Gas Assisted Mechanical Expression of Cocoa Nibs

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GAS ASSISTED MECHANICAL EXPRESSION OF COCOA NIBS

DISSERTATION

to obtain
the doctor's degree at the University of Twente,
on the authority of the rector magnificus,
prof. dr. W.H.M. Zijm,
on account of the decision of the graduation committee,
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by

Magdalena Jacomina Venter

born on 18 February 1978

in Pretoria, South Africa

This dissertation is approved by the promoter
Prof. dr. ir. A.B. de Haan

and the assistant promoter
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Loof die Here, want Hy is goed. Aan Sy liefde is daar geen einde nie.

Give thanks to the Lord, for He is good. His love endures forever.

Psalm 136: 1

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28 June 2006

Contents

Summary

The objective of this thesis was to investigate the expression of cocoa nibs and a way to optimise the cocoa butter yield (defined as the mass of cocoa butter recovered as a percentage of the total cocoa butter content) obtainable from cocoa nibs without modifying the composition of the cocoa butter. Currently the majority of cocoa butter produced commercially is obtained by pressing cocoa liquor in hydraulic filter presses. This requires the cocoa nibs to be finely grinded to liquor prior to pressing. Considerable savings are possible if cocoa nibs can be pressed instead of cocoa liquor. Therefore the expression behaviour of cocoa nibs was studied in a custom built hydraulic filter press as function of temperature, the applied mechanical pressure, the mechanical pressure profile and the moisture content. The maximum cocoa butter yield is achieved at 100 °C and a pressure of 60 MPa. The cocoa butter yield increases with pressure up till 60 MPa, but remains virtually constant when the pressure is increased further. At this pressure a cocoa butter yield of 80 % was obtained when dry cocoa beans were used. Industrial expression operations normally utilises a linearly increasing pressure profile at the beginning, whereafter the pressure is kept constant for the remaining time of pressing. However, our experiments showed that this does not increase the cocoa butter yield compared to experiments where a constant pressure was used for the entire pressing time. The mass of nibs being pressed as well as the duration of the pressing time also do not significantly influence the cocoa butter yield. The optimum moisture content with respect to cocoa butter yield is 1.3 wt. % (wet basis). Using cocoa nibs at this moisture content result in an absolute increase in cocoa butter yield of around 5%. The rate of expression increases with an increase in temperature or a decrease in moisture content. Higher cocoa butter yields (up to 90 %) were achieved when cocoa liquor was pressed instead of cocoa nibs at a temperature of 100 °C.

A predictive mathematical model can aid in the optimisation and understanding of the expression behaviour of cocoa nibs. Therefore the ability of the Shirato model to describe the expression of dry cocoa nibs in a hydraulic press at pressures of 20 – 80 MPa was compared with that of a numerically solved conservation laws model based on mass and momentum balances. The Shirato model is an analytical solution of the conservation laws model that assumes constant material properties (porosity and filtration resistance). Furthermore the model also assumes the expression process to consist of two stages. In the first stage, the primary consolidation stage, the material is assumed to exhibit only elastic behaviour. During the second stage, the so-called secondary consolidation stage, creep is assumed to occur as well. During creep the material exhibits viscous-elastic behaviour. The numerically solved conservation laws model assumes the porosity and filtration resistance to be the result of purely elastic

material behaviour and to vary within the filter cake as a result of the solids compressive pressure profile within the cake.

Experimental data were used to determine the four material constants involved in both models at 40, 80 and 100 °C. The Shirato model more accurately describes the final average porosity at different pressures when dry cocoa nibs are expressed. It was therefore decided not to do any further calculations with the numerically solved conservation laws model. The calculation results of the Shirato model followed the experimentally observed trends when calculations were made for different pressures, pressing times and mass of cocoa nibs pressed. The Shirato model was also used to describe the expression behaviour of cocoa liquor at 100 °C and pressures of 20-70 MPa. Cocoa liquor is a slurry containing solid particles (cocoa solids) in a free-flowing liquid (cocoa butter), and therefore the transition time between filtration and expression needs to be determined first. It was calculated that the filtration stage is absent when cocoa liquor is expressed at pressures of 20 MPa and higher. However, the behaviour of cocoa liquor can only be accurately described with the Shirato model for the last part of the expression process (> 100 s).

In view of the relatively low cocoa butter yields obtained for cocoa nibs with conventional expression, it was decided to also investigate the performance of Gas Assisted Mechanical Expression (GAME). In GAME the solubility of supercritical CO_2 in cocoa butter is utilised to enhance the cocoa butter yields of mechanical expression. In a hydraulic press GAME consists of a CO_2 dissolution stage, a press stage and a depressurisation stage. GAME experiments with cocoa nibs were performed at 40-100 °C, CO_2 pressures of 0-20 MPa and effective mechanical pressures (defined as the difference between the applied mechanical pressure and the CO_2 pressure at the end of the experiment) of 20-50 MPa. GAME has a substantially higher yield than conventional mechanical expression for the recovery of cocoa butter from dry cocoa nibs, with the highest yield (87.1 %) obtained at 100 °C, a CO_2-pressure of 10 MPa and an effective mechanical pressure of 50 MPa. The cocoa butter yield increases with increasing CO_2 pressure until 10 MPa. The yield remains approximately constant for higher CO_2 pressures. In contrast to conventional expression GAME also allows the recovery of cocoa butter from cocoa nibs at temperatures below the melting point of pure cocoa butter. The melting point of CO_2-saturated cocoa butter decreases from 35 °C (pure cocoa butter) at atmospheric pressure to 23 °C at CO_2 pressures higher than 5 MPa. The influence of several process parameters on GAME of cocoa nibs was also investigated. It was found that neither the mass of cocoa nibs used, the duration of the press stage nor the mechanical pressure profile has a significant influence on the final cocoa butter yield. However, the moisture content of the nibs determines the behaviour of the solid structure during the press stage. It therefore determines the cocoa butter yield that can be achieved as well

as the rate with which it can be obtained. The maximum yield is obtained at a moisture content of 1.3 wt. % (wet basis). Lower moisture contents result in a faster compression of the cake. At 100 °C and moisture contents higher than 5.5 wt. % the cocoa solids are extruded through the filter medium. Similar yields were obtained when cocoa liquor and cocoa nibs were used in GAME experiments at the same conditions. Higher cocoa butter yields can be achieved when multi-stage GAME is used instead of single stage GAME. An absolute increase in cocoa butter yield of 7 – 10 % was achieved when two-stage GAME was used instead of single stage GAME. GAME allows shorter process times to be used than conventional expression, and therefore increases the process capacity.

It was experimentally found that the pressing stage always ends with approximately the same liquid volume inside the filter cakes for both conventional expression and GAME experiments performed at the same temperature and effective mechanical pressure. However, in GAME a large part of the cocoa butter is replaced with CO_2 due to the high solubility of CO_2 in the cocoa butter. This CO_2 is removed through depressurisation and only the cocoa butter remains in the filter cake, resulting in an increased cocoa butter yield. In order to quantify this replacement effect a static analytical procedure was used to measure the solubility of CO_2 in cocoa butter, as well as the density and the viscosity of CO_2-saturated cocoa butter at 40, 80 and 100 °C and pressures of 2-35 MPa in a novel autoclave set-up. The highest solubility of CO_2 in cocoa butter (36 wt. %) occurs at 40 °C and 35 MPa. The measured solubilities differ from those previously reported in literature. This is attributed to differences in the cocoa butter used for measurements. The density of CO_2-saturated cocoa butter increases with pressure, whereas the viscosity decreases. The Grunberg equation was used to correlate the viscosity of CO_2-saturated cocoa butter. The theoretical GAME yields calculated with the measured data indicate that the cocoa butter yield is always underestimated with the assumption of equal volumes of liquid in GAME and conventional filter cakes at the end of the pressing stage. The mechanism is therefore more complex than replacement of the cocoa butter alone.

Cocoa butter consists of different triacylglycerols (TAG) with POP, POS and SOS accounting for the majority of the TAG. The cocoa butter produced with GAME was found to have the same POS/POP and SOS/POP ratios compared to conventionally expressed cocoa butter. Therefore it can be concluded that higher cocoa butter yields can be achieved with GAME without altering the composition of the cocoa butter when compared to conventional expression. When conventional expression is used yields of 90 % or higher can only be achieved when cocoa liquor is expressed. The optimum cocoa butter yield (> 90 %) when hydraulic presses are used to defatten cocoa nibs can be achieved by using GAME at 100 °C with a CO_2 pressure of 10 MPa in combination with an effective mechanical pressure of 60 MPa or higher and cocoa

nibs with a moisture content of 1.3 % (wet basis). The cocoa butter yield can be increased further by using the same conditions in a multi-stage GAME operation. This makes the future use of continuous extruders instead of batch wise operating hydraulic filter presses an attractive option.

Samenvatting

Het doel van dit proefschrift was het onderzoeken van de expressie van cacaonibs (geschilde, gebroken bonen) en het vinden van een manier om de cacaoboteropbrengst (gedefinieerd als de massa gewonnen cacaoboter als percentage van het totale cacaobotergehalte) van cacaonibs te optimaliseren zonder de samenstelling van de boter te veranderen. Momenteel wordt het merendeel van de commercieel geproduceerde cacaoboter gewonnen door het persen van cacaomassa in hydraulische filterpersen. Hiervoor dienen de cacaonibs fijngemalen te worden voor het persen. Wanneer cacaonibs geperst kunnen worden in plaats van cacaomassa, kan een aanzienlijke besparing gehaald worden. Daarom is het expressiegedrag van cacaonibs bestudeerd als een functie van temperatuur, de opgelegde mechanische druk, het drukprofiel en het vochtgehalte in een op maat gemaakte hydraulische filterpers. Bij 100 °C en 60 MPa werd de maximale hoeveelheid cacaoboter gewonnen. Bij drukken tot 60 MPa neemt de opbrengst toe, verder verhogen van de druk leverde een vrijwel constante opbrengst. Bij deze druk bedroeg de cacaoboteropbrengst 80% wanneer droge cacaonibs gebruikt werden. In de industriële praktijk wordt normaliter een lineair oplopende druk gebruikt in het begin van het expressieproces, waarna de druk constant gehouden wordt voor de resterende duur van de persing. Uit onze experimenten bleek echter dat dit de cacaoboteropbrengst niet verhoogt ten opzichte van het gebruik van een constante druk gedurende de hele periode. Zowel de hoeveelheid geperste cacaonibs als de duur van de persing hebben geen significante invloed op de cacaoboteropbrengst. Het optimale vochtgehalte wat betreft de cacaoboteropbrengst is 1.3 gewichtsprocent (natte basis). Bij gebruik van cacaonibs met dit vochtgehalte neemt de cacaoboteropbrengst toe met ongeveer 5 procentpunt. De snelheid van de expressie neemt toe met een toenemende temperatuur of een afnemend vochtgehalte. Bij een temperatuur van 100 °C werden hogere opbrengsten (tot 90%) gehaald wanneer cacaomassa werd geperst in plaats van cacaonibs.

Een voorspellend wiskundig model kan behulpzaam zijn bij het optimaliseren en begrijpen van het expressiegedrag van cacaonibs. Daarom is de mate waarin het Shiratomodel de expressie van droge cacaonibs in een hydraulische filterpers beschrijft bij drukken van 20 tot 80 MPa vergeleken met een numeriek opgelost model gebaseerd op de behoudswetten van massa en momentum. Het Shiratomodel is een analytische oplossing van het op behoudswetten gebaseerd model, waarbij is aangenomen dat de materiaaleigenschappen (porositeit en filtratieweerstand) constant zijn. Daarnaast is aangenomen dat het expressieproces opgedeeld kan worden in twee stadia. In het eerste stadium, primaire consolidatie, is aangenomen dat het materiaal alleen elastisch gedrag vertoont. In het tweede stadium vindt daarnaast ook kruip plaats. Het materiaal vertoont tijdens de kruip visco-elastisch gedrag. In het numeriek opgeloste model is aangenomen dat de porositeit en filtratieweerstand slechts het resultaat zijn van puur

elastisch gedrag en dat deze variëren in de koek als functie van de lokale druk op de vaste stof.

Om de vier materiaalconstanten te bepalen voor beide modellen is gebruik gemaakt van experimentele data bij 40, 80 en 100 °C. Het Shiratomodel beschrijft de uiteindelijke gemiddelde porositeit van droge cacaonibs bij verschillende drukken het beste. Op basis hiervan is besloten geen verdere berekeningen te doen met het numeriek opgeloste behoudswet-model. De met het Shiratomodel berekende resultaten volgden de experimentele trends wat betreft verschillende drukken, perstijden en geperste massa. Tevens is het Shiratomodel gebruikt om het expressiegedrag van cacaomassa te beschrijven bij een temperatuur van 100 °C en drukken van 20-70 MPa. Omdat cacaomassa een suspensie is van vaste (cacao)deeltjes in een vrij-vloeiende vloeistof (cacaoboter), dient allereerst de overgangstijd van filtratie naar consolidatie bepaald te worden. Berekeningen leerden dat geen filtratie plaatsvindt tijdens de expressie van cacaomassa bij drukken van 20 MPa en hoger. Desondanks is het Shiratomodel alleen in staat om het laatste stadium(>100 sec.) van het expressieproces accuraat te beschrijven.

In het licht van de relatief lage cacaoboteropbrengsten die met conventionele expressie behaald zijn, is besloten om tevens de mogelijkheden van Gas-geAssisteerde Mechanische Expressie (GAME) te onderzoeken. Bij GAME wordt gebruik gemaakt van de oplosbaarheid van superkritisch koolstofdioxide in cacaoboter om de cacaoboteropbrengst van mechanische expressie te verhogen. GAME bestaat in een hydraulische pers uit een CO_2-oplosfase, een persfase en drukaflaatfase. GAME-experimenten met cacaonibs zijn uitgevoerd bij temperaturen van 40-100 °C, CO_2-drukken van 0 tot 20 MPa en effectieve mechanische drukken (gedefinieerd als het verschil tussen de opgelegde mechanische druk en de CO_2-druk op het eind van het experiment) van 20-50 MPa. GAME resulteert in aanzienlijk hogere cacaoboteropbrengsten dan conventionele mechanische expressie van droge cacaonibs, waarbij de hoogste opbrengst (87.1%) werd gehaald bij 100°C, een CO_2-druk van 10 MPa en een effectieve mechanische druk van 50 MPa. Tot 10 MPa stijgt de cacaoboteropbrengst met stijgende CO_2-druk, hierboven blijft de opbrengst ongeveer constant. In tegenstelling tot conventionele expressie is het met GAME mogelijk om cacaoboter te winnen bij temperaturen onder het smeltpunt van cacaoboter. Het smeltpunt van cacaoboter verzadigd met CO_2 daalt van 35 °C bij atmosferische druk (pure cacaoboter) tot 23 °C bij CO_2 drukken hoger dan 5 MPa. Tevens is de invloed van een aantal procesparameters op het GAME-proces bepaald. Zowel de gebruikte hoeveelheid cacaonibs, de duur van de persing als het gebruik van een drukprofiel hadden geen significante invloed op de cacaoboteropbrengst. Het vochtgehalte daarentegen bepaald de structuur van de vaste stof tijdens de persing. Daarom bepaald dit zowel de maximaal haalbare cacaoboteropbrengst als de snelheid waarmee dit

bereikt kan worden. De maximale opbrengst wordt bereikt bij een vochtgehalte van 1.3 gewichtsprocent (natte basis). Bij lagere vochtgehaltes treed een snellere compactie van de koek op. Bij 100 °C en een vochtgehalte hoger dan 5.5 gewichtsprocent wordt de vaste stof door het filtermedium geperst. Met het GAME-proces worden bij gelijke condities vergelijkbare opbrengsten gehaald voor zowel cacao massa als cacaonibs. Door gebruik te maken van meerstaps-GAME worden hogere cacaoboteropbrengsten gehaald dan wanneer slechts enkelstaps-GAME gebruikt wordt. Door gebruik te maken van GAME, kunnen kortere procestijden gehanteerd worden dan bij conventionele expressie en daarmee een hogere productiecapaciteit gehaald worden.

Uit de experimenten is gebleken dat de persstap voor conventionele expressie en GAME bij gelijke temperatuur en effectieve druk resulteert in een vrijwel gelijk vloeistofvolume in de perskoek. Bij GAME is echter een groot deel van de cacaoboter verdrongen door CO_2, vanwege de hoge oplosbaarheid van CO_2 in de cacaoboter. Door het aflaten van de CO_2-druk wordt deze verwijderd en blijft alleen cacaoboter achter in de perskoek, wat resulteert in een hogere cacaoboteropbrengst. Om dit verdringingseffect te kwantificeren is een statisch analytische methode gebruikt om zowel de oplosbaarheid van CO_2 in de cacaoboter als de dichtheid en viscositeit van cacaoboter verzadigd met CO_2 te bepalen bij 40, 80 en 100 °C en drukken van 2-35 MPa in een vernieuwende autoclaafopstelling. De hoogste oplosbaarheid (36 gewichtsprocent) werd gevonden bij 40 °C en 35 MPa. De gemeten oplosbaarheden verschillen van eerder in de literatuur gerapporteerde waarden. Dit verschil wordt toegeschreven aan de verschillen in de gebruikte cacaoboter. De dichtheid van cacaoboter verzadigd met CO_2 stijgt als functie van de druk, terwijl de viscositeit daalt. De Grunberg-vergelijking is gebruikt om de viscositeit van de cacaoboter verzadig met CO_2 te beschrijven. De theoretische GAME-opbrengsten berekend met de gemeten waarden geven aan dat de cacaoboteropbrengst altijd wordt onderschat onder de aanname van gelijke uiteindelijke vloeistofhoeveelheden in zowel de conventionele als de GAME perskoeken. Het mechanisme is daarom complexer dan alleen het verdringen van cacaoboter.

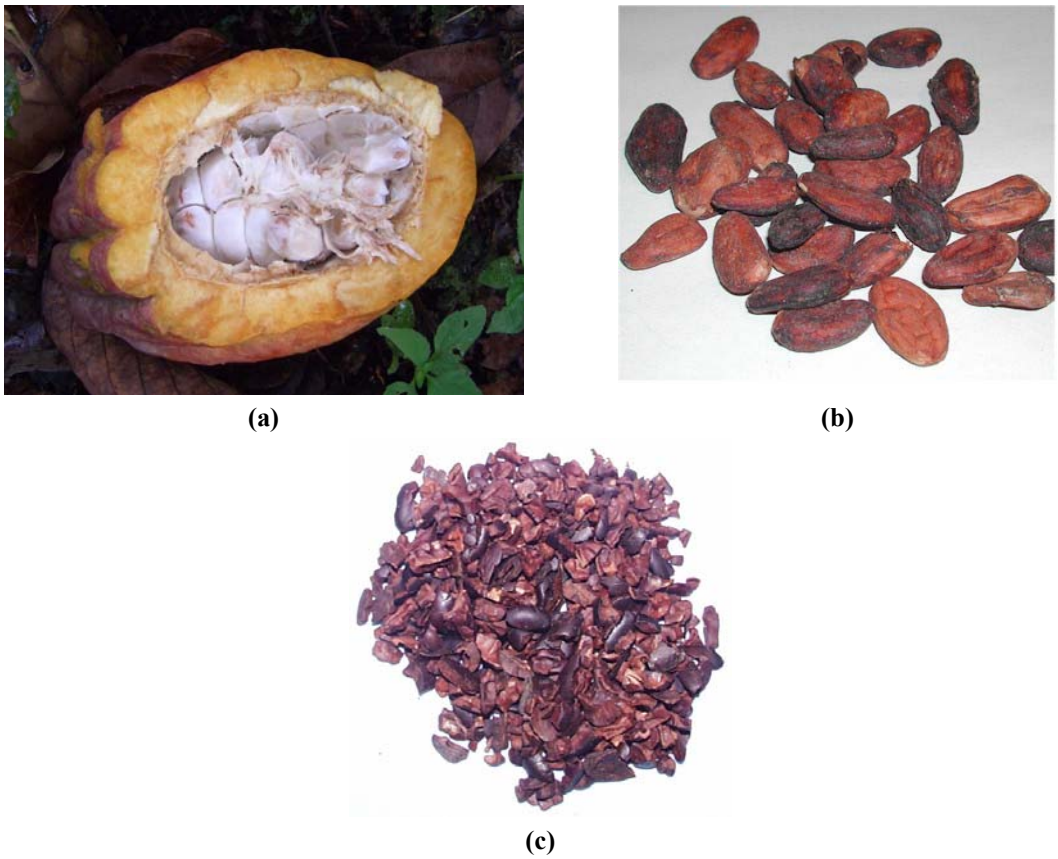
Cacaoboter bestaat uit een mengsel van diverse triacylglyceriden (TAG), waarbij het merendeel bestaat uit POP, POS en SOS. De met GAME gewonnen cacaoboter had dezelfde POS/POP en SOS/POP verhoudingen als de cacaoboter gewonnen met conventionele expressie. Hieruit kan worden geconcludeerd dat met GAME hogere cacaoboteropbrengsten kunnen worden gehaald zonder de samenstelling van de cacaoboter te veranderen ten opzichte van conventionele expressie. De met hydraulisch persen van cacaomassa maximaal haalbare opbrengst van 90% of hoger kan door GAME gehaald worden door gebruik van cacaonibs met een vochtgehalte van 1.3 gewichtsprocent (natte basis) bij een temperatuur van 100 °C in combinatie met een CO_2-druk van 10 MPa en een effectieve mechanische druk van 60 MPa of hoger. Door

gebruik te maken van meerstaps-GAME kan de cacaoboteropbrengst nog verder verhoogd worden. Dit maakt het toekomstig gebruik van continue opererende extruders in plaats van batchverwerkende hydraulische filterpersen een aanlokkelijke optie.

1 Introduction

1.1 Cocoa butter

When the Spanish came upon cocoa in South America they labelled it “food of the gods”. The consumer statistics of today suggest that modern society agrees with this opinion: in 2003/2004 3.5 million tons of cocoa beans were produced, with more than 90 % of the total production being processed for further use [1]. Cocoa processing is mainly done in Europe and North America with the Netherlands and the United States as the world’s two leading cocoa processing countries. Approximately two-thirds of the cocoa bean production is used to make chocolate and one-third to make cocoa powder [1]. Cocoa butter is the most important ingredient in chocolate in terms of determining its physical and chemical properties [2].



(a) **(b)** **(c)**

Figure 1-1: (a) The fruit of the cocoa tree, cut open to show the cocoa beans. (b) Dried, fermented cocoa beans. (c) Cocoa nibs.

Cocoa beans are the dried and fermented seeds of the *Theobroma cacao* tree which grows in equatorial regions. Cocoa nibs are broken cocoa bean cotyledons. Figure 1-1 shows photographs of a fresh cocoa fruit, cocoa beans and cocoa nibs. Cocoa nibs consist of 52-56 wt. % cocoa butter [3]. Most of the cocoa butter produced in the world

is used in chocolate manufacturing, although a small percentage of cocoa butter is also used in the manufacturing of cosmetics [1,3]. Cocoa butter is a unique plant lipid in that it has a melting point of 34-36 °C, which gives chocolate its pleasant melt-in-the-mouth texture [2,3]. Cocoa butter consists mainly of triacylglycerols (TAG's). TAG's are trieseters of glycerol and three fatty acids. The physical and chemical properties of a lipid are determined by its fatty acid and triglyceride compositions. Cocoa butter consists of approximately 90 % symmetrical TAG, with 1 – palmitoyl – 2 – oleoyl – 3 – stearoylglycerol (POS), 1,3 – stearoyl – 2 – oleoylglycerol (SOS) and 1,3 – palmitoyl – 2 – oleoylglycerol (POP) accounting for most of the TAG content of cocoa butter [2-6]. Because of this cocoa butter has a relative narrow melting point. Figure 1-2 shows the structures of glycerol, the three fatty acids oleic acid, palmitic acid and stearic acid and the TAG POP.

1.2 Current technologies for the production of cocoa butter

High quality cocoa butter is required to produce chocolate. Most of the high quality cocoa butter is produced with hydraulic pressing [3,5]. The main steps involved in this process are shown in Figure 1-3.

Prior to pressing the cocoa beans must be cleaned and de-shelled. During winnowing the difference in density between the cocoa nibs and the shell pieces is used to remove the shells. The remaining pieces of cocoa beans are known as cocoa nibs. Roasting, and optionally alkalisation with potassium or sodium carbonate, develops the flavour and colour of the cocoa nibs [3,5,7]. The nibs are grinded to create cocoa liquor. During the grinding step the cocoa butter is freed from the cell structure. Therefore cocoa liquor consists of fine cocoa particles suspended in cocoa butter.

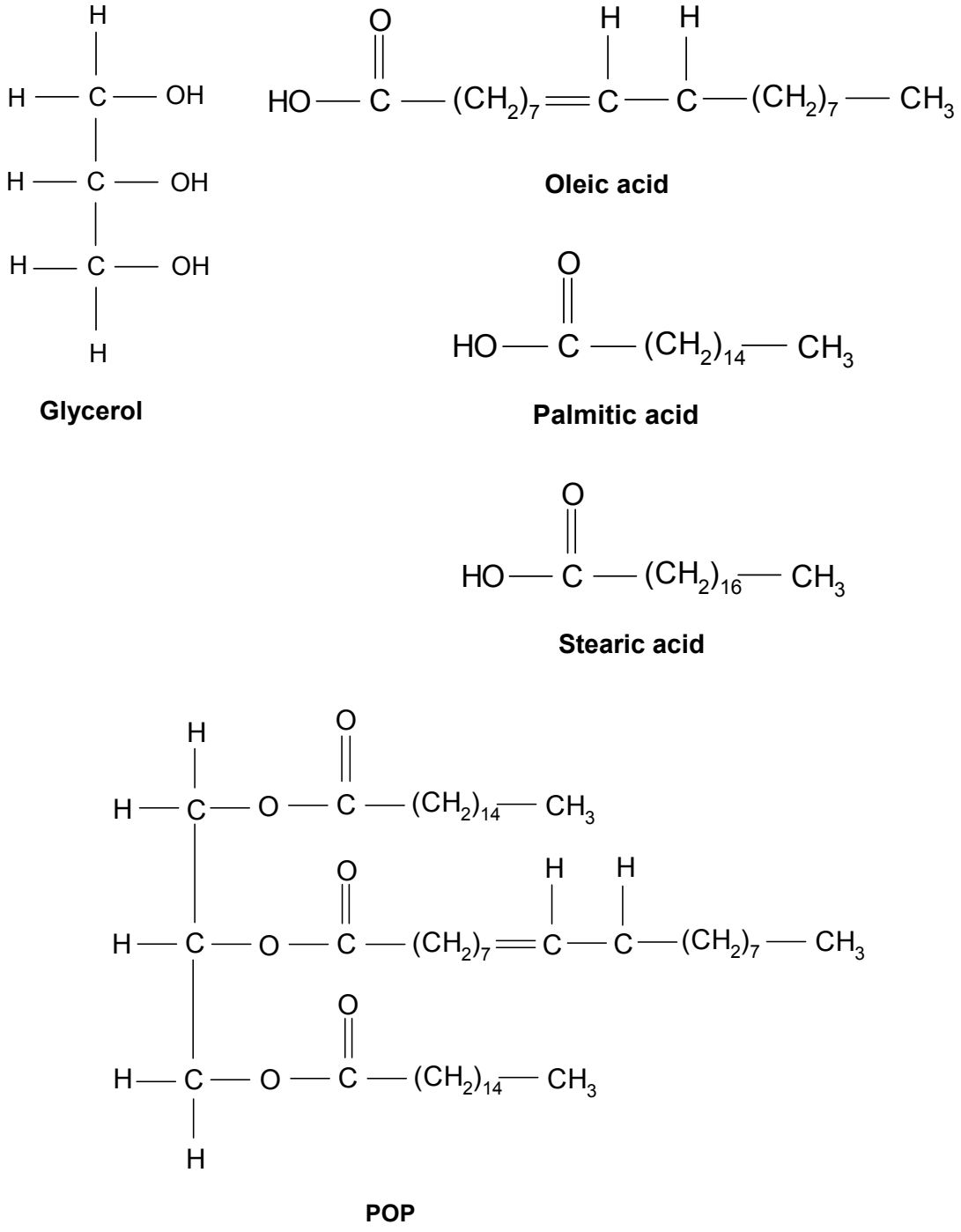


Figure 1-2: Glycerol, palmitic, stearic and oleic acid and the TAG POP consisting of glycerol attached to the fatty acids via ester links.

Roasting and alkalisation can be performed on cocoa beans, cocoa nibs or cocoa liquor depending on the desired colour and flavour. Both roasting and alkalisation only changes the nature of the cocoa solids, and not that of the cocoa butter.

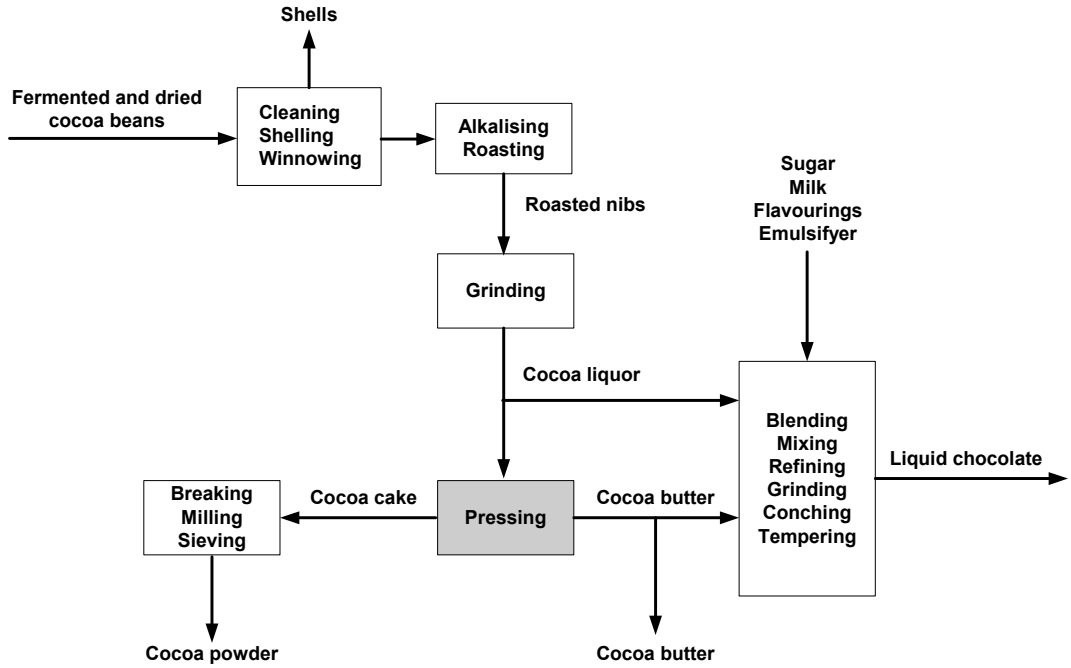


Figure 1-3: Summary of the processing steps involved in making chocolate, cocoa butter and cocoa powder.

Hydraulic pressing is performed with large horizontal hydraulic filter presses consisting of twelve or more filter pots connected in series. Screw presses, often known as expellers, can also be used, but their use is usually limited to whole bean pressing [3,5]. Figure 1-4 shows a schematic picture of a hydraulic cocoa press. Each filter pot contains two drainage surfaces. Each drainage surface is covered with a filter medium to prevent the cocoa solids from being entrained in the cocoa butter. Usually pressing is performed at 95-105 °C [3, 5]. The cocoa liquor is pumped into the press at a pressure of 1.5 to 2 MPa, thereby forcing some of the cocoa butter through the filter media. In the process a fine layer of cocoa solids deposits on the filter media, effectively creating the first layer of the cocoa filter cake. Once filled, the filter pots are slowly squeezed together, increasing the pressure on the cocoa liquor to levels of up to 100 MPa. This causes the cocoa butter to flow through the filter cake and the filter media, thereby defattening the cocoa liquor. This method of separating a solid and a liquid is known as expression. Typically a press cycle of 15 minutes is used to obtain filter cakes with a cocoa butter content of 22-24 %, while 25 to 30 minutes are needed to produce filter cakes with fat contents of 10-12 % cocoa butter. The lowest practical fat content of the cocoa press cakes is 8 % (92 % of the total cocoa butter removed), lower fat contents will require too long press cycles to be economically feasible [3]. At the end of the press cycle the filter pots are opened and the filter cakes removed. The filter cakes are cooled down and broken to form a free-flowing powder that can be sold as cocoa powder. The taste and colour of cocoa powder does not

depend on the fat content. However, cocoa powders with lower fat contents are easier to handle and clump less.

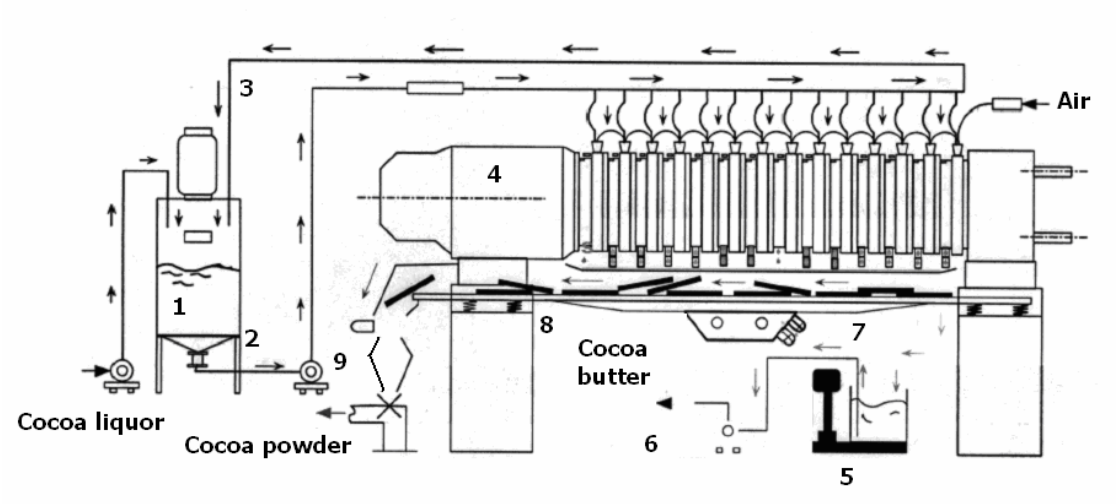


Figure 1-4: Schematic depiction of a cocoa press [9]. 1: Cocoa liquor conditioning tank. 2: Cocoa liquor pump. 3: Pipe for cocoa liquor. 4: Hydraulic cocoa press. 5: Cocoa butter scale. 6: Cocoa butter pump. 7: Cocoa butter pipe. 8: Cocoa cake conveyor. 9: Cocoa powder milling system.

The cocoa butter pressed from the cocoa liquor is collected as a pale yellow oil. It is usually filtered to remove any entrained solid particles, whereafter it is tempered and packaged. Cocoa butter sells at a price approximately 2 times higher than that of cocoa powder [8]. It is therefore desirable to operate at conditions ensuring the maximum cocoa butter yield.

Mechanical pressing produces cocoa butter of high quality, and can easily remove 80 to 85 % of the cocoa butter from the cocoa liquor [3]. Solvent extraction can be used to produce cocoa butter at yields of 98 % or higher. Generally n-hexane, a toxic and flammable compound, is used as a solvent [10]. Usually cocoa corns created with an expeller are used for solvent extraction to ensure good percolation of the solvent. Solvent extraction requires rigorous, energy-intensive solvent recovery processes to lower the solvent levels to acceptable levels in both the oil and the solid residue. Solvent extracted cocoa butter is commonly lye refined, bleached and deodorised. These processes remove desirable components (e.g. some anti-oxidants and volatile substances responsible for certain taste and flavour characteristics), thereby changing the quality of the oil [11,12]. Solvent extracted cocoa butter often has inferior keeping properties due to the destruction of natural anti-oxidants [13]. This, together with the safety precautions that must be taken due to the flammable and explosive nature of hexane and the risk of toxic residue in the cocoa butter and cocoa powder, have caused hexane extraction to be used only to a limited extent in the cocoa industry [2,15].

Supercritical fluid extraction (SFE) can be performed with supercritical carbon dioxide (SC-CO_2) to extract cocoa butter from cocoa nibs. High yields are possible (> 98 %) [2,14] and the cocoa butter is considered to be of an excellent quality. However, large amounts of SC-CO_2 are required due to the low solubility of cocoa butter in SC-CO_2 (0.5-1.5 wt. %) at the conditions normally used in SFE plants (25-30 MPa, 40-60 °C) [2,12,14-20]. The SC-CO_2 must be recycled, and the re-pressurising of the CO_2 to supercritical conditions requires a lot of energy and economic investment. It is therefore widely acknowledged that SFE is more suitable for the recovery of high-value, speciality products like essential oils than commodity oils such as cocoa butter [20,21].

Rural extraction processes often make use of aqueous extraction. The yield obtainable with this process is relatively low [23]. Enzymes can be used to weaken the cell walls and free the cocoa butter from the cell structure in order to increase the yield, but the cost of the enzymes, as well as the hygiene requirements of a wet process and the cost of demulsification and water removal from the final products have a negative impact on the industrial feasibility of enzyme assisted aqueous extraction [23-26].

1.3 Scope of this thesis

There is a need for a new cocoa butter recovery process that combines the advantages of the current industrial methods without their respective disadvantages. The positioning of such a process in terms of product quality, cocoa butter yield and its suitability for commercial use on a large scale is shown in Table 1-1.

The solubility of SC-CO_2 in plant oils is much higher than the solubility of the same oils in SC-CO_2 [30,31]. A number of patents have proposed the use of the solubility of SC-CO_2 in plant oils to enhance the oil yield during expression [27-29]. Figure 1-5 shows the phase diagram of cocoa butter/CO_2 at 40 °C. From the phase diagram it can be seen that the solubility of SC-CO_2 in cocoa butter (left side of the diagram, marked GAME) is substantially higher than the solubility of cocoa butter in SC-CO_2 (right side of the diagram, marked SFE). It is clear that less CO_2 will be needed when the solubility of SC-CO_2 in cocoa butter is utilised in a process instead of the solubility of cocoa butter in the SC-CO_2. In fact, 464 times more CO_2 is needed in SFE than when the solubility of SC-CO_2 in cocoa butter is used at 40 °C and 10 MPa. The viscosities of CO_2-saturated plant oils are also lower than those of the corresponding pure oils [21]. Furthermore SC-CO_2 can cause cell rupture [32,33] and causes melting point depression [21,22]. All these factors can contribute to an increase in the oil yield during pressing. However, no systematic investigation on this topic could be found in open literature.

Table 1-1: Positioning of cocoa butter recovery processes in terms of product quality, oil yield and commercial use. + indicates good, + + excellent and – indicates poor to very poor.

Process	Cocoa butter quality	Solids residue quality	Cocoa butter yield	Commercial use
Mechanical expression	+ +	+ +	+	+ +
Aqueous extraction	+	+	-	-
Solvent extraction	-	-	+ +	+
SC-CO_2 extraction	+ +	+ +	+ +	-
Ideal process	+ +	+ +	+ +	+ to + +

Another question that arises is whether it is possible to press cocoa nibs instead of cocoa liquor. The filter cakes can then be grinded to the desired fineness to make cocoa powder. This will result in savings due to the smaller volume of material that needs to be grinded. Even more savings are possible if the filter cakes instead of the cocoa beans or cocoa liquor are alkalised and roasted. In this thesis the focus is on the removal of cocoa butter from cocoa material, and all pre- and post-expression operations are neglected.

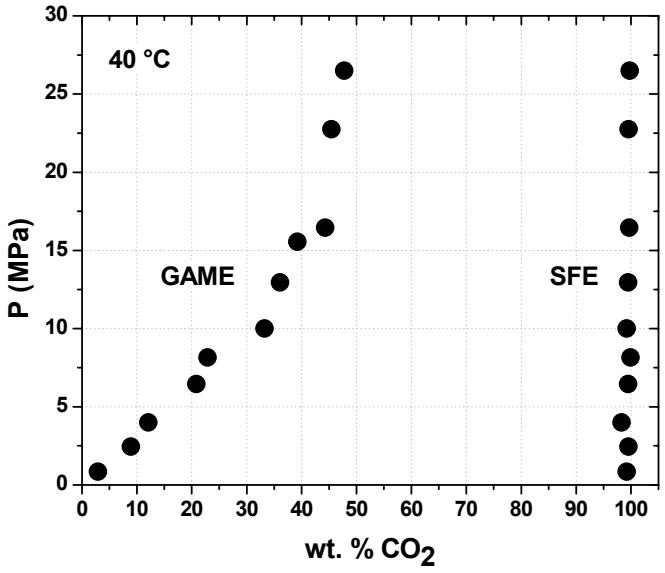


Figure 1-5: A typical phase diagram for the system CO_2/cocoa butter [30].

It is necessary to understand the expression process and the influence of process parameters on it before the process can be modified. In **Chapter 2** the expression behaviour of cocoa nibs is investigated and compared to that of cocoa liquor. The influence of different process parameters on the expression behaviour of the nibs is also studied.

The ability to accurately describe the expression process with a mathematical model facilitates optimisation and understanding of the expression process. In **Chapter 3** the modelling of expression and the experimental validation of such models are discussed.

In **Chapter 4** the process called Gas Assisted Mechanical Expression (GAME) is introduced. In this process CO_2-saturated cocoa nibs are pressed. GAME is compared with conventional expression, and the probable mechanism involved in GAME is discussed. The influence of temperature and CO_2-pressure on the cocoa butter yield are shown.

GAME can only be understood if the properties of CO_2-saturated cocoa butter are known. **Chapter 5** shows the viscosity and density of CO_2-saturated cocoa butter and the solubility of CO_2 in cocoa butter at different temperatures and pressures. These data are also used to calculate the theoretical GAME cocoa butter yields.

Several process parameters aside from the temperature and CO_2-pressure can influence the expression behaviour of cocoa nibs during GAME. In **Chapter 6** these parameters and their influence on GAME of cocoa nibs are discussed. GAME of cocoa liquor is also compared with GAME of cocoa nibs. Furthermore the possibility to increase cocoa butter yields even further by using multi-stage GAME is investigated.

Finally, **Chapter 7** presents the conclusions of this thesis and recommendations for future work.

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2 Conventional expression of cocoa butter from cocoa nibs

Abstract

The effect of temperature (40-110 °C), applied mechanical pressure (20-80 MPa), applied pressure profile (constant / linearly increasing) and moisture content (0-8 wt. %, wet basis) on the conventional expression of cocoa nibs was investigated. The maximum cocoa butter yield is achieved at 100 °C. The optimum moisture content with respect to cocoa butter yield is 1.3 wt. %. The cocoa butter yield increases with pressure up till 60 MPa where it has a value of 80 % when dry cocoa beans are used. Neither the use of higher pressures nor the use of a linearly increasing pressure profile cause any further increases in the cocoa butter yield when the total pressing time is kept constant. The rate of expression increases with an increase in temperature or a decrease in moisture content. Higher cocoa butter yields (up to 89 %) were achieved when cocoa liquor was pressed instead of cocoa nibs.

2.1 Introduction

Cocoa butter is used in the manufacturing of chocolate, making it one of the most important ingredients used by the confectionery industry [1]. Since 1828, when Van Houten developed a press to partially defatten cocoa beans [2], mechanical pressing has been used to produce good quality cocoa butter from cocoa beans. Mechanical pressing can be done with either hydraulic presses or screw presses, but hydraulic filter presses are traditionally used for defattening cocoa beans. Mechanical pressing makes use of the unit operation expression, where the expressible liquid is expressed from a liquid - bearing mixture or matrix (in this case the cocoa nibs) by applying external pressure to deform and compress the mixture. Cocoa beans contain approximately 54 wt. % cocoa butter [2]. Usually the cocoa beans are cleaned, winnowed, roasted, alkalised and grinded to a fine paste known as cocoa liquor before being pressed.

In industry cocoa liquor is pumped into the press chamber at 1.5-2 MPa. Once the press chamber is filled the pressure is linearly increased to the required end pressure. The applied pressure is then kept constant for approximately 10 minutes before the filter cake is removed. Industrial hydraulic presses consists of twelve or more filter pots with an inner diameter of 425-600 mm [3], and invariably operates at temperatures of 90-110 °C to optimise the yield [2,4]. After pressing the cocoa liquor, the filter cakes are broken into smaller pieces, grinded and sold as cocoa powder. The taste and colour of cocoa powder does not depend on the fat content. Cocoa powders with lower fat contents are easier to handle and clump less. Cocoa butter is a more valuable raw material than cocoa powder, selling at a price approximately 2 times higher than that of cocoa powder [5]. The optimisation of the cocoa butter yield is therefore desirable.

Roasting and alkalisation are performed to obtain specific colour and flavour characteristics in the cocoa solids, and theoretically do not influence the taste, flavour or characteristics of the cocoa butter. The particle size of the cocoa powder is achieved during the liquor grinding. Any grinding performed after pressing only reduces the size of the compacted aggregates formed during pressing. Considerable savings are possible if cocoa nibs (broken, de-hulled cocoa bean cotyledons) are pressed instead of cocoa liquor, whereafter the cocoa filter cakes are grinded, alkalised and roasted to obtain the desired flavour and colour. Pressing cocoa nibs will also avoid some of the problems encountered with pressing ultra-fine cocoa liquor; especially the entrainment of solid particles into the cocoa butter stream, clogging of the filter medium and malfunctioning of the felt sealing rings used in the press chambers [6].

Up to date very little research has been done on the expression of cocoa nibs. Gros et al. [7] only investigated the influence of roasting and alkalisation on the expression of

cocoa butter from cocoa nibs at pressures between 9 and 11 MPa and temperatures of 90 and 100 °C. They removed 24 % of the total cocoa butter content by pressing untreated nibs. Alkalisation, roasting and an increase in the pressing temperature all increased the yield. This is probably due to damage of the cell structure, which causes more of the cocoa butter to be freed from the cell structure.

Cocoa beans contain lipid components, and can therefore be defined as an oilseed. It is known that several factors influence the yield obtainable by pressing oleaginous seeds. Pre-treatment, temperature, pressure and moisture content are known to be the most important expression parameters [2,7-23]. The optimum temperature and moisture content is unique for each oilseed [9,12-17,20-25]. However, it is not only the oil yield, but also the rate at which this yield is achieved that determines the performance of an expression operation. The rate can be quantified with the consolidation ratio U_C, defined as

$$U_C(t) = \frac{L(t) - L_0}{L_{final} - L_0} \tag{2-1}$$

where $L(t)$ is the filter cake thickness at time t, L_0 the initial filter cake thickness and L_{final} the filter cake thickness at the end of pressing.

In this chapter the influence of the temperature, pressure, pressure profile and moisture content on the press behaviour of cocoa nibs is investigated. First the default operational settings that should be used are determined, whereafter the parameters are varied one at a time. Furthermore the press behaviour of cocoa nibs is compared to that of cocoa liquor. Both the yield (defined as the mass of cocoa butter removed as a percentage of the total mass of cocoa butter contained in the cocoa nibs) and the rate at which the yield is achieved are studied. The rate of pressing is only discussed in cases where it is significantly influenced by the parameter being studied.

2.2 Materials and methods

2.2.1 Experimental set-up

Figure 2-1 shows the laboratory scale press with one drainage area constructed for this study. It consists of a hydraulic plunger (4) that can exert pressures of up to 100 MPa on the material and moves uni-axially in a cylinder with a diameter of 30 mm. The cocoa nibs are placed on top of a sieve plate (7) covered with a fine wire mesh acting as a filter medium (6). The filter medium is woven from 0.6 mm thick chromium steel (type 430) wires in a configuration of 13 bundles of 3 threads per 25.4 mm, with 212

wires per 25.4 mm perpendicular to these bundles. When cocoa liquor is pressed two layers of fast speed filter paper (No 4. Whatman International Ltd., Maidstone, Kent, UK) are placed beneath the wire mesh. The filter medium is kept in place inside the sieve plate with a Teflon ring, which also prevents solids from being extruded into the collection chamber. The expressed cocoa butter is collected in the collection chamber (8) below the sieve plate. The press is fitted with two jackets (9) in which a heating medium can be circulated to enable isothermal operation (± 1 °C) at elevated temperatures (30-100 °C). The hydraulic pressure is regulated electronically with a type SRX controller (RKC Instruments, Tokyo, Japan). The set points for the controller are set with the electronic interface SpecView Plus (SpecView, Ltd., East Sussex, United Kingdom). The distance the plunger has advanced is continuously measured with a position transducer (2) (SPH-50, WayCon Positionsmesstechnik GmbH, Unterhaching, Germany) in order to determine the actual thickness of the filter cake (accuracy ± 0.01 mm). All data is recorded digitally with a memo-graph (Visual Data Manager, Endress & Hauser B.V., Naarden, The Netherlands) at a frequency of 1 Hz.

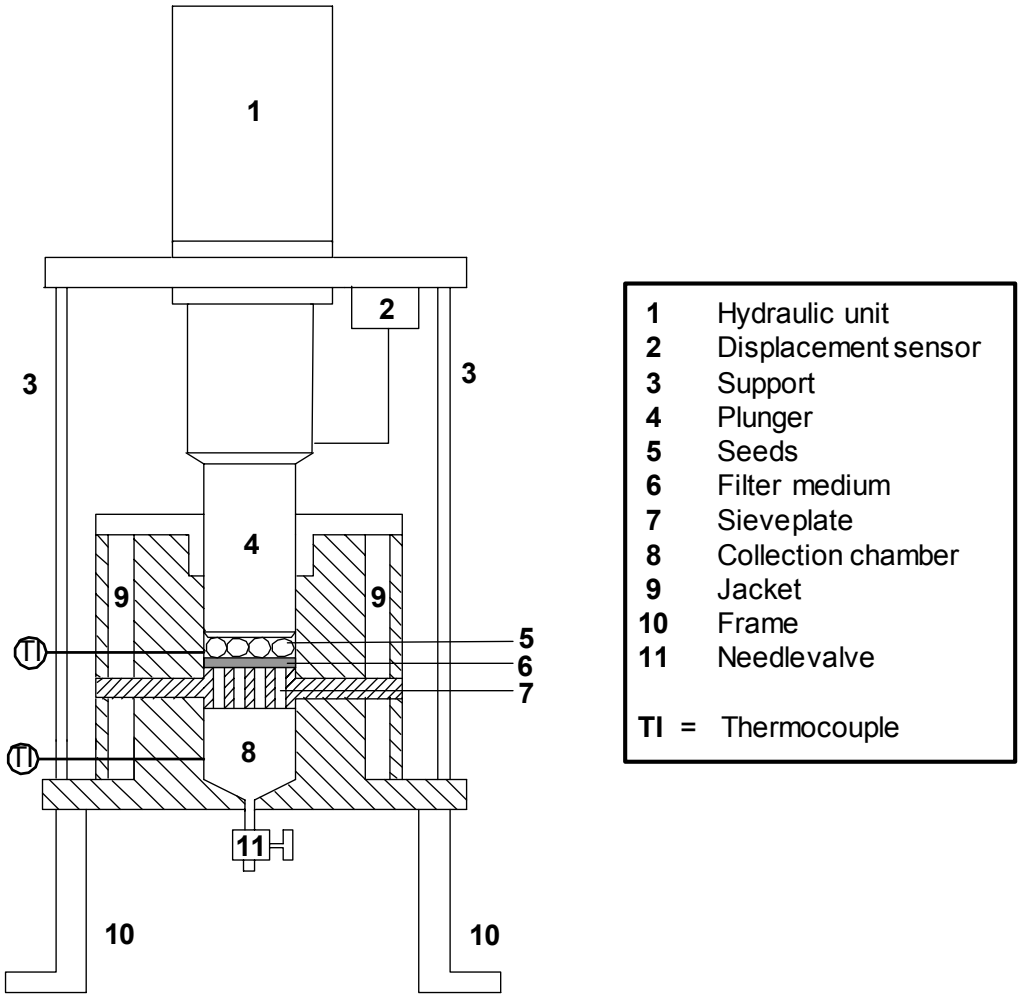


Figure 2-1: Schematic depiction of the laboratory press (not to scale).

2.2.2 Experimental procedure

Unless stated otherwise, the cocoa nibs were dried at 103 ± 1 °C until completely dry to ensure that all press experiments were performed at the same moisture content. The influence of moisture content on the expression of cocoa nibs was also investigated. The desired mass of nibs was placed on top of the filter medium. The plunger was lowered to the level of the nibs after which the nibs were allowed to equilibrate for 30 minutes to the temperature of pressing (40-100 °C). The plunger exerted no pressure on the nibs during the time required for reaching thermal equilibrium.

Pressing was performed directly after reaching thermal equilibrium by adjusting the hydraulic pressure exerted on the plunger to ensure that the desired mechanical pressure (20-80 MPa) was exerted on the nibs. Unless stated otherwise the mechanical pressure was increased in two seconds and then kept constant for 10 minutes. This pressing time was chosen to allow the cocoa filter cake thickness to be constant for some time. The needle valve in the bottom of the collection chamber was left open to allow the cocoa butter to drain into a sample container. After the pressing stage the plunger was raised. The filter cake was then removed and analysed to determine the fat content. The same experimental procedure was followed for cocoa liquor.

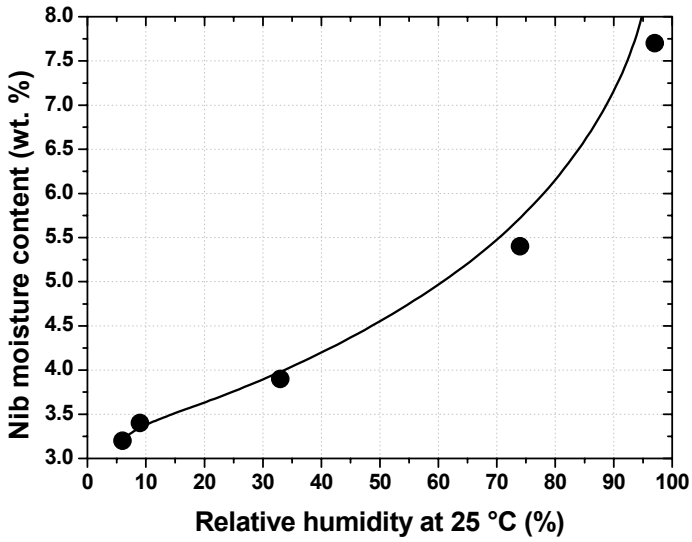


Figure 2-2: Sorption isotherm of cocoa nibs. Moisture contents are reported on a wet basis. Relative humidities associated with the saturated salt solutions are taken from [28]. Line only serves as a visual aid.

Cocoa nibs with different moisture contents were obtained by equilibrating the nibs for at least a week in an atmosphere of constant humidity by placing nibs together with a saturated salt solution inside an exsiccator. Kaya and Kahyaoglu [26] followed a

similar method to condition sesame seeds to specific moisture contents. Low moisture contents (< 3 wt. %) were obtained by equilibrating cocoa nibs with zeolite A4 in the same manner. The zeolite was dried overnight at 200 °C in order to ensure that it was completely dry before it was used. All moisture contents were determined according to the DGF standard method [27]. Figure 2-2 shows the moisture content of the cocoa nibs as a function of the relative humidity.

The viscosity of the cocoa butter was measured with an Ubelohde viscometer (capillary diameter 1.13 mm) purchased from Schott (Mainz, Germany). The viscometer was placed in a constant temperature bath (set point ± 0.1 °C).

2.2.3 Materials

Winnowed cocoa nibs (56.2 wt. % cocoa butter, dry basis), cocoa butter and cocoa liquor (53.9 wt. % cocoa butter, dry basis) were obtained from Gerkens Cacao (Wormer, The Netherlands). Zeolite A4 was kindly donated by Tosoh Europe B.V. (Amsterdam, The Netherlands). Sodium hydroxide, potassium hydroxide and magnesium chloride were bought from Aldrich (Amsterdam, The Netherlands), potassium sulphate was bought from Acros (Amsterdam, The Netherlands) and sodium nitrate and petroleum ether (boiling range 40-60 °C) were bought from Merck (Amsterdam, The Netherlands).

2.2.4 Analysis

The filter cakes resulting from pressing moist cocoa nibs were broken and dried overnight at 103 ± 1 °C before determining the fat content of the cakes. The standard method for the determination of the fat content of cocoa powder by soxhlet extraction as proposed by the International Office of Cocoa, Chocolate and Sugar Confectionary (IOCCC) [29] was modified to be suitable for the analysis of cocoa filter cakes. For filter cakes formed by pressing cocoa nibs, these modifications include soaking the filter cake in a small quantity of petroleum ether for at least 4 hours before grinding. This prevents the excessive formation of fines during grinding due to the brittle nature of the dried nibs. Furthermore a wad of cotton wool was placed in the bottom of the cellulose fibre extraction thimble to prevent fines from passing through the thimble. The pre-soaked filter cakes were grinded together with a small volume of petroleum ether for 20 s at 16 Hz in a ball mill (Type MM 301, Retsch GmbH & Co, Haan, Germany).

The filter cakes formed by pressing cocoa liquor do not require grinding, but can be placed directly into the extraction thimbles. Due to the fineness of the solids glass fibre thimbles need to be used. These thimbles are more fragile than the cellulose fibre

thimbles, but have a finer pore structure. The rest of the analysis procedure is the same as that used for determining the fat content of cocoa nib filter cakes. All fat contents are reported on a dry basis.

2.2.5 Accuracy and reproducibility of experimental results

In order to evaluate the experimental error three pressing experiments were done at 40 °C and a pressure of 60 MPa. The average yield for these experiments was 74.9 %. The absolute standard deviation in the determined yields was calculated as 0.6 %. Duplication of random experiments at other conditions always resulted in an absolute standard deviation of less than 0.9 %. Furthermore the cocoa butter contents of cocoa powders with a known cocoa butter content were determined with an accuracy of ± 0.5 wt. %. In view of this the absolute experimental error made in calculating the yield is taken as ± 1 %.

2.3 Results and discussion

2.3.1 Default press settings

2.3.1.1 Degree of grinding

Table 2-1: Influence of the degree of grinding on the final yield. All press experiments were done with 15 g of material at 70 °C and 30 MPa.

Material	Ball mill settings	Yield (% oil/oil)
Nibs	0 s	60.0%
	7.5 Hz, 15 s	62.0%
	10 Hz, 15 s	61.5%
	10 Hz, 50 s	60.9%
	10 Hz, 180 s	62.3%
Cocoa liquor	-	71.9%

Table 2-1 shows that, with the exception of cocoa liquor, the degree of grinding does not have a noticeable influence on the yield. Cocoa liquor is a viscous slurry, in which the fine cocoa solids are dispersed in free-flowing cocoa butter. It is known that any pre-treatment that ruptures cell walls will improve the efficiency of the expression process [14,19,23]. It was visually observed that grinding cocoa nibs for longer times or at higher frequencies resulted in finer particles as long as the cocoa solids did not agglomerate on the walls of the grinding chamber. However, even at longer grinding times or higher frequencies no free-flowing cocoa butter was observed. Therefore the cocoa butter was expected to still be contained inside the cellular structure of the cocoa solids. It can be concluded that, with the ball mill that was used and the grinding times

and frequencies that were studied, the oil cell structures inside the cocoa nibs are not ruptured when the cocoa nibs are grinded in the ball mill. It is not unusual for particle size reduction processes to disrupt the integrity of the cellular matrix without breaking the cell walls except at the particle surfaces [24]. It was therefore decided to do all further press experiments with nibs without grinding the cocoa nibs.

2.3.1.2 Mass pressed

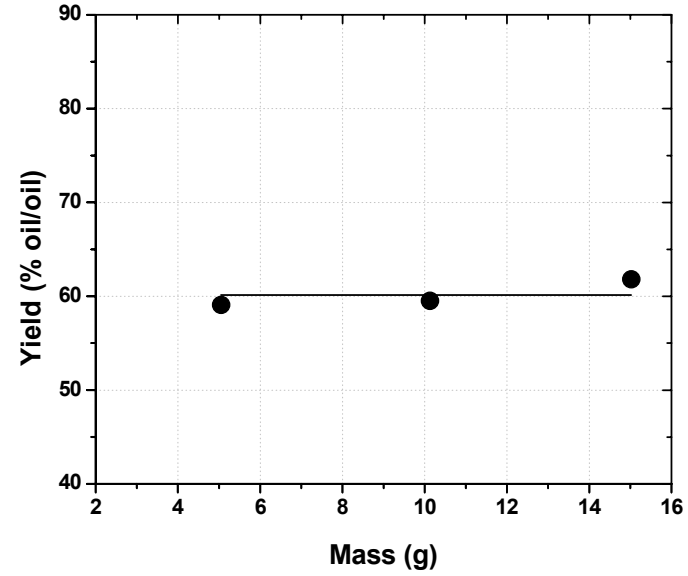
Press experiments were performed with different amounts of cocoa nibs in order to determine if the amount of material being pressed has an influence on the yield. Figure 2-3 (a) shows that there is no difference in the yield obtained for 5, 10 and 15 g of cocoa nibs pressed at the same conditions. For analysing the fat content of the filter cakes the preferred mass of filter cake is at least 5 g [29]. At least 10 g of cocoa nibs or liquor must be used in the press experiments to obtain a filter cake of 5 g or more. It was therefore decided to do all press experiments with 10 g of cocoa nibs.

Figure 2-3 (b) shows that pressing more material slows down the rate of expression. This does not influence the final yield when the press time is sufficiently long to enable the filter cake to reach its equilibrium thickness. Short press times (in this case < 200 s) will however result in lower yields when 15 g of material is pressed.

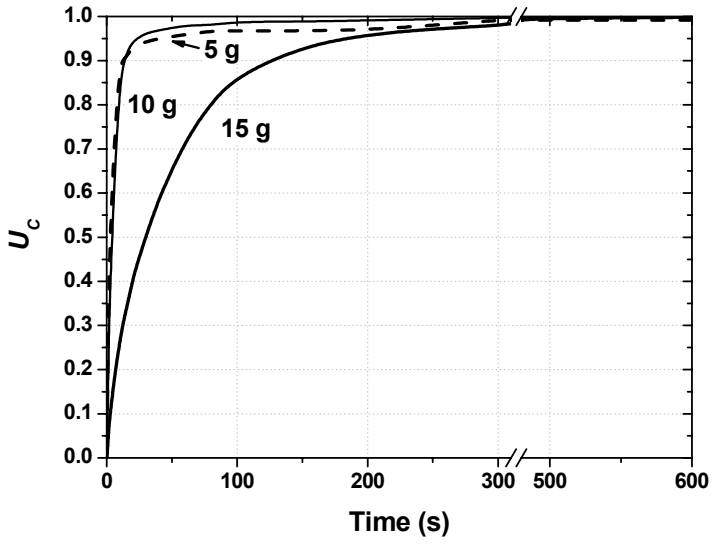
2.3.1.3 Pressing time

Koo [16] found that the pressing time has little influence on the oil yield for several types of oilseeds (soybeans, cottonseeds, rapeseeds, peanuts, tung nuts, sesame seeds and castor beans) for pressing times varying between 30 minutes and 4 hours. The pressing time also has little influence on the yield when cocoa nibs are pressed, as can be seen in Figure 2-4. Up till 600 seconds (10 minutes) the cocoa butter yield increases with an increasing pressing time, whereafter there is no appreciable increase in the yield when the time of pressing is increased.

In order to understand this it is necessary to study the displacement of the plunger in more detail. A constant hydraulic pressure is applied to the plunger throughout the experiment, causing a constant mechanical pressure to be exerted to the nibs being pressed. This causes the nibs to compact, and the plunger to move downwards. Oil is removed as long as the plunger is moving: once the plunger has stopped moving equilibrium has been reached and no further oil is removed. After approximately 450 seconds there is almost no further plunger movement. This means that the use of longer pressing times will not increase the yield. Furthermore the pressing time does not influence the rate of expression. All further press experiments were therefore performed with pressing times of 10 minutes (600 s).



(a)



(b)

Figure 2-3: Influence of the amount of material being pressed on the press behaviour of the cocoa nibs. All press experiments were done at 70 °C and 30 MPa. (a) The yield as a function of the mass being pressed (line shows the average yield). (b) U_C as a function of the mass being pressed.

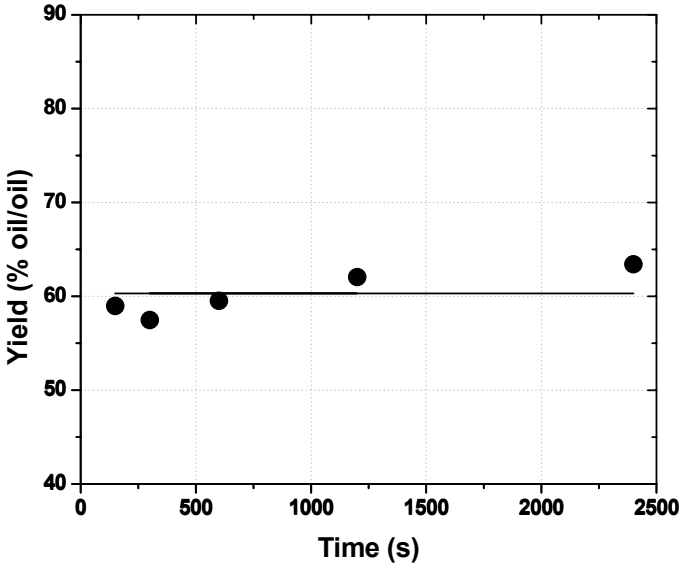


Figure 2-4: The yield as a function of the time of pressing (line shows the average yield). All experiments were done with 10 g of cocoa nibs at 70 °C and 30 MPa.

2.3.2 Process parameters

2.3.2.1 Temperature

Figure 2-5 shows that the viscosity of cocoa butter decreases exponentially with temperature. It is expected that the decreased viscosity of the cocoa butter will cause the cocoa butter to flow more easily when higher temperatures are used during pressing, thereby enhancing the yield. However, the temperature has no influence on the yield when cocoa nibs are pressed at temperatures below 100 °C (Figure 2-6(a)). At 100 °C there is an appreciable increase in yield. The reduced viscosity of the cocoa butter cannot explain this.

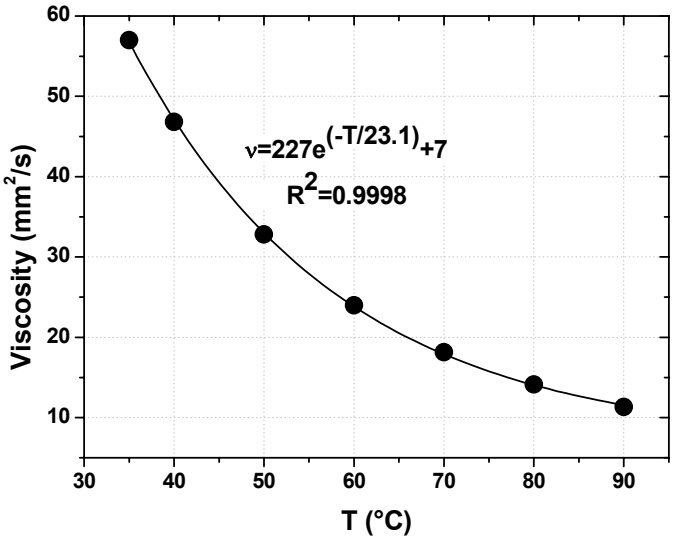
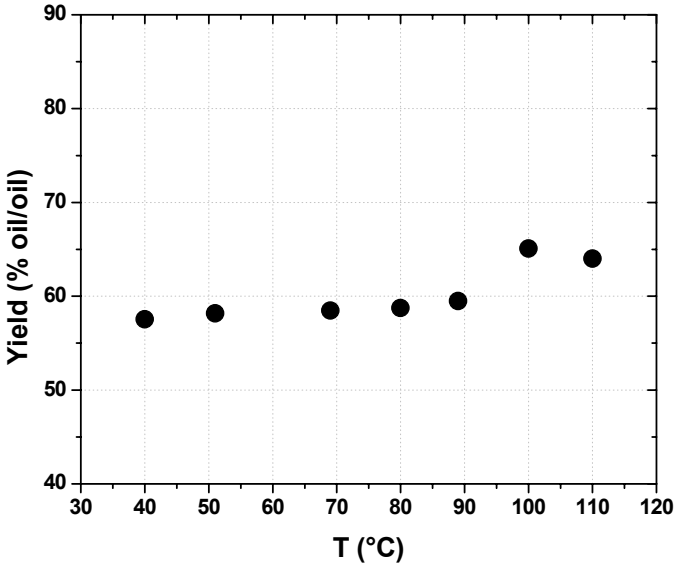
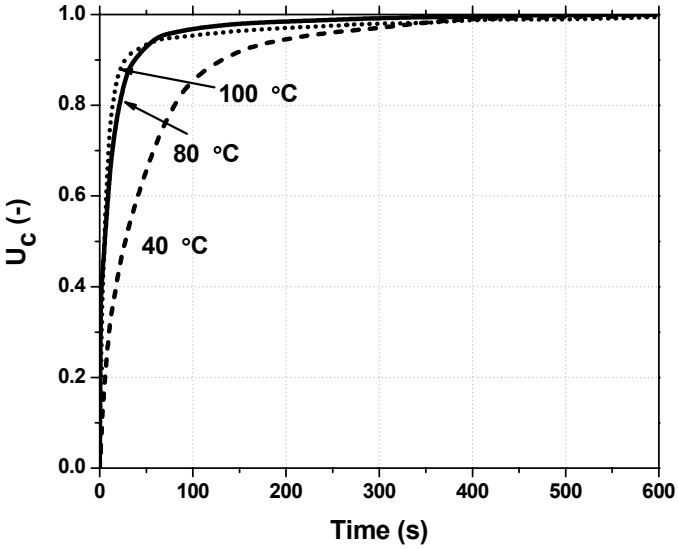


Figure 2-5: Kinematic viscosity (v) of cocoa butter as a function of temperature (T).

An increase in temperature not only influences the properties of the cocoa butter, but also that of the cocoa solids. Faborode and Favier [24] found that heating seeds softens the seed tissues, thereby enhancing the compressibility of the material. Higher temperatures may cause cell walls to weaken and proteins to coagulate, and therefore also influences the elasticity of the solid matrix [20]. The compressibility of the material influences the speed with which equilibrium is reached. Very compressible materials, or very brittle materials, will reach equilibrium faster than soft materials or materials with a low compressibility. This will result in a very fast decrease in the filter cake thickness during the initial pressing period. In Figure 2-6 (b) the consolidation ratios of experiments done at different temperatures and the same mechanical pressure are shown. It can be seen that equilibrium is only reached after 300 seconds at 40 °C, while equilibrium is reached more than 100 seconds earlier at 80 and 100 °C. From this it can be deduced that the change in the characteristics of the solids due to the increased temperature has a bigger influence on the press behaviour of the cocoa nibs than the decreased viscosity of the cocoa butter.



(a)



(b)

Figure 2-6: The influence of temperature on the press behaviour of cocoa nibs. All experiments were done with 10 g of cocoa nibs and pressed at 30 MPa. a) The yield as a function of the temperature of pressing. b) U_C as a function of temperature. - - - 40 °C, --- 80 °C, – 100°C.

2.3.2.2 Pressure

It is well known that the use of higher pressures during the expression of oilseeds will result in a higher oil yield [14,16-22]. This is also the case for cocoa, as is shown in Figure 2-7. A higher mechanical pressure imparts a bigger force on the cocoa butter, thereby forcing more of the cocoa butter to flow through the filter cake. Higher mechanical pressures also cause the cocoa solids to fracture more and the filter cake to be more compacted. All these factors attribute to the increase in cocoa butter yield observed at higher pressures.

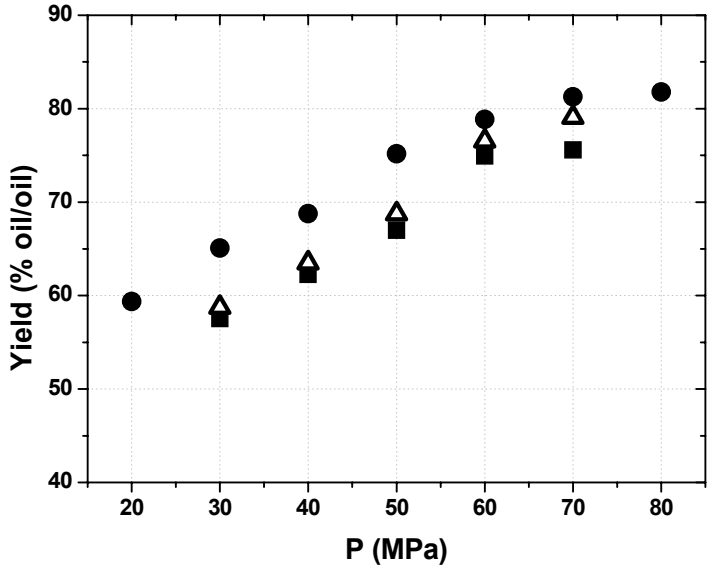


Figure 2-7: The cocoa butter yield as a function of the applied pressure. The symbols indicate the following temperatures: ■ 40 °C , △ 80 ° C and ● 100 °C.

The same profile for the consolidation ratio as a function of time was obtained for all experiments performed at one temperature, regardless of the pressure that was used. Therefore the mechanical pressure does not influence the rate at which equilibrium is reached. There is however a big difference in the decrease of the filter cake thickness over time between the different experiments, as can be seen in Figure 2-8. At higher pressures the plunger moves further downwards, resulting in a thinner filter cake. As a result the porosity (the volume fraction of non-solids) of filter cakes produced at higher pressures is lower than those produced at lower pressures. This explains the increase in cocoa butter yield with increasing pressure.

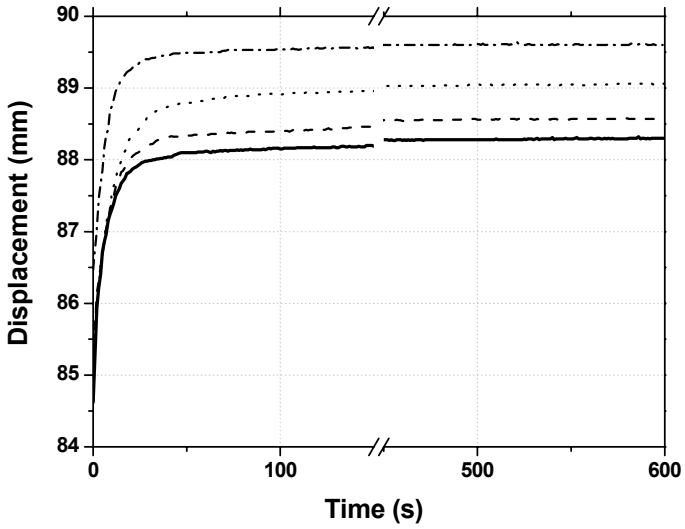


Figure 2-8: The displacement of the plunger as a function of time for experiments done at different pressures and 100 °C. – 30 MPa, - - - 40 MPa, ··· 50 MPa, -·- 60 MPa.

2.3.2.3 Pressure profile

In the industrial pressing of cocoa liquor the pressure is increased linearly at a rate of 0.1 – 0.3 MPa/s until the desired maximum pressure, whereafter it is kept constant [2,7,30,31]. This raises the question whether it would be advantageous to use the same press curve for pressing cocoa nibs. When the pressure is increased at a lower rate the time during which the filter cake is pressed at the maximum pressure shortens if the total time of pressing is kept constant. This leads to the expectation that lower rates of pressure increase would result in lower cocoa butter yields. Figure 2-9 however shows that the rate with which the pressure is increased to the maximum pressure does not influence the yield. This confirms that the pressing time has little influence on the yield (see paragraph 2.3.1.3).

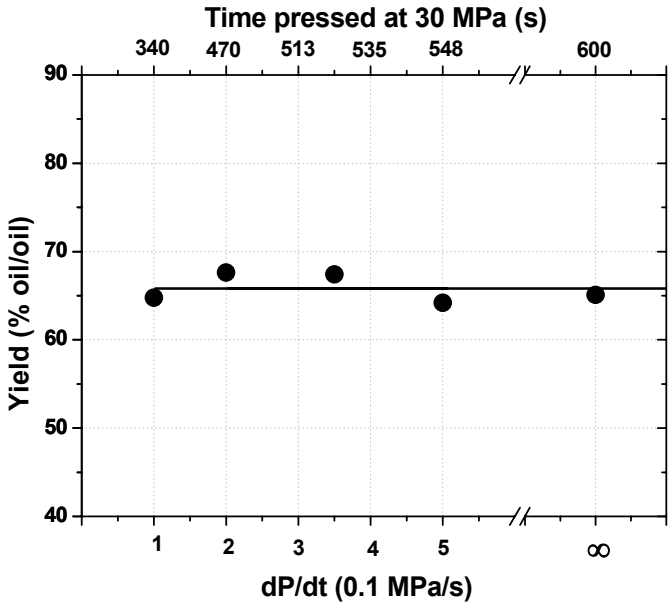
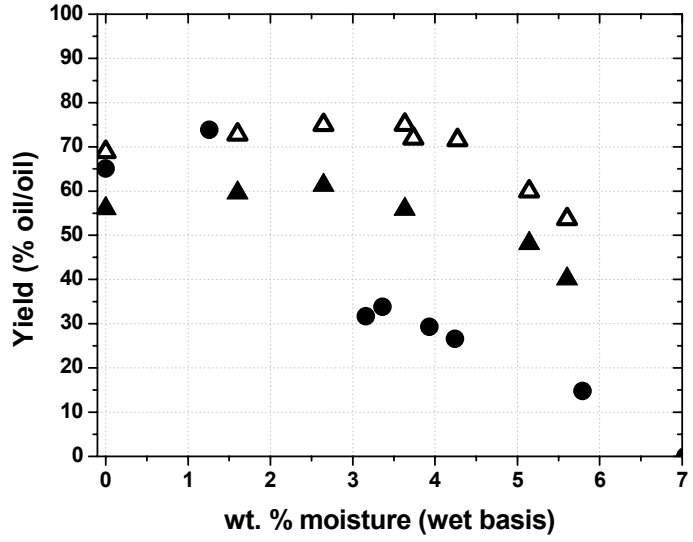


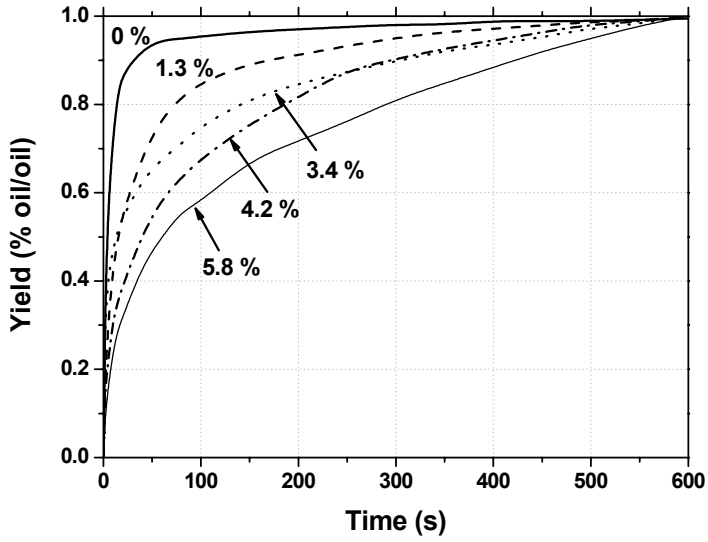
Figure 2-9: Influence of the applied pressure profile on the yield for a total pressing time of 10 minutes. Line shows the average yield. All experiments were done at 100 °C and a maximum pressure of 30 MPa.

2.3.2.4 Moisture content

The optimum moisture content for the expression of oil from oilseeds is unique for each oilseed [9,12-14,17,20-25]. The moisture content influences the mechanical strength, elasticity and compressibility of the seed material [12,15,25]. Figure 2-10 (a) shows that, for the expression of cocoa butter from cocoa nibs, the optimum moisture content with respect to yield lies in the region of 1.3 wt. % for 100 °C. There is no clear maximum in yield at 40 °C, even though the yield decreases at moisture contents above 3.5 wt. %. In industry cocoa liquor is pressed at 90-110 °C and moisture contents between 1 and 1.5 wt. % [2,8,30]. The nature of the cellular structure of the cocoa beans is such that the cocoa beans must either be grinded to a very fine paste (i.e. cocoa liquor, see paragraph 2.3.1) or be dry and therefore brittle in order to free the maximum amount of cocoa butter from the cellular structure and enable it to be expressed from the cocoa material. As the moisture content of the cocoa nibs increase the nibs become more elastic. Therefore a bigger part of the applied pressure is utilised to deform and compress the solid structure than when dry (and therefore brittle) nibs are expressed. This can be seen in Figure 2-10 (b): the higher the moisture content, the longer the filter cake takes to reach its equilibrium thickness. The longer this process takes the more energy is spent in deforming the solid structure. At 7.0 wt % moisture the solids starts to be extruded through the filter medium, causing the consolidation ratio to increase faster than expected.



(a)



(b)

Figure 2-10: (a) The yield as a function of the moisture content. All moisture contents are reported on a wet basis. The symbols indicate the following conditions: ▲ 40 °C and 30 MPa, △ 40 ° C and 50 MPa, ● 100 °C and 30 MPa. (b) U_C as a function of time for experiments performed with cocoa nibs with varying moisture contents at 100 °C and 30 MPa.

The different dependence of yield on moisture content at 100 °C when compared to 40 °C can be explained by the boiling of water. The moist cocoa nibs will effectively be cooked during the time required to reach thermal equilibrium, thereby changing the

nature of the solid structure. Possibly chemical reactions will change the structure of the cell walls, and will cause the cocoa butter to be adsorbed onto the solids, making it non-expressible. At higher moisture contents (> 7 wt. %) the cocoa material is extruded through the filter medium and sieve plate, making it impossible to recover any cocoa butter at these conditions.

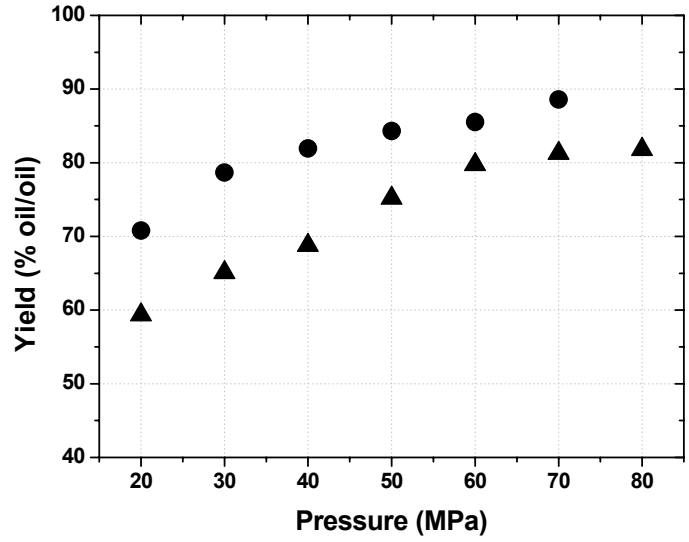
2.3.3 Comparison of cocoa nibs with cocoa liquor

In industry cocoa liquor is pressed at 35 MPa to obtain a yield of 73 %. Pressures higher than 50 MPa are used to obtain yields of 88 % or higher [2]. Figure 2-11 (a) shows that pressing dry cocoa liquor in the laboratory press results in comparable cocoa butter yields as those obtained with industrial presses despite the differences between the two types of equipment. The laboratory press is much smaller and contains one drainage area whereas each filter pot in an industrial press contains two drainage areas. Furthermore a constant pressure profile was used for the entire pressing time in the experiments. Industrial filter presses usually utilise linearly increasing pressure profiles. It is not expected that the use of pressures above 60 MPa will cause a substantial increase in the yield due to the apparent logarithmic dependence of the yield on the pressure.

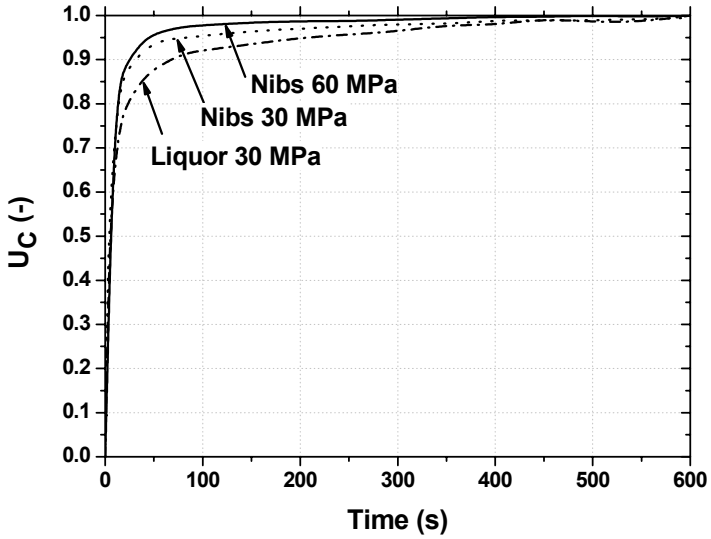
When the yields obtained by pressing cocoa liquor are compared with those of experiments done with nibs at the same pressure it can be seen that pressing cocoa liquor always results in a higher yield, although the additional increase in yield decreases at higher pressures. This makes it doubtful that the cocoa industry will use nib pressing for producing cocoa powder with low fat contents. In order to obtain the same yield when pressing cocoa nibs the pressure must approximately be doubled. In Figure 2-11 (b) it can be seen that cocoa nibs reach the equilibrium filter cake thickness much faster than cocoa liquor when pressed at the same temperature and pressure. This is probably due to the limited ability of the hydraulic press to crush the solid structure of the nibs.

The yield is higher for cocoa liquor due to the fact that most of the cocoa butter is already freed from the cell structure, and all the applied mechanical energy is used to force the cocoa butter through the filter cake. In cocoa nibs the cocoa butter is still contained in the cell structure. Cell wall rupture is not a precondition for oil expression due to the permeable nature of the cell wall [19]. However, the cell walls offer resistance against the flow of the cocoa butter, thereby slowing and limiting the expression process when cocoa nibs are pressed. In cocoa liquor the cocoa butter is freed from the cell structure, and is therefore expressed more easily. Furthermore the utilisation of the mechanical energy is different when cocoa nibs and cocoa liquor are pressed. In nib expression the mechanical energy must first crush the nibs and remove

the air between the nib particles before the cocoa butter will start to flow through the filter cake. When cocoa liquor is pressed the mechanism is filtration (due to the free-flowing liquid cocoa butter) followed by expression (compaction of the solids and removal of the remaining cocoa butter) [31]. In the case of cocoa nibs the mechanism is expelling of air, crushing (causing some, but not all, of the cell structures to rupture) and expression [32].



(a)



(b)

Figure 2-11: Comparison of the press behaviour of cocoa nibs (▲) and cocoa liquor (●) at 100 °C. (a) The cocoa butter yield as a function of pressure. (b) Comparison of U_C graphs of liquor and nibs experiments.

2.4 Conclusions

The dimensions and design of the hydraulic press have little influence on the cocoa butter yield. Yields comparable to those achieved in industrial presses operating with a linearly increasing pressure profile were achieved when cocoa liquor was pressed at a constant pressure in the laboratory press. For cocoa nibs the mass of nibs pressed had little influence on the yield. Grinding the cocoa nibs in a ball mill also does not influence the cocoa butter yield. In contrast pressing cocoa liquor always results in a higher cocoa butter yield. This can be attributed to the freeing of the cocoa butter from the solid matrix when the cocoa nibs are grinded to a very fine paste.

The cocoa butter yield increases with the applied pressure up till a pressure of 60 MPa, whereafter it remains constant. Temperatures below 100 °C have no influence on the cocoa butter yield, whereas pressing cocoa nibs at temperatures of 100 °C or higher results in a noticeably increased cocoa butter yield. Therefore the cocoa butter viscosity has little influence on the yield, whereas the elasticity and compressibility of the solid matrix plays an important role in determining the achievable cocoa butter yield. This is confirmed by the influence of the moisture content on the cocoa butter yield. The maximum yield is reached at moisture contents around 1.3 wt. %. At higher moisture contents, where the nibs are more elastic, the yield decreases dramatically. Furthermore it was shown that at 100 °C higher moisture contents facilitates cooking of the solids, which causes the nibs to extrude through the sieve plate. It is therefore not possible to express cocoa butter from cocoa nibs in a hydraulic press at high moisture contents.

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3 Modelling and experimental evaluation of high-pressure expression of cocoa nibs

Abstract

The ability of the Shirato model to describe the expression of dry cocoa beans in a hydraulic press at pressures of 20 – 80 MPa was compared with that of a numerically solved conservation laws model based on mass and momentum balances. The Shirato model is an analytical solution of the conservation laws model assuming constant material properties. It also assumes the expression process to consist of two stages, namely the primary consolidation stage and the secondary consolidation stage. Creep is assumed to occur only during the secondary consolidation stage. Therefore the Shirato model assumes the material to exhibit viscous-elastic behaviour. In contrast the numerically solved conservation laws model assumes the porosity and filtration resistance to be the result of purely elastic material behaviour and to vary within the filter cake as a result of the solids compressive pressure profile within the cake.

Experimental data were used to determine the material constants involved in both models at 40, 80 and 100 °C. The Shirato model more accurately describes the final average porosity at different pressures when dry cocoa nibs are expressed. It was therefore decided to use the Shirato model to calculate the influence of certain process parameters on the expression of dry cocoa nibs. The calculation results followed the experimentally observed trends when calculations were made for different pressures, pressing times and mass of cocoa nibs pressed. The Shirato model was also used to describe the expression behaviour of cocoa liquor at 100 °C and pressures of 20-70 MPa. Cocoa liquor is a slurry containing solid particles (cocoa solids) in a free-flowing liquid (cocoa butter), and therefore the transition time between filtration and expression needs to be determined first. It was calculated that the filtration stage is absent when cocoa liquor is expressed at pressures of 20 MPa and higher. However, the behaviour of cocoa liquor can only be accurately described with the Shirato model for the last part of the expression process (> 100 s).

3.1 Introduction

Expression of oilseed material in hydraulic filter presses or screw presses is widely used in the food industry to separate oil from the solid material [1-3]. The oils recovered in this way are usually several times more valuable than the original oilseeds, and the optimisation of the oil yield is therefore considered highly desirable in the oilseeds industry. This is also true in the cocoa industry, where the cocoa butter is approximately twice as valuable as the cocoa nibs or the resultant filter cake [4]. Expression is a unit operation in which a liquid is separated from a solid-liquid mixture or liquid bearing matrix by mechanical compression due to the movement of a retaining wall. The compaction and deliquoring occurring to the solid mixture during expression is often referred to as consolidation. A predictive model can aid in the optimisation of the cocoa butter yield and understanding of the high-pressure expression of cocoa nibs.

The general theoretical description of expression is based on consolidation theories originally developed for soil mechanics [5]. Several studies have been made on the modelling of oilseed expression, resulting in the development of empirical models [6-9], Terzaghi-type models [10,11], and models based on the nature of the cell structure of the oilseeds [12-14]. Empirical models enable the prediction of oil yields, but can often only describe the behaviour of a few species of oilseeds expressed in a specific apparatus. The Terzaghi-type models allow good description of the expression process, but the assumptions made in this model are not representative of reality [11,15] Bargale et al. [11] modified the Terzaghi model by using time-varying properties for the oilseed material. However, this requires knowledge of the cumulative volume of oil expressed. This volume is difficult to measure accurately due to the inability to completely remove the oil from the walls of the collecting chamber and sample lines during an expression experiment. Models based on the cell structure provide good insight into the expression process, but require knowledge of the cell structure and cell dimensions of the oilseeds. These measurements are difficult and expensive to make, and the lack of data on the cellular dimensions and properties of oilseeds makes it difficult to apply such models. Lanoisellé investigated the expression of cocoa liquor (finely grinded cocoa nibs) in industrial hydraulic presses and developed an empirical model for the expression of cocoa liquor [9]. Data on the modelling of expression of cocoa nibs have not been found in literature. Gros and co-workers [16] investigated the effect of several parameters on the compressibility modulus of cocoa nibs, but did not present any modelling results for cocoa nibs.

The aim of this chapter is to establish a general model suitable for the description of high-pressure expression of cocoa nibs. In order to do this the ability of two models, a conservation laws model that needs to be solved numerically and the Shirato model

[17-19] that has an analytical solution, to accurately describe the cocoa nib expression process is compared. The conservation laws model takes the changes of the solid compressive pressure and the pressure- dependent material properties throughout the filter cake and during the expression process into account. The Shirato model is a limiting case of the conservation laws model, as a number of assumptions need to be made in order to be able to produce an analytical solution. The most important assumption is that of a constant solid compressive pressure throughout the filter cake. However, the Shirato model is more generally applicable than the Terzaghi model [15]. An advantage of the Shirato model is that the decrease in filter cake thickness as a function of time is used as a variable in the model. The decrease in filter cake thickness is relatively easy and inexpensive to measure. The material constants involved in the constitutive equations describing the pressure-dependent material properties were determined from expression experiments with dry cocoa nibs performed in a laboratory scale hydraulic press at 40, 80 and 100 °C and pressures of 30 – 80 MPa. The modelling results are given in terms of the consolidation ratio and the final average porosity, both easily measurable quantities. The expression behaviour calculated by the selected model is shown for different expression times, pressures and initial mass of cocoa nibs. The ability of the model to describe the expression behaviour of cocoa liquor (finely grinded cocoa beans) is also investigated.

3.2 Theory

Cocoa nibs are de-shelled, broken cocoa bean cotyledons and contain 52-56 wt. % cocoa butter. Cocoa butter has a melting point of around 34 °C [20], and expression can therefore only be performed at elevated temperatures. Figure 3-1 (see paragraph 3.2.1.1) illustrates the expression process. During expression an external load is applied to the cocoa nibs. The forces applied in this way are carried only by the cocoa nibs, and cause a decrease in the porosity. In the case of cocoa nibs this decrease is initially due to the rearrangement of the nibs, causing the bed of nibs to become more compacted due to the expulsion of air [21]. After a short time the nibs are crushed, whereby the cell structures containing the cocoa butter is damaged and the cocoa butter is freed. This allows the cocoa butter to drain through the bed of crushed nibs, thereby partially defattening the crushed nibs. During this stage both the solid matrix of crushed nibs and the freed cocoa butter carry the external load.

The distribution of the external load causes both a liquid pressure gradient and a solid compressive pressure gradient. The liquid pressure gradient is the driving force for the liquid flow through the cake, while the gradient in the solid compressive pressure causes a gradient in the local porosity. At equilibrium the gradients have disappeared, and the solids carry the complete external load.

It is not possible to determine how much of the cocoa butter contained within the cocoa nibs has been freed from the cell structure at different times of the expression process. Therefore, for the purposes of this chapter, the entire cocoa butter content of the cocoa nibs will be considered as the liquid, while the solids are defined as the solid content of the cocoa nibs. The compacted, partially defattened bed of crushed nibs will be called "filter cake".

3.2.1 Conservation laws model

Mathematically the expression process can be described by material independent equations, derived from the mass and momentum balances of the liquid and solid parts, and a set of material dependent equations, the so-called constitutive equations describing the pressure dependency of the permeability and compressibility of the material being expressed [15,22-29].

In the following paragraphs these equations will be derived. The following assumptions are made in this derivation:

- The expression process is one-dimensional.
- The effect of gravity and inertia is negligible compared to that of the externally applied load.
- The resistance of the filter medium is negligible compared to that of the filter cake.
- Only point contact exists between particles.
- No solids pass through the filter medium.

3.2.1.1 Mass and momentum balances

Cartesian coordinates

Consider a one-dimensional expression process, with the filter medium at $x = 0$, and the externally applied load at $x = L$ (see Figure 3-1). The load is applied by an impermeable, movable wall. Then the rate of the flow of liquid in at x ($u_L(x,t)$) minus the rate of flow of liquid out at $x = 0$ ($u_L(0,t) \equiv u_1(t)$) equals the rate of change of liquid in distance x:

$$u_L(x,t) - u_1(t) = -\frac{\partial}{\partial t}\int_0^x \varepsilon(x,t)\,dx \tag{3-1}$$

ε is the local porosity, and is related to the solidosity by equation (3-2).

$$\varepsilon = 1 - \varepsilon_S \tag{3-2}$$

In a similar way equation (3-3) can be derived when it is assumed that no solids pass through the filter medium.

$$u_S(x,t) = -\frac{\partial}{\partial t}\int_0^x \varepsilon_S(x,t)dx \tag{3-3}$$

where u_S is the superficial velocity of the solids based on the total surface area. Differentiation of equations (3-1) and (3-3) yields equations (3-4) and (3-5) when it is assumed that ε is a smooth function of x and t:

$$\left(\frac{\partial u_L}{\partial x}\right)_t = -\left(\frac{\partial \varepsilon}{\partial t}\right)_x \tag{3-4}$$

$$\left(\frac{\partial u_S}{\partial x}\right)_t = \left(\frac{\partial \varepsilon}{\partial t}\right)_x \tag{3-5}$$

Combination of equations (3-4) and (3-5) yields the following continuity equation:

$$\left(\frac{\partial u_L}{\partial x}\right)_t + \left(\frac{\partial u_S}{\partial x}\right)_t = 0 \tag{3-6}$$

The corresponding integral form is:

$$u_L(x,t) + u_S(x,t) = u_1(t) \tag{3-7}$$

The one-dimensional Navier-Stokes equation is used for the momentum balances of both the solid and the liquid phase. The liquid and (intrinsic) solid density is taken to be constant, since the compressibilities of these phases are much smaller than that of the filter cake. The liquid phase is also assumed to be Newtonian, a reasonable assumption for pure cocoa butter [30,31]. Furthermore the momentum transfer to the wall (i.e. wall friction) is ignored. This is valid when the ratio of cake thickness to diameter is less than 0.6 [10], which is always the case for the experiments used for this chapter. Previous studies proved the acceleration, convective, viscous, gravitational and buoyancy terms to be negligible with respect to the pressure terms for expression [15]. From the resultant momentum balance (see equation (3-8)) it follows that the change in the liquid pressure gradient equals the negative change in the solid compressive pressure gradient.

$$\left(\frac{\partial P_L}{\partial x}\right)_t + \left(\frac{\partial P_S}{\partial x}\right)_t = 0 \tag{3-8}$$

Note that P_L and P_S are based on the overall cross-sectional area of the filter medium. Integration of (3-8) yields:

$$P_L(x,t) + P_S(x,t) = P(t) \tag{3-9}$$

P(t) is the externally applied load. A relation between the liquid velocity and the liquid pressure gradient is also needed. This is dependent on the local cake permeability, *K*, which is a function of the local porosity. Darcy's law can be used to describe the relation between the liquid velocity and the liquid pressure drop if the liquid flow can be assumed to be laminar. In this case the liquid velocity relative to the solid velocity is used:

$$\frac{\partial P_L}{\partial x} = -\frac{\mu}{K}(u_L - u_S) \tag{3-10}$$

where μ is the dynamic viscosity of the liquid. The permeability is dependent on the characteristics of the expressed material, which in turn is influenced by the expression conditions. It is defined as:

$$K = \frac{1}{\rho_S \alpha (1-\varepsilon)} \tag{3-11}$$

ρ_S is the solids density. The specific cake resistance, α, is dependent on the size and shape of the particles in the filter cake, as well as the cake porosity.

Equations (3-8), (3-10) and (3-11) can be combined to yield:

$$\frac{\partial P_S}{\partial x} = \mu \rho_S \alpha (1-\varepsilon)(u_L - u_S) \tag{3-12}$$

Therefore the liquid velocity, at a certain time and spatial coordinate, equals:

$$u_L = \left(\frac{\partial P_S}{\partial x}\right)\frac{1}{\mu \rho_S \alpha (1-\varepsilon)} + u_S \tag{3-13}$$

When equation (3-13) is substituted into equation (3-4) together with the assumption that α and ε are functions of P_S only, the following equation results:

$$\frac{\partial}{\partial x}\left(u_S + \frac{1}{\mu\rho_S\alpha(1-\varepsilon)}\left(\frac{\partial P_S}{\partial x}\right)\right) = -\frac{\partial \varepsilon}{\partial t} \tag{3-14}$$

or:

$$\frac{\partial u_S}{\partial x} + \frac{1}{\mu\rho_S\alpha(1-\varepsilon)}\left(\frac{\partial^2 P_S}{\partial x^2}\right) + \frac{1}{\mu\rho_S}\left(\frac{\partial P_S}{\partial x}\right)^2\left\{\frac{-1}{\alpha^2(1-\varepsilon)}\frac{\mathrm{d}\alpha}{\mathrm{d}P_S} + \frac{1}{\alpha(1-\varepsilon)^2}\frac{\mathrm{d}\varepsilon}{\mathrm{d}P_S}\right\} + \frac{\mathrm{d}\varepsilon}{\mathrm{d}P_S}\left(\frac{\partial P_S}{\partial t}\right) = 0 \tag{3-15}$$

Equation (3-5) can be substituted into equation (3-15) to yield:

$$\frac{1}{\mu\alpha\rho_S(1-\varepsilon)}\left(\frac{\partial^2 P_S}{\partial x^2}\right) - \frac{1}{\mu\alpha^2\rho_S(1-\varepsilon)}\frac{\mathrm{d}\alpha}{\mathrm{d}P_S}\left(\frac{\partial P_S}{\partial x}\right)^2 + \frac{1}{\mu\alpha\rho_S(1-\varepsilon)^2}\frac{\mathrm{d}\varepsilon}{\mathrm{d}P_S}\left(\frac{\partial P_S}{\partial x}\right)^2 + 2\frac{\mathrm{d}\varepsilon}{\mathrm{d}P_S}\left(\frac{\partial P_S}{\partial t}\right) = 0 \tag{3-16}$$

Simplification after rearrangement leads to the final equation:

$$\left(\frac{\partial^2 P_S}{\partial x^2}\right) - \left(\frac{\partial P_S}{\partial x}\right)^2\left\{\frac{1}{\alpha}\frac{\mathrm{d}\alpha}{\mathrm{d}P_S} + \frac{1}{(1-\varepsilon)}\frac{\mathrm{d}\varepsilon}{\mathrm{d}P_S}\right\} + 2\mu\alpha\rho_S(1-\varepsilon)\frac{\mathrm{d}\varepsilon}{\mathrm{d}P_S}\left(\frac{\partial P_S}{\partial t}\right) = 0 \tag{3-17}$$

Material coordinates

During expression the cake thickness is a function of time, introducing a moving boundary when Cartesian coordinates are used. It is more convenient to simulate with fixed boundaries. Therefore material coordinates must be introduced. The material coordinates are defined in terms of ω; the volume of the solid phase between an arbitrary position in the cake and the filter medium, divided by the filter area. Since the total volume of the solid phase remains constant the boundary values of ω are also constant. This is known as a convective coordinate system [15,26,27]. Figure 3-1 shows the relationship between the Cartesian and the convective coordinate systems.

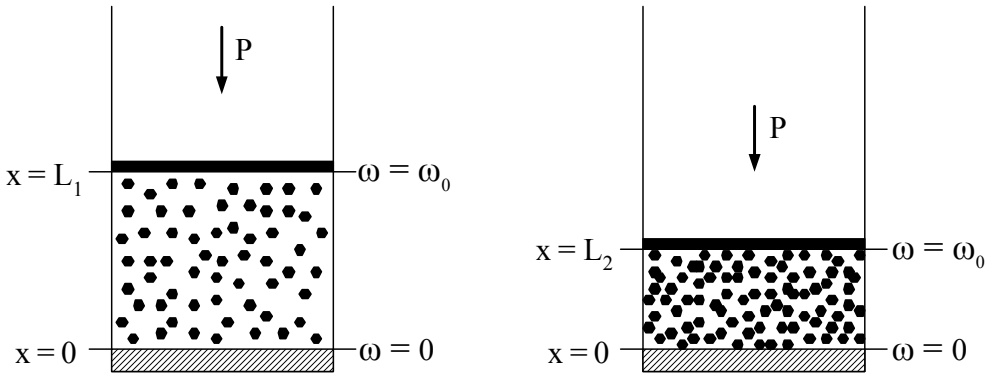


Figure 3-1: The expression in terms of the Cartesian and the convective coordinate systems. L_1 is the original cake thickness; L_2 is the thickness of the compressed filter cake; ω_0 is the total volume of solids per filter area; P is the applied pressure.

Equation (3-18) can be used to transform equation (3-17) into ω-coordinates.

$$\mathrm{d}\omega = (1-\varepsilon)\mathrm{d}x \tag{3-18}$$

With the aid of equation (3-18) the following equation results:

$$\left(\frac{\partial^2 P_S}{\partial \omega^2}\right) - \frac{1}{\alpha}\frac{\mathrm{d}\alpha}{\mathrm{d}P_S}\left(\frac{\partial P_S}{\partial \omega}\right)^2 + \frac{2\mu\alpha\rho_S}{(1-\varepsilon)}\frac{\mathrm{d}\varepsilon}{\mathrm{d}P_S}\left(\frac{\partial P_S}{\partial t}\right) = 0 \tag{3-19}$$

Equation (3-19) is the differential equation that, together with the appropriate constitutive relationships, describes the expression process.

3.2.1.2 Constitutive equations

The constitutive equations are empirical relationships that describe the pressure dependency of the permeability and compressibility of the material being expressed. In this chapter a continuum approach will be used, that is, it is assumed that the dimensions of the particles are small compared to that of the equipment. The compressibility and permeability are therefore macroscopic properties of the filter cake. It is conventionally assumed that equations (3-20) and (3-21) describe the pressure dependency of the filtration resistance and the porosity, respectively [18,26-29,32-35]:

$$\alpha = \alpha_0\left(1+\frac{P_S}{P_a}\right)^{n_\alpha} \tag{3-20}$$

$$(1-\varepsilon)=(1-\varepsilon_0)\left(1+\frac{P_S}{P_a}\right)^{\beta} \tag{3-21}$$

where α_o, P_a, n_α, ε_0 and β are material constants. These relationships assume that the material is elastic, i.e. that the material behaviour is time-independent and that instantaneous changes to P_s will cause instantaneous changes in the porosity and filtration resistance.

3.2.1.3 Boundary and initial conditions

Equation (3-19) is a second order partial differential equation, requiring one initial and two boundary conditions to be fulfilled.

Initial condition

The hydraulic pressure distribution in filter cakes of moderate compressibility can be approximated with a sinusoidal curve [17,18]. Therefore the initial solid compressive pressure distribution in filter cakes of moderate compressibility can also be approximated with a sinusoidal curve. For the case of uni-axial expression performed in a filter press with a single drainage area it can be written as [17,18]:

$$P_S(\omega,0)=P(0)\left(1-\sin\left(\frac{\pi}{2}\frac{\omega}{\omega_0}\right)\right) \tag{3-22}$$

where ω_0 is the total volume of solids per filter area.

Boundary condition at the filter medium

The solid compressive pressure at the filter medium equals the applied pressure when the liquid pressure drop across the filter can be neglected with respect to the liquid pressure drop of the cake. It is reasonable to assume that this is the case due to the low flow rate of liquid in the case of expression [15,17,18,26]. Therefore:

$$P_s(0,t)=P(t) \tag{3-23}$$

Boundary condition at the top of the filter cake

At the top of the filter cake (i.e. the surface where the external load is applied) the superficial liquid velocity relative to the solid velocity is zero since the liquid and the solid move with the same velocity [15,17,18,26]. From Darcy's law (equation (3-10))

it follows that the gradient of the solid compressive pressure also equals zero at the cake surface. Therefore:

$$\left.\frac{\partial P_S}{\partial \omega}\right|_{\omega=\omega_0} = 0 \tag{3-24}$$

3.2.1.4 Relation with the consolidation ratio

Equation (3-18) can be used to determine the filter cake thickness L at time t once the model has been solved numerically. $L(t)$ is the value of x at ω_0 at time t. The consolidation ratio $U_C(t)$ can then be calculated from equation (3-25):

$$U_C(t) = \frac{L(0) - L(t)}{L(0) - L(t_{end})} \tag{3-25}$$

where t_{end} is the final time of the expression process.

3.2.2 Shirato model

Terzaghi published the first consolidation theory [5,15]. In this model it is assumed that the filter cake thickness, compressibility and permeability remain constant throughout the process [23]. This is almost never true and limits the theory to systems with small strains. Shirato [17-19,21-24] developed a model for the consolidation of solid/liquid mixtures and semi-solids based on that of Terzaghi in which the consolidation process is divided into two stages: primary consolidation and secondary consolidation. This avoids the assumption of instantaneous mechanical equilibrium made in the Terzaghi model. It is assumed that creep effects are negligible during primary consolidation (i.e. the local void ratio depends on the solid compressive pressure only). The secondary consolidation stage, assumed to occur at a much slower rate than that of primary consolidation, involves creep of the solid phase (i.e. the local void ratio depends on both the solid compressive pressure and time) [17-19]. The model of Shirato is more generally applicable than that of Terzaghi [15]. The primary consolidation stage is described with a Terzaghi-type model, while it is assumed that the rheological behaviour of the secondary consolidation stage can be described by a Voigt element. Figure 3-2 shows a schematic diagram of the Voigt model. The spring accounts for the effect of elasticity, while the dashpot takes the effect of viscous behaviour into account. In this way the visco-plastic behaviour of the material (i.e. the instantaneous change in the porosity due to a sudden change in the compressive

pressure as well as the inability of the material to return to its original state after the load has been released) can be described.

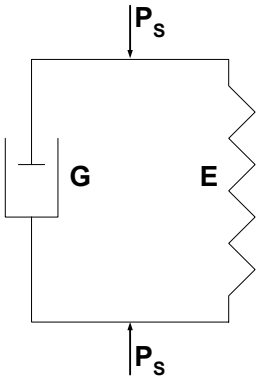


Figure 3-2: Schematic diagram of the Voigt model. E is the elasticity of the spring in Pa, G is the viscosity of the dashpot in Pa.s.

The natural volume strain S is defined as the relative volume change of the solid phase:

$$\mathrm{d}S = \frac{\mathrm{d}V}{V} \tag{3-26}$$

where V is the specific cake volume. For a constant solid phase density the mass balance of the solid phase leads to the relationship between the void ratio, e, and the strain, S, as shown in equation (3-27).

$$\mathrm{d}e = (1+e)\,\mathrm{d}S \tag{3-27}$$

The void ratio is related to the porosity, ε, by equation (3-28):

$$e = \frac{\varepsilon}{1-\varepsilon} \tag{3-28}$$

The Voigt model assumes the following relationship between the solids compressive pressure P_S, time t and natural volume strain S for a constant solids compressive pressure [15]:

$$S = -\frac{P_S}{E}\left(1-\exp\left(\frac{-E}{G}t\right)\right) \tag{3-29}$$

The Voigt model is a linear viscoelastic model, and therefore the Boltzmann superposition principle can be applied to calculate the strain of the creeping material as a function of an arbitrary pressure history. This leads to the following equation [15]:

$$S(t)=\int_0^t \frac{\partial S\left(P_S,t-\tau\right)}{\partial P_S}\frac{\partial P_S(\tau)}{\partial \tau}d\tau \tag{3-30}$$

where τ is a dummy variable. Combination of equations (3-27) to (3-30) and differentiation with respect to t leads to:

$$\frac{\partial e}{\partial t}=-\int_0^t \frac{1+e}{E}\left\{1-\exp\left(-\frac{E}{G}(t-\tau)\right)\right\}\frac{\partial P_S}{\partial \tau}d\tau \tag{3-31}$$

The mass balance is considered as a sum of the mass balances for the primary and the secondary consolidation stages. The effect of convection is neglected. This leads to equation (3-32), where $(\partial e/\partial t)_E$ and $(\partial e/\partial t)_c$ are the time rate of change in e due to primary and secondary consolidation, respectively [15].

$$\frac{\partial e}{\partial t}=\left(\frac{\partial e}{\partial t}\right)_E+\left(\frac{\partial e}{\partial t}\right)_c=-\frac{\partial\left(u_L-u_S\right)}{\partial \omega} \tag{3-32}$$

The Terzaghi model with a convective coordinate system is used for $(\partial e/\partial t)_E$, while equation (3-31) is used for $(\partial e/\partial t)_c$:

$$\left(\frac{\partial e}{\partial t}\right)_E=C_e\cdot\frac{\partial^2 e}{\partial \omega^2} \tag{3-33}$$

C_e is the modified coefficient of consolidation. The same initial and boundary conditions as described in paragraph 3.2.1.3 are used to solve the equations. The analytical solution of the Shirato model for the case of one drainage surface, assuming that the time rate of secondary consolidation is much smaller than that of primary consolidation, is shown in equation (3-34) [17-19]:

$$U_c(t)\equiv\frac{L(0)-L(t)}{L(0)-L\left(t_{end}\right)}=(1-B)\left\{1-\exp\left(-\frac{\pi^2}{4}\frac{C_e}{\omega_0^2}t\right)\right\}+B\left\{1-\exp\left(-n\cdot t\right)\right\} \tag{3-34}$$

where B is the ratio of secondary to primary consolidation ($0 < B < 1$), ω_0 is the volume of solids in the cake per filter area, t is time and n (= E/G) is the creep

constant (the ratio of the rigidity and the viscosity) of the Voigt model. $U_C(t)$ is the consolidation ratio at time t. The modified coefficient of consolidation, C_e, is assumed to be constant throughout the entire consolidation process in order to obtain the analytical solution. C_e is defined as:

$$C_e = \frac{1}{\mu\rho_s\alpha\left(-\frac{\mathrm{d}e}{\mathrm{d}P_s}\right)} \tag{3-35}$$

However, it is a well-known fact that the local solid compressive pressure (P_s) changes throughout the consolidated cake and with time [24], and C_e may therefore change substantially with time and position during the consolidation process.

The following equation holds for $t >> 0$ when the deliquoring rate due to secondary consolidation is much smaller than that due to primary consolidation [17-19]:

$$n \ll C_e\left(\frac{\pi}{2\omega_0}\right)^2 \tag{3-36}$$

Equation (3-34) can be simplified to:

$$U_c(t) = 1 - B\left\{\exp\left(-n\cdot t\right)\right\} \tag{3-37}$$

Therefore the values of B and η can be found from the experimental results by plotting $\ln(1\text{-}U_c)$ against t for $t >> 0$. The value of C_e can then be found by a fitting method when equation (3-34) is rearranged as follows [17-19]:

$$\frac{\left(L(0)-L(t)\right)-B\left(L(0)-L(t_{end})\right)\left\{1-\exp\left(-n\cdot t\right)\right\}}{(1-B)\left(L(0)-L(t_{end})\right)} = 1-\exp\left(-\frac{\pi^2 C_e}{4\omega_0^2}t\right) \tag{3-38}$$

In actual fact the Shirato model is the analytical solution that is obtained by assuming the solid compressive pressure P_S, and hence the filtration resistance and porosity, to be constant throughout the filter cake at any given time. It is therefore a limiting case of the conservation laws model. The model does not reflect reality, where the pressure distribution, and as a consequence the filtration resistance and porosity, not only varies throughout the filter cake but also with time. However, the material constants are determined from the experimental data. The experimental apparatus does not allow measurement of the pressure profiles within the cake, and therefore only the final average porosity and the decrease in filter cake thickness can be used in these

calculations. The material constants determined in this way will reflect the equilibrium conditions and the conditions at the filter cake surfaces, and not the pressure and porosity profiles within the cake. The Shirato model is therefore not necessarily less accurate in its description of equilibrium expression behaviour than the conservation laws model.

3.2.3 Modelling parameter determination

Table 3-1 shows the nature of the parameters involved in the two models. For both models the material constants need to be known before any modelling calculations can be done. The material constants of the conservation laws model were determined via iteration by fitting the calculated U_c graphs and final average porosities for each temperature and different pressures to the experimental ones.

The values of B and n in the Shirato model were determined at each pressure for every temperature. The average values of B and n at each temperature were used in subsequent calculations. C_e was determined from the experimental filter cake decrease data at each pressure. The value of α was calculated from the value of C_e at each pressure. α_0 and n_α were calculated by plotting α against $\ln(1+P_S/P_a)$. ε_0 and β were determined from the cocoa butter contents of the filter cakes. ε_0 and β were determined from the cocoa butter contents of the filter cakes.

Table 3-1: Parameters and solution procedures involved in the conservation laws and the Shirato models.

	Conservation laws model	**Shirato model**
Input	$L\,(t)$ $P\,(t)$ ω_0 μ ρ_S Final ε	$L\,(t)$ $P\,(t)$ ω_0 μ ρ_S Final ε
Assume	P_a	P_a
Fit	α_o n_α ε_0 β	ε_0 β B n C_e
Calculate from fitted parameters		α_o n_α

3.3 Experiments

3.3.1 Experimental apparatus and procedure

A laboratory scale press with one drainage area was constructed to provide the experimental data. The inner diameter of the press chamber is 30 mm. Figure 3-3 shows a schematic depiction of the filter press. Details of the equipment and the experimental procedure can be found in Chapter 2. Expression experiments were done with 10 g of dry cocoa nibs at 40, 80 and 100 °C and pressures of 20-80 MPa. Experiments were also done with dry cocoa liquor at 100 °C and pressures of 20-80 MPa. In all cases the pressure was kept constant for 10 minutes, whereafter the filter cake was removed and analysed. The decrease of filter cake thickness was measured with an accuracy of 0.01 mm and was recorded digitally at a frequency of 1 Hz.

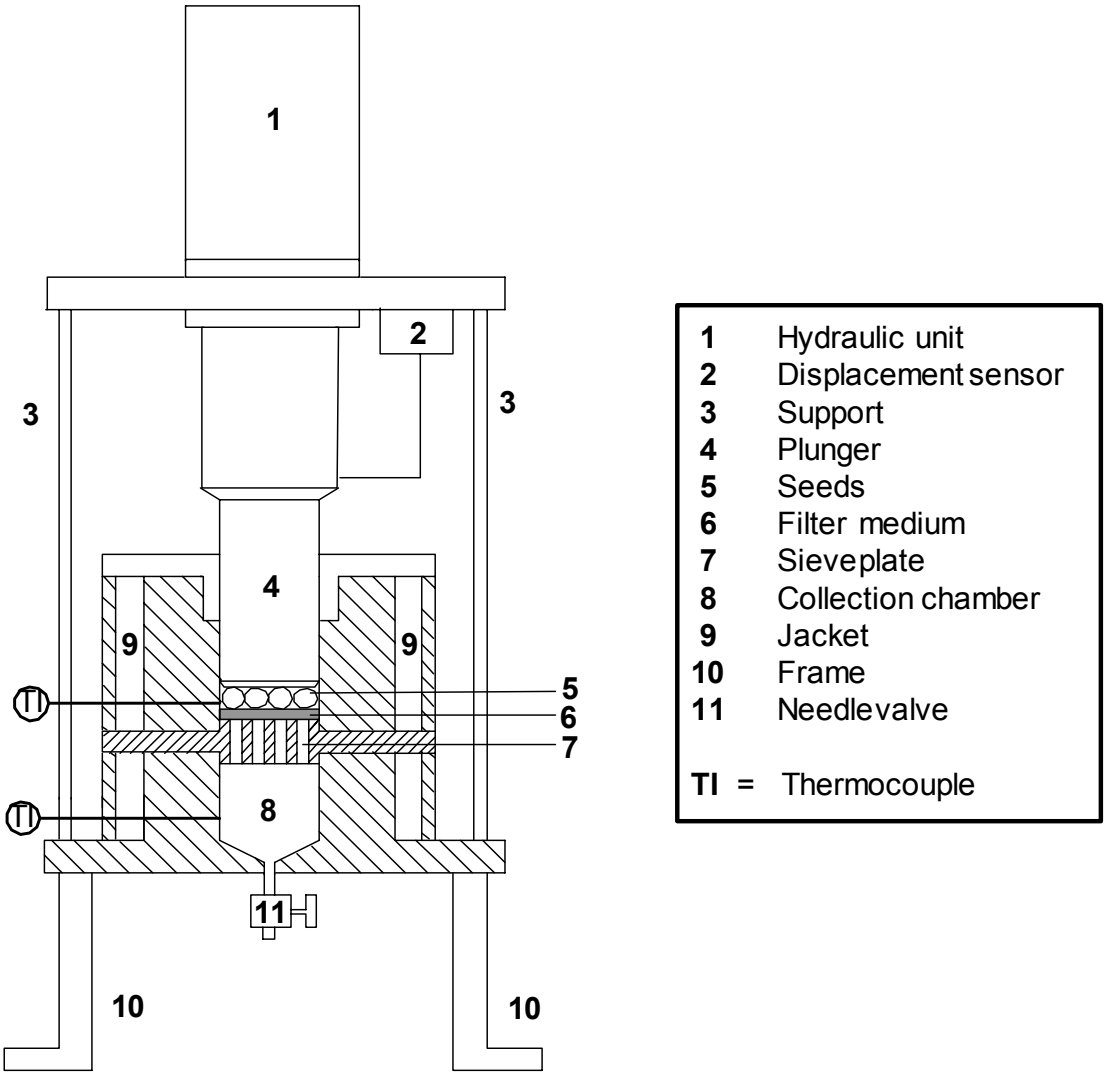


Figure 3-3: Schematic drawing of the laboratory press (not to scale).

In order to evaluate the experimental error three pressing experiments were done at 40 °C and a pressure of 60 MPa. The average yield (defined as the percentage of the total mass of oil that has been expressed) for these experiments was 74.9 %. The absolute standard deviation in the determined yields was calculated as 0.6 %. Duplication of random experiments at other conditions always resulted in an absolute standard deviation of less than 0.9 %. In view of this the absolute experimental error made in calculating the yield is taken as ± 1 %.

The viscosity of the cocoa butter was measured with an Ubelohde viscometer (capillary diameter 1.13 mm) purchased from Schott (Mainz, Germany). The viscometer was placed in a constant temperature bath (set point ± 0.1 °C). The density of the cocoa butter was measured at different temperatures with a density meter (DMA 5000, Anton Paar, Graz, Austria) with an accuracy of 0.005 kg/m^3. A pycnometer (AccuPyc 1330, Micromeritics, Norcross, GA, USA) was used to determine the density of the cocoa nibs.

3.3.2 Analysis

The standard method for the determination of the fat content of cocoa powder by soxhlet extraction as proposed by the International Office of Cocoa, Chocolate and Sugar Confectionary (IOCCC) [37] was modified to be suitable for the analysis of cocoa filter cakes. These modifications include soaking the filter cake in a small quantity of petroleum ether for at least 4 hours before grinding to prevent the excessive formation of fines during grinding. Furthermore a wad of cotton wool was placed in the bottom of the cellulose fibre extraction thimble to prevent fines from passing through the thimble. The pre-soaked filter cakes were grinded together with a small volume of petroleum ether for 20 s at 16 Hz in a ball mill (Type MM 301, Retsch GmbH & Co, Haan, Germany). Filter cakes from cocoa liquor were not grinded in the ball mill, but placed inside glass fibre thimbles with cotton wool on top and then extracted in the conventional manner.

3.3.3 Materials

Winnowed cocoa nibs (56.2 wt. % cocoa butter, dry basis), cocoa liquor (53.9 wt. % cocoa butter, dry basis) and cocoa butter were obtained from Gerkens Cacao (Wormer, The Netherlands). The density of the cocoa liquor was reported as 1110 kg/m^3 at 100 °C. Petroleum ether (boiling range 40-60 °C) was bought from Merck (Amsterdam, The Netherlands).

3.3.4 Modelling

The conservation laws model was solved with a second order centered finite difference method using the software package gPROMS® version 2.3.4 (Process Systems Enterprise Limited, London, UK). The material constants (ε_0, β, α_0 and n_α) were determined using the parameter estimation subroutine of gPROMS® with a constant variance model. The decrease in filter cake thickness as a function of time (standard deviation 0.00001 m) and the final average porosity (as calculated from the oil content of the filter cakes) (standard deviation 0.001) were used as measured quantities in the calculations.

The Shirato model was simple enough to solve in spreadsheet format using Microsoft Excel® with the method described in paragraph 3.2.2.

3.4 Results and discussion

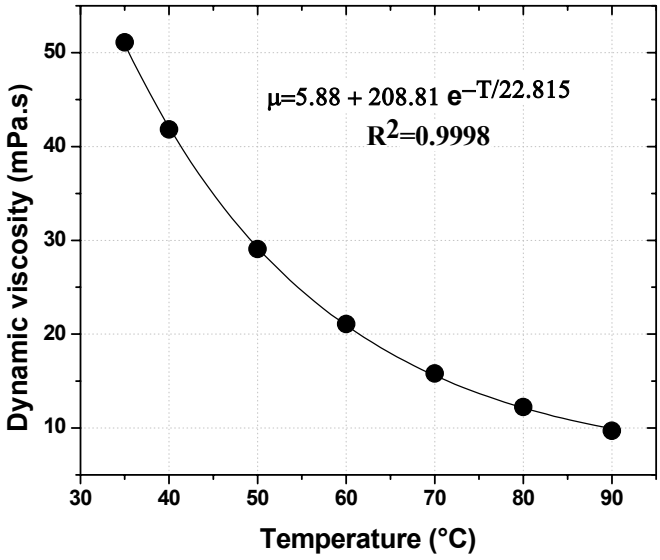
3.4.1 Physical properties

The true density of the cocoa nibs (ρ_{nibs}) was measured as 1100 kg/m^3 at 25 °C. The density of solid cocoa butter (ρ_{cb}) is 961 kg/m^3 [20]. The density of the cocoa solids (ρ_{solids}) was calculated as 1350 kg/m^3 with the following equation:

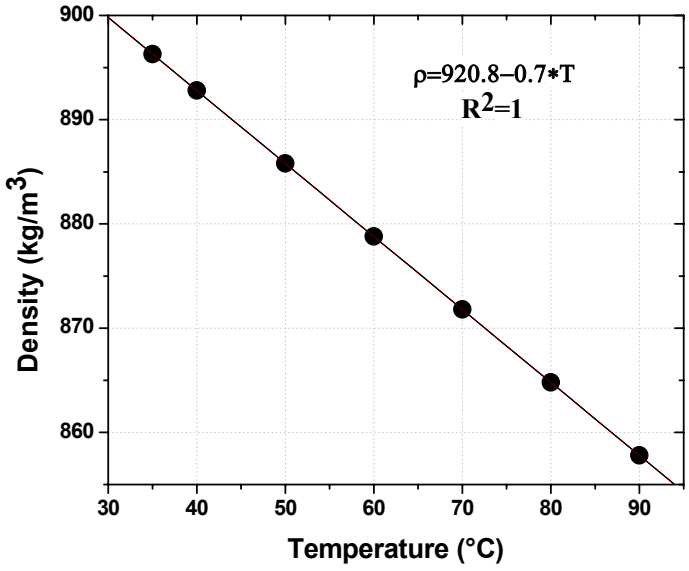
$$\frac{1}{\rho_{nibs}} = \frac{x_{cb}}{\rho_{cb}} + \frac{x_{solids}}{\rho_{solids}} \tag{3-39}$$

x_{cb} and x_{solids} are the mass fraction of the cocoa butter and the cocoa solids, respectively. It was assumed that the density of the cocoa solids will remain constant with temperature. The density of the cocoa nibs at 40, 80 and 100 °C was calculated with equation (3-39) using the measured cocoa butter densities and the density of cocoa solids.

Figure 3-4 shows the viscosity and density of cocoa butter as functions of temperature. For the calculations at 100 °C the density and viscosity reported by Fang et al. [30] were used due to limitations of the experimental set-ups used to measure the atmospheric properties of cocoa butter.



(a)



(b)

Figure 3-4: Physical properties of cocoa butter. T has units of °C. (a) Viscosity (μ). (b) Density (ρ).

3.4.2 Model selection

In this paragraph the material constants determined for both the conservation laws model and the Shirato model are shown. These constants were used to calculate the final average porosity and U_c-graphs at different temperatures and pressures. The

calculated and experimental values are compared in order to determine which of the two models gives the most accurate description of the expression of cocoa nibs.

3.4.2.1 Material constants

Conservation laws model

Table 3-2 shows the material constants used in the conservation laws model as determined with the parameter estimation routine of gPROMS®. In all cases P_a was assumed to have a value of 10 MPa. In filtration theory P_a is the threshold pressure above which the cake would deform [28]. In the case of oilseed expression P_a should therefore be close to the pressure at which oil first start to be expressed. Initial experiments showed that it is not possible to express cocoa butter from cocoa nibs at pressures below 10 MPa, while it is possible to express oil at 20 MPa [36]. It is therefore reasonable to assume P_a to have a value of 10 MPa.

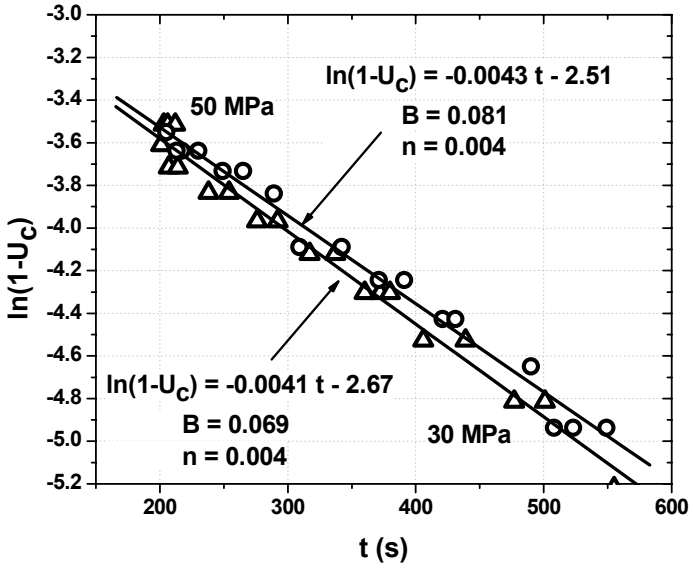
Shirato model

Table 3-2 shows the material constants used in the Shirato model that were determined from the experimental data according to the procedure described in paragraphs 3.2.2 and 3.2.3. At each temperature the values of B and n are the averages of the values determined for the experiments at different pressures. C_e has to be calculated for every pressure at each temperature. In all cases the value of C_e is in the order of 1×10^{-7} m^2/s. It was assumed that the constitutive equations have the same form as those used in the conservation laws model (see equations (3-20) and (3-21)) with the exception that the applied pressure P was used instead of the solid compressive pressure P_s. This is a reasonable assumption: the amount of free-flowing liquid at any time of the expression process is very small compared to the amount of solids. The value of P_s will therefore always be close to P (see equation (3-9)). P_a was assumed to be equal to 10 MPa for the reasons mentioned before. The values of ε_0 and β were calculated by plotting the experimentally determined final average porosity, as calculated from the cocoa butter content of the filter cakes, versus pressure for each temperature. It is important to note that for the Shirato model the porosity calculated with equation (3-21) is the final average porosity. The cocoa butter contents of the filter cakes were used to determine the constants β and ε_0 in equation (3-21), and therefore this equation can only be used to calculate the porosity of the filter cake at the end of the expression experiment. The porosity at time t can also be calculated from the measured decrease in filter cake thickness if the initial porosity is known. Knowledge of the porosity as a function of time gives insight into the speed of the expression process. This is however an indirect method, and does not provide additional information compared to a calculation of the final average porosity and the consolidation ratio U_C as a function of

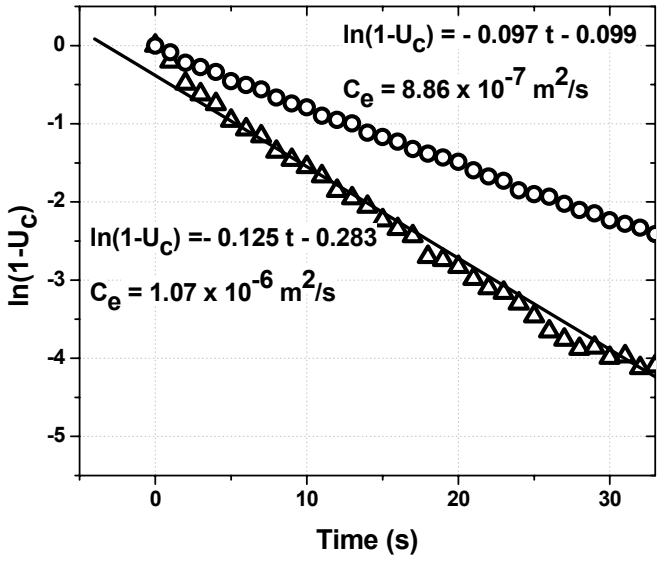
time. It was therefore decided not to calculate the porosity as a function of time. Figure 3-5 shows typical graphs made to determine the material constants B and n (Figure 3-5 (a)), ε_0 and β (Figure 3-5 (c)) and α_0 and n_α (Figure 3-5 (d)).

Discussion

The values of the different material constants differ for the two models, but are of the same order of magnitude and show the same trend. The difference in the values can be attributed to the assumption made in the Shirato model that the value of C_e is constant throughout the entire expression process. The relatively high values of n_α and β indicate that cocoa nibs can be considered to be highly compressible material at the conditions studied [3,27,29,34]. The calculated filtration resistances are of the same order of magnitude as those reported for cellular biological solids in Schwartzberg [3]. The different values of ε_0 for 40, 80 and 100 °C can be attributed to the change of compressibility of the cocoa nibs with temperature. The consolidation and permeability properties of oilseed material often vary with temperature [38,39]. Furthermore it must be noted that P_a used in equations (3-20) and (3-21) is a constant that makes these equations dimensionless, and that the value used for P_a influences the value of ε_0. It can also be seen that the contribution of secondary consolidation to the expression process is much smaller at 100 °C than at 40 and 80 °C. This indicates that the cocoa nibs are weaker at 100 °C, causing the nibs to fracture more easily than at lower temperatures. This confirms that the temperature influences the nature of the solid structure and its behaviour during expression. It has previously been observed that the change in the characteristics of the solids due to the increased temperature has a bigger influence on the press behaviour of the cocoa nibs than the decreased viscosity of the cocoa butter [36].

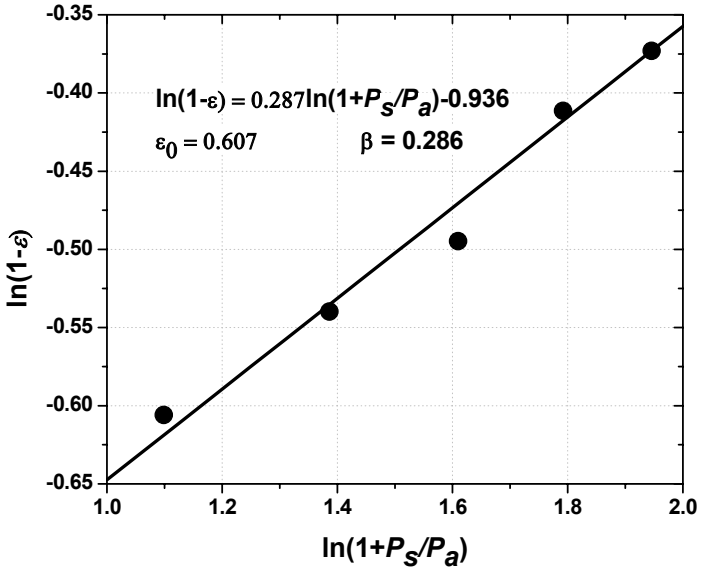


(a)



(b)

Figure 3-5 (continued on next page).



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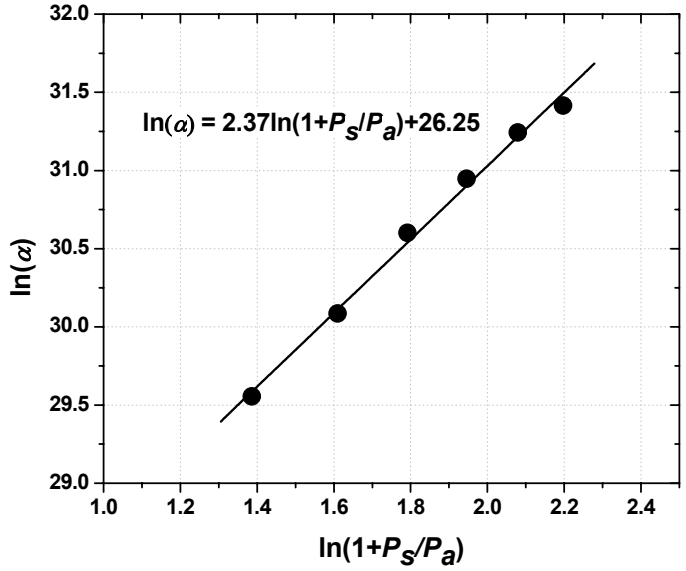


(d)

Figure 3-5: Typical graphs made from the experimental data to determine the material constants for cocoa nibs expressed at 100 °C and pressures of 30 (△) and 50 (○) MPa for the Shirato model. In all cases ω_0 = 0.0046 m^3/m^2. (a) Determination of *β* and *n* according to equation (3-37), (b) C_e according to equation (3-38), (c) the material constants involved in equation (3-21), (d) the material constants involved in equation (3-20).

Table 3-2: Material constants used in the Shirato (S) and the conservation laws (C) models for pressures of 20-80 MPa. The minimum and maximum values for *B* and *n* are also shown.

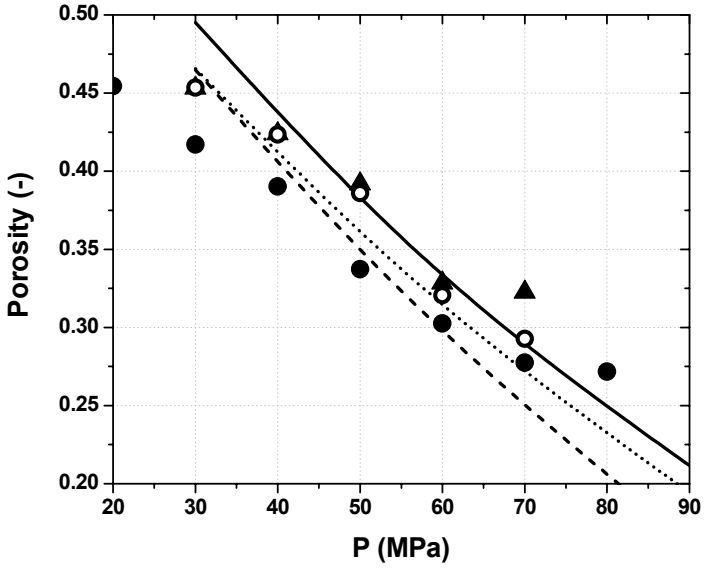
	Units	40 °C		80 °C		100 °C	
		S	C	S	C	S	C
B	-	0.17	-	0.19	-	0.08	-
min		0.10		0.14		0.02	
max		0.28		0.23		0.14	
n	s^{-1}	0.007	-	0.008	-	0.005	-
min		0.006		0.007		0.004	
max		0.007		0.009		0.007	
ε_0	-	0.67	0.75	0.62	0.72	0.61	0.71
β	-	0.36	0.51	0.31	0.49	0.29	0.45
$\alpha_0 \times 10^{-11}$	m/kg	1.84	2.04	1.44	5.28	2.50	6.15
n_α	-	2.28	2.34	2.30	1.93	2.37	1.85

3.4.2.2 Model comparison

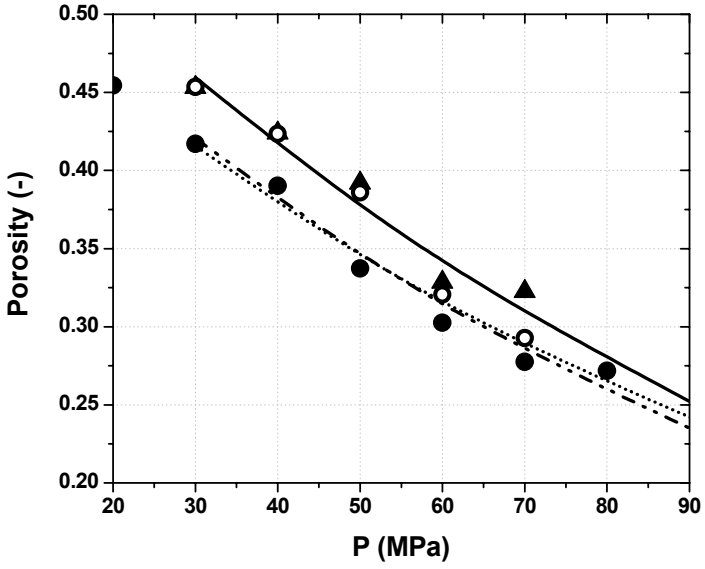
The applied pressure is an important parameter in determining the yield attainable when cocoa nibs are pressed [36]. Therefore the ability of the Shirato and conservation laws model to accurately reflect the influence of the expression pressure on the behaviour of the cocoa nib filter cake determines the usefulness of the model. In Figure 3-6 the calculated final average porosities (equal to the volume fraction of cocoa butter in the filter cake at the end of the expression process) are compared to the experimentally determined final average porosities. The calculated porosities of both the Shirato and the conservation laws model are similar for lower pressures. However, at higher pressures the porosities calculated with the conservation laws model continue to decrease approximately linearly with an increase in pressure, whereas those calculated with the Shirato model follow a more logarithmic trend with pressure. It is expected that the porosity will decrease with an increase in pressure, but that it will reach a minimum whereafter a further increase in pressure will not cause any further decrease in the porosity. It has previously been shown that the cocoa butter yield reaches an apparent maximum at 60 MPa [36], and it is therefore reasonable to expect the final average porosity to reach a minimum at this pressure. The experimental data used for determining the material constants in the constitutive equations were taken from experiments performed at 20 – 80 MPa. Therefore the conservation laws model will be most accurate in this pressure range, and the deviations of the calculated porosities from the actual porosities can therefore be expected to decrease when the material constant calculations include experiments at higher pressures.

Figure 3-7 compares the experimental and calculated U_c curves. Once again the calculations made with the Shirato model more accurately follow the experimental data. This is a direct consequence of the inclusion of viscous material properties in the fitting parameters of the Shirato model. The inability of the conservation laws model to accurately describe the expression of cocoa nibs can therefore be attributed to the assumption that cocoa nibs display elastic behaviour. La Heij [40] has made similar observations for sludge expression.

Replacing the constitutive equations (see paragraph 3.2.1.2) with equations taking the viscous properties of the material in account will improve the conservation laws model. However, the equations used for describing visco-elastic behaviour are at best an approximation of the probable plastic behaviour, and the relation between the constants used in these equations, the porosity and the definition of strain necessary for describing the material behaviour is not clear [40]. In view of this and the inability to determine any pressure profiles within the filter cake during the expression process it was decided not to investigate the conservation laws model any further, but to select the Shirato model for further calculations.

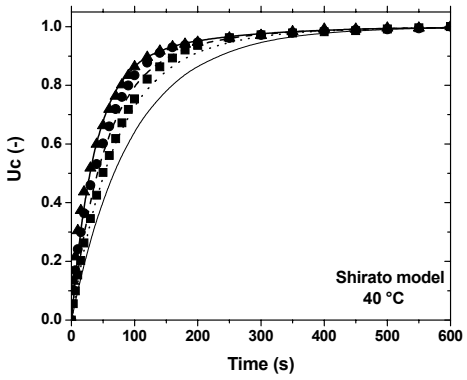


(a)

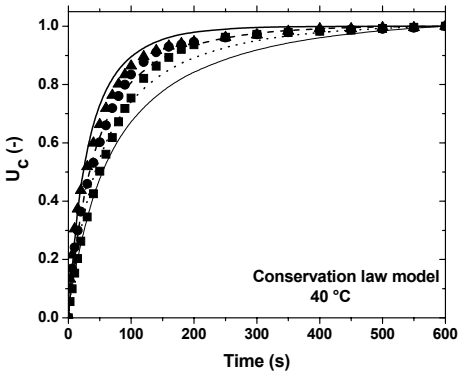


(b)

Figure 3-6: Calculated (lines) and experimental (symbols) final average porosities for different pressures and 40 °C (▲, -), 80 °C (○, ----) and 100 °C (●, ···). (a) Conservation laws model. (b) Shirato model. In all cases ω_0 = 0.0046 m^3/m^2 and t_{end} = 600 s.



(a)



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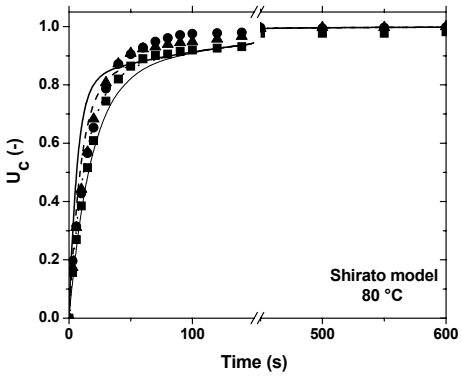

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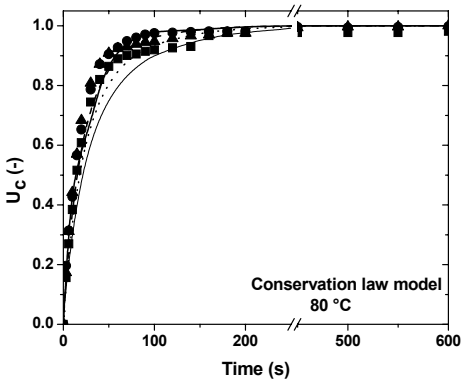

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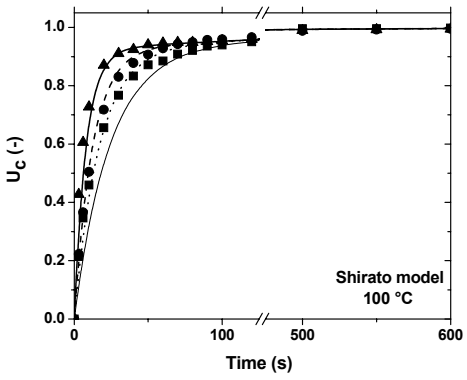

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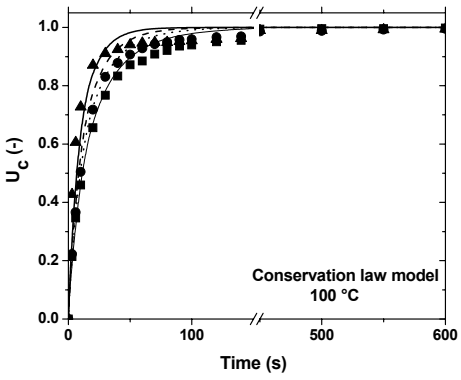


(f)

Figure 3-7: Calculated (lines) and experimental (symbols) U_c curves for both the Shirato model (a, c, e) and conservation laws model (b, d, f) for 40 °C (a, b), 80 °C (c, d) and 100 °C (e, f). The symbols indicate the following pressures: 30 MPa (—,▲), 50 MPa (- - - ,●), 70 MPa (…,■) and 100 MPa (-).

3.4.3 Shirato model calculations

3.4.3.1 Cocoa nibs

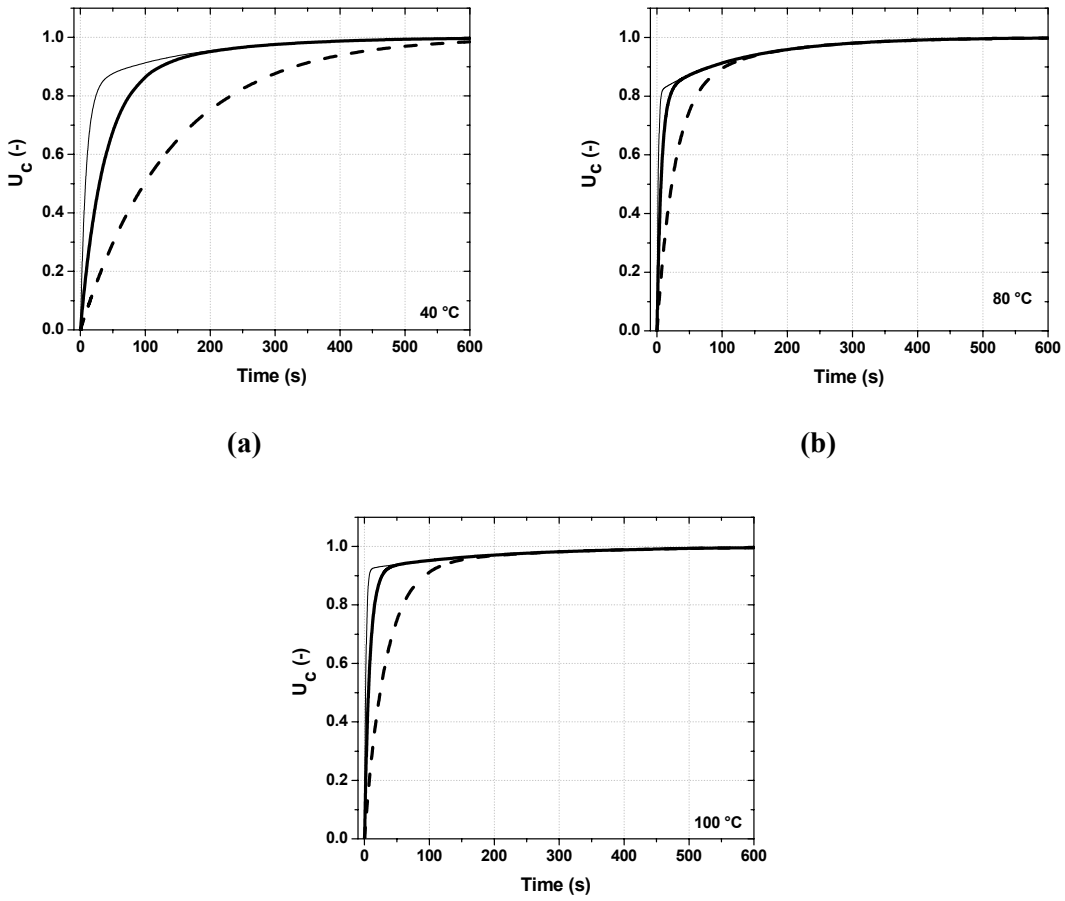
Mass pressed

Experimentally the mass of cocoa nibs being pressed has no influence on the yield when expression is performed at 70 °C and a pressure of 30 MPa [36]. The same conclusion is reached when calculations are made for different values of solids content with the Shirato model for temperatures of 40, 80 and 100 °C and a pressure of 30 MPa. The resulting U_c and average porosity curves are shown in Figure 3-8.

The Shirato model calculates the same final porosity, and therefore yield, regardless of the amount of nibs being pressed due to the absence of a mass related term in the equation used for calculating the porosity (see equation (3-21)). The speed with which the final filter cake thickness (U_C = 1) is reached increases with a decrease in ω_0. For 40 °C there is a more marked difference between the curves calculated for different values of ω_0 than at 80 and 100 °C. Notably the filter cake thickness continues to decrease for a longer period of time, a result of the less brittle nature of cocoa nibs at 40 °C than at 100 °C. The quotient C_e/ω_0^2 is in fact a time constant and therefore the time necessary for equilibrium to be reached is inversely proportional to ω_0^2.

Duration of pressing

Experimentally the duration of the expression process has little influence on the final yield when expression is performed at 70 °C and 30 MPa [36]. Calculations made with the Shirato model for a pressure of 30 MPa and temperatures of 40, 80 and 100 °C and pressing times of 150 to 2400 s confirm this observation. In all cases the calculated U_c graphs coincided with each other. Furthermore the final average porosity was not influenced by the pressing time. The calculated final average porosities were 0.46 for 40 °C and 0.42 for 80 and 100 °C. It comes as no surprise that the Shirato model shows the porosity to be independent of the pressing time, since the equation used for calculating the final porosity (see equation (3-21)) does not contain a time dependent term when the solids compressive pressure is assumed to be constant throughout the filter cake and the expression process.



(a) **(b)**

(c)

Figure 3-8: Calculated U_c curves at 40 °C (ε = 0.46) (a), 80 °C (ε = 0.42) (b) and 100 °C (ε = 0.42) (c) for different masses of cocoa nibs and a pressure of 30 MPa. The lines indicate the following solids contents: ω_0 = 0.0023 m^3/m^2 (-), ω_0 = 0.0046 m^3/m^2 (—) and ω_0 = 0.0092 m^3/m^2 (- - -).

3.4.3.2 Cocoa liquor

Industrial cocoa pressing is usually done with cocoa liquor, which consists of finely grinded cocoa nibs [20]. It is therefore of interest to determine whether the Shirato model can also describe the expression behaviour of cocoa liquor.

Cocoa liquor is a slurry consisting of cocoa solids and free-flowing cocoa butter [20]. Expression processes of slurries consist of a filtration and a consolidation stage. The filtration stage can be described with normal filtration theory and the consolidation stage with the Shirato model. However, if the solids content of the slurry is high enough the expression process consists only of consolidation and the slurry is labelled as a semi-solid. The transition between the filtration and consolidation stages can be determined graphically by plotting $\Delta L/\Delta t^{0.5}$ versus t when the expression is done at a

constant pressure [17]. During filtration $\Delta L/\Delta t^{0.5}$ has a constant value over time. At the transition point the value of $\Delta L/\Delta t^{0.5}$ starts to decrease with time. Figure 3-9 shows typical plots for cocoa liquor. The expression stage starts instantaneously ($t < 2$ s), and therefore the cocoa liquor can be considered as a semi-solid.

Table 3-3 shows the fitted and calculated parameters for cocoa liquor at 100 °C. The calculations were made in the same way as those for cocoa nibs. When the values of the parameters are compared with those of cocoa nibs at 100 °C (see Table 3-2) it can be seen that secondary consolidation plays a more important role in the expression of cocoa liquor than in the expression of cocoa nibs, while the importance of creep is approximately the same for both materials. This is probably due to the presence of free-flowing cocoa butter in cocoa liquor due to the grinding process. The solid particles in the cocoa liquor slowly rearrange as the cocoa butter is expressed from the cocoa liquor, causing a delayed response on the applied load. There is no free-flowing cocoa butter present in cocoa nibs - the applied load must crush the nibs and thereby free the cocoa butter. Rearrangement of particles is more likely to be caused by the crushing effect than by the removal of cocoa butter, hence the less important role of secondary consolidation in the expression of cocoa nibs. Cocoa liquor has a lower initial porosity (ε_0) than cocoa nibs due to the absence of air between the particles in cocoa liquor. The magnitude of the filtration resistance of cocoa liquor is two orders of magnitude lower than that of cocoa nibs (10^9 compared to 10^{11}). This can be explained by the location of the cocoa butter in the two materials. In cocoa nibs the cocoa butter is enclosed within the cell structure, and the particles needs to be crushed before the cocoa butter is free to flow through the cake and be expressed, while the cocoa butter in cocoa liquor is already freed from the cell structure.

Table 3-3: Material constants for cocoa liquor.

	Units	**100 °C**
$\boldsymbol{B}$	-	0.17 (0.03-0.33)
$\boldsymbol{n}$	s^{-1}	0.006 (0.003-0.008)
$\boldsymbol{\varepsilon_0}$	-	0.49
$\boldsymbol{\beta}$	-	0.23
$\boldsymbol{\alpha_0}$	m/kg	1.88×10^9
$\boldsymbol{n_\alpha}$	-	4.98

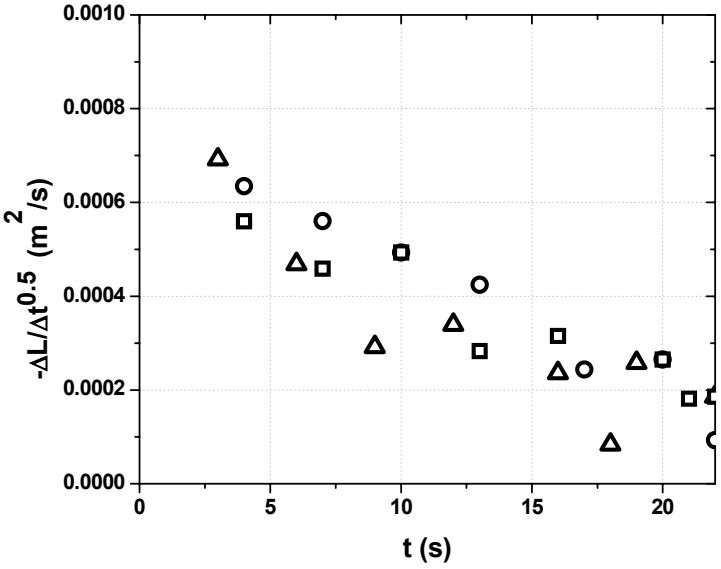
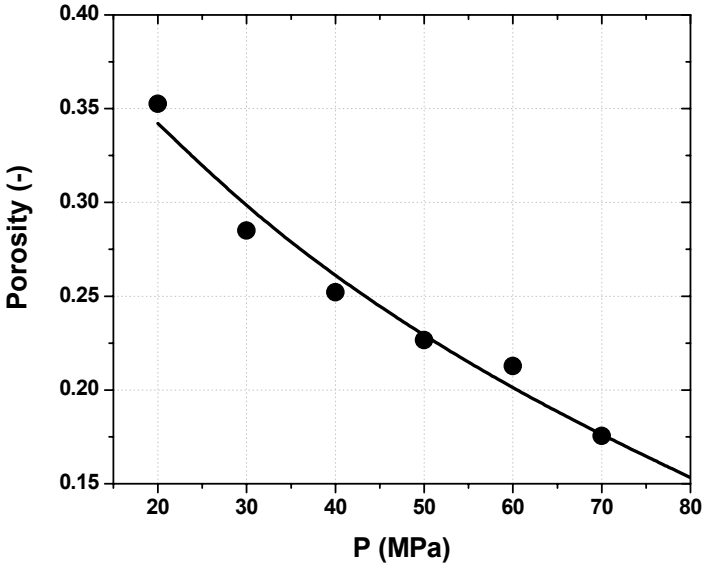
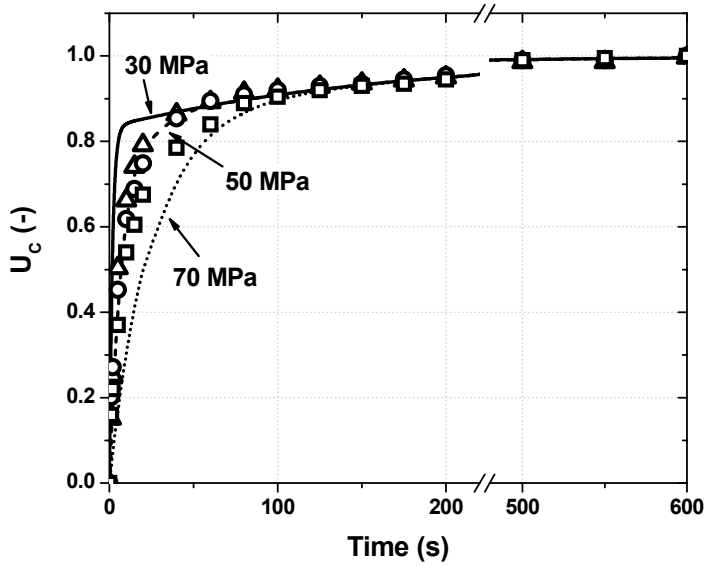


Figure 3-9: Determination of the transition point between filtration and consolidation for cocoa liquor expressed at 100 °C and pressures of 30 (△), 50 (○) and 70 (□) MPa.

Figure 3-10 compares the experimental and calculated expression behaviour of cocoa liquor. There is a good agreement between the calculated and experimental porosities. For t > 100 s the calculated consolidation ratios correlate well with the experimental ones. At shorter times the calculated consolidation ratios deviate from the experimental ones for pressures of 30 and 70 MPa. At 30 MPa the calculated U_c increases too fast, while at 70 MPa it increases too slow. Calculations at other pressures also showed deviations from the experimental observations. The reason for this deviation is not clear, although it can be caused by rearrangement of the particles to their final packing structure during the initial stages of expression. Despite this the Shirato model can be useful for describing the expression behaviour of cocoa liquor since it is unlikely that any expression process will last less than 100 s.



(a)



(b)

Figure 3-10: Calculated (lines) and experimental (symbols) expression behaviour of cocoa liquor at 100 °C. (a) Porosity as a function of pressure. (b) U_C as a function of time for 30 (—, △), 50 (╍,○) and 70 (▪▪▪,□) MPa.

3.5 Conclusions

The expression behaviour of dry cocoa nibs is described more accurately with the Shirato model than with the conservation laws model, despite the assumption of

constant material properties. This can be attributed to the incorporation of viscous material behaviour in the Shirato model, whereas the conservation laws model assumes the cocoa nibs to be purely elastic. It was calculated that there is no difference in the yield when the time of pressing is varied between 150 and 2400 s, and that the same yield is achieved by pressing different amounts of cocoa nibs when pressing times longer than 300 s are used. This is in agreement with the experimental results reported earlier [36]. The Shirato model is also able to accurately describe the expression behaviour for cocoa liquor for expression times longer than 100 s.

Nomenclature list

B	ratio of secondary to total consolidation	[-]
C_e	modified consolidation coefficient	[m^2/s]
e	void ratio	[m^3 non-solids/m^3 solids]
K	permeability	[m^2]
L	filter cake thickness at time t	[m]
n	creep constant of the Voigt model	[s^{-1}]
n_α	material constant for filtration resistance	[-]
P	externally applied load	[Pa]
P_L	liquid pressure	[Pa]
P_s	solid compressive pressure	[Pa]
q_L	actual velocity of the liquid based on the area occupied by the liquid	[m/s]
t	time	[s]
t_{end}	duration of expression	[s]
U_c	consolidation ratio	[-]
u_L	superficial velocity of the liquid based on the total surface area = $\varepsilon \cdot q_L$	[m/s]
u_s	superficial velocity of the solids based on the total surface area = $\varepsilon_s \cdot q_s$	[m/s]
V	specific cake volume	[m^3/kg]
α	filter cake resistance	[m/kg]
α	specific cake resistance	[m/kg]
α_0	material constant for filtration resistance	[m/kg]
β	material constant for porosity	[-]
ε	porosity	[m^3 non-solids / m^3 total]
ε_0	material constant for porosity	[m^3 non-solids / m^3 total]
ε_s	solidosity= 1-ε	[m^3 solids / m^3 total]
μ	liquid viscosity	[Pa.s]
ρ_s	solid density	[kg/m^3]
ω_0	total solid volume in the cake per unit sectional area	[m^3/m^2]

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4 Gas assisted mechanical expression (GAME) of cocoa butter from cocoa nibs

Abstract

The current methods used to recover high quality oil from oilseeds have low yields (mechanical expression, aqueous extraction), require the use of toxic chemicals and rigorous purification processes that can reduce the quality of the oil (solvent extraction with hexane) or are unsuitable for the recovery of commodity oils due to the low solubility of plant oils in environmentally benign solvents (supercritical extraction with CO_2). Gas Assisted Mechanical Expression (GAME) utilises the much higher solubility of supercritical CO_2 in the oil to enhance the extraction yields of mechanical expression. GAME experiments with cocoa nibs were performed at 40-100 °C, CO_2 pressures of 0-20 MPa and effective mechanical pressures of 20-50 MPa. The maximum yield with conventional expression (71.8 %) was obtained at a mechanical pressure of 50 MPa and a temperature of 100 °C. It is shown that GAME has a substantially higher yield than conventional mechanical expression for the recovery of cocoa butter from cocoa nibs, with the highest yield (87.1 %) obtained at 100 °C, a CO_2-pressure of 10 MPa and an effective mechanical pressure of 50 MPa. The cocoa butter yield increases with increasing CO_2 pressure until 10 MPa but remains almost constant for higher CO_2 pressures. In contrast to conventional expression GAME also allows the recovery of cocoa butter from cocoa nibs at temperatures below the melting point of pure cocoa butter. The cocoa butter produced with GAME was found to be unfractionated and is therefore of the same high quality as mechanically expressed cocoa butter.

4.1 Introduction

Vegetable oils are valuable raw materials that are widely used in the food, pharmaceutical and cosmetic industries. Currently good quality oil is recovered from oilseeds by performing mechanical expression (separation of liquid from a solid-liquid mixture by mechanical compression) in hydraulic filter presses or screw presses [1-5]. Although this process delivers high-quality, unadulterated oils, the economically obtainable yield (defined as the mass of oil recovered as a percentage of the total mass of oil in the oilseeds) is low compared to that of solvent extraction [1,2,5,6]. Aqueous extraction, a process that is used in many rural oil extraction processes, yields oil of high quality. Unfortunately the yields obtainable with this process are relatively low [7]. Certain enzymes can be used to weaken the cell walls, thereby freeing the oil and increasing the yield. However, the cost of the enzymes, as well as the hygiene requirements of a wet process and the cost of demulsification and water removal from the final products have a negative impact on the industrial feasibility of enzyme assisted aqueous extraction [7-10]. Solvent extraction is normally performed with hexane, a toxic and flammable organic solvent [11]. Solvent extraction can however yield oils with different compositions due to the co-extraction of non-fat components. In addition solvent extraction requires rigorous, energy-intensive solvent recovery processes to lower the solvent levels to acceptable levels in both the oil and the solid residue. These processes remove desirable components (e.g. some anti-oxidants and volatile substances responsible for certain taste and flavour characteristics), thereby changing the quality of the oil [5,12]. Alternatively, extraction with environmentally benign solvents such as supercritical carbon dioxide (SC-CO_2) can be used to produce oil at high yields [11-14]. The oil produced in this way is of high quality, but can be fractionated when the process conditions favour selective extraction of certain triglyceride fractions [13,15-24]. Supercritical extraction utilises the solubility of the vegetable oil in SC-CO_2. This solubility is dependent on the oil under consideration as well as the temperature and pressure, but generally it is in the order of only 1-5 wt. % under normal extraction conditions (25-30 MPa, 40-60 °C) [12-14,25]. Supercritical extraction therefore requires the use of large volumes of carbon dioxide [24,26] and is consequently only feasible for high value, low volume speciality products like essential oils and flavours [17,22]. Therefore there is a need for a new process that combines the advantages of the current industrial methods without their respective disadvantages.

In this chapter a new process called Gas Assisted Mechanical Expression (GAME) is introduced. GAME has the potential to overcome some of the disadvantages of other technologies as discussed above. In GAME mechanical expression is performed on oilseed material that has been saturated with SC-CO_2. Therefore a gas-expanded liquid (the CO_2-saturated oil) is expressed from the oilseed material. The solubility of SC-

CO_2 in vegetable oils is considerably higher than the solubility of the oils in SC-CO_2; up to 50 wt. % depending on the temperature, pressure and type of oil [12,13]. Consequently a much smaller volume of SC-CO_2 is needed than in supercritical extraction. The viscosity of CO_2-saturated oils is considerably lower than that of the pure oils at the same temperature [26,27]. Therefore less energy will be needed to express CO_2-saturated oils from oilseeds compared to the expression of pure oils from the oilseeds. The dissolving SC-CO_2 causes the oil to swell, and consequently CO_2-saturated vegetable oils occupy a larger volume than the pure oils due to the dissolved CO_2. This causes the cell structures containing the oil to swell when SC-CO_2 dissolves in the oil, eventually causing these structures to rupture due to their low mechanical strength, thereby freeing the oil. During expression only oil liberated from the cell structure can be recovered: the higher the proportion of the oil contained in the seeds that are liberated from the cell structure, the higher the yield will be. The lower liquid viscosity and high percentage of the oil freed from the cell structure enhance the recovery of oil in GAME. It is expected that a higher SC-CO_2 solubility in the oil will result in a higher oil yield. Solids often melt substantially below their atmospheric melting points in the presence of SC-CO_2 [28]. GAME therefore offers the additional advantage that oilseeds containing lipid components with atmospheric melting points higher than ambient temperature can be processed at lower temperatures than those currently used in conventional expression.

The main objective of this chapter was to experimentally compare the performance of GAME with conventional expression for the recovery of cocoa butter from cocoa nibs (broken cocoa beans). Cocoa nibs contain between 50 and 55 wt. % cocoa butter [29,30]. Cocoa butter is a complex mixture of triacylglycerols (TAG), with POP (1,3-dipalmitoyl-2-oleoylglycerol), POS (1-palmitoyl-2-oleoyl-3-stearoylglycerol) and SOS (1,3-stearoyl-2-oleoylglycerol) accounting for more than 90 % of the TAG [15,16,31]. The possibility therefore exists that one, or more, of the TAG will be preferentially extracted when SC-CO_2 is used. Due to the presence of several TAG cocoa butter has polymorphic behaviour, but it is generally accepted that it is completely melted at 35 °C at atmospheric conditions [29,30]. This places a lower limit on the temperature that can be used in conventional expression. It is known that the applied mechanical pressure as well as the temperature has an influence on the yield obtainable with conventional expression [1,32-38]. The CO_2 pressure and the process temperature have an influence on the solubility of CO_2 in the cocoa butter [39]. The applied mechanical pressure, temperature and CO_2-pressure are therefore important process parameters, and their influence on both the yield and quality of the processed cocoa butter will be evaluated. The quality of the GAME recovered cocoa butter will be determined by comparing the composition of this butter to that of mechanically expressed cocoa butter from the same batch of nibs. Finally the experimental results are used to explain the mechanism of GAME.

4.2 Materials and methods

4.2.1 Materials

Winnowed cocoa nibs (moisture content 5.5 %, wet basis) were obtained from Gerkens Cacao (Wormer, The Netherlands). The moisture content of the cocoa nibs was determined according to the DGF standard method [40]. The cocoa butter content of the cocoa nibs, as determined by soxhlet extraction with petroleum ether (boiling range 40-60 °C, Merck, Amsterdam, The Netherlands), was found to be 56.2 wt. % (dry basis). Details of the soxhlet extraction procedure are given in paragraph 4.2.4. CO_2 (purity 99.995 %) was obtained from Hoekloos (Schiedam, The Netherlands). n-Hexane (purity ≥ 99 %) was purchased from Merck (Amsterdam, The Netherlands).

4.2.2 Experimental set-up

A laboratory scale press (Figure 4-1) with one drainage area was constructed to provide the experimental data. It consists of a hydraulic plunger (9) that can exert pressures of up to 100 MPa on the material and moves uni-axially in a cylinder with a diameter of 30 mm. The cocoa nibs are placed on top of a sieve plate (5) covered with a fine wire mesh acting as a filter medium (6). The filter medium is woven from 0.6 mm thick chromium steel (type 430) wires in a configuration of 13 bundles of 3 threads per 25.4 mm, with 212 wires per 25.4 mm perpendicular to these bundles. The filter medium is kept in place inside the sieve plate with a Teflon ring, which also prevents solids from being extruded into the collection chamber. The expressed liquid (cocoa butter or CO_2-saturated cocoa butter) is collected in the collection chamber (4) below the sieve plate. Turcon Variseal seal rings (Busak & Shamban, The Netherlands) are used to ensure a gas-tight set-up. Gas pressure is measured with an accuracy of ± 0.1 MPa with a pressure transducer (Nova Swiss 5.1539.016, Nova Werke, Effretikon, Switzerland).

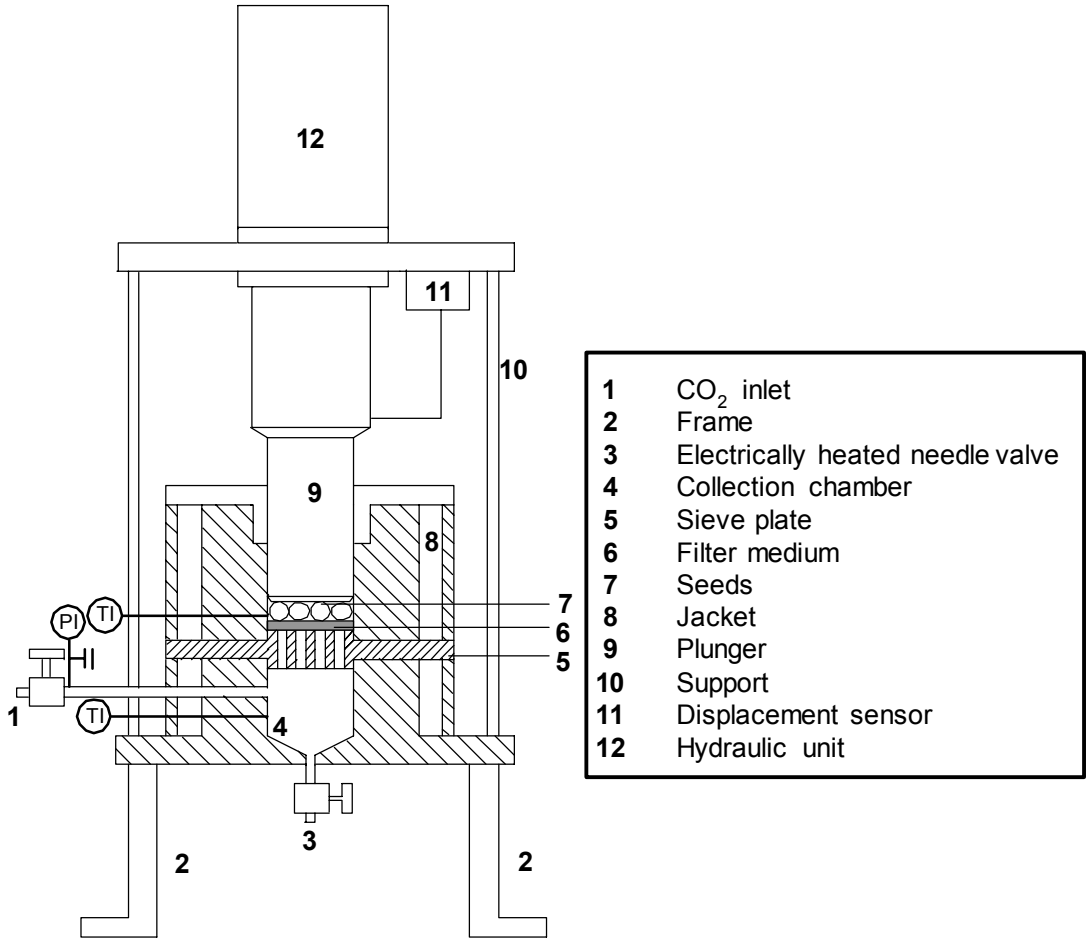


Figure 4-1: Schematic depiction of the laboratory press (not to scale). TI = thermocouple, PI = pressure transducer, || = rupture disk.

The press can withstand gas pressures of up to 45 MPa. CO_2 is added up to the required pressure with the aid of a handpump (Sitec Hand Pump 750.1060, Sitec Sieber Engineering, Zürich, Switzerland). The fluid chamber of the handpump is cooled to 10 ± 1 °C. An electrically heated needle valve (3) is fitted to the collection chamber to enable depressurisation and collection of the expressed cocoa butter. The press is fitted with two jackets (8) in which a heating medium can be circulated to enable isothermal operation (± 1 °C) at elevated temperatures (30-100 °C). The hydraulic pressure is regulated electronically with a type SRX controller (RKC Instruments, Tokyo, Japan). The set points for the controller are set with the electronic interface SpecView Plus (SpecView, Ltd., East Sussex, United Kingdom). The distance the plunger has advanced is continuously measured with a position transducer (11) (SPH-50, WayCon Positionsmesstechnik GmbH, Unterhaching, Germany) in order to determine the actual thickness of the filter cake (accuracy ± 0.01 mm). All data are recorded digitally with a memo-graph (Visual Data Manager, Endress & Hauser B.V., Naarden, The Netherlands) at a frequency of 1 Hz.

4.2.3 Experimental procedure

The cocoa nibs were dried at 103 ± 1 °C until completely dry to ensure that all experiments were performed at the same moisture content. Approximately 10 g of the dried nibs were placed on top of the filter medium resulting in a filter cake thickness of roughly 14 mm. The plunger was lowered to the level of the nibs after which the nibs were allowed to equilibrate for 30 minutes to the temperature of pressing (40, 80 or 100 °C). The plunger exerted no mechanical pressure on the nibs during the time required for reaching thermal equilibrium.

Conventional pressing was performed directly after reaching thermal equilibrium by adjusting the hydraulic pressure exerted on the plunger to ensure that the desired mechanical pressure (30, 40 or 50 MPa) was exerted on the nibs. The mechanical pressure was kept constant for 10 minutes. This pressing time was chosen to allow the cocoa filter cake thickness to be constant for some time. The needle valve in the bottom of the collection chamber was left open to allow the cocoa butter to drain into a sample container. The cocoa butter collected in this way was saved for analysis. After the pressing stage the plunger was raised. The resultant filter cake was then removed and analysed to determine the fat content. No visible solids were observed in the expressed liquid, and the liquid was therefore not analysed for solid content.

GAME experiments require an additional equilibrium time to ensure that the CO_2 has enough time to dissolve in the cocoa butter (which is enclosed in the cell structure of the cocoa nibs) before pressing proceeds. In order to accomplish this the needle valve in the bottom of the collection chamber was closed to create a gas-tight pressure vessel once the cocoa nibs have reached thermal equilibrium. CO_2 was then added to the desired pressure (8, 10, 15 or 20 MPa) with the aid of the hand pump. During the entire equilibration stage no mechanical pressure was exerted on the cocoa nibs. Preliminary experiments showed that an equilibration time of 30 minutes must be used. Upon completion of the phase equilibration stage the mechanical pressure was increased to the desired level by adjusting the hydraulic pressure. After 10 minutes the mechanical pressure was set to zero. The needle valve in the bottom of the collection chamber was then opened in a controlled manner to allow the mixture of CO_2 and expressed cocoa butter to be released. The cocoa butter was collected in a sample container and saved for analysis. After complete depressurisation the filter cake was removed and analysed to determine the fat content.

The mechanism responsible for the increased yields obtained with GAME was determined by doing experiments in which the order of the different stages used in the GAME experiments (pressurisation and equilibration with CO_2, pressing and depressurising) was changed.

4.2.4 Analysis

The standard method for the determination of the fat content of cocoa powder by soxhlet extraction as proposed by the International Office of Cocoa, Chocolate and Sugar Confectionary (IOCCC) [41] was modified to be suitable for the determination of the fat content of filter cakes. These modifications include soaking the filter cake in a small quantity of petroleum ether for at least 4 hours before grinding. This prevents the excessive formation of fines during grinding due to the brittle nature of the dried nibs. Furthermore a wad of cotton wool was placed in the bottom of the extraction thimble to prevent fines from passing through the thimble. The pre-soaked filter cakes were ground together with a small volume of petroleum ether for 20 s at 16 Hz in a ball mill (Type MM 301, Retsch GmbH & Co, Haan, Germany).

The POP, POS and SOS content of the cocoa butter was determined by gas chromatographic (GC) analysis using a Varian CP-3800 chromatograph fitted with a SGE HT5 column (12 m × 0.32 mm, 0.1 μm) (Bester, Amstelveen, The Netherlands) and a flame ionisation detector (340 °C, 8×10^{-12}). The cocoa butter was dissolved in n-hexane (1 g / 20 g hexane) and the mixture was used for analysis. A splitless injector (325 °C, 0.5 μl) was used. The carrier gas was hydrogen (152.3 cm/s). The column temperature was programmed to rise from 200 °C to 370 °C at a rate of 10 °C/min and then held constant for 5 minutes.

4.2.5 Accuracy and reproducibility of experimental results

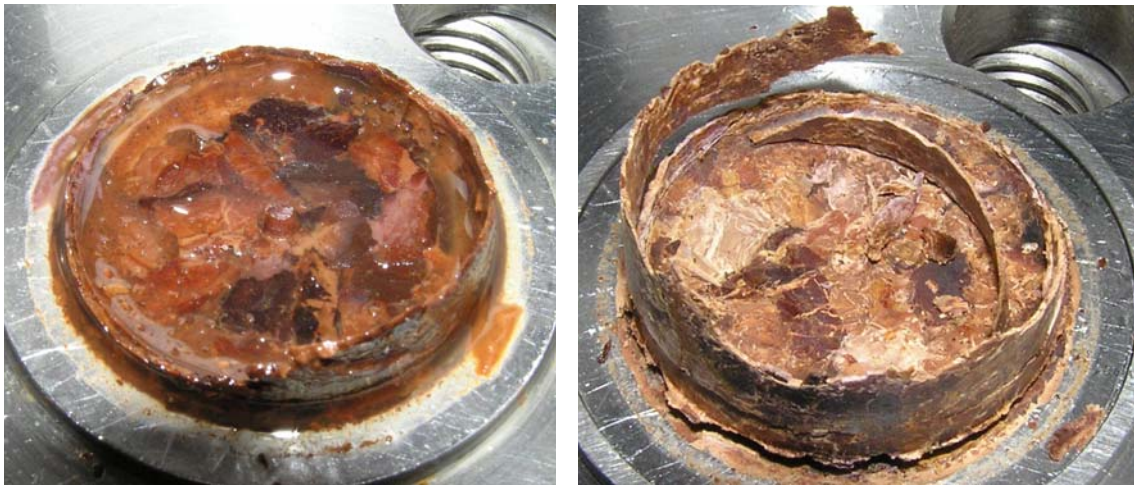
In order to evaluate the experimental error four experiments were done at 80 °C with 10 MPa CO_2 and an effective mechanical pressure of 29 MPa. The effective mechanical pressure is defined as the difference between the applied mechanical pressure and the CO_2 pressure. It takes into account that the CO_2 pressure acts against the mechanical force being exerted by the plunger, thereby decreasing the effective mechanical force experienced by the cocoa nibs. The CO_2 pressure at the end of the pressing stage was used in the calculation of the effective mechanical pressure to take into account the compression of the CO_2 resulting from the movement of the plunger. The CO_2 pressures reported in this paper refer to the initial CO_2 pressure of the experiment. The average yield for these four experiments was 78.2 %. The absolute standard deviation in the determined yields was calculated as 0.6 %. Duplication of random experiments at other conditions always resulted in an absolute standard deviation of less than 0.9 %. Furthermore the cocoa butter contents of cocoa powders with known cocoa butter contents were determined within ± 0.5 wt. %. In view of this the absolute experimental error made in calculating the yield is taken as ± 1 %.

4.3 Results and discussion

4.3.1 Cocoa butter yield

Figure 4-2 shows photographs of a conventional expression and a GAME filter cake resulting from experiments performed at 100 °C with an effective mechanical pressure of 50 MPa. A CO_2 pressure of 10 MPa was used for the GAME experiment. It can be seen that the surfaces of GAME filter cake are much drier than that of the conventional filter cake.

The yields obtained with conventional expression and GAME at CO_2 pressures of 8, 10, 15 and 20 MPa as a function of effective mechanical pressure are shown in Figure 4-3 (a), (b) and (c) at temperatures of 40, 80 and 100 °C respectively. The yield increases with an increasing effective mechanical pressure for both conventional expression and GAME. This is a well-known phenomenon for conventional expression [1,32-38]. A higher effective mechanical pressure not only results in a higher energy input to the freed oil, but also causes more of the oil cell structures to rupture. Both of these effects cause a higher percentage of the oil to be expressed from the filter cake.



Conventional filter cake GAME filter cake

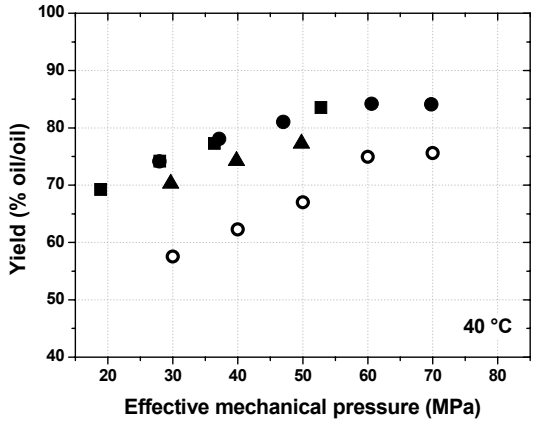
Figure 4-2: Photographs of a conventional expression and a GAME filter cake, both created at 100 °C and an effective mechanical pressure of 50 MPa with dry cocoa nibs. A CO_2 pressure of 10 MPa was used in the GAME experiment.

GAME shows a much higher yield than conventional expression for all three temperatures and all CO_2 pressures. Figure 4-3 shows that there is an absolute increase of 10-20 wt. % in the cocoa butter yield when the 8 MPa CO_2 GAME experiments are compared with the conventional expression experiments. At 40 and 100 °C the additional increase in yield for the 10 MPa GAME experiments is much smaller. At these temperatures increasing the CO_2 pressure to 15 MPa does not result in an

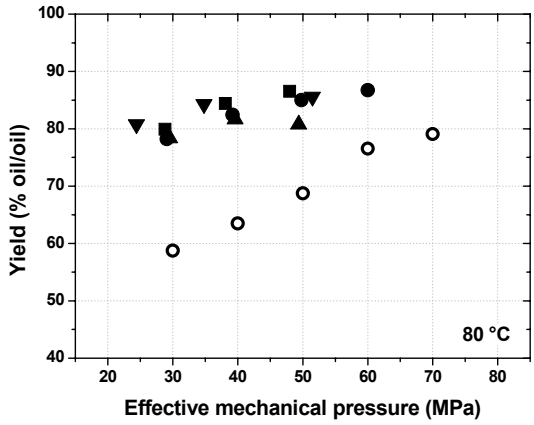
appreciable increase in the cocoa butter yield compared to the yields obtained with 10 MPa GAME experiments. It is therefore concluded that, for the CO_2 pressures studied, GAME performed with 10 MPa CO_2 offers the optimal increase in cocoa butter yield at temperatures of 40 and 100 °C. Figure 4-3 (b) shows that the yield does not follow the trend observed with other CO_2 pressures and temperatures at 80 °C and CO_2-pressures of 8 and 10 MPa. The yield remains approximately constant instead of increasing with an increasing effective mechanical pressure. This behaviour might originate from the phase behaviour but cannot be explained from the current knowledge of the CO_2-cocoa butter system [39]. At CO_2 pressures of 15 and 20 MPa the yield once again increases with increasing effective mechanical pressure, and the cocoa butter yield at these pressures are also slightly higher than those achieved at 10 MPa.

The temperature of pressing is known to influence the yields obtainable by conventional expression. This is also the case for GAME, as can be seen in Figure 4-3. It is even clearer in Figure 4-4, where data for experiments performed at 30 °C are also included. The highest yields are obtained at 100 °C, which is comparable to the temperature of 95-105 °C that is used in industrial cocoa pressing operations [29].

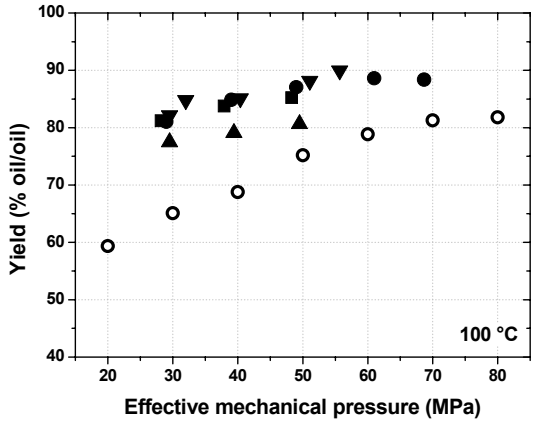
The yields obtained with GAME performed at 30 °C (see Figure 4-4) are noteworthy. Pure cocoa butter is a solid at 30 °C, and conventional expression of cocoa nibs at this low temperature will therefore not be able to remove any cocoa butter from cocoa nibs. The presence of CO_2 decreases the melting point of cocoa butter to 22.1-27.1 °C; depending on the CO_2 pressure [39]. This is the reason why GAME is able to express cocoa butter from cocoa nibs at this low temperature. The combination of a lower cocoa butter melting point and a lower cocoa butter viscosity makes it feasible to operate GAME at lower temperatures than that used in industry for conventional mechanical expression (95-105 °C, [29]).



(a)



(b)



(c)

Figure 4-3: Cocoa butter yield as a function of the effective mechanical pressure for conventional expression and GAME experiments at different CO_2 pressures. (a) 40 °C, (b) 80 °C, (c) 100 °C. The symbols indicate the following CO_2 pressures: ○ 0 MPa, ▲ 8 MPa, ● 10 MPa, ■ 15 MPa, ▼ 20 MPa.

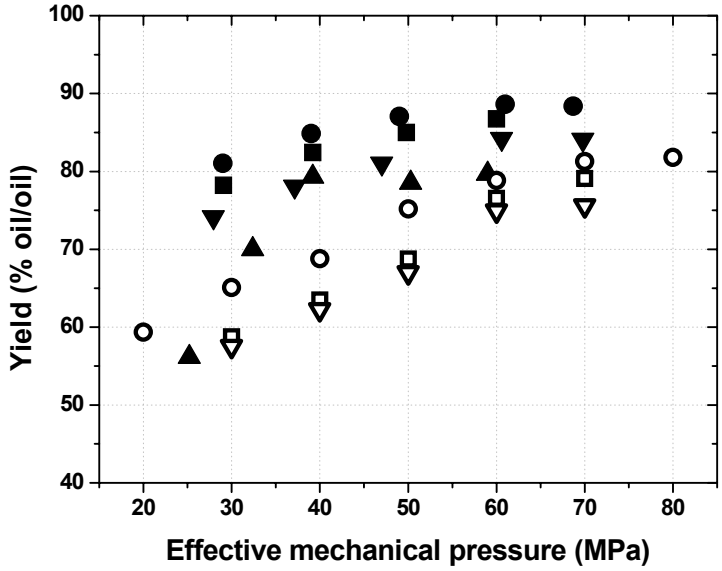


Figure 4-4: The influence of temperature on the cocoa butter yield obtained with conventional expression (open symbols) and GAME (closed symbols). All GAME experiments were performed at a CO_2 pressure of 10 MPa. The symbols indicate the following temperatures: ▲ 30 ° C; ▽ , ▼40 °C; ■ ,□ 80 °C and ○ , ● 100 °C.

4.3.2 Cocoa butter composition

The collected cocoa butter was analysed for POP, POS and SOS content due to the fact that these TAG account for more than 90 % of the TAG content of the cocoa butter. Changes in the effective mechanical pressure will have no influence on the cocoa butter composition, while changes in the CO_2 pressure could possibly cause fractionation of the cocoa butter. There was no noticeable difference in the ratios of both POS/POP and SOS/POP for all the conditions studied in the experiments (30-100 °C, 0-20 MPa CO_2). The average value for the POS/POP ratio is 2.49 ± 0.02 and that for the SOS/POP ratio is 1.77 ± 0.03. Therefore no fractionation of the cocoa butter occurred during the GAME experiments.

4.4 Mechanism of GAME

As discussed in the introduction several factors can be responsible for the increase in oil yield when GAME instead of conventional expression is used to recover the oil:

- A lower viscosity of the liquid being expressed
- Removal of oil through depressurisation
- Freeing of oil from the cell structure through disruption of oil cell structures
- Replacement of part of the oil contained in the filter cake with SC-CO_2

Initially it was assumed that the lower viscosity of CO_2-saturated oils compared to that of pure oils causes the increase in yield observed with GAME. If this is the case the decrease in the filter cake thickness will be much faster for GAME experiments than that observed for conventional expression experiments, in the same way that the decrease in filter cake thickness is faster at higher temperatures for conventional expression due to a decreased oil viscosity. The decrease in the filter cake thickness is measured as the distance the plunger has moved downwards. Typical plunger displacement graphs for cocoa nibs are shown in Figure 4-5. As expected an increase in temperature causes the filter cake thickness to decrease at a faster rate for conventional expression. There is however no difference between the displacement graphs measured for conventional expression and GAME experiments at the same temperature. The lower viscosity can therefore not be the reason for the increase in yields observed for the GAME process. Consequently the different behaviour of the filter cakes at different temperatures when conventional expression is used can also not be explained by the change in the viscosity of the cocoa butter. A higher temperature not only changes the physical properties of the oil, but also the properties of the solid structure of the oilseeds. Cell walls are denatured at temperatures above 50 °C, which causes the cells to break apart easily when subjected to stress [5]. This not only liberates a higher percentage of the oil contained in the cell structure, but also causes the solid structure of the oilseeds to be more compressible, which explains both the increased rate of filter cake decrease and the higher yields observed at higher temperatures for both conventional expression and GAME.

Another possible explanation for the increase in the yield of GAME experiments compared to conventional experiments is the removal of oil from the filter cake through depressurisation. This hypothesis assumes that the CO_2 replaces the freed oil in the filter cake, similar to the replacement of filtrate by a washing liquid during the washing stage performed in filtration operations. In this case a similar increase in yield should be observed if the intact filter cake obtained by conventional expression is equilibrated with CO_2, whereafter the CO_2 is removed by depressurisation.

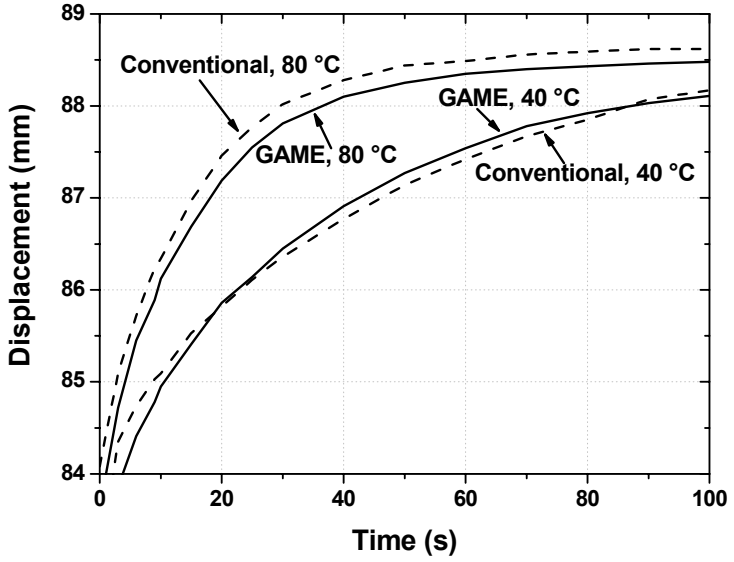


Figure 4-5: Typical plunger displacements measured during the experiments performed with cocoa nibs. All experiments were performed at an effective mechanical pressure of 40 MPa. GAME experiments were performed with 10 MPa CO_2.

The increased yield obtained with GAME experiments can also be due to the disruption of oil cells by the CO_2. Cocoa butter must be freed from the cell structure of the cocoa nibs before it can be separated from the cocoa solids, only freed cocoa butter can be removed from the cocoa nibs. This is true for all seeds [5]. Mechanical pressure has a limited ability to free the cocoa butter from the cell structure. It is known that SC-CO_2 can be used to disrupt oil cells [42], and it is thought that this also may happen during the GAME process. In this case a similar increase in yield than that observed with GAME experiments should be obtained by equilibrating the cocoa nibs with CO_2, depressurising and subsequently pressing the nibs.

A series of experiments with cocoa nibs in which the order of pressurisation and equilibration with CO_2, pressing and depressurisation of the original GAME experimental procedure was changed were used to test the above hypotheses. By equilibrating the nibs with CO_2, de-pressurising and then pressing the influence of oil cell rupture on the oil yield is tested. Pressing the nibs and thereafter equilibrating the filter cake with CO_2 evaluates the influence of the removal of oil during depressurisation on the oil yield. In Figure 4-6 it can be seen that none of the experiments in which the order of equilibration with CO_2, pressing and depressurising were changed gave yields as high as that observed with the GAME experiment performed at the same conditions. Oil cell rupture (experiment 2 in Figure 4-6) and the removal of oil during depressurisation (experiment 3 in Figure 4-6) increase the yield

when compared to conventional expression (experiment 1 in Figure 4-6), but this increase was small compared to the increase obtained with a GAME experiment (experiment 4 in Figure 4-6).

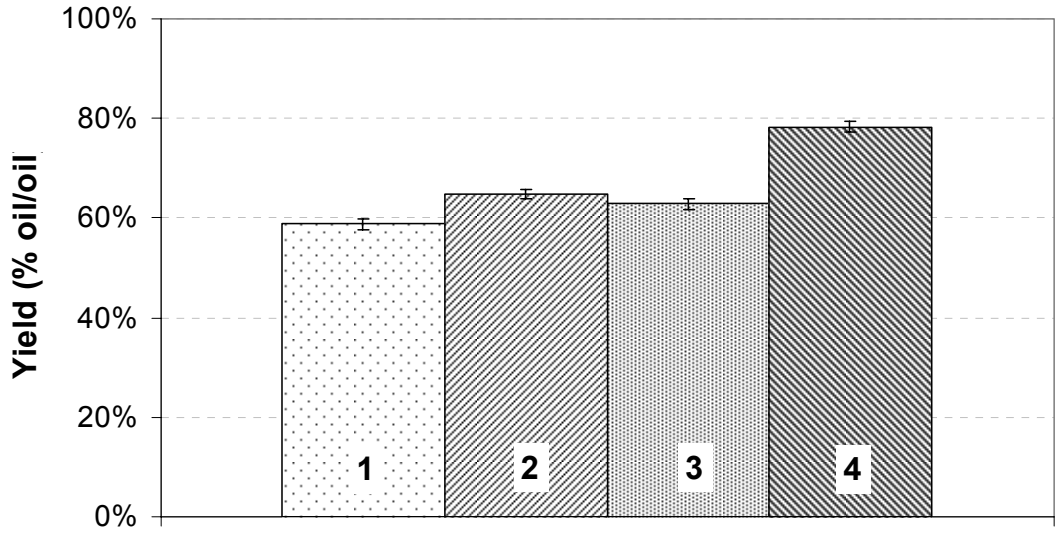


Figure 4-6: Influence of the order of pressurising, de-pressurising and pressing on the cocoa butter yield. A CO_2 pressure of 10 MPa and an effective mechanical pressure of 30 MPa were used throughout. All experiments were performed at 80 °C. 1) Conventional pressing, no CO_2. 2) Equilibrate nibs with CO_2, de-pressurise and press. 3) Press, equilibrate filter cake with CO_2 and de-pressurise. 4) Equilibrate nibs with CO_2, press and de-pressurise (GAME).

SEM pictures were taken from cocoa nibs and GAME filter cakes in an attempt to determine whether GAME causes widespread cell rupture. Figure 4-7 shows some of these pictures. However, no conclusive evidence of cell rupture or the lack thereof could be made from these pictures.

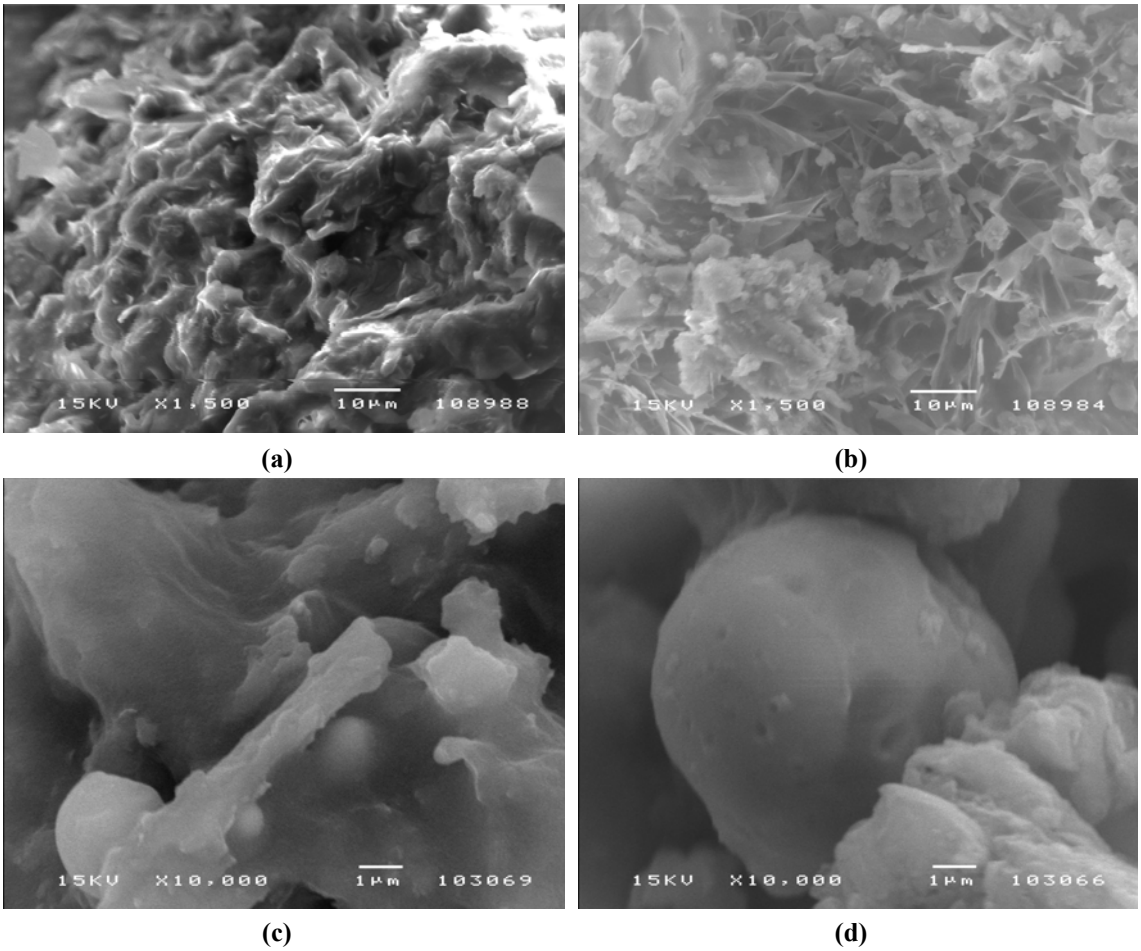
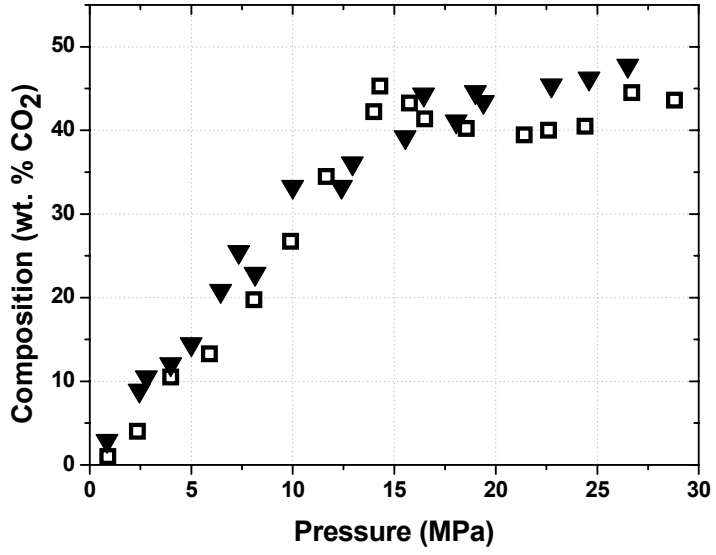
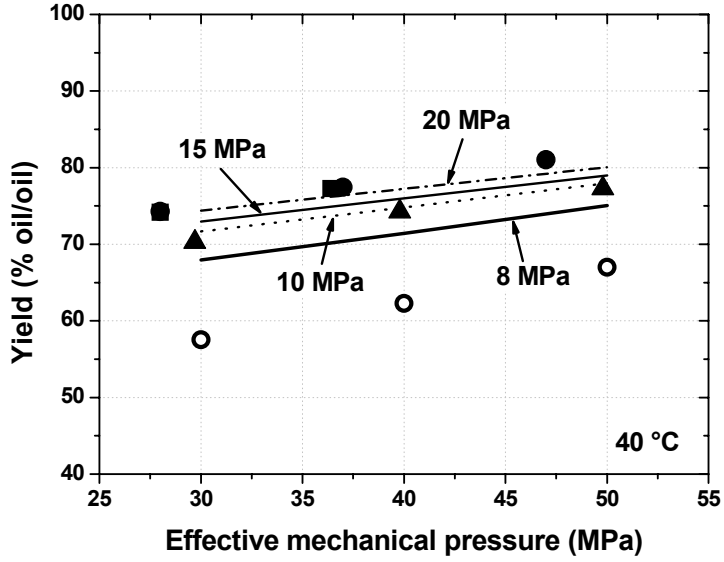


Figure 4-7: SEM pictures of cocoa nibs ((a) and (c)) and GAME filter cakes ((b) and (d)) created at a temperature of 100 °C with 10 MPa CO_2 and an effective mechanical pressure of 300 MPa.

It is clear that neither the lower viscosity of the CO_2-saturated cocoa butter compared to that of the pure cocoa butter, the washing of the filter cake with CO_2 nor even the freeing of cocoa butter from the cell structure by the CO_2 explains the increase in cocoa butter yield observed with GAME experiments. The only remaining explanation for this increase can be that the filter cakes always contain similar volumes of liquid at the end of both conventional expression and the pressing stage of GAME experiments (i.e. before depressurisation). In the case of conventional expression this liquid consists only of cocoa butter, but in the case of GAME the liquid consists of CO_2-saturated cocoa butter.



(a)



(b)

Figure 4-8: Prediction of GAME yields for cocoa butter as a function of CO_2-pressure and effective mechanical pressure. a) CO_2 solubility in cocoa butter as a function of pressure for 40 °C (▼) and 60 °C (□) [30]. b) Measured (markers) and predicted (lines) GAME yields for 40 °C. The symbols indicate the following CO_2 pressures: ○ 0 MPa, ▲ 8 MPa, ● 10 MPa, ■ 15 MPa.

An increasing solubility of CO_2 in the cocoa butter will cause a lower amount of cocoa butter to remain in the cake after depressurisation, resulting in an increasing cocoa

butter yield. This can easily be seen when the cocoa butter-CO_2 phase equilibrium data measured by Kokot and co-workers [39] are used to predict the cocoa butter yield for GAME from the yields obtained with conventional expression. In these calculations it is assumed that the same amount of liquid will be present in the GAME filter cakes before depressurisation. Furthermore the CO_2-saturated cocoa butter is assumed to have the same density as pure cocoa butter at the same temperature. The results from these calculations, as well as the VLE data, for a temperature of 40 °C are shown in Figure 4-8. The measured yields followed the same trend as the predicted yields. The difference between the measured and the predicted yields can be attributed to the assumption of an equal cocoa butter and CO_2-saturated cocoa butter density. The solubility increases with CO_2 pressure until a pressure of roughly 15 MPa, whereafter it remains almost constant with an increasing pressure [39]. Therefore the amount of cocoa butter left in the filter cake will not significantly decrease when higher CO_2 pressures are used. The optimal increase in yield is therefore expected to occur at a CO_2 pressure of 15 MPa. However, experiments showed that the optimal increase in yield already occurs at a CO_2 pressure of 10 MPa.

4.5 Conclusions

GAME experiments consistently give higher yields when cocoa butter is recovered from cocoa nibs compared to conventional expression experiments performed at the same temperature and effective mechanical pressure. The optimal increase in cocoa butter yield is achieved with a CO_2 pressure of 10 MPa. An increase in temperature and effective mechanical pressure also leads to an increase in yield. GAME can be used to recover cocoa butter from cocoa nibs at temperatures below the melting point of pure cocoa butter. The cocoa butter produced with GAME experiments has the same POS/POP and SOS/POP ratios compared to the cocoa butter recovered with conventional mechanical expression experiments, and is therefore of the same quality as that produced by mechanical expression. Therefore GAME is a promising process for recovering high-quality vegetable oils at high yields. Experiments indicate that the pressing stage always ends with the same liquid volume inside the filter cakes for both conventional expression and GAME experiments performed at the same temperature and effective mechanical pressure. In the case of GAME a large part of the cocoa butter is replaced with CO_2 due to the high solubility of CO_2 in the cocoa butter. This CO_2 is removed through depressurisation and only the cocoa butter remains in the filter cake, resulting in an increased cocoa butter yield.

4.6 References

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5 Phase equilibria and physical properties of CO_2-saturated cocoa butter mixtures at elevated pressures

Abstract

The melting point and phase behaviour of cocoa butter under CO_2-pressure were observed in a high-pressure view cell. The melting point decreases from 35 °C to 23 °C at CO_2 pressures higher than 5 MPa. A static analytical procedure was used to measure the solubility of CO_2 in cocoa butter at 40, 80 and 100 °C and pressures of 2-35 MPa in an autoclave set-up. The density and viscosity of the CO_2-saturated cocoa butter was measured simultaneously in this set-up. The experimental procedure was first validated by comparing the data measured for the systems CO_2/hexadecane with literature data. The highest solubility of CO_2 in cocoa butter (36 wt. %) occurs at 40 °C and 35 MPa. The measured solubilities differed from those previously reported in literature. This can be attributed to differences in the cocoa butter used for the measurements. The density of CO_2-saturated cocoa butter increases with pressure, whereas the viscosity decreases. The Grunberg equation was used to correlate the viscosity of CO_2-saturated cocoa butter. The measured data were used to estimate the theoretical gas assisted mechanical extraction (GAME) yields. These yields deviate from the experimental ones due to the oversimplification of the mechanism involved in GAME.

5.1 Introduction

Cocoa butter is used in the manufacturing of chocolate, making it one of the most important ingredients used by the confectionery industry [1]. Since 1828, when Van Houten developed a press to partially defatten cocoa beans [2], mechanical pressing has been used to generate good quality cocoa butter from cocoa beans. However, mechanical pressing can only remove a limited amount of cocoa butter from the cocoa beans [2-4]. Recently a new process, Gas Assisted Mechanical Expression (GAME), has been proposed as an improved method for obtaining good quality cocoa butter from cocoa beans at high yields [4]. In this process supercritical carbon dioxide (SC-CO_2) saturated cocoa beans are mechanically pressed. In GAME the high solubility of SC-CO_2 in cocoa butter is used to increase the cocoa butter yield that can be obtained with mechanical pressing. This is in contrast to supercritical extraction, where the solubility of the cocoa butter in SC-CO_2 is the important parameter. Data on the solubility of SC-CO_2 in cocoa butter, as well as on the viscosity and density of SC-CO_2 - saturated cocoa butter are needed for the characterisation and design of a GAME process. The GAME cocoa butter yields can be predicted from the yields obtained with conventional expression at the same effective mechanical pressure when the CO_2-content and density of the CO_2-saturated cocoa butter are known.

Limited information on the properties of SC-CO_2-saturated cocoa butter could be found in literature. Kokot and co-workers [5] investigated the melting point of SC-CO_2 - saturated cocoa butter as well as the solubility of SC-CO_2 in cocoa butter at 30, 40, 60 and 80 °C. This data was previously used to predict GAME yields from conventional expression yields with a reasonable accuracy [4]. However, no data could be found for the density and the viscosity of SC-CO_2 - saturated cocoa butter or the properties of SC-CO_2-saturated cocoa butter at 100 °C.

In this chapter a new experimental set-up consisting of an autoclave fitted with a magnetically coupled stirrer, an inline quartz viscosimeter and an external density sensor was developed to simultaneously measure the CO_2-content, density and viscosity of CO_2 - saturated cocoa butter at 40, 80 and 100 °C and pressures of 2-35 MPa. This set-up allows equilibrium to be reached at shorter times (~ 5 min) than those necessary for shaken autoclaves (~ 30 min) like the one used in [5]. Cocoa butter was considered as a single compound for the purposes of this chapter, following the example of others who measured phase equilibria of plant oils/SC-CO_2 [5-9]. The experimental procedure was first validated by comparing the measured CO_2 solubility in n-hexadecane as well as the viscosity of CO_2 - saturated n-hexadecane at 40 and 60 °C and pressures of 2 – 22 MPa with literature values. n-Hexadecane was used as a test compound as it is a non-volatile organic compound, and can therefore be expected to behave in a similar way as cocoa butter. The ability to reproduce literature data was

used as a proof of acceptable experimental procedure and analysis. The melting point depression of cocoa butter in the presence of SC-CO_2 was investigated in a high pressure view cell. Qualitative observations of the phase behaviour of cocoa butter/CO_2 were also made with the view cell.

5.2 Materials and methods

5.2.1 Experimental set-up and procedure

A high-pressure cell with a total interior volume of 25 cm^3 was used for qualitative phase behaviour observations. This cell contains two glass sight windows and can withstand pressures of up to 20 MPa. A heating jacket allows operation at a constant temperature ± 0.5 °C. The temperature is measured with a thermocouple fitted to the upper third of the cell. A magnetic stirrer enables mixing of the substances inside the view cell. The melting point of pure and CO_2-saturated cocoa butter was also visually observed with this set-up by loading the cell with a small amount of cocoa butter and slowly increasing the temperature with and without CO_2 present. It is expected that the melting point found in this way will not differ from the solidification temperature measured by decreasing the temperature, since cocoa butter does not display hysteresis [5].

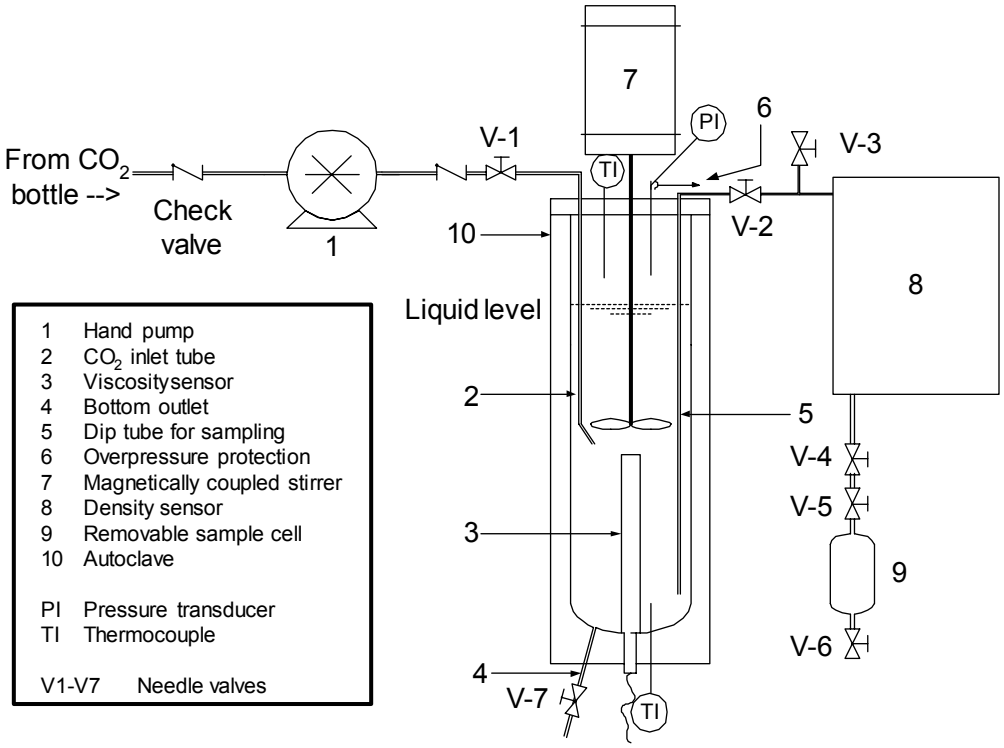
Details of the static analytic set-up used for phase equilibrium, density and viscosity measurements are shown in Figure 5-1. The apparatus consists of a 500 ml autoclave (10) fitted with a quartz viscosimeter (3) allowing continuous viscosity measurement (QVis 01/o, Flucon, Clausthal-Zellerfeld, Germany) and a magnetically coupled stirrer (7) (Cyclone 075, Büchiglasuster, Uster, Switzerland). The pressure was measured with a pressure transducer (PTX7517, maximum pressure 70 MPa, accuracy ± 5 % full scale, Druck Nederland, Barendrecht, The Netherlands). Teflon seal rings were used to ensure a gas-tight set-up. A dip tube (5) enables sampling of the heavy phase inside the autoclave. The sampling line is connected to an external oscillating density meter (8) (DMA 512P, Anton Paar, Graz, Austria). The temperature of the set-up is kept constant within ± 1 °C by circulating thermal oil through the jackets of the autoclave and density sensor. A removable sample cell (9) is connected to the density sensor. The system can withstand pressures up to 45 MPa and temperatures up to 120 °C. A relief valve is connected to the autoclave to protect the system against overpressures. A bursting disk is also present in case the relief valve malfunctions.

The density sensor was calibrated with air and n-hexadecane. The calibration of the viscosity sensor was checked with the atmospheric cocoa butter viscosity data measured at different temperatures. The atmospheric viscosity of the cocoa butter at temperatures of 35 – 90 °C was measured with an Ubelohde viscometer (capillary

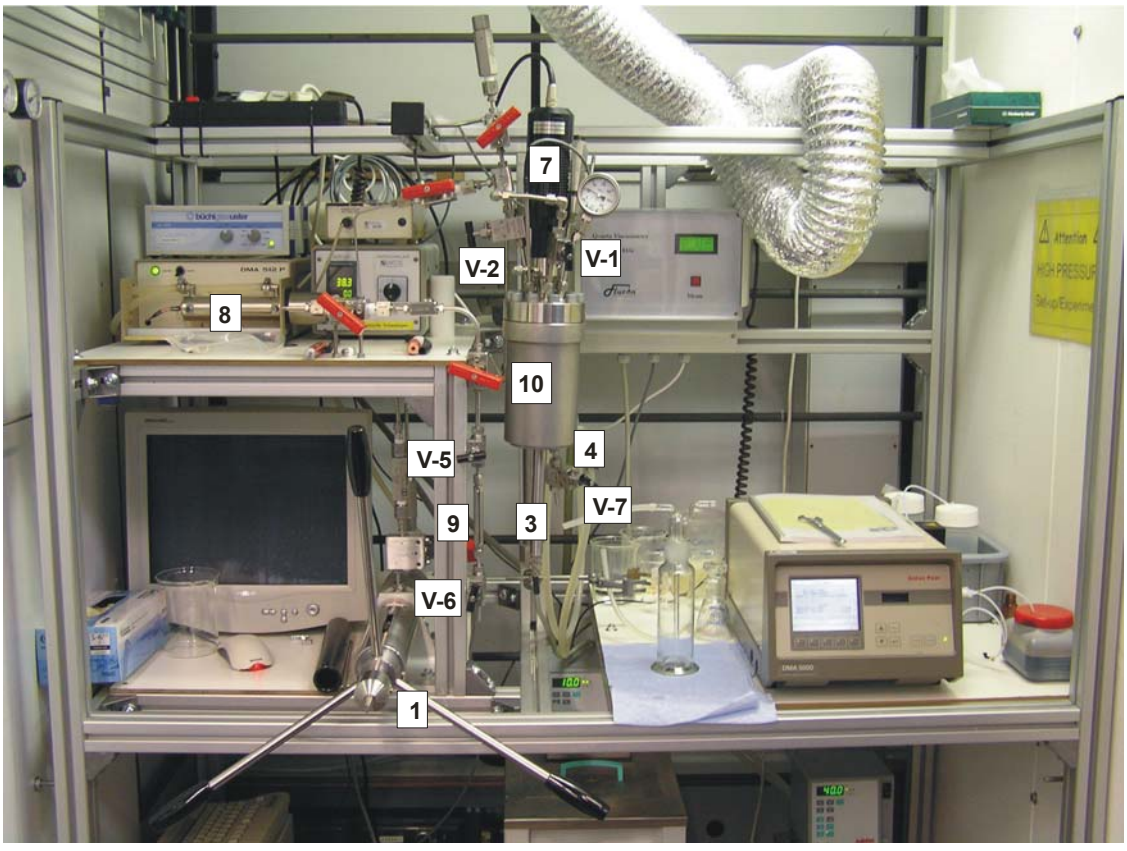
diameter 1.13 mm) purchased from Schott (Mainz, Germany) placed in a constant temperature bath (set point ± 0.1 °C). The atmospheric density of the cocoa butter at temperatures of 35 – 90 °C was measured with an oscillating densimeter (DMA5000, Anton Paar, Graz, Austria).

The autoclave (10) was loaded with 200-300 ml of test compound and allowed to reach the desired temperature before CO_2 from the supply cylinder was added with a hand pump (1) (Sitec Hand Pump 750.1060, Sitec Sieber Engineering, Zürich, Switzerland), of which the fluid chamber is cooled to 10 ± 1 °C. In all cases the CO_2 had to diffuse into the unsaturated liquid. The mixture in the autoclave was stirred at 500 rpm for at least 5 minutes to ensure that phase equilibrium has been reached. Letourneau *et al.* [10] used similar equilibrium times in their cocoa butter micronisation study. A settling period of at least 20 minutes was observed to be necessary for phase separation. This procedure (stirring and settling) was repeated if the viscosity deviated more than 1.5 % from any chosen measured value in a time period of 1 min after the settling period.

Once equilibrium has been reached the system was purged via valve V-6 to ensure that the entire system up to the sample cell was at the same conditions. The density was then measured, whereafter the sample cell (consisting of V-5, (9) and V-6) was removed. The sample cell was weighed and depressurised into a wash bottle containing hexane. The sample cell was thoroughly rinsed with petroleum ether to ensure transference of all the material. The CO_2 content of the mixture was determined gravimetrically by emptying and rinsing the wash bottle into a round bottom flask and evaporating the petroleum ether over an oil bath at 100 ± 1 °C. The flasks were placed overnight in an oven at a temperature of 103 ± 1 °C to ensure complete evaporation of the solvent. Initial experiments indicated that negligible amounts of test compound are lost when transferred from the sample cell to the wash bottle and from the wash bottle to the flask (< 0.025 g (≈ 0.7 % of typical contents)). Less than 0.1 g of n-hexadecane (≈ 0.18 % of typical contents) evaporates during typical conditions used to remove the hexane. At least three measurements were made for each pressure. The CO_2-content, density and viscosity of the mixture were determined with each measurement. The solubility measurement was considered to be satisfactory when the weight fractions of at least two of the samples differed less than 1 mass %. The measurement was repeated if this was not the case.



(a)



(b)

Figure 5-1: The autoclave set-up. (a) Schematic diagram (not to scale). (b) Photograph of the set-up.

Phase equilibrium and density measurements were done with n-hexadecane and CO_2 at 40 and 60 °C and pressures of 2 – 22 MPa in order to validate the experimental procedure. Thereafter measurements were done with the CO_2-cocoa butter system for pressures of 2 – 35 MPa and temperatures of 40, 80 and 100 °C. At higher temperatures there is an increased pressure drop in the lines connecting the autoclave to the external density cell and removable sample cell. This can cause phase separation in these lines as well as in the density sensor. This results in a measured density that is notably lower than the expected value for the heavier phase. Therefore density measurements cannot be made at 100 °C. However, phase composition measurements can still be done by connecting the sample cell (9) directly to the bottom outlet (4) of the autoclave. This ensures that the sample is always at the same conditions as that of the lower phase in the autoclave.

5.2.2 Materials

Cocoa butter was obtained from Gerkens Cacao (Wormer, The Netherlands). Petroleum ether (boiling range 40-60 °C) was bought from Merck (Amsterdam, The Netherlands). Hexadecane (99 % pure) was bought from Acros (Geel, Belgium). Liquid CO_2 with a purity ≥ 99.995 % was bought from Hoek Loos (Schiedam, The Netherlands).

5.2.3 Accuracy and reproducibility of experimental results

An error analysis was performed on the measured data. In these calculations the errors made in weighing the different components as well as the evaporation of the substance being measured were taken into account. It was experimentally determined that a maximum of 0.03 g of n-hexadecane (0.01 % of the total amount) will evaporate at the conditions used during evaporation of the solvent. Cocoa butter is less volatile than n-hexadecane, and will not evaporate during the evaporation stage. The absolute error made in calculating the mass fraction of substance present in the sample was always calculated as less than 0.8 mass %.

5.3 Results and discussion

5.3.1 Validation of the experimental procedure

The experimental procedure was validated by comparing the measured properties of the n-hexadecane/CO_2 system at 40 and 60 °C with literature data. Figure 5-2 shows the density of CO_2 - saturated n-hexadecane at 40 and 60 °C. There is an excellent agreement between the measured values and those reported in [11]. The measurements made at 40 °C show the importance of the density measurements as a check that the

correct phase has been sampled. Around 10 – 12 MPa there is an irregularity in the measurements. This is the pressure where a third phase develops in the CO_2 / n-hexadecane system, as can be seen in Figure 5-3. The dip tube (number (5) in Figure 5-1) obviously did not extend to the level of the heaviest phase, resulting in samples being taken from the lighter phase as is evident from both the density and phase equilibrium measurements made at these pressures. It is difficult to draw this conclusion without the density measurements when experiments are done with systems of which it is not known whether more than two phases exist at a given temperature and pressure. The density measurements can also indicate when the level of the heavier phase becomes too low for sampling.

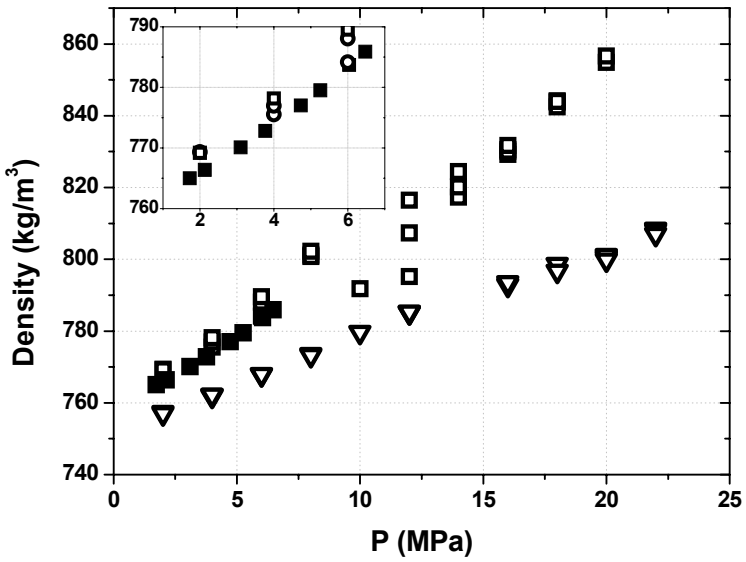
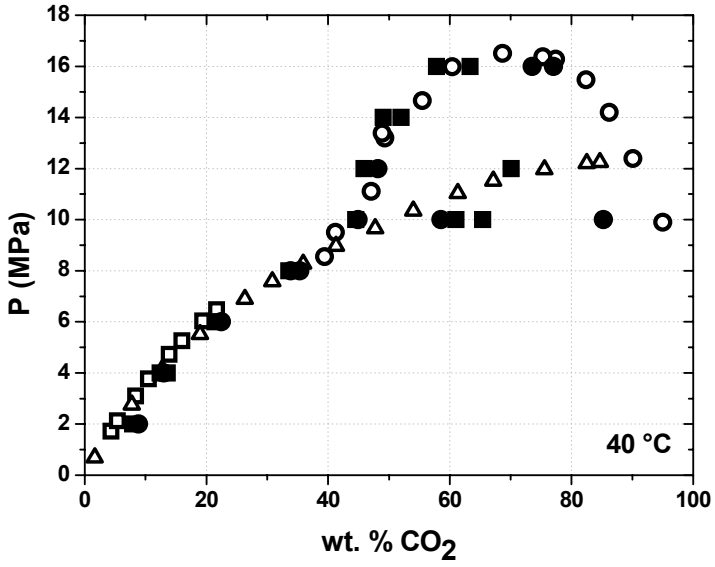
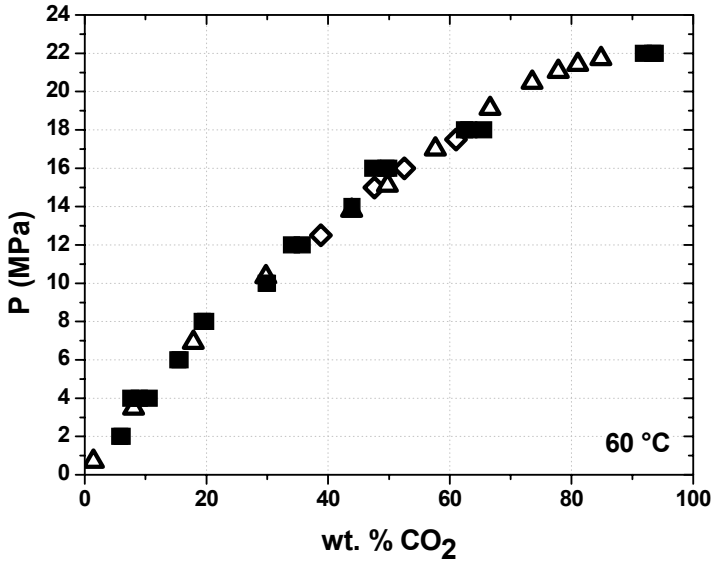


Figure 5-2: Liquid phase densities of the system n-hexadecane + CO_2 at 40 °C (measured (□) and literature values (■, taken from [11]) and 60 °C (measured,▽).

Figure 5-3 compares the measured phase equilibrium compositions with the literature values for 40 and 60 °C. It can be seen that there is an excellent agreement between the measured and literature values at pressures where only two phases exists. From this it can be concluded that the experimental procedure can be used to produce accurate data for the heavier phase of unknown systems.



(a)



(b)

Figure 5-3: Comparison of the measured (closed symbols) and literature values (○ taken from [12], □ taken from [11], △ taken from [13] and ◇, taken from [14]) for the phase equilibrium composition of n-hexadecane + CO_2 at (a) 40 °C and (b) 60 °C.

5.3.2 Characterisation of the CO_2 – cocoa butter system

5.3.2.1 Melting point

The melting point of pure cocoa butter as well as that of CO_2-saturated cocoa butter at different CO_2 pressures was visually determined by placing the samples in a thermostated view cell. For pure cocoa butter it was found that melting starts at 34 °C and that the cocoa butter is completely melted at 35 °C. Cocoa butter does not have a sharp melting point due to the presence of different triacylglycerols. The re-crystallised sample exhibited the same melting behaviour as the original sample.

Figure 5-4 compares the melting points measured in this chapter with that reported in [5]. It is clear that the presence of CO_2 decreases the melting point of cocoa butter. It was found that CO_2-saturated cocoa butter starts to melt at 21 °C and is completely molten at 23 °C, independent of the CO_2 pressure for pressures higher than 5 MPa. The measured values correspond to the literature values if the experimental accuracy is taken into account.

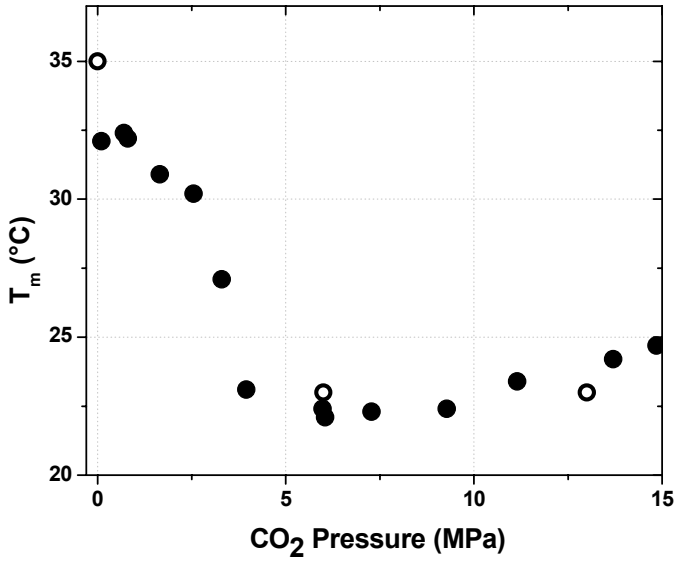


Figure 5-4: Melting temperature of cocoa butter with and without CO_2. Open symbols were measured in this chapter, closed symbols taken from [5].

5.3.2.2 Solubility of CO_2 in cocoa butter

The phase behaviour of cocoa butter in the presence of CO_2 was studied visually with the aid of a view cell in order to determine whether phase inversion or the formation of a third phase is likely to occur at the temperatures and pressures under consideration. It

was already known that this does not happen at temperatures up to 80 °C and pressures up to 30 MPa [5]. Figure 5-5 shows that this is also the case for 90 °C. The volume of the heavier phase increases considerably with pressure. This is due to the increased solubility of CO_2 in cocoa butter at higher pressures. Furthermore it can be seen from the shape of the meniscus that the surface tension of the CO_2-saturated cocoa butter is a function of the CO_2 pressure. The surface tension of the heavier phase decreases with increasing pressure, corresponding to the increasing dissolution of CO_2 in the cocoa butter.

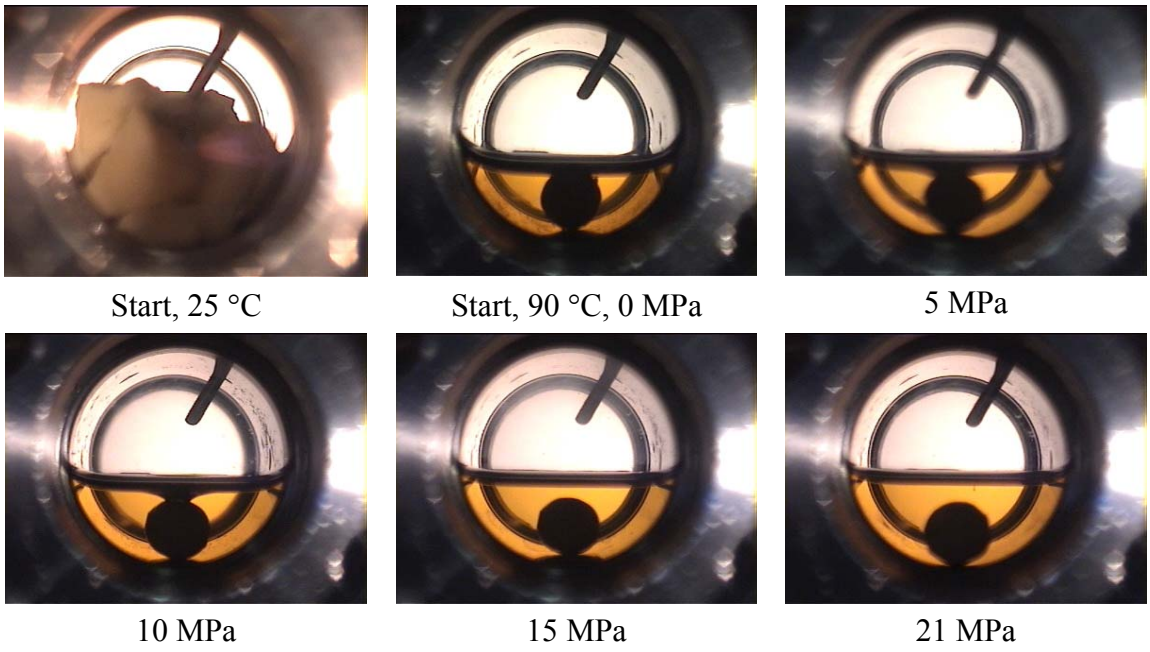
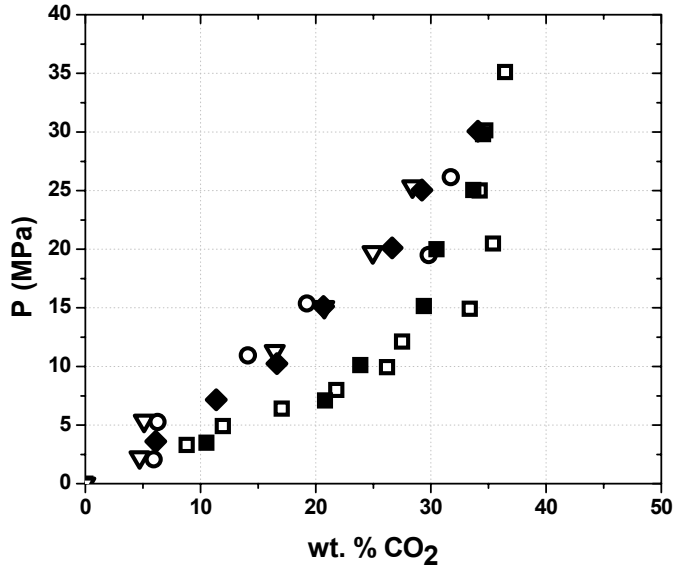


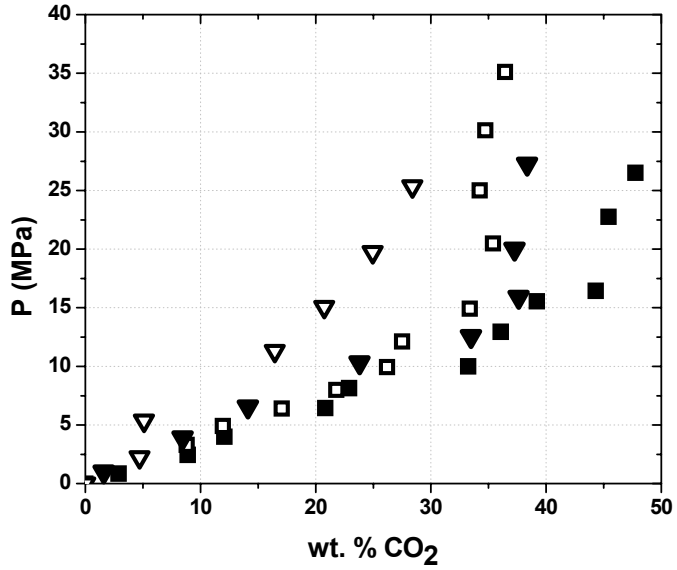
Figure 5-5: The phase behaviour of the CO_2-cocoa butter system at 90 °C.

Figure 5-6 shows the solubility of CO_2 in cocoa butter at different pressures at 40, 80, 90 and 100 °C. The solubility of CO_2 increases with a decreasing temperature, and also increases with an increasing CO_2 pressure. At 40 °C the CO_2 solubility reaches a maximum of 36 wt. % at a pressure of 20 MPa. The CO_2 solubility remains constant at higher pressures. However, at higher temperatures the CO_2 solubility continues to increase with pressure. The same behaviour, as well as solubilities of similar magnitudes, is reported for sesame seed oil [8], rapeseed oil [15] and palm oil [16].

There is a marked difference between the measured data and the data previously published in [5]. The reported maximum deviation (2.5 %) between measurements made at the same conditions [5] is larger than that of the measurements made for this chapter (1 %). Furthermore the measured data correspond to those measured with the same batch of cocoa butter in another lab with the autoclave set-up described in [17].



(a)



(b)

Figure 5-6: The solubility of CO_2 in cocoa butter at different pressures and 40 (■,□), 80 (▼,▽), 90 (◇) and 100 °C (○). (a) Comparison of the data measured in the autoclave set-up (open symbols) and that measured in the set-up described in reference [17] (closed symbols). (b) Comparison of the data measured in the autoclave set-up (open symbols) and the data reported in reference [5] (closed symbols).

It is possible that the difference between the two sets of data can be attributed to the different batches of cocoa butter that was used. It is known that growing conditions, age of the plant, the production process of the cocoa butter from the cocoa beans and subsequent refining all influences the composition of cocoa butter [1,18]. These differences in composition influence the physical properties [18], and it is therefore not unreasonable to expect the solubility of CO_2 in cocoa butter also to be influenced by these differences.

5.3.2.3 Density

Figure 5-7 shows the atmospheric density of cocoa butter at different temperatures. The density decreases linearly with an increase in temperature, as was expected. The change of density as a function of temperature corresponds to that reported for other common plant oils (0.67 kg/m^3) [19].

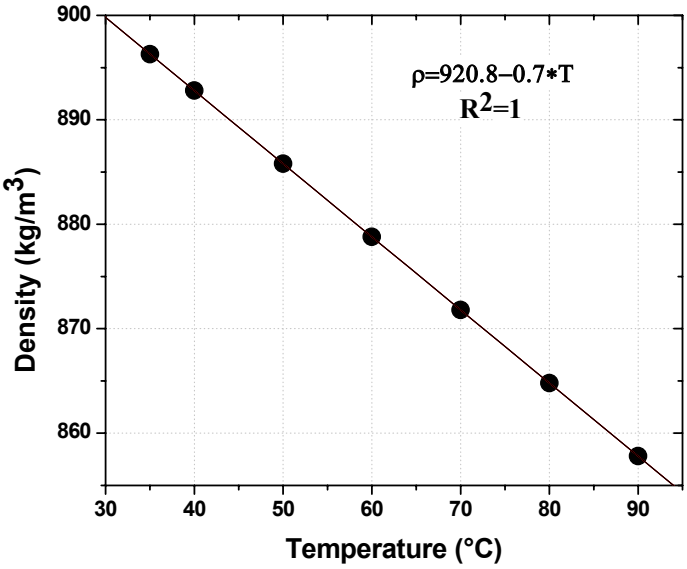


Figure 5-7: The density of cocoa butter at different temperatures and atmospheric pressure. T has units of °C.

Figure 5-8 shows the density of CO_2-saturated cocoa butter at different pressures and temperatures. The density of CO_2-saturated cocoa butter increases linearly with increasing CO_2-pressure for pressures above 5 MPa, and decreases with an increase in temperature. However, the magnitude of the density increase for increasing CO_2 pressure is relatively small. The density increase with pressure follows the same behaviour for both 40 and 80 °C, and depends only on CO_2 pressure. This is common behaviour for SC-CO_2-saturated triglycerides [25]. Densities of the same magnitude,

as well as similar values of density increase, were measured for corn oil [20], soybean oil [22], coconut oil [21], palm kernel oil [21], castor oil [21], linseed oil [21], olive oil [21] and palm oil [20-23]. The non-linear behaviour at 40 °C for pressures below 5 MPa was also observed for corn oil [20]. This behaviour can be attributed to difference of the properties of CO_2 close to the critical point and at higher pressures where the properties of CO_2 changes more gradually with increasing pressure and temperature.

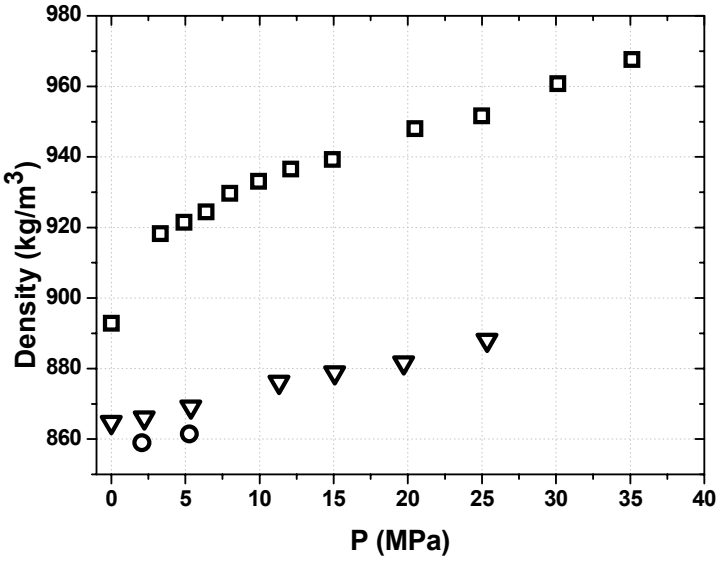


Figure 5-8: The density of CO_2-saturated cocoa butter at different pressures and 40 (□), 80 (▽) and 100 °C (○).

5.3.2.4 Viscosity

Figure 5-9 shows the atmospheric viscosity of cocoa butter at different temperatures. The viscosity decreases exponentially with temperature, as is normal for Newtonian fluids.

Figure 5-10 shows the viscosity of CO_2-saturated cocoa butter at different temperatures. The viscosity decreases with increasing CO_2-pressure and to a lesser extent with an increase in temperature. This corresponds to an increase in the amount of dissolved CO_2. The viscosity of the CO_2-saturated cocoa butter reaches a lower limit at a pressure of approximately 15 MPa, regardless of the temperature. The viscosity reduction due to the presence of CO_2 is more pronounced at a lower temperature. This is normal for systems in which the pure components are Newtonian fluids [25].

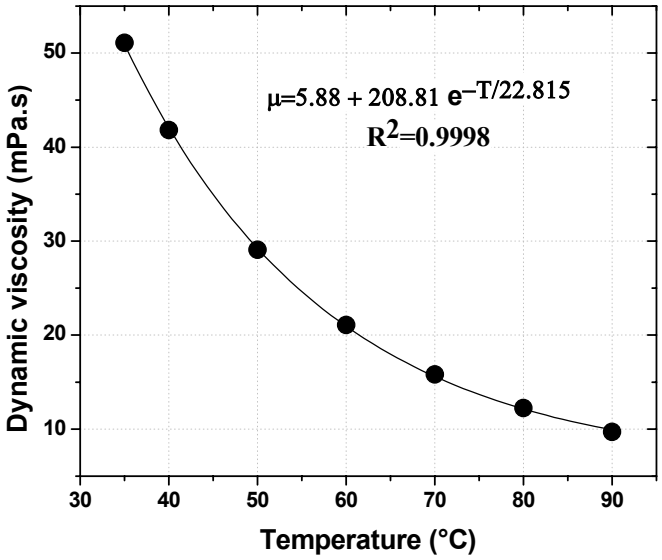
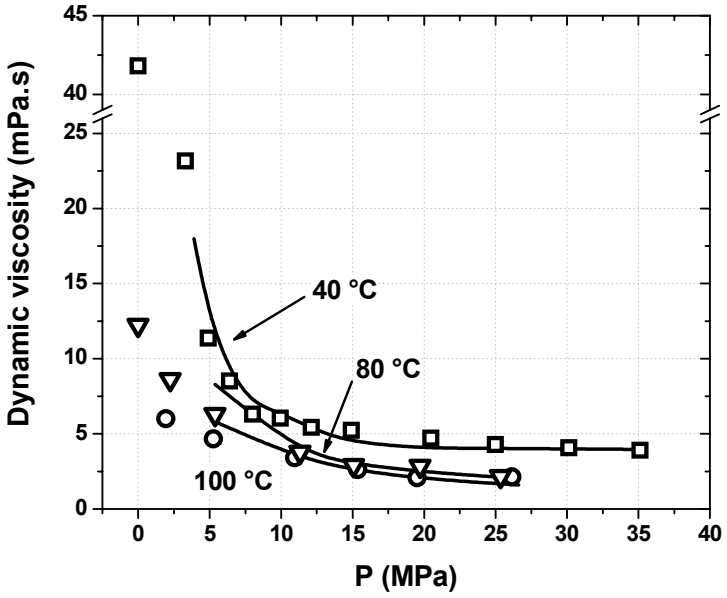


Figure 5-9: The dynamic viscosity of cocoa butter at different temperatures and atmospheric pressure. T has units of °C.

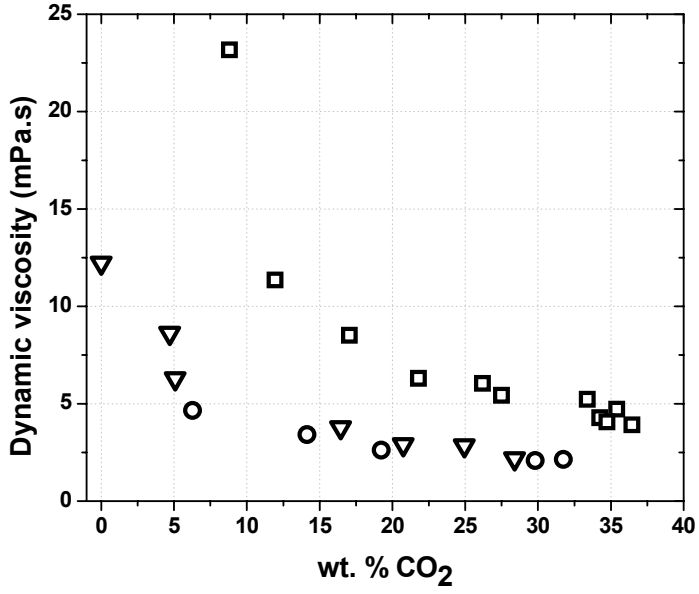
Empirical parabolic equations with one adjustable interaction parameter are often used to calculate the mixture viscosities of liquid mixtures with reasonable accuracy [24]. The Grunberg equation is such an equation that can be used to predict the viscosity of saturated phases [25,26]. For a binary mixture the equation can be written as follows:

$$\mu_m = \mu_1^{x_1} \mu_2^{x_2} \exp\left(G_{12} x_1 x_2\right) \tag{5-1}$$

where μ_m is the viscosity mixture, μ_i the viscosity of component i at the system conditions, x_i is the mass fraction of component i and G_{12} is an interaction coefficient. G_{12} is temperature dependent and can be used as a fitting parameter. The Grunberg equation is in fact a modification of the Arrhenius-type equation. The Arrhenius equation describes ideal mixtures. The interaction coefficient in the Grunberg equation takes deviations from ideal behaviour into account. G_{12} is system, and often also temperature, dependent.



(a)



(b)

Figure 5-10: The dynamic viscosity of CO_2-saturated cocoa butter for 40 (□), 80 (▽) and 100 °C (○). (a) As a function of CO_2-pressure also showing the viscosities calculated with equation (5-1). (b) As a function of CO_2 solubility.

No data is available on the viscosity of pure cocoa butter at elevated pressures. Equation (5-1) was therefore fitted to the experimental data for pressures above the critical pressure of CO_2 (7.4 MPa) using the measured atmospheric viscosities of cocoa butter at 40 and 80 °C, and the viscosity reported by Fang *et al.* [27] for 100 °C due to limitations of the experimental set-up that was used. The pure CO_2 viscosities at different pressures and 40, 80 and 100 °C were taken from reference [28]. The absolute average deviation (AAD) can be used to quantify the goodness of the fit. The percentage AAD is defined as:

$$\text{AAD}=\frac{1}{\text{N}}\sum\left|\frac{\mu_{calculated}-\mu_{measured}}{\mu_{measured}}\right|\times 100 \qquad (5\text{-}2)$$

where N is the number of points, $\mu_{calculated}$ is the calculated viscosity and $\mu_{measured}$ is the corresponding experimentally measure mixture viscosity. The fitting results are reported in Table 5-1. The viscosities calculated with equation (5-1) are shown in Figure 5-10.

The negative values of G_{12} at 40 and 80 °C indicate that the interaction of the molecules in the mixture is less than would be expected from the individual component viscosities. However, there is no obvious temperature dependence for the G_{12} values. Attempts to determine G_{12} with group contribution methods have failed [29]. The Grunberg equation is therefore purely correlative, and not predictive. This severely limits the usefulness of the method.

Table 5-1: Fitting results for the Grunberg equation.

Temperature	G_{12}	AAD (%)
40 °C	-0.8	13.8
80 °C	-1.1	4.8
100 °C	0.3	4.7

Other authors found similar AAD for lipid/CO_2 systems [29,30]. Size and polarity differences between the CO_2 and lipid compounds cause relatively large errors when equation (5-1) is used to estimate the mixture viscosity for lipid/CO_2 systems [29]. It is not thought that the use of predictive viscosity equations incorporating the excess Gibbs free energy will improve the fit due to the assumptions that are made in these models (i.e. that the components in the mixture mixes isometrically) [30].

5.3.3 Predicted GAME yields

Higher cocoa butter yields are achieved when GAME is used to remove cocoa butter from cocoa nibs than with conventional expression of cocoa nibs [4]. The filter cakes created with GAME contain the same volume of liquid as those created with conventional expression at the same effective mechanical pressure [4]. However, in GAME filter cakes a large part of the liquid consists of SC-CO_2, which is removed during depressurisation. Therefore the yields for GAME can be predicted from the yields obtained with conventional expression at the same effective mechanical pressure and the solubility of SC-CO_2 in cocoa butter at the conditions used.

The volume of liquid left in the filter cake (V_{liquid}) can be calculated with equation (5-3) if the mass fraction of cocoa butter in the conventional expression filter cake (x_1), the original cocoa butter content of the cocoa nibs (x_0), the mass of nibs (m_1) and the atmospheric density of the cocoa butter (ρ_{cb}) are known.

$$V_{liquid} = x_1 \cdot m_1 \cdot \frac{(1-x_0)}{(1-x_1)} \cdot \frac{1}{\rho_{cb}} \tag{5-3}$$

The mass of cocoa butter left in a GAME filter cake (m_{cb}) can then be calculated from the solubility of CO_2 in cocoa butter and the density of CO_2-saturated cocoa butter ($\rho_{cb\text{-}CO2}$). Equation (5-4) is used for this calculation:

$$m_{cb} = V_{liquid} \cdot \rho_{cb-CO2} \cdot (1-y_1) \tag{5-4}$$

where y_1 is the mass fraction of CO_2 in the CO_2-saturated cocoa butter. The cocoa butter yield (Y, equal to the percentage of the total cocoa butter removed) can then be calculated with equation (5-5).

$$Y = \frac{x_1 \cdot m_1 - m_{cb}}{x_0 \cdot m_1} \cdot 100 \tag{5-5}$$

The results of these calculations are shown in Figure 5-11. Surprisingly the calculated GAME yields are rather low compared to the experimental yields, especially at 100 °C. The same calculations were made with the values reported in [5] for the solubility of CO_2 in cocoa butter and the density measured densities of the CO_2-saturated cocoa butter. There is still a considerable difference between the predicted and measured yields, even though the difference is smaller than when the measured solubilities are used.

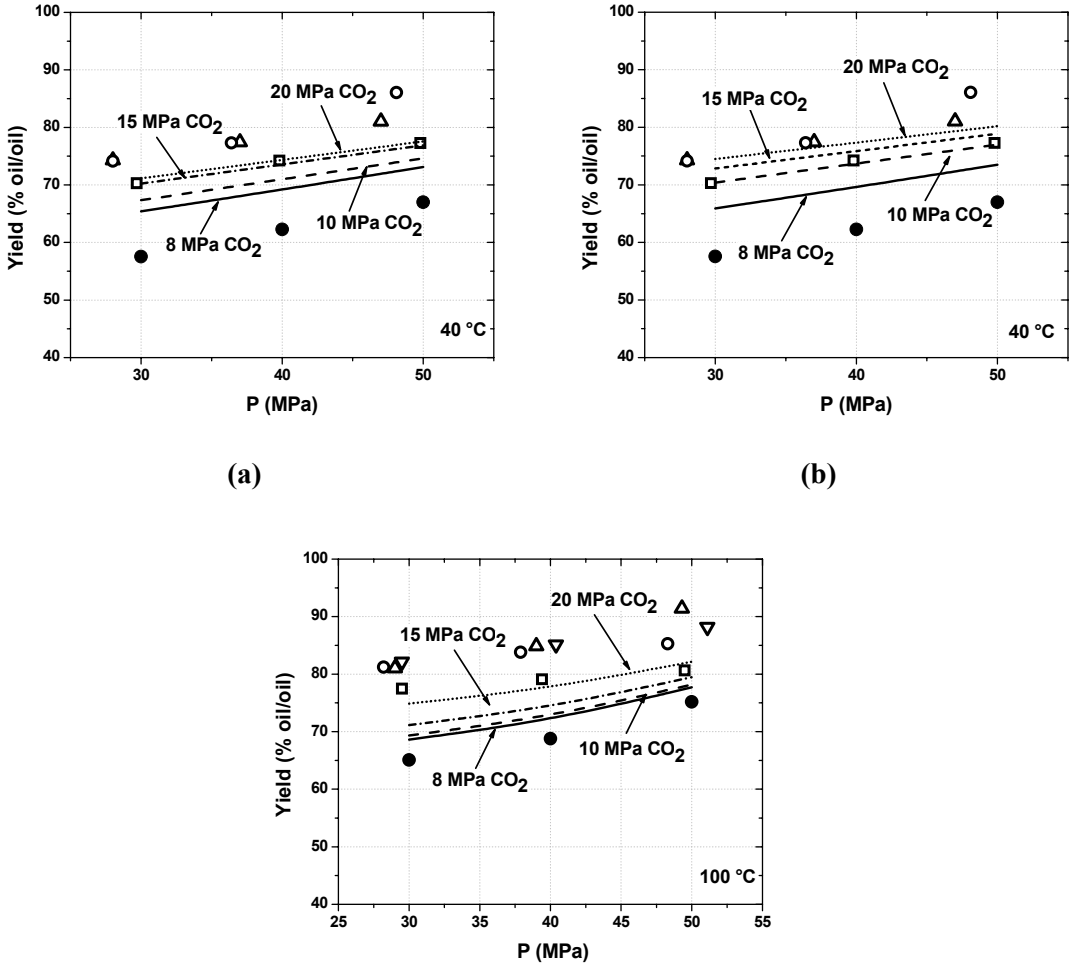


Figure 5-11: Comparison of the experimental GAME yields (open symbols, reported in [3,4]) for CO_2 pressures of 8 MPa (□), 10 MPa (△), 15 MPa (○) and 20 MPa (▽) and the cocoa butter yields calculated (lines) from the conventional mechanical expression yields (●). (a) For 40 °C using the solubilities measured in this chapter. (b) For 40 °C using the solubilities reported in [5]. (c) For 100 °C using the solubilities measured in this chapter.

The discrepancy between the experimental and predicted cocoa butter yields points to the complexity of the process. Other effects apart from the replacement of cocoa butter by SC-CO_2 when GAME is used also come into play to increase the cocoa butter yield compared to the yield obtainable with conventional expression. Although the removal of cocoa butter by entrainment during depressurisation and the rupturing of cocoa butter containing cell structures play minor roles in GAME [4], these effects do contribute to enhancing the cocoa butter yield when GAME is used. It has been suggested that CO_2 increases the permeability of cell membranes, and that this increase is more pronounced at higher temperatures [31]. This will also contribute to increasing the yield when GAME is used compared to the yield obtainable with conventional

expression by allowing more cocoa butter to be removed from the cell structure. This also explains the larger deviation between the calculated and experimental yields at 80 and 100 °C compared to the deviation at 40 °C.

5.4 Conclusions

It is shown that the new experimental set-up can be used to accurately measure the equilibrium composition, density and viscosity of the heavier phase of a gas-liquid mixture at elevated pressures and temperatures. Although the experimental set-up has a limitation due to the lack of a sight window, it is also suitable for measuring multi-phase mixtures due to the simultaneous measurement of density, viscosity and phase composition data.

The presence of CO_2 causes the melting point of the cocoa butter to decrease from its atmospheric value of 34 – 35 °C to 21 – 23 °C at CO_2 pressures above 5 MPa. The solubility of CO_2 in cocoa butter increases with pressure, but decreases with temperature. Qualitative observations of phase behaviour in a high-pressure view cell indicated complete miscibility with CO_2 and no phase inversion for the conditions that were studied. A maximum solubility of 36 wt. % was measured at 20 MPa and 40 °C. The density of CO_2-saturated cocoa butter increases slightly with pressure, and decreases with temperature. The viscosity of CO_2-saturated cocoa butter decreases with temperature and increasing CO_2 pressure up till 15 MPa where it reaches a minimum value of 2 – 5 mPa.s depending on the temperature.

The cocoa butter yields calculated for the GAME process indicate that the solubility of CO_2 in cocoa butter varies between batches. Comparison of the calculated and measured yields also showed that the increased yield when GAME is used cannot be attributed to replacement of part of the cocoa butter with CO_2 alone.

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6 The influence of process parameters on Gas Assisted Mechanical Expression (GAME) of cocoa nibs

Abstract

It is known that increased cocoa butter yields can be achieved with Gas Assisted Mechanical Expression (GAME) of cocoa nibs when compared to conventional expression of cocoa nibs [1]. In a hydraulic press the GAME operation consists of a CO_2 dissolution stage, a press stage and a depressurisation stage. In this chapter the influence of the process parameters involved with the press stage on the final cocoa butter yield is investigated. All GAME experiments were performed with 10 MPa of CO_2. It is shown that neither the mass of cocoa nibs used, the duration of the press stage nor the mechanical pressure profile has a significant influence on the final cocoa butter yield. The moisture content of the nibs determines the behaviour of the solid structure during the press stage, thereby determining the cocoa butter yield that can be achieved as well as the speed with which it can be obtained. The maximum yield is obtained at a moisture content of 1.3 wt. % (wet basis). Lower moisture contents result in a faster compression of the cake. It is impossible to recover cocoa butter with GAME at 100 °C when nibs with moisture contents higher than 5.5 wt. % are used due to the extrusion of the cocoa solids through the filter medium. Similar yields were obtained when cocoa liquor and cocoa nibs were used in GAME experiments at the same conditions. Lastly it is shown that higher yields can be achieved when multi-stage GAME is used instead of single stage GAME. An absolute increase in cocoa butter yield of 7 – 10 % was achieved when two-stage GAME was used instead of single stage GAME.

6.1 Introduction

Cocoa butter is an important ingredient in the confectionary industry [2,3]. Usually cocoa nibs (broken cocoa beans containing approximately 54 wt. % cocoa butter) are grinded to a fine paste known as cocoa liquor before being pressed in hydraulic filter presses to remove the cocoa butter [2]. It is important to maximise the cocoa butter yield, as cocoa butter is at least twice as valuable as the residual filter cake [4].

Gas assisted mechanical expression (GAME), a process introduced in Chapter 4, offers increased cocoa butter yields (defined as the mass of oil extracted as a percentage of the total mass of oil in the oilseeds) when compared to the mechanical expression of cocoa nibs. In this process the cocoa nibs are saturated with supercritical carbon dioxide (SC-CO_2) before being mechanically expressed. At the end of the pressing stage of the GAME process the same volume of liquid remains in the filter cake as when the cocoa nibs are pressed conventionally. Due to the high solubility of SC-CO_2 in cocoa butter a large part of this liquid consists of CO_2, which is removed during the depressurisation stage. Therefore the filter cakes resulting from GAME have lower cocoa butter contents than those created by conventional expression. The high yields of GAME lead to the question whether using different conditions can increase the cocoa butter yield even more. It is therefore of interest to determine the optimum conditions at which GAME can be performed on cocoa nibs.

The decrease in filter cake thickness follows the same trend over time for both GAME and conventional pressing [1]. It can therefore be expected that the parameters influencing the expression behaviour during conventional expression will also have an influence on the expression behaviour in GAME processes. The effect of these parameters on conventional expression was investigated in Chapter 2.

Besides the mechanical pressure, temperature and seed pre-treatment the following parameters also influence the conventional expression of oilseeds [2, 6-29]:

- Duration of pressing
- Mass of material being pressed
- Pressure profile of the applied mechanical pressure
- Moisture content of the oilseeds

In GAME the effective mechanical pressure has to be used instead of the mechanical pressure. The effective mechanical pressure is defined as the difference between the applied mechanical pressure and the CO_2-pressure and corrects for the counteracting force of the CO_2-pressure. Apart from these parameters the CO_2-pressure also influences the oil yield in GAME [1].

The aim of this chapter is to study GAME in more detail. A CO_2 pressure of 10 MPa is used throughout since this is the pressure at which the maximum increase in oil yield is obtained [1]. The influence of the pressing time, the mass of cocoa nibs pressed, the mechanical pressure profile and the moisture content of the cocoa nibs on the cocoa butter yield obtainable by GAME of cocoa nibs are investigated. The effect of the moisture content on the rate of filter cake compression is also investigated. The rate of compression is not affected by the mass of nibs being pressed or the pressing time. Furthermore the behaviour of nibs is compared to that of cocoa liquor. Lastly the feasibility of using multi-stage GAME to further increase the cocoa butter yield is investigated by re-using already pressed filter cakes in GAME experiments at different conditions.

6.2 Materials and methods

6.2.1 Equipment and experimental procedure

A detailed description of the experimental set-up, experimental method and analysis procedure was presented in Chapter 4. Figure 6-1 shows the laboratory press with one drainage area and an inside diameter of 30 mm that was used to perform the experiments. The uniaxially moving plunger can exert mechanical pressures of up to 100 MPa on the material being pressed. The displacement of the plunger is recorded digitally at a frequency of 1 Hz with an accuracy of 0.01 mm. Gas pressures of up to 45 MPa can be used. A fine wire mesh is used as filter medium.

Each experiment consists of the following stages:

- A thermal equilibration stage of 30 minutes during which the nibs are allowed to reach the desired temperature (40 or 100 °C).
- A CO_2 – equilibration stage where CO_2 is added to the press and allowed to diffuse into the cocoa nibs. During this stage the CO_2 dissolves in the cocoa butter contained in the solids cocoa matrix. It was experimentally determined that 30 minutes is sufficient to reach phase equilibrium. A CO_2 pressure of 10 MPa was used in all experiments.
- A pressing stage during which the mechanical pressure is increased to the desired level (300-800 MPa) and then kept constant. Unless otherwise stated the mechanical pressure is increased instantaneously and maintained constant for 10 minutes.
- A depressurisation stage, during which the CO_2 is released.

The default settings (using 10 g of dry cocoa nibs or cocoa liquor and a pressing time of 10 minutes) used in conventional expression [25] are used unless stated otherwise. The CO_2 pressure at the end of the pressing stage was used in the calculation of the

effective mechanical pressure to take into account the compression of the CO_2 resulting from the movement of the plunger. The CO_2 pressures reported in this chapter refer to the initial CO_2 pressure of the experiment.

The fat contents of the filter cakes were determined by soxhlet extraction with petroleum ether following the procedure described in Chapter 2 [25]. The moisture content of the cocoa nibs was controlled by equilibrating them in a closed exsiccator with a saturated salt solution as described in Chapter 2 [25]. By using different salts different moisture contents were obtained.

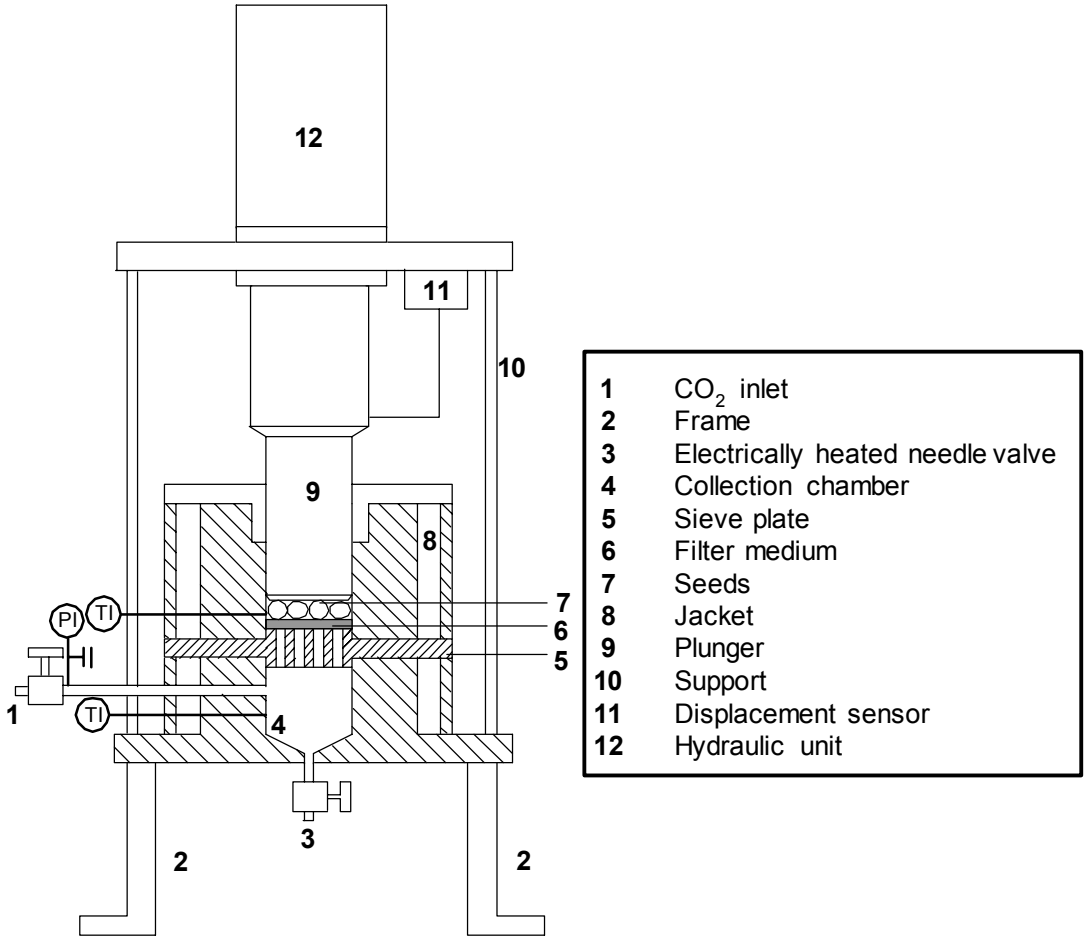


Figure 6-1: A schematic depiction of the laboratory press (not to scale).

In order to evaluate the experimental reproducibility four experiments were done with dry nibs at 80 °C with 10 MPa CO_2 and an effective mechanical pressure of 29 MPa. The average yield for these four experiments was 78.2 %. The absolute standard deviation in the determined yields was calculated as 0.6 %. Duplication of random experiments at other conditions always resulted in an absolute standard deviation of less than 0.9 %. In view of this the absolute experimental error made in calculating the yield is taken as ± 1 %.

6.2.2 Materials

Winnowed cocoa nibs and cocoa liquor were obtained from Gerkens Cacao (Wormer, The Netherlands). The original moisture contents were determined according to the DGF standard method [5] and are presented in Table 6-1. The fat contents of the cocoa material are also shown in Table 6-1. All fat contents are reported on a dry basis.

Table 6-1: Properties of the cocoa material.

Native material	Moisture content (wt. %,wet basis)	Fat content (wt. %, dry basis)
Cocoa nibs	5.5	56.2
Cocoa liquor	1.9	53.9

Zeolite A4 was kindly donated by Tosoh Europe B.V. (Amsterdam, The Netherlands). Sodium hydroxide, potassium hydroxide and magnesium chloride were purchased from Aldrich, potassium sulphate was purchased from Acros and sodium nitrate as well as petroleum ether (boiling range 40-60 °C) were purchased from Merck.

6.3 Results and discussion

6.3.1 Time of pressing

It is known that the pressing time generally has little influence on the yield in the conventional expression process [15,25]. Previously it has been determined that conventional expression and GAME of cocoa nibs follow the same mechanism, with the only difference that the liquid remaining in the GAME filter cakes consists not only of cocoa butter but also of SC-CO_2 [1]. It is therefore reasonable to expect the duration of the GAME press stage to have little influence on the yield. Figure 6-2 confirms that the pressing time indeed has little influence on the cocoa butter yield when pressing times longer than 150 s are used. Therefore 10 minutes is a reasonable choice for the default duration of the pressing stage.

6.3.2 Mass of nibs

Figure 6-3 shows that the mass of nibs has no influence on the cocoa butter yield obtained with GAME. The same trend was already observed for the conventional expression of cocoa nibs [25]. Therefore the default mass of material being pressed (10 g) used for conventional expression experiments is also a good choice for GAME experiments.

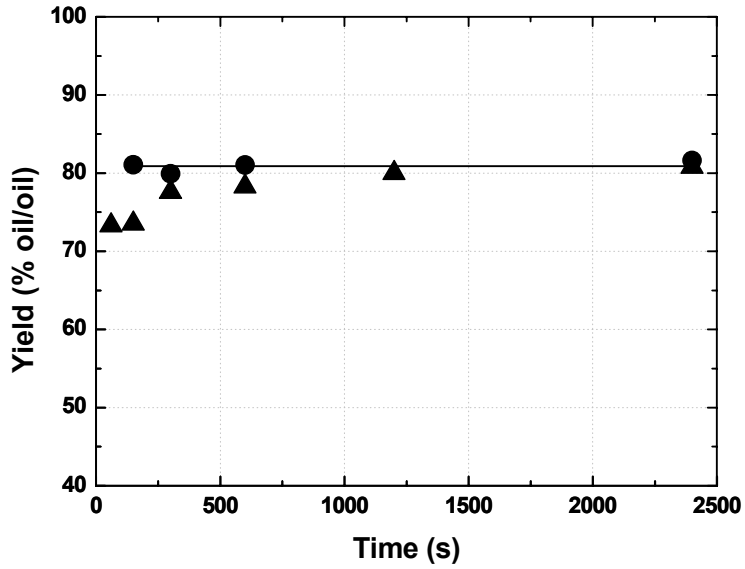


Figure 6-2: The yield as a function of the duration of the press stage for experiments done at 40 °C and 50 MPa effective pressure (▲) and 100 °C and 30 MPa effective pressure (●) with 10 MPa CO_2. The line shows the average yield at 100 °C.

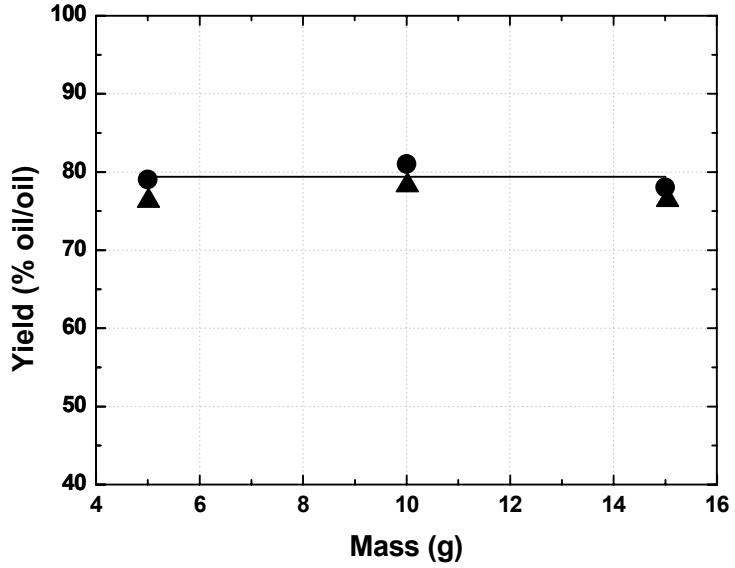


Figure 6-3: The yield as a function of the mass of nibs being pressed at 40 °C and 50 MPa effective pressure (▲) and 100 °C and 30 MPa effective pressure (●) with 10 MPa CO_2. The line shows the average yield at 100 °C.

6.3.3 Mechanical pressure profile

In traditional industrial pressing of cocoa liquor the mechanical pressure is increased linearly at a rate of 0.1-0.3 MPa/s until the desired maximum pressure has been reached, whereafter it is kept constant until the pressing stage ends [2,6,23,24]. Figure 6-4 shows typical examples of constant and linearly increasing pressure profiles.

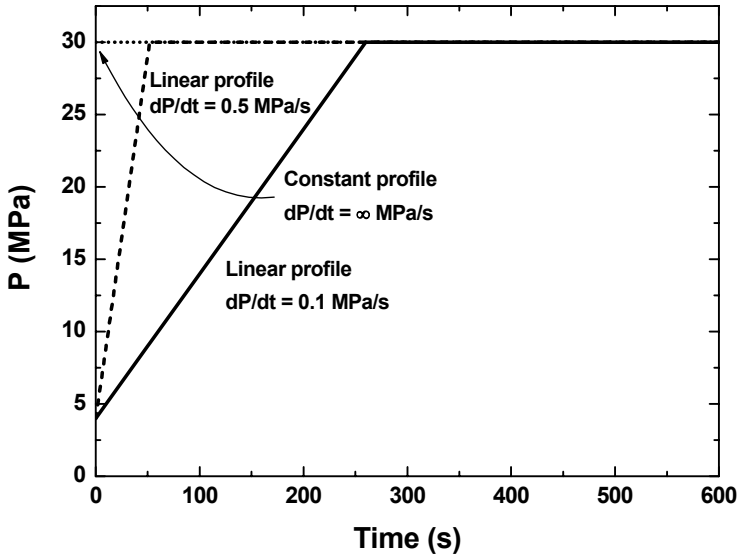


Figure 6-4: Typical mechanical pressure profiles for a total pressing time of 10 minutes as used in the GAME experiments.

When the mechanical pressure is increased at a slower rate the time during which the filter cake experiences the maximum effective pressure is shorter. Figure 6-5 shows the yields obtained with GAME experiments in which the mechanical pressure is increased at different rates when a total pressing time of 10 minutes is used. The cocoa butter yield obtained when the slowest linearly increasing pressure profile was used (i.e. $dP/dt = 0.1$ MPa.s^{-1}) is lower than those of the other rates, but still falls within the error margins of the other yields. Therefore the rate at which the effective mechanical pressure is increased does not influence the cocoa butter yield if the same total pressing time is used in GAME experiments. This confirms that the duration of pressing has little influence on the final cocoa butter yield (see also paragraph 6.3.1).

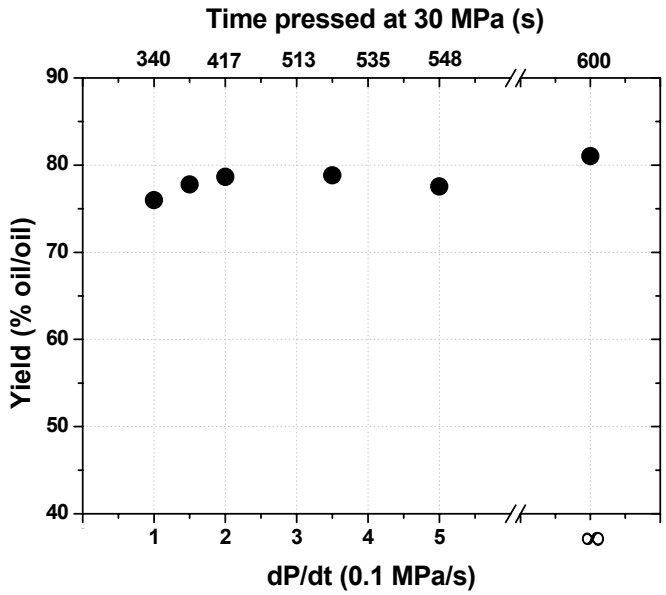


Figure 6-5: Influence of the mechanical pressure profile on the yield for a total pressing time of 10 minutes. All experiments were done at 100 °C with 10 MPa CO_2 and a maximum effective pressure of 30 MPa.

6.3.4 Moisture content

The maximum cocoa butter yield (73.9 %) is obtained with a moisture content of 1.3 wt. % (wet basis) when cocoa nibs are conventionally expressed at 100 °C. At 40 °C there is no clear optimal moisture content as long as the moisture content is less than 3.5 wt. % (wet basis) [25]. It is expected that the optimum moisture contents of cocoa nibs will be the same for GAME since there is no discernable difference between the decrease of the filter cake thickness as a function of time when GAME and conventional expression experiments are performed at the same temperature [1]. This is confirmed in Figure 6-6 (a). At moisture contents above 5.5 wt. % (wet basis) the filter cake is extruded through the sieve plate. It is therefore not possible to use GAME to recover cocoa butter from cocoa nibs at moisture contents higher than 5.5 wt. %. For the conventional expression of cocoa nibs the upper limiting moisture content is 7.0 wt. %. This difference can be attributed to the amount of time the cocoa nibs are kept at the elevated temperatures. In conventional expression experiments the total equilibration time before the pressing stage commences amounts to 30 minutes [25], whereas it is equal to 60 minutes in GAME experiments. The cellular material of moist cocoa nibs softens due to cooking when the nibs are exposed to elevated temperatures. This softening process is more noticeable with longer exposure times. Soft cellular material offers less resistance against compression and is more easily extruded through porous media. Long cooking times (> 15 min) at temperatures around 100 °C also

adversely affects the oil yields of other seeds in conventional expression [29]. Furthermore the dissolution of CO_2 in the water contained in the cell structure causes acidification. This causes proteins to denaturate, which also influences the behaviour of the cellular material during compression by making the material less elastic.

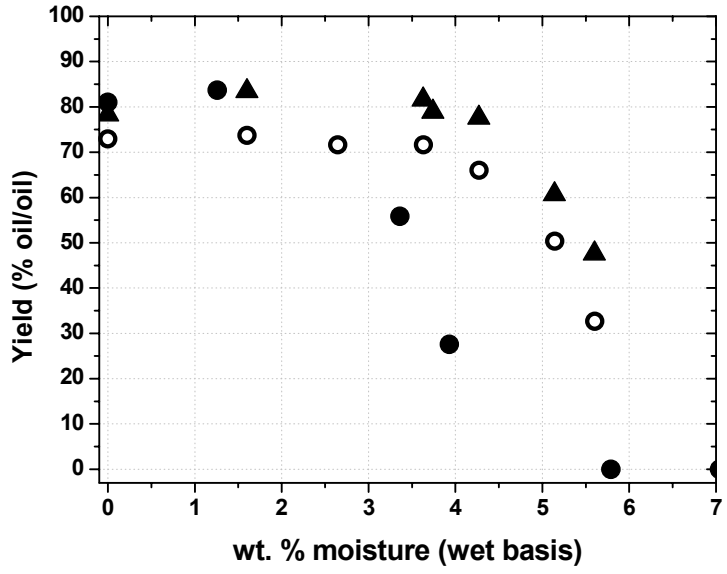
The difference between the behaviour of the cocoa nibs at 40 °C and 100 °C is probably also due to the cooking of the cocoa solids during the equilibrium and press stages of the GAME operation at 100 °C. This weakens the solid structure, making it more pliable and elastic and therefore increases the oil point [28]. This results in a lower yield at the same moisture content than when lower temperatures are used.

In any expression process the material being compressed shows time-dependent behaviour. The rate of compression can be quantified with the so-called consolidation ratio U_C. U_C is defined as:

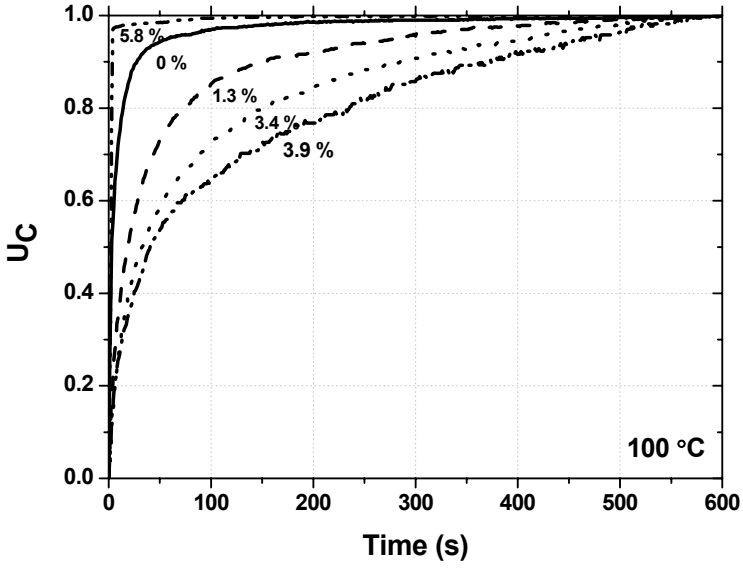
$$U_C(t) = \frac{L(t) - L_0}{L_{final} - L_0} \tag{6-1}$$

where $L(t)$ is the filter cake thickness at time t, L_0 the initial filter cake thickness and L_{final} the filter cake thickness at the end of pressing. U_C is 0 at the start of the process and 1 at the end of the process. A fast increase in U_C indicates that the maximum attainable yield can be achieved in a shorter time than for a material with a slow increase in U_C. When U_C equals 1, or has values close to 1, for an extended period of time before the end of pressing, equilibrium has been reached and the maximum yield for the conditions being used in the process has been achieved.

When the U_C – time graphs of the experiments performed at different moisture contents are compared it can be seen that the rate of compression decreases as the moisture content increases (Figure 6-6(b)). The only exception is the experiment done at 5.8 wt. % moisture where the final filter cake thickness (U_C = 1) is reached almost instantaneously. This is above the threshold moisture content where the solids start to extrude through the sieve plate. It is clear that the nature of the solid structure plays an important role in determining the maximum attainable cocoa butter yield.



(a)



(b)

Figure 6-6: Influence of moisture content on the behaviour of cocoa nibs during GAME performed with 10 MPa CO_2 (a) Cocoa butter yield for 40°C using effective mechanical pressures of 30 MPa (○) and 50 MPa (▲) and for 100 °C and 30 MPa effective mechanical pressure (●). (b) U_C as a function of time for GAME performed at 100 °C at various moisture contents and an effective mechanical pressure of 30 MPa.

6.3.5 Liquor versus nibs

Cocoa liquor is the term used for finely grinded cocoa nibs. It resembles baking chocolate, and is a viscous slurry above its melting point. It is usually assumed that the vigorous grinding required to produce cocoa liquor ruptures the cell wall and frees the cocoa butter from the solid structure [2,23]. Substantially higher cocoa butter yields (an absolute increase of 7-14 % (oil/oil) in cocoa butter yield) can be achieved when cocoa liquor is conventionally expressed than when cocoa nibs are pressed at the same conditions [25]. Figure 6-7 shows that this is not the case for GAME. An absolute increase of 3-6 % (oil//oil) in cocoa butter yield is obtained when cocoa liquor is used in GAME instead of cocoa nibs. As mentioned before (see paragraph 6.1) the increase in cocoa butter yield with GAME can be attributed to the presence of CO_2-saturated cocoa butter in the filter cake at the end of the pressing stage. The roughly comparable yields achieved with cocoa liquor and cocoa nibs when GAME is used therefore indicate that the solid structure of the cocoa nibs does not hinder the diffusion of the SC-CO_2 into the oil-containing cell structures. Freeing the oil from the cell structure will therefore not increase the cocoa butter yield. This is confirmed by the U_C – time graphs of the different experiments, which shows no difference at all between the cocoa nibs experiments and the cocoa liquor experiments.

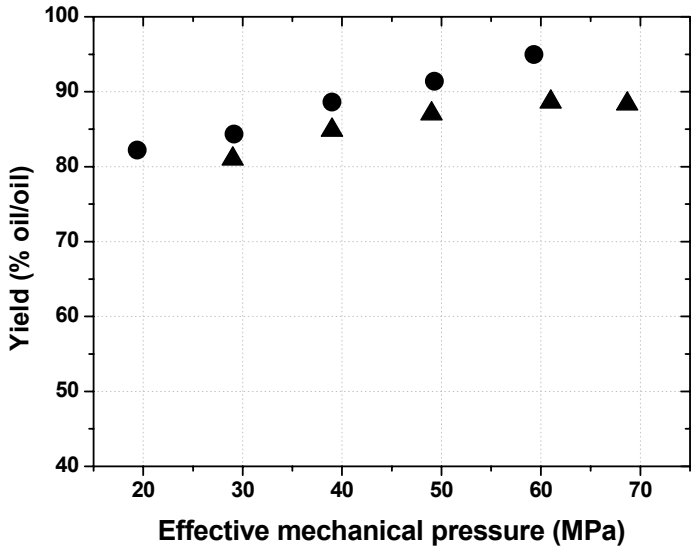


Figure 6-7: Comparison of the yield obtained with nibs (▲) versus that obtained with liquor (●) at 100 °C and different effective mechanical pressures when 10 MPa of CO_2 is used.

6.3.6 Multi-stage GAME

In order to get an indication of the yields that can be expected with multi-stage GAME operations the filter cakes produced by several experiments were broken in smaller pieces and mixed. 10 g of this mixture was then used in a new GAME experiment. Two configurations were investigated:

1. Two-stage GAME performed at the same conditions (100 °C, 10 MPa CO_2 and an effective mechanical pressure of 30 MPa).
2. Isothermal (100 °C) two-stage operation consisting of conventional expression performed at 30 MPa mechanical pressure followed by GAME performed with 10 MPa CO_2 and an effective mechanical pressure of 50 MPa.

The first configuration simulates an extruder operating with nibs pre-saturated with SC-CO_2. The second configuration imitates a two-stage extruder using cocoa nibs as a feed material.

In the first configuration a cocoa butter yield of 87.5 % was achieved, compared to the yield of 81.0 % of a single stage GAME experiment at the same conditions. In the second configuration a cocoa butter yield of 89.9 % was achieved. This is higher than both the yield achieved with conventional expression at 100 °C and 30 MPa mechanical pressure (65.1 %) and the yield achieved with GAME at 100 °C with 10 MPa CO_2 and an effective mechanical pressure of 50 MPa (87.1 %).

Filter cakes created at the same effective mechanical pressure contains equal volumes of liquid for GAME and conventional expression [1]. Therefore the yield of multi-stage GAME operations can be predicted from the conventional expression yields at the same effective mechanical pressure when the solubility of CO_2 in cocoa butter as well the density of CO_2-saturated cocoa butter ($\rho_{cb,CO2}$) are known. The volume of liquid ($V_{liq,i}$) remaining in the filter cake after i GAME stages can be calculated from equation (6-2) if it is assumed that the percentage decrease in the liquid volume remains constant in all stages.

$$V_{liq,i} = \left(\frac{x_1}{x_0} \left(\frac{1-x_0}{1-x_1} \right) \right)^i \frac{x_0 \cdot m_0}{\rho_{cb}} = \left(\frac{x_1}{x_0} \left(\frac{1-x_0}{1-x_1} \right) \right)^i V_{cb,0} \tag{6-2}$$

x_0 is the initial mass fraction of cocoa butter in the cocoa nibs, x_1 is the mass fraction of cocoa butter in the filter cake produced with conventional expression at the same temperature and effective mechanical pressure, m_0 is the mass of nibs being pressed, ρ_{cb} is the density of pure cocoa butter at the temperature of pressing and $V_{cb,0}$ is the initial volume of cocoa butter present in the cocoa nibs.

The yield (Y_i) after *i* stages can then be calculated with equation (6-3):

$$Y_i = \frac{x_0 \cdot m_0 - V_{liq,i} \cdot \rho_{cb,CO2} \cdot (1 - y_1)}{x_0 \cdot m_0} \cdot 100 \qquad (6\text{-}3)$$

where y_1 is the mass fraction of CO_2 in the CO_2-saturated cocoa butter at the temperature and CO_2 pressure being used.

Figure 6-8 shows the predicted yields of multi-stage GAME operations performed with the same effective mechanical pressure in all stages at 100 °C with 10 MPa of CO_2. The data reported in Chapter 5 were used for the calculations. The deviations between the experimental and calculated GAME yields were also observed in Chapter 5. The deviations are attributed to the complex nature of the GAME process, which makes it difficult to accurately specify the mechanism of GAME responsible for the increase in cocoa butter yields compared to conventional expression. The absolute increase in yield decreases between successive stages. It is predicted that the maximum yield (100 %) will be obtained with 3 stages when an effective mechanical pressure of 50 MPa is used, and with 4 stages with an effective mechanical pressure of 30 MPa.

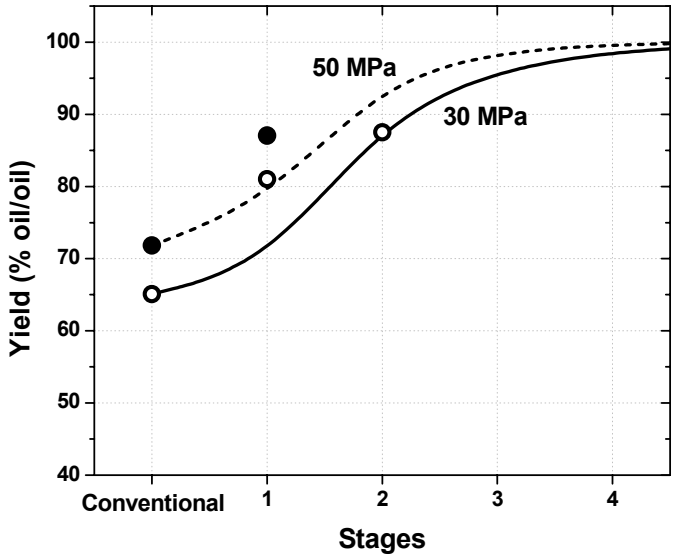


Figure 6-8: Theoretical prediction of the cocoa butter yield after multiple stages of GAME with 10 MPa of CO_2 from experimental conventional expression yields (taken from Chapter 4) at 100 °C and effective mechanical pressures of 30 (○) and 50 MPa (●).

Multi-stage GAME can easily be performed with extruders. In addition, a continuous GAME process may be realised in an extruder. Continuous processes are preferred

above batch processes due to their increased capacity. In conventional expression of oilseeds screw presses are often used. Screw presses are specialised extruders that allow for the removal of the expressed oil. Due to the modular construction of extruders it is easy to have multiple stages operating at different mechanical pressures. It is also possible to add high-pressure components along the screw when the screw profile causes the material being processed to form a dynamic plug. The relative low costs of such extruders and the ability to use multi-stage processing make them attractive for the performance of continuous multi-stage GAME. During the first stage the cocoa nibs will be expressed at a relatively low mechanical pressure and a dynamic plug of partly-defattened and broken cocoa nibs will form. In the second stage SC-CO_2 will be added and a higher mechanical pressure will be used. It is clear that further investigation into the GAME process performed with extruders is necessary.

6.4 Conclusions

Both the duration of the press stage and the mass of cocoa nibs pressed have little influence on the cocoa butter yield obtained with GAME. The mechanical pressure profile used during the pressing stage also has little influence on the cocoa butter yield.

The moisture content of the cocoa nibs changes the behaviour of the solid structure, and therefore determines the maximum attainable cocoa butter yield. The highest yield of cocoa butter is obtained when nibs with a moisture content of 1.3 wt. % (wet basis) are used in GAME. Comparison of the U_C – time graphs of GAME experiments performed with nibs of different moisture contents at the same conditions shows that lower moisture contents results in a faster expression process. The increase in yield at the optimal moisture content decreases when GAME is performed at 100 °C. This is attributed to cooking of the nibs during the equilibrium stages. It is impossible to recover cocoa butter with GAME at moisture contents above 5.5 % at 100 °C.

In contrast to conventional expression there is a relatively small increase in the cocoa butter yield (an absolute increase of 3-6% (oil/oil) compared to an absolute increase of 7-14 % (oil/oil)) when cocoa liquor instead of cocoa nibs is used in GAME experiments at the same conditions. It can therefore be concluded that the cocoa solids do not hinder the diffusion of SC-CO_2 into the oil-containing cell structures. Pressing cocoa nibs instead of cocoa liquor can save grinding costs, as the volume of the filter cakes is less than that of the cocoa nibs.

Multi-stage GAME operations, performed by mixing filter cakes and using this mixture in GAME experiments, increase the cocoa butter yield substantially. This makes the use of continuous extruders instead of batch wise operating hydraulic filter presses an attractive option.

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7 Conclusions and recommendations for future work

7.1 Conclusions

The objective of this thesis was to find a way to optimise the cocoa butter yield when cocoa butter is recovered from cocoa nibs. Most of the high quality cocoa butter used in the food and confectionary industry is produced by expressing cocoa liquor, a slurry consisting of finely ground cocoa nibs, in hydraulic filter presses. Considerable savings are possible if cocoa nibs instead of cocoa liquor are used as a raw material. Therefore the expression of cocoa nibs was studied in a laboratory scale hydraulic press.

The maximum cocoa butter yield (defined as the mass of cocoa butter expressed as a percentage of the total cocoa butter content) when cocoa nibs are expressed is achieved when cocoa nibs with a moisture content of 1.3 wt. % (wet basis) is pressed with mechanical pressures of 60 MPa or higher at a temperature of at least 100 °C. Cocoa butter yields of 80-84 % can easily be reached. Increasing the pressing time beyond 600 s does not result in higher yields, and relatively short pressing times are therefore sufficient to reach high yields. However, higher yields (~ 90 %) will still be achieved when cocoa liquor is used at the same conditions and the loss of income due to the lower cocoa butter yields needs to be compared with the costs saved by pressing cocoa nibs instead of cocoa liquor before a decision is made with regards to the material used in the expression process.

The experimental results lead to the conclusion that the elasticity and compressibility, and therefore the preconditioning, of the solid matrix play an important role in determining the achievable cocoa butter yield. This is confirmed by the material constants calculated with the Shirato model, which shows a dependence on temperature. Comparison of the calculation results of the Shirato model with that of the numerically solved conservation laws model highlights the importance of an accurate description of the behaviour of the solids structure. A truly predictive model is only possible if representative equations are used for describing the changes of the filtration resistance and the porosity with solids compressive pressure in the conservation laws model. These equations must be able to describe both the viscous and the elastic component of the material behaviour of the solids structure.

Gas assisted mechanical expression (GAME) utilises the solubility of CO_2 in cocoa butter to enhance the cocoa butter yield achievable with expression. GAME experiments consistently give higher yields when cocoa butter is recovered from cocoa nibs compared to conventional expression experiments performed at the same temperature and effective mechanical pressure. The increased cocoa butter yields obtained with GAME are mostly due to the replacement of part of the cocoa butter in

the filter cake with CO_2. However, the cocoa butter yield is always underestimated when the theoretical GAME cocoa butter yield is calculated with the assumption of equal volumes of liquid in GAME and conventional filter cakes at the end of the pressing stage. The mechanism is therefore more complex than replacement of the cocoa butter alone.

The cocoa butter recovered with GAME has the same composition as conventionally expressed cocoa butter. GAME also offers the opportunity to operate at lower temperatures due to the lower melting point of CO_2-saturated cocoa butter. The optimal increase in cocoa butter yield is achieved with a CO_2 pressure of 10 MPa. The optimum process conditions with regards to cocoa butter yield are the same as that of conventional expression (100 °C, an effective mechanical pressure of 60 MPa or higher and nibs with a moisture content of 1.3 wt. % (wet basis)), with the exception that 10 MPa of CO_2 must be used as well. Yields of around 90 % can be achieved in this way. Contrary to conventional expression the use of cocoa liquor instead of cocoa nibs does not substantially increase the cocoa butter yield. Using cocoa nibs in GAME is therefore recommended. Multi-stage GAME experiments, performed by mixing filter cakes and using this mixture in GAME experiments, have substantially higher cocoa butter yields than single stage GAME experiments. Operating at the optimum moisture content and optimum pressure combinations can increase the cocoa butter yield even further, and it is not unreasonable to expect yields of 95 % or even higher. This makes the future use of continuous extruders instead of batch wise operating hydraulic filter presses an attractive option.

7.2 Recommendations for future work

7.2.1 Modelling

In this thesis the modelling of conventional expression of dry cocoa nibs was done with the Shirato model. This analytical solution of the conservation laws model discussed in Chapter 3 assumes constant material properties for the entire expression process, something that is not true in reality. In Chapter 3 it was stated that the poor description of the final average porosity by the conservation laws model is due to the assumption of elastic material properties, whereas the inclusion of visco-elastic material properties in the Shirato model improves the agreement of the theoretical porosities with the experimentally measure ones. Using constitutive equations including visco-elastic properties in the conservation laws model should improve its accuracy. It is therefore recommended that future investigations into the modelling of conventional expression of cocoa nibs take this into account. It is also recommended to extend the modelling to include not only the expression of dry cocoa nibs, but also the expression of cocoa nibs at other moisture contents.

Currently there is no good model for GAME. It was thought that the model for conventional expression could be extended to describe GAME as well by calculating the final average porosity from the calculated conventional expression porosity when the solubility of CO_2 in the cocoa butter as well as the density of the CO_2-saturated cocoa butter is known. However, Chapter 5 shows that the mechanism of GAME is more complicated than initially assumed. Modelling of GAME will only be possible once the mechanism of GAME is known and understood. It is therefore recommended to further investigate the mechanism of GAME, especially the influence of CO_2 on cell wall permeability and its effect on GAME, and to develop a model describing GAME once the mechanism is known.

7.2.2 Extruders

GAME was shown to be a promising process for recovering high-quality cocoa butter at high yields. One of the major advantages of GAME is that shorter process times are feasible compared to conventional expression. Figure 7-1 shows that higher cocoa butter yields can be achieved with GAME compared to conventional expression even at times as short as 100 s. This can be used in the design of a continuous GAME process performed with an extruder. Due to the short times necessary for achieving high yields with GAME a relatively short residence time is required inside the extruder. This makes it feasible to use an extruder design where the cocoa nibs are partially defattened and crushed in the first part of the extruder (which contains a slotted barrel to facilitate removal of the cocoa butter), whereafter the cocoa material is compressed to form a dynamic plug and CO_2 is added. Mixing elements will ensure that complete dissolution of the CO_2 in the cocoa nibs is achieved within a short time period. Thereafter the screw can be designed to ensure that the mechanical pressure is increased. Depressurisation can occur along the screw axis, which allows the CO_2 to be recycled.

Extruders are commonly used at high pressures in the polymer industry, and the addition of (high-pressure) gases as well as degasification along the screw axis is an existing and proven technology. Slotted barrel extruders (also known as screw-presses) are commonly used in the oilseeds industry. It should therefore be relatively easy to adapt current technologies to incorporate GAME in an extruder. It is recommended to experimentally investigate the performance of GAME in an extruder.

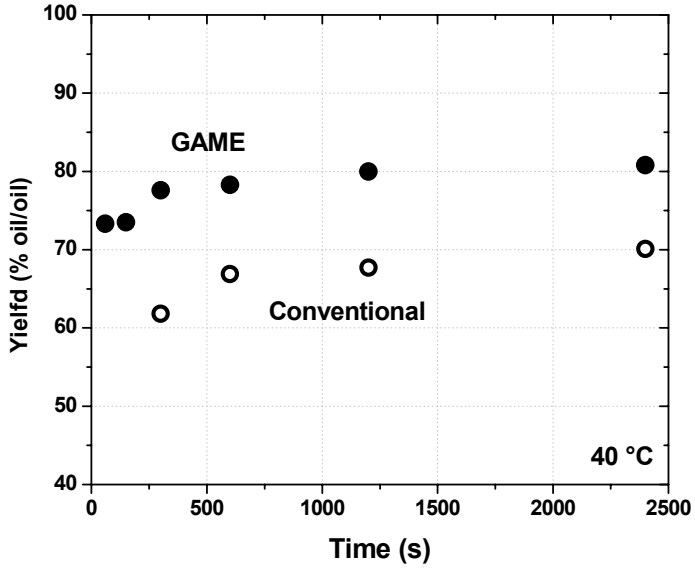

Figure 7-1: Comparison of the cocoa butter yields of GAME and conventional expression performed at an effective mechanical pressure of 50 MPa at 40 °C. A CO_2 pressure of 10 MPa was used in the GAME experiments.

7.2.3 Other oilseeds

The positive results for the recovery of cocoa butter from cocoa nibs with GAME led to the question whether the same increase in oil yield will be observed for other oilseeds. The generic feasibility of GAME was investigated by comparing the yields obtained with GAME to that of conventional expression for the recovery of oils from linseed and de-hulled sesame seed. The seeds were donated by Dipasa (Enschede, The Netherlands). The fat content of the filter cakes of sesame seed and linseed was determined according to the DGF standard method [1]. The properties of the seeds are shown in Table 7-1.

Table 7-1: Fat and moisture contents of the oilseeds.

Seed	Moisture content (native material) (wt. %, wet basis)	Fat content (wt. %, dry basis)
Linseed	5.3	43.8
Sesame seed, de-hulled	3.5	51.5

Figure 7-2 shows that comparable increases were obtained for the different oilseeds when the oil yields of GAME experiments performed at 40 °C with 10 MPa CO_2 are compared to that of conventional mechanical expression performed at 40 °C. Both conventional expression and GAME were performed at an effective mechanical pressure of 30 MPa. These results point to the generic feasibility of the GAME process. Not only do all the oilseeds have similar yields, but the yields also all follow the same trend as a function of effective mechanical pressure. The higher relative increase in yields observed for linseed compared to the yields obtained with conventional expression can be explained by the presence of hulls on the linseeds. The hulls offer an additional resistance to oil flow, to the extent that a part of the freed oil is adsorbed on the hulls when the oil is removed with conventional expression. In the GAME process this oil is also removed. The decreased viscosity of the CO_2-saturated oil allows the oil to drain more easily through the filter cake. The adsorbed oil is also replaced with CO_2-saturated oil, of which the dissolved CO_2 is removed during depressurisation. This causes an additional increase in the oil yield.

In view of the generic feasibility of GAME it is strongly recommended to investigate the performance of GAME for other oilseeds as well. The investigation should also include GAME of oilseeds in extruders, as well as the influence of the extruder geometry and the moisture contents of the oilseeds on both the oil yield and the rates at which these yields are achieved.

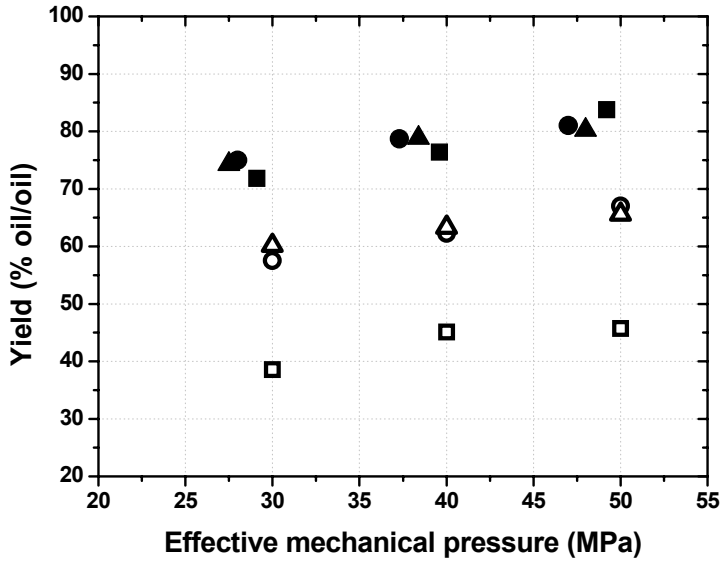

Figure 7-2: Comparison of the yields obtained with conventional expression (open symbols) and GAME (closed symbols) for dry cocoa nibs (○ , ●), dry linseed (□ , ■) and dry sesame seed (△ , ▲) at 40 °C and an effective mechanical pressure of 30 MPa. All GAME experiments were performed with a CO_2 pressure of 10 MPa.

7.3 Reference

1. Deutsche Einheitsmethoden zur Untersuchung von Fetten, Fettprodukten, Tensiden und verwandten Stoffen, DGF-Einheitsmethoden, Wissenschaftliche Verlagsgesellschaft, Stuttgart, 2002, B-I-5: Ölgehalt.