apparatus used by Costa et al [30].

The apparatus can be divided in three zones: Carbon dioxide (CO₂) admission zone; Calibrated volume zone and Phase Equilibria zone.

2.2.3. Experimental Procedures

The solubility was measured through a Synthetic Method. The synthetic methods consist in the determination of all the conditions of pressure, temperature and composition where a change of
phase occurs without the need of extract samples from the system.

The experimental procedure in this type of methods consists in putting known quantities of the compounds in a cell with variable volume, and by varying the volume adjusts the pressure and temperature of the system a homogenous phase (phase transition) is achieved. In this way, with visual detection of bubble, dew and fusion points or transition for supercritical state it is possible to get equilibria lines \((P, T \text{ and } x)\) \cite{28}.

2.2.4. Results and Discussion

2.2.4.1. Solubility of SC-CO\(_2\) in cocoa butter

Figure 8 shows the solubility of CO\(_2\) (weight percentage) in cocoa butter at different pressures at 40°C and 50°C.

![Figure 8: The solubility of CO\(_2\) in cocoa butter at different pressures at 40°C and 50°C.](image)

Figure 15: The solubility of CO\(_2\) in cocoa butter at different pressures at 40 and 50°C.

The increase of solubility with pressure is explained by the Henry’s law states. According to this law, the solubility of a gas in a liquid is directly proportional to the pressure of that gas above the surface of the solution. By increasing pressure, the CO\(_2\) molecules are induced to solubilise in cocoa butter in order to relief the pressure that has been applied.

In another way, the increasing of temperature takes to a decrease of solubility. The increase of temperature augments the kinetic energy, which increases the motion of the molecules that break intermolecular bonds and escape from the solution.

The variation of the solubility with the pressure is in the agreement which what was already referred. The increase of solubility justifies why the increase of density of the mixture CO\(_2\)-cocoa butter is sharper than for cocoa butter (figure 17). The increase of solubility was also verified through the low volume expansion of the heavy phase during the density measurements.

2.2.4.2. Comparison of experimental data with bibliography data

Figure 17 presents the experimental data obtained in this work at 40°C and data from Venter \textit{et al.} \cite{4}, Kokot \textit{et al.} \cite{3} and Calvignac \textit{et al.} (data not published) \cite{37} in order to compare the different results.

![Figure 16: The solubility of CO\(_2\) in cocoa butter at 40°C from different references (Venter \textit{et al.} \cite{4}, Kokot \textit{et al.} \cite{3} and Calvignac \textit{et al.} \cite{37}).](image)

Analyzing the figure 17 it is possible to observe that the data points at low pressure are very similar, with small differences. However, for high pressures the solubility differences increase, showing a different trend.

The solubility data of Venter \textit{et al.} \cite{4} reaches a maximum of 36 wt % at 200 bar and remains constant at higher pressures. According to Venter \textit{et al.} \cite{4}, the same behaviour was already observed in seed oil, rapeseed oil and palm oil. In the other cases, the solubility doesn’t reach any maximum, showing a growing trend. In Kokot \textit{et al.} \cite{3} the solubility at high pressures continues with a sharp growing.

As it is possible to observe in figure 17, the solubility of CO\(_2\) in cocoa butter in Calvignac \textit{et al.} \cite{37} is lower than the other data. The solubility shows a growing trend and it seems that is near to reach a maximum. In this experimental work, the solubility shows a trend very similar to Kokot \textit{et al.} \cite{3}.

A possible reason to explain the differences of the experimental data obtained of the bibliography data is the cocoa butter used. Despite the fact that the supplier was the same of Venter \textit{et al.} \cite{4} (Gerkens Cacao), the cocoa butter could be from different batches, which can influence de composition. Besides that, the cocoa butter composition depends also of its origin and the age of the plant. Another possible reason is the experimental method used. In the previous works, all the solubility measurements were carried out by analytical methods, with an autoclave. In the present work, the solubility was measured through a synthetic method, which can justify the differences between the data obtained.
2.2.5. Modelling of solubility with Peng-Robinson Equation of State

The next step of this work is to model the solubility of CO$_2$ in cocoa butter with the Peng-Robinson Equations of State (equation (4)), which is recommended in Valderrama et al. [14] for mixtures with a supercritical component. For that, the critical properties of cocoa butter (such as $P_C$, $T_C$, $T_B$ and $\omega$) are required.

$$P = \frac{RT}{V - b} - \frac{a(T)}{V(V + b) + b(V - b)}$$

where $a(T) = a_a(T_a, \omega) \left[ 1 + m(T_a - T_C)^2 \right]$

$$a_a = 0.45724 \frac{RT^{1.5}}{P_C}$$

$$b = 0.07780 \frac{RT}{P_C}$$

$T_C$ and $P_C$ were estimated through the definition and $\omega$ estimation was done after the estimation of other critical properties due to its dependency on those critical values. The next table presents the estimated values.

The cocoa butter is a vegetable fat composed by three main triglycerides: POS, POP and SOS, which account respectively for 34-45, 21-29.5 and 12.2-21.5% of the total triglycerides. For the modelling it was assumed that the cocoa butter properties are the same of POS because it is the triglyceride in majority. Besides, the three triglycerides are very similar, they are monounsaturated in sn-2 carbon (oleic acid – which means that they have similar dispositions) and the carboxylic acids of carbons sn-1 and 3 have similar properties (palmitic and stearic acid) [21].

There is a lack of information about triglycerides and the POS critical properties are unknown. In this way, the properties of POS have to be estimated.

2.2.5.1. Properties Estimation

The POS properties were estimated through a program (Aspen Plus 2006.5) using four methods, which are: Constatinou-Gani, Joback, Ambrose and Fedors methods. The table 2 shows the results obtained.

<table>
<thead>
<tr>
<th>Triglyceride</th>
<th>Method</th>
<th>$T_C$ (K)</th>
<th>$P_C$ (bar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>POS</td>
<td>Constatinou-Gani</td>
<td>917.526</td>
<td>3.379</td>
</tr>
<tr>
<td></td>
<td>Joback</td>
<td>917.526</td>
<td>3.379</td>
</tr>
<tr>
<td></td>
<td>Ambrose</td>
<td>917.526</td>
<td>3.379</td>
</tr>
<tr>
<td></td>
<td>Fedors</td>
<td>917.526</td>
<td>3.379</td>
</tr>
<tr>
<td>Tripalmitin</td>
<td>817.768</td>
<td>917.526</td>
<td>3.379</td>
</tr>
<tr>
<td></td>
<td>1636.180</td>
<td>917.526</td>
<td>3.379</td>
</tr>
<tr>
<td></td>
<td>1868.246</td>
<td>917.526</td>
<td>3.379</td>
</tr>
<tr>
<td></td>
<td>1811.830</td>
<td>917.526</td>
<td>3.379</td>
</tr>
<tr>
<td></td>
<td>905.559</td>
<td>917.526</td>
<td>3.379</td>
</tr>
<tr>
<td></td>
<td>762.400</td>
<td>917.526</td>
<td>3.379</td>
</tr>
<tr>
<td></td>
<td>889.140</td>
<td>917.526</td>
<td>3.379</td>
</tr>
<tr>
<td>Tripalmitin</td>
<td>Lee Kesler</td>
<td>1.3863678</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Definition</td>
<td>1.220611</td>
<td></td>
</tr>
<tr>
<td>Tripalmitin</td>
<td>1.650000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tripalmitin</td>
<td>1.819471</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tripalmitin</td>
<td>1.800400</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tripalmitin</td>
<td>1.686230</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tristearin</td>
<td>1.737092</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Comparing the values of the table 2 with the predicted values in Weber et al. [18] and Lim et al. [22] of Tripalmitin, Tristearin and Tristearin it is evident that the $T_B$ and $T_C$ values estimated by the Constatinou-Gani method are more similar than those predicted by the other methods. Besides that, according to Araújo et al. [17] the properties of fatty acids estimated with the Constatinou-Gani method were more accurate than the values predicted by methods that used experimental boiling temperature. Therefore, the chosen method to predict $T_B$ and $T_C$ was the Constatinou-Gani method.

The $P_C$ value predicted by the Constatinou-Gani method is also similar to those predicted in Lim et al. [32] for Tripalmitin and Tristearin. This same method was chosen to predict the $P_C$ of fatty acids and fatty acid esters in Araújo et al. [17].

These choices had been made according to predicted and experimental values obtained for other triglycerides. It is possible that the predicted value of other methods was better that the chosen values.

For the estimation of the acentric factor ($\omega$) the program Aspen Plus 2006.5 was used. The $\omega$ estimation was done through the definition of $\omega$ and Lee Kesler vapour pressure correlations. The estimation of acentric factor was done after the estimation of other critical properties due to its dependency on those critical values. The next table presents the estimated values.

Table 3: Acentric Factor estimated through the definition and Lee Kesler vapour pressure relations for POS, and Acentric Factor estimated for Tripalmitin, Tristearin and Tristearin [18], [22]

<table>
<thead>
<tr>
<th>Triglyceride</th>
<th>Method</th>
<th>$\omega$</th>
</tr>
</thead>
<tbody>
<tr>
<td>POS</td>
<td>Lee Kesler</td>
<td>1.863678</td>
</tr>
<tr>
<td></td>
<td>Definition</td>
<td>1.220611</td>
</tr>
<tr>
<td>Tripalmitin</td>
<td>1.650000</td>
<td></td>
</tr>
<tr>
<td>Tripalmitin</td>
<td>1.819471</td>
<td></td>
</tr>
<tr>
<td>Tripalmitin</td>
<td>1.800400</td>
<td></td>
</tr>
<tr>
<td>Tristearin</td>
<td>1.686230</td>
<td></td>
</tr>
<tr>
<td>Tristearin</td>
<td>1.737092</td>
<td></td>
</tr>
</tbody>
</table>

Analyzing table 3, it is possible to conclude that both values are higher values than expected. According to the definition, the acentric factor measures the complexity of a molecule with respect to both geometry and polarity. Therefore, large molecules (such as triglycerides) have usually high $\omega$ values. Comparing both values with the bibliography values [18], [32], the $\omega$ value obtained by the Lee Kesler vapour pressure relations is more similar than the value obtained by the definition.

2.2.5.2. Interaction Parameters

In this work, the van der Waals (vdW) and Panagiotopoulos-Reid (P&R) were the mixing rules
used. The Peng-Robinson equation of state with P&R mixing rules is recommended by Valderrama et al. [14]. This recommendation was based on literature information and on the author experience. In this way, the P&R and vdW mixing rules were tested in order to compare the results obtained by both mixing rules and to chose which mixture rules should be used.

The vdW mixing rules have two binary parameters and it is also known as a quadratic mixing rule. The P&R mixing rule is nonquadratic with three binary parameters and is characterized by the introduction of a second interaction parameter, by making the $k_{ij}$ parameter concentration-dependent, transforming by this way in a nonquadratic mixing rule – Table 3.

The binary parameters (interaction parameters) of the mixing rules are determined by the minimization of the differences between predicted and experimental values. These calculations (binary parameters determination) were done with the program PE2000 (Phase Equilibria 2000), which was developed in the Professor Brunner’s research group at the Technical University of Hamburg-Harburg [33]. This program has been presented in many conferences and publications and often leads to a better convergence than Aspen.

The Phase Equilibria 2000 is a program that offers more than 40 different equations of state with up to 7 mixing rules, to correlate and predict phase equilibria. This program can be used for pure components and for mixtures (binary and ternary systems).

The binary parameters were obtained through the minimization of the equation (5) – AAD² absolute average deviation.

\[ AAD^2 = \frac{1}{n} \sum_{i=1}^{n} (x_{i}^{exp} - x_{i}^{calc})^2 \]

Where, $x_i$ is the mole fraction of the component I, $exp$ and $calc$ are the experimental and the calculated values, respectively. Beyond this, it was only considered the liquid phase data for the minimization of the equation (5) because the vapour phase wasn’t studied during the experimental work. Next table presents the interactions parameters and the respective error for mixing rules, vdW and P&R, at 40°C.

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>Mixing rule</th>
<th>Interaction parameters</th>
<th>AAD² (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>313.15</td>
<td>vdW</td>
<td>$k_0 = 0.0284$</td>
<td>2.0</td>
</tr>
<tr>
<td></td>
<td>P&amp;R</td>
<td>$k_0 = 0.0017$</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$k_0 = 0.0564$</td>
<td>4.7</td>
</tr>
<tr>
<td></td>
<td>vdW</td>
<td>$k_0 = 0.0533$</td>
<td>4.6</td>
</tr>
<tr>
<td></td>
<td>P&amp;R</td>
<td>$k_0 = 0.0207$</td>
<td>4.1</td>
</tr>
</tbody>
</table>

Analyzing and comparing the results obtained with the two mixing rules, it is evident that the error obtained with vdW with two parameters at 313.15 K is lower than with P&R with three parameters. At 323.15 K, the P&R mixing rule error is lower than the vdW error, but the values are very similar. According to these results, despite P&R mixing rule having three parameters fitted to the experimental measurements it didn’t produce better results than the vdW mixing rules. In this way, the vdW mixing rule was chosen for the modelling of the solubility of CO₂ in cocoa butter with the Peng-Robinson Equation of State due its simplicity and lower correlation deviations ($AAD^2$).

Usually, it is considered that the interactions parameters are temperature independent. However, as it is possible to observe in Table 4, that the interaction parameters of both mixing rules vary with temperature, which makes impossible to use the same interaction parameters at various temperatures.

**2.5.3. Solubility Modelling**

Figure 18 present the modelling of solubility using the PR equation and vdW mixing rules.

As it is possible to observe in figure 18, the models show a different trend from the experimental points at both temperatures. According to the models, the solubility reaches a maximum at 105 and 128 bar, at 313.15 and 323.15 K, respectively. After this maximum, the solubility starts to decrease with the increase of pressure. At the same pressures, the Peng-Robinson equation of state predicts that the vapour – liquid equilibria changes to liquid – liquid equilibria. However, during the experimental procedure this phenomenon wasn’t observed, which justify the different trends of the results and models.

Despite this phenomenon wasn’t observed during the experimental procedure, it was observed and predicted by Weber et al. [18], in the studies of
vapour – liquid equilibria of tristearin, tripalmitin and triolein in CO₂. Besides, in this work it was assumed that cocoa butter properties were the same as of POS (since this triglyceride is the major component and the other triglycerides are very similar), which can’t correspond to reality. On other hand, Peng-Robinson Equation of State may not be the best equation of state to describe this system. Adding to this, all the POS properties were predicted by estimation methods, which mean that there is an inherent error.

3. Conclusions

According to the obtained results, the densities of the binary and cocoa butter increases with the increase of pressure and decreases with the increase of temperature. However, the increase of density in the binary is sharper than for cocoa butter, due to the increase of CO₂ solubility. The Tait and Modified Tait Equation revealed to be a good tool to modelling the density and compressibility in function of pressure. The better correlations (lower deviations) were obtained with the Tait Equation. However, these equations are empirical, without physical mean, making difficult to evaluate its parameters.

The CO₂ solubility in cocoa butter increases with the increase of pressure and with the decrease of temperature, as expected. These phenomena were also observed in the density measurements, through the volume expansion of the heavy phase. The solubility behaviour was in the agreement with the Henry’s law states.

The last step was to model the solubility in function of pressure with the Peng-Robinson EoS using van der Waals (vdW) and Panagiotopoulos & Reid (P&R) mixing rules. Lower deviations were obtained with the vdW mixing rules, which have only two interaction parameters. The Peng-Robinson Equation modelling didn’t describe the obtained results, showing a different trend and predicting a phase change that wasn’t observed.

5. References

[3]. Kokot K.; Knez, Ž.; Bauman, D.; Petkov, S.; Brunner, G.; and Panagiotopoulos & Reid (P&R) mixing rules. Lower deviations were obtained with the vdW mixing rules, which have only two interaction parameters. The Peng-Robinson Equation modelling didn’t describe the obtained results, showing a different trend and predicting a phase change that wasn’t observed.

5. References

[3]. Kokot K.; Knez, Ž.; Bauman, D.; Petkov, S.; Brunner, G.; and Panagiotopoulos & Reid (P&R) mixing rules. Lower deviations were obtained with the vdW mixing rules, which have only two interaction parameters. The Peng-Robinson Equation modelling didn’t describe the obtained results, showing a different trend and predicting a phase change that wasn’t observed.

5. References

[3]. Kokot K.; Knez, Ž.; Bauman, D.; Petkov, S.; Brunner, G.; and Panagiotopoulos & Reid (P&R) mixing rules. Lower deviations were obtained with the vdW mixing rules, which have only two interaction parameters. The Peng-Robinson Equation modelling didn’t describe the obtained results, showing a different trend and predicting a phase change that wasn’t observed.

5. References

[3]. Kokot K.; Knez, Ž.; Bauman, D.; Petkov, S.; Brunner, G.; and Panagiotopoulos & Reid (P&R) mixing rules. Lower deviations were obtained with the vdW mixing rules, which have only two interaction parameters. The Peng-Robinson Equation modelling didn’t describe the obtained results, showing a different trend and predicting a phase change that wasn’t observed.

5. References

[3]. Kokot K.; Knez, Ž.; Bauman, D.; Petkov, S.; Brunner, G.; and Panagiotopoulos & Reid (P&R) mixing rules. Lower deviations were obtained with the vdW mixing rules, which have only two interaction parameters. The Peng-Robinson Equation modelling didn’t describe the obtained results, showing a different trend and predicting a phase change that wasn’t observed.


[32]. Lim, C.S., Manan, Z.A., Sarmidi, M.R., Simulation Modelling of the Phase Behaviour of Palm Oil-Supercritical Carbon Dioxide, JAOCs, 2003:Vol. 80, no. 11.


