Gas
Assisted
Mechanical
Expression of Oilseeds

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GAS ASSISTED MECHANICAL EXPRESSION OF OILSEEDS

PROEFSCHRIFT

ter verkrijging van
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en de assistent-promotor

Dr. ir. N.J.M. Kuipers

Contents

Summary

It is the objective of this thesis to show the general applicability of the Gas Assisted Mechanical Expression (GAME) process for recovery of oil from oilseeds with high yields. In this process, the oilseeds are saturated with supercritical CO_2 before mechanical pressing. The CO_2 displaces part of the oil during the pressing and therefore increases the oil yield. To prove the general applicability of GAME, a number of oilseeds with a wide range of properties was chosen: sesame, linseed, jatropha, palm kernel and rapeseed. These seeds all produce high added value oils with a low market volume and their properties range from soft (sesame) to hard (jatropha, palm kernel) and from high (sesame) to low oil contents (palm kernel). A lab scale hydraulic press was used to determine the oil yields and expression rates that can be obtained for both conventional expression and GAME expression under a wide range of process conditions.

Hydraulic pressing experiments were performed for all seeds to provide a benchmark for the GAME process. The influence of pressure, pressure profile, temperature and moisture content on the oil yield and rate of conventional hydraulic expression of sesame and linseed is discussed as well as the influence of pressure and temperature for rapeseed, palm kernel, jatropha and dehulled jatropha. Yield increased with increasing pressure and temperature. For both sesame and linseed maximum oil yield was obtained at a moisture content of about 4 wt%. Maximum yields obtained were 45-55 wt% (oil/oil) for hulled seeds (linseed, rapeseed, palm kernel and jatropha) and 70-75 wt% (oil/oil) for dehulled seeds (sesame and dehulled jatropha). Rate of expression increased with increasing temperature and decreasing moisture content. Furthermore, the rate of pressing was described by the Shirato model. The material properties obtained from the Shirato model correspond nicely with general notion of hard (palm kernel, jatropha) and soft seeds (sesame) and cake hardening phenomena (cocoa). The increased creep, and thus decreased rate of pressing, observed with increased moisture content of sesame and linseed was satisfactorily described by the Shirato model.

The general applicability of GAME was demonstrated by experiments with sesame, linseed, rapeseed, palm kernel and jatropha (hulled and dehulled) at 40 °C and varying mechanical pressures (10-70 MPa). Furthermore, the influence of moisture content, temperature and CO_2-pressure on yield and rate of pressing was investigated. Yields obtained with GAME were up to 30 wt% higher than conventional expression at the same conditions (40 °C, 10-30 MPa effective mechanical pressure and 10 MPa CO_2 for GAME experiments). GAME yields for hulled and dehulled seeds were very similar, despite the lower yields for hulled seeds in conventional expression. The influence of moisture content and temperature on GAME was similar to their influence on conventional expression. Yield increased

significantly with CO_2 pressure up to 10 MPa. At higher pressures the improvement was minimal. The displacement of oil by dissolved CO_2 was identified as the major cause of increased oil yields for dehulled seeds. For hulled seeds the entrainment of oil by CO_2 during depressurisation also plays a significant role in the increase of the oil yields.

In order to predict the performance of the GAME process, the solubility of CO_2 in the oils and the density and viscosity of the CO_2 saturated oils are required. Therefore, the CO_2 content as well as the viscosity and density of CO_2-saturated oils of palm kernel, jatropha and linseed were measured between 2 and 30 MPa at 40 °C. The solubility of CO_2 in these oils was very similar, despite differences in average triglyceride length and degree of unsaturation. All oils showed a strong increase in solubility until approximately 10 MPa after which the increase was less strong. The solubilities reached a limit of approximately 35 wt% CO_2 at 30 MPa. Viscosity of all CO_2/oil mixtures decreased sharply until about 5 mPa.s at 10 MPa, after which the decrease was more gradual. Above 10 MPa the viscosity of the three CO_2-saturated oils was very similar. Density showed an almost linear increase with pressure above 5 MPa, which was similar for the three oils.

The GAME oil yields for dehulled seeds could be predicted very well from the conventional oil yields at the same effective mechanical pressure and the solubility of the CO_2 in the oil at the given conditions. For dehulled seeds this prediction always underestimated the GAME yield, because entrainment of oil by the escaping CO_2 was not included in the calculation.

It is expected that an industrial scale application of GAME will be in an extruder, since this is a continuous process and less problems are expected with containment and dissolution of CO_2. It is therefore desirable to have information of the performance of an extruder suited for GAME. As a first step towards the development of such an extruder based process, a mathematical model was developed that predicts the performance (yield, throughput) of a conventional extruder. Together with the data obtained on the performance of GAME for the various oilseeds, the model is used to predict the performance of GAME in an extruder. A mathematical model from literature was adapted to predict the pressure profile and oil yield for canola in a lab-scale extruder. Changing the description of the expression process from filtration to consolidation significantly improved the performance and physical meaning of the model. The model predicts the trends in pressure and residual oil content with varying screw rotational speed and choke opening very well, but the residual oils content is always overestimated. The model was unable to describe the influence of temperature on pressure and residual oil content.

With the developed model, four extruder designs were compared based on the resulting residual oil contents at the same process conditions (feed temperature 40

°C, 90 rpm): a single stage and a double stage conventional extruder, a single stage GAME extruder and an extruder with a conventional first stage and a second stage with GAME. The last layout was found to result in the lowest residual oil content (14.5 wt%) compared to a conventional residual oil content of 19 wt%. These residual oil contents correspond to oil yields of 69 wt% oil/oil for conventional extrusion and 78 wt% oil/oil for the GAME extruder. This increase in oil yield is similar to the increase observed in hydraulic pressing.

Samenvatting

Het doel van het in dit proefschrift beschreven onderzoek is om de generieke toepasbaarheid aan te tonen van Gas geAssisteerde Mechanische Expressie (GAME) voor het met hoge opbrengst verkrijgen van olie uit oliehoudende zaden. Bij deze techniek worden de zaden voorafgaande aan de mechanische persing verzadigd met superkritisch CO_2. De CO_2 verdringt een deel van de olie tijdens de persing en zal hierdoor de olieopbrengst verhogen. Om de generieke toepasbaarheid aan te tonen, zijn een aantal verschillende zaden gekozen voor experimenteel onderzoek: sesam, lijnzaad, jatropha, palmpit en raapzaad. Uit al deze zaden wordt een olie geproduceerd met hoge toegevoegde waarde. De eigenschappen van de zaden variëren van zacht (sesam) tot hard (jatropha, palmpit) en van een hoog (sesam) tot een laag oliegehalte (palmpit). De olieopbrengsten en perssnelheden voor zowel conventioneel persen als GAME zijn voor diverse condities bepaald met behulp van een hydraulische pers op labschaal.

Met alle zaden zijn conventionele mechanische persingen uitgevoerd om als maatstaaf te dienen voor de GAME-experimenten. De invloed van druk, drukprofiel, temperatuur en vochtgehalte op de olieopbrengst en perssnelheid van sesam en lijnzaad zijn onderzocht. Daarnaast zijn ook de invloed van temperatuur en druk op de opbrengst en perssnelheid van raapzaad, palmpit en jatropha bekeken. De olieopbrengst nam toe met toenemende druk en temperatuur voor alle zaden. Voor zowel sesam als lijnzaad wordt de hoogste olieopbrengst verkregen bij een vochtgehalte van ongeveer 4 gewichtsprocent. De maximale olieopbrengst voor ongeschilde zaden (lijnzaad, raapzaad, palmpit en jatropha) was 45-55 gewichtsprocent (olie/olie), terwijl voor de geschilde zaden (sesam, geschilde jatropha) olieopbrengsten van 70-75 gewichtsprocent (olie/olie) mogelijk waren. De perssnelheid nam toe met toenemende temperatuur en afnemend vochtgehalte. Naast dit experimentele onderzoek, is de perssnelheid ook beschreven met behulp van het Shirato-model. De materiaalparameters die met dit model verkregen zijn, komen goed overeen met het algemeen geldende beeld van de materiaaleigenschappen zoals harde (palmpit, jatropha) en zachte zaden (sesam). Verstening, bekend uit de persing van cacao, werd ook teruggevonden in de verkregen materiaalparameters. Het Shirato-model was daarnaast ook goed in staat om de toenemende kruip (en de daardoor veroorzaakte lagere perssnelheid) bij toenemend vochtgehalte te beschrijven.

Persingen van sesam, lijnzaad, raapzaad, palmpit en jatropha bij 40 °C en variabele mechanische druk (10-70 MPa) zijn gebruikt om de generieke toepasbaarheid van GAME aan te tonen. Daarnaast is de invloed van temperatuur, vochtgehalte en CO_2-druk op de olieopbrengst en perssnelheid onderzocht. De met GAME verkregen olieopbrengsten waren tot 30 gewichtsprocent (olie/olie) hoger dan voor

conventionele persingen bij dezelfde condities (40 °C, 10-30 MPa effectieve mechanische druk en 10 MPa CO_2 bij de GAME experimenten). De olieopbrengsten voor geschilde en ongeschilde zaden waren vergelijkbaar, ondanks de lagere olieopbrengsten voor de ongeschilde zaden onder conventionele condities. De invloed van vochtgehalte en temperatuur op olieopbrengst en perssnelheid bij GAME waren vergelijkbaar met de invloed van deze parameters bij conventionele persingen. Tot een CO_2-druk van 10 MPa nam de olieopbrengst aanzienlijk toe, boven deze druk was de toename echter minimaal. Voor geschilde zaden is de verdringing van olie door de opgeloste CO_2 het belangrijkste mechanisme voor de toegenomen olieopbrengst. Bij ongeschilde zaden speelt daarnaast meesleuren van de olie door de CO_2 tijdens het aflaten van de druk ook een grote rol.

De oplosbaarheid van de CO_2 in de olie en de dichtheid en viscositeit van het olie/CO_2 mengsel zijn noodzakelijk om de opbrengsten bij het GAME proces te kunnen voorspellen. Daarom zijn deze bepaald voor palmpitolie, jatropha-olie en lijnzaadolie, verzadigd met CO_2 bij een temperatuur van 40 °C en drukken van 2-30 MPa. Ondanks de verschillen in het gemiddelde molecuulgewicht en de mate van verzadiging van de triglycerides in de diverse oliën was de oplosbaarheid van CO_2 in de oliën vergelijkbaar. De oplosbaarheid in alle oliën nam sterk toe met stijgende druk tot een CO_2-druk van ongeveer 10 MPa. Hierboven was de toename minder sterk. De oplosbaarheid nam toe tot ongeveer 35 gewichtsprocent bij 30 MPa. De viscositeit van alle olie/CO_2 mengsels daalde sterk tot ongeveer 5 mPa.s bij 10 MPa, waarna ook deze afname minder sterk werd. Bij drukken boven 10 MPa was de viscositeit van alle oliën vergelijkbaar. Bij drukken boven 5 MPa nam de dichtheid van de olie/CO_2 mengsels lineair toe met de druk, waarbij de toename voor alle oliën hetzelfde was. De olieopbrengsten van geschilde zaden onder GAME condities konden zeer goed voorspeld worden uit de olieopbrengsten voor conventionele persingen bij dezelfde effectieve druk en de oplosbaarheid van de CO_2 in de olie bij de heersende condities. Voor ongeschilde zaden werd altijd een te lage opbrengst voorspeld omdat het meesleuren van de olie in de expanderende CO_2 niet meegenomen is in de berekeningen.

Naar verwachting zal bij industriële toepassing van GAME gebruik gemaakt worden van een extruder. In dit continue proces worden namelijk minder problemen verwacht met het insluiten en oplossen van de CO_2 in de apparatuur. Voor deze toepassing is het daarom van belang een indicatie te hebben van de prestaties van GAME in een extruder. Om de doorzet en het restoliegehalte te voorspellen, is een wiskundig model ontwikkeld voor een conventionele extruder, als eerste stap in de ontwikkeling van een GAME proces gebaseerd op een extruder. Samen met de experimentele data verkregen voor de diverse oliezaden met de hydraulische pers kan dit model gebruikt worden om een uitspraak te doen over het gedrag van een extruder onder GAME condities. Hiervoor is een model uit de literatuur, dat de drukprofielen, doorzet en olieopbrengsten voor een labschaal extruder van canola voorspelt, aangepast. De originele beschrijving van de expressie van de olie met behulp van filtratie is vervangen door een beschrijving op basis van consolidatie. Hierdoor zijn zowel de prestaties van het model alsook de fysische betekenis van het model verbeterd. De trends in druk en restoliegehalte als functie van schroefsnelheid en choke-opening worden goed beschreven door het model. Het restoliegehalte wordt echter altijd overschat. Het model was niet in staat om de invloed van temperatuur op de drukken en restoliegehaltes goed te beschrijven.

Met het ontwikkelde model zijn vier extruder-ontwerpen vergeleken op basis van het restoliegehalte bij dezelfde condities (voedingstemperatuur 40 °C, schroefsnelheid 90 toeren/min): een enkelstaps en een tweestaps conventionele extruder, een enkelstaps GAME extruder en een extruder met een conventionele stap gevolgd door een GAME stap. Dit laatste ontwerp resulteerde in het laagste restoliegehalte (14.5 gewichtsprocent) vergeleken met een restoliegehalte van 19 gewichtsprocent in de conventionele extruder. Deze restoliegehaltes corresponderen met olieopbrengsten van respectievelijk 69 (conventioneel) en 78 (GAME) gewichtsprocent (olie/olie). Deze toename in olieopbrengst is vergelijkbaar met de toename verkregen met de hydraulische pers.

1 Introduction

1.1 Background

Vegetable oils are one of the oldest classes of chemical compounds known to mankind and even the famous Homer concerned himself with the use of vegetable oils[1]. Numerous references and clues are found that indicate the use of these oils during stone age and bronze age. During the Egyptian times, the sesame plant had a mythical status. In certain ceremonies, black sesame seeds were used to represent problems and regrets and were ritually burned[2]. Nowadays, the view on oilseeds and oils is slightly more down to earth: the oils are used in food, paint and the market for renewable fuels is growing rapidly. World market for oils and fats is approaching 400 million metric tons of seed produced every year, resulting in a total amount of oil of around 100 million ton[3]. The relative contribution of the major oils is given in figure 1-1 (data from 2001)[3,4].

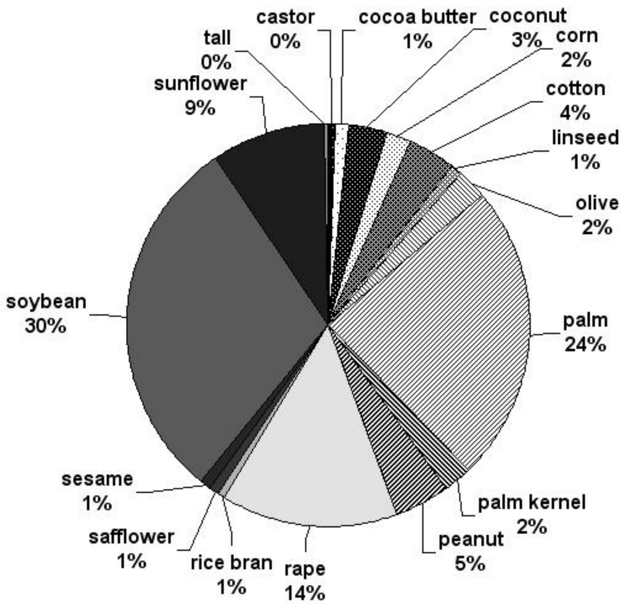

Figure 1-1 *World production of vegetable oil differentiated to source in 2000/2001 (total amount = 100 million ton/y)*[3,4]

In increasing markets, such as the one for vegetable oils, improvement of the production process is always pursued. In this case improvement can be obtained in three areas: oil yield, oil quality and production costs. Apart from research into optimisation of existing technologies, new technologies are developed as well. Given the maturity of the existing technologies, optimisation will not result in huge improvements. When large improvements are required, new technologies have to be developed.

1.2 Present industrial scale technologies

1.2.1 Mechanical expression

Mechanical expression is the oldest method used for oil extraction from seeds. The seeds are placed between permeable barriers and mechanical pressure is increased by reducing the volume available for the seeds. This way oil is squeezed from the seeds. In practice, this operation can take two shapes: a hydraulic, uni-axial press or a screw press (also called extruder or expeller). The advantages of a screw press compared to a hydraulic press are its slightly higher yield and its continuous mode of operation. Mechanical expression results in high quality oil, but has a relatively low yield. Generally it is only used for smaller capacity plants, speciality products[4,5] or as a pre-press operation in a large scale solvent extraction plant.

1.2.2 Solvent extraction

In a (continuous) solvent extraction process, the seeds are contacted with a solvent, generally hexane. The oil contained in the seeds is dissolved in the solvent after which solvent and solids are separated. The solvent/oil mixture (usually 20-33 wt% oil)[5] is sent to the solvent recovery operation, where solvent is removed by evaporation. The residual cake is sent to a desolventiser/toaster, which also removes the solvent by evaporation. Both oil and solids therefore undergo a heat treatment, which is detrimental for the oil and cake quality. The co-extraction of undesired components further reduces the quality of the oil. However, with this method it is possible to recover almost all of the oil from the seeds. Generally, this method is used in the high(est) capacity plants. To further improve the efficiency of the process, the extraction can be preceded by a pre-pressing step. Here part of the oil is recovered by a screw press, which reduces the size of the extractor and improves the permeability of the solids for the solvent.

1.2.3 Supercritical extraction

When the pressure and temperature of a compound are increased beyond the so-called critical values, the interface between the liquid and vapour phase disappears. This is the supercritical state, in which properties like density and viscosity can be varied continuously between those of the liquid and the vapour state by adjusting temperature and pressure. This also allows for a large change in solubility of solutes with a relatively small change in pressure and/or temperature. This makes supercritical fluids interesting candidates as extraction solvents. CO_2 has been the most used solvent up to now, because of its relatively low critical pressure and temperature (7.38 MPa and 31 °C resp.), availability, low toxicity and low cost.

The principle of extraction itself is similar to normal solvent extraction, however the use of high pressure has a number of complications. Up to now, no continuous feeding system for solids at high pressure is available necessitating the extraction vessels to be depressurised for feeding and pressurised (sometimes up to 70 MPa) for the extraction. This makes it a semi-batch process by nature. Furthermore, the solubility of vegetable oils in supercritical CO_2 ($SCCO_2$) is limited to a few weight percent[6,7] and a large amount of solvent is required for the extraction. To overcome this discontinuous operation, research is ongoing into the use of extruders as a unit operation for SCE[8,9]. The amount of solvent required is still very large.

Apart from one exception[10], SCE-plants for oils are focussed on essential oils, which have a different composition, higher solubility in $SCCO_2$, lower concentration in the raw material and higher added value than (glyceridic) vegetable oils.

1.2.4 Limitations of present technologies

All of the above technologies have some advantages: mechanical expression and supercritical extraction produce high quality oil, solvent extraction and supercritical extraction give high yields. However, these techniques also have their limitations: mechanical expression has a low yield, solvent extraction a reduced oil and meal quality and supercritical extraction requires a huge amount of CO_2. It is desirable to find a technique that combines the high yields of (supercritical) solvent extraction and the high oil quality of hydraulic pressing and SCE, but does not require the large quantities of solvent used in SCE. An overview of the advantages and disadvantages of these techniques is given in table 1-1, together with a new technique called Gas Assisted Mechanical Expression.

Table 1-1 *Advantages and disadvantages of various oil production processes*

Technique	Oil yield	Oil quality	Solvent requirement per kg oil (kg, order of magnitude)
Mechanical expression	-	+	0
Solvent extraction	+	-	2 (organic)
Supercritical extraction	+	+	100 (CO_2)
Gas Assisted Mechanical Expression (GAME)	+	+	1 (CO_2)

1.3 Gas Assisted Mechanical Expression

Recently a new technique has been described for obtaining cocoa butter from cocoa nibs[11-13]. This technique, called Gas Assisted Mechanical Expression (GAME), is a combination of mechanical expression and the use of supercritical CO_2 (hence gas assisted). It was shown that GAME can increase the oil yield from cocoa nibs beyond values obtained in industry at milder conditions than generally used without the need for large quantities of carbon dioxide[11].

The principle of GAME is illustrated in figure 1-2. In the GAME process, CO_2 is dissolved in the oil contained in the seeds before pressing. After equilibration, the oil / CO_2 mixture is expressed from the seeds. It was shown for cocoa that the dissolved CO_2 displaces part of the oil during pressing[14]. It was concluded that at the same effective mechanical pressure (absolute mechanical pressure minus the actual CO_2 pressure) the *liquid* content is the same in both conventional and GAME press cakes. The liquid in the GAME press cake is saturated with CO_2 (which can be up to 30 wt% CO_2), reducing the oil content compared to the conventional cake by the same amount. The amount of this effect increases with increasing solubility of the CO_2 in the oil. Furthermore, the dissolved CO_2 reduces the viscosity of oil by an order of magnitude, which increases the rate of pressing. After pressing, the CO_2 is easily removed from the cake and oil by depressurisation. During depressurisation of the cake, some additional oil is removed by entrainment in the gas flow.

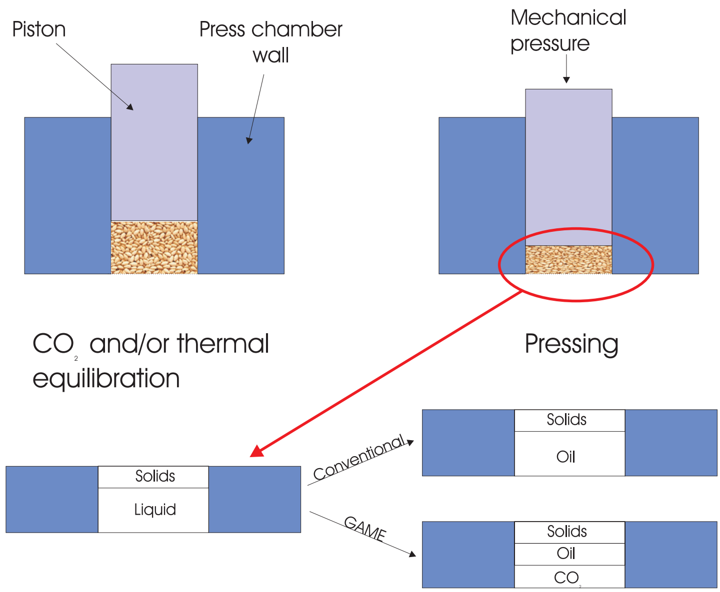

Figure 1-2 *Principle of GAME*

The advantages of GAME include:

- Mechanical pressure can be lower than conventional pressing (50 MPa compared to 100 MPa) while still obtaining higher yields
- Required CO_2 pressure is lower than for supercritical extraction (10 MPa compared to 45-70 MPa)
- The amount of CO_2 required is much lower than for supercritical extraction (around 1 kg CO_2 per kg oil compared to 100 kg CO_2 per kg oil)
- A virtually solvent free product, remaining solvent is not detrimental to consumer health
- It is suggested by several authors that CO_2 at the conditions employed has a sterilising effect[15,16]

Preliminary experiments have shown that GAME is also able to increase the oil yields for sesame and linseed by up to 30 wt%, as shown in figure 1-3[14]. These results suggest that GAME will also be applicable to other seeds with equally good results. The increased number of applications this would yield for GAME renders further investigation into the general applicability of GAME worthwhile.

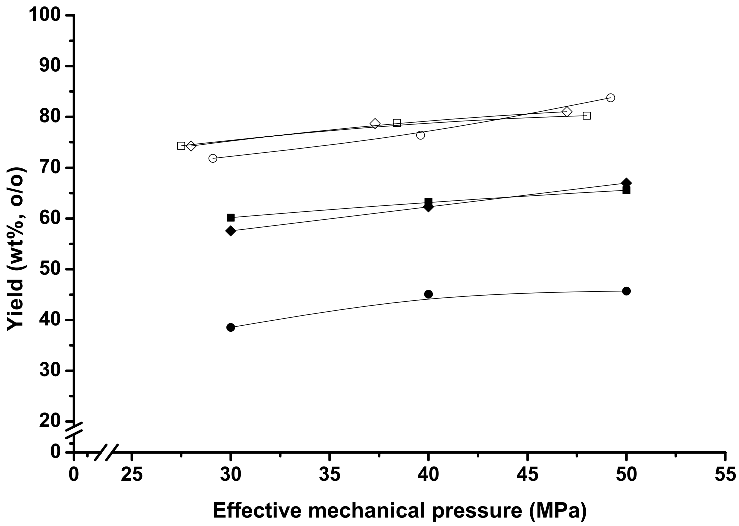

Figure 1-3 *Oil yields for conventional expression (closed symbols) and GAME with P_{CO2} = 10 MPa for cocoa nibs (◆, ◇), sesame (■, □) and linseed (●, ○)[14]. Lines serve as visual aid only*

1.4 Objective and outline

The GAME process has been shown to be effective in increasing the yield of cocoa butter from cocoa nibs[11] and preliminary experiments for sesame and linseed were very promising. It is the objective of this thesis to show the general applicability of the GAME process for recovery of oil from oilseeds with high yields. For this purpose a number of oilseeds with a wide range of properties was chosen: sesame, linseed, jatropha, palm kernel and rapeseed. These seeds all produce high added value oils with a low market volume and their properties range from soft (sesame) to hard (jatropha, palm kernel) and from high (sesame) to low oil contents (palm kernel). A lab scale hydraulic press was used to determine the oil yields that can be obtained for both conventional expression and GAME expression under a wide range of process conditions.

It is expected that in an industrial scale application, GAME will be performed in an extruder, since this is a continuous process and less problems are expected with containment and dissolution of CO_2. It is therefore desirable to have information of the performance of an extruder suited for GAME. As a first step towards the development of such an extruder based process, a mathematical model was developed that predicts the performance (yield, throughput) of a conventional extruder. Together with the data obtained on the performance of GAME for the various oilseeds, the model is used to predict the performance of GAME in an extruder.

To reach the objective, the following chapters are included in this thesis:

- In ***Chapter 2***, a systematic study into the conventional expression of oilseeds is provided. The influence of mechanical pressure, temperature, moisture content and dehulling is investigated experimentally. Results are correlated using the Shirato model, previously used to describe the expression of cocoa nibs[17].
- ***Chapter 3*** describes an experimental investigation into the performance of the GAME process for all the seeds. Apart from the parameters investigated for the conventional expression, the influence of equilibrium time and CO_2 pressure are also investigated. The chapter concludes with a prediction of the oil yields obtained with GAME from the experimental data for conventional expression and the solubility data of CO_2 in the various oils.
- As not all necessary data were available in literature, ***Chapter 4*** contains the solubility data, density and viscosity of CO_2 saturated linseed, jatropha and palm kernel oil.
- The extruder model is developed in ***Chapter 5***, in which it is also compared to literature data. Various extruder configurations are explored to determine the most promising configuration for GAME.
- ***Chapter 6*** presents the conclusions of this work and an outlook for further development of the process.

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2 Hydraulic pressing of oilseeds

The influence of pressure, temperature and moisture content on the oil yield and rate of conventional hydraulic expression of sesame and linseed is discussed as well as the influence of pressure and temperature for rapeseed, palm kernel, jatropha and dehulled jatropha. Yield increased with increase in pressure and with increase in temperature. For both sesame and linseed maximum oil yield was obtained at a moisture content of about 4 wt%. Maximum yields obtained were 45-55 wt% (oil/oil) for hulled seeds (linseed, rapeseed, palm kernel and jatropha) and 70-75 wt% (oil/oil) for dehulled seeds (sesame and dehulled jatropha). Rate of expression increased with an increase in temperature and a decrease in moisture content. Furthermore, the rate of pressing was described by the Shirato model. The increased creep, and thus decreased rate of pressing, observed with increased moisture content was satisfactorily described by the Shirato model.

2.1 Introduction

Vegetable oils have been used by mankind for centuries, for both food and non-food applications[1]. For most of this time, the only option to recover the oil from the seeds has been mechanical expression (pressing). The oil obtained via this method is of a high quality, but the attainable yield is limited to roughly 80 wt% of the oil originally present[1]. It is only in the last century that solvent extraction has been used in this field[1]. The advantage of solvent extraction is the high yield that can be obtained economically with this method (>99 wt%), but this is at the expense of a reduced oil quality. This quality reduction is caused by the extensive solvent recovery processes that are necessary and the fact that the solvent co-extracts undesired components from the cell walls. Especially for high value added oils this quality reduction is unacceptable, limiting the production process to mechanical expression. Maximizing the yield is then limited to optimising the preconditioning and maximizing the pressure. Since a cocoa filter press is able to achieve higher pressures (up to 100 MPa) than conventionally used presses[2,3], the use of a laboratory scale cocoa press[4] was studied for its ability to attain high yields for oils from high value added seeds.

For this study, sesame, linseed, palm kernel and jatropha were chosen, because these seeds represent a wide range of physical properties and produce high value added oils. They range from soft to hard and from high to relatively low oil content. Furthermore rapeseed was included as a representative of the bulk oilseeds. An overview of the seeds used in this work and their properties is given in table 2-1.

Table 2-1 *Overview of seeds*[5-9]

Seed	Composition (wt%, d.b.)				Oil point (MPa)	Hard -ness	World Market volume (10^6 ton) (2000)
	Oil content (measured)	Protein	Fibre	Ash			
Sesame	51.5	20-25	4-10	5		soft	2.4
Linseed	43.8	20-25	20-30	3-4		hard	2.5
Palm kernel	31.6	8	5	2	3.91	hard	9.7
Jatropha	37.2	19	38	5		hard	very low
Rapeseed	46.7	25-35	30-50	5	6.7-8.4	hard	44.7

In order to identify all the parameters that influence the pressing behaviour of the seeds, an overview of the available literature was made. This is shown in table 2-2, in which type of seed and experimental conditions are reported. Although it is not intended to be complete, it provides a good overview of the field. A number of general conclusions can be drawn from these studies:

- With increasing pressure the yield increases reaching a limit at higher pressures. This limit is dependent on the type of seed, seasonal variations, pre-treatment of the seed and the equipment used. Most data available in literature are limited to pressures below 35 MPa, with a few exceptions[10-12].
- Quality requirements for the oil or the meal may restrict the maximum allowable temperature to prevent undesired cell wall components polluting the oil. It is therefore desirable to reach high yields at lower temperatures. For the seeds considered in this study, literature data on the influence of temperature are lacking (linseed, jatropha) or limited to single temperatures (rapeseed) or higher temperature (palm kernel).
- Starting from dry seeds, increasing the moisture content (MC) of the seeds increases the yield until a seed-specific maximum. Increasing the moisture content beyond this optimum decreases the yield again. This is due to two counteracting phenomena. Increasing the moisture content of the seeds is reported to make the cell walls more permeable[13] (which increases the yield), but also to cause a plasticization of the seed material which reduces the oil yield[14]. Therefore an optimum moisture content exists for the yield. Results for sesame at moisture contents below 6 wt% are not available, for linseed only a few points are available covering a wide moisture content range.
- Time is a factor of influence, although for small-scale operations over 95% of the attainable yield is obtained in the first ten minutes[11,15].

The results in this work present a variety of small market volume oilseeds, of which limited data are available in literature. This paper presents a systematic study of the influence of pressure, pressure profile, temperature, time and moisture content on the pressing behaviour of sesame, linseed, jatropha, palm kernel and rapeseed in a laboratory scale cocoa filter press. The ranges for which experimental data are available in literature are extended for sesame (P > 20 MPa, T = 100 °C, <6 wt% moisture), linseed (P < 66 MPa, T = 40-100 °C), palm kernel (P > 25 MPa, T = 40 °C) and rapeseed (P= 20-50, 60-70 MPa, T= 40, 100 °C). These experiments were done to exclude the influence of the apparatus[16] and variety of the seeds[17] when comparing conventional experiments to the GAME results in Chapter 3.

Table 2-2 *Overview of hydraulic pressing studies available in open literature*

Seed	P (MPa)	T (°C)	MC (wt% d.b.)	Yield range (%)
Cocoa [18]	10, 20…70	40-100	0-5.6	
Conophor[19]	10, 15…25	50-110	8-17	8-40 w/wtot
Groundnut[20]	8, 15, 22, 31	35-80	3.5 - 13	20-38 w/wtot
Linseed[11]	66, 89, 118, 148	NA	0.5, 3.1, 7.8, 16	4.4-57
Palm[21]	5,10…35	80, 100, 120, 140	NA	2-50
Palm kernel[15]	50, 10…25	80, 90, 100	NA	5-30 v/vtot
Rapeseed[22]	7.5, 15	95	NA	NA
Rapeseed[12]	56.6	16	NA	NA
Sesame[23]	15, 20	40, 55, 70, 85	6.1, 9.1, 12.0	65.7 o/o
Soybean, cotton, rape, peanuts, sesame, tung, castor[24]	max. 34	18-125	3-14	62 (soy), 80 (sesame), 64 (rape)
Soybean, sunflower[10]	20, 40, 60	22, 60, 90	3.7	60-85

NA= not available/mentioned

w/wtot = mass of oil recovered as percentage of original seeds weight

v/vtot = volume of oil recovered as percentage of original seeds volume

o/o = oil recovered as percentage of amount originally present

To the best of the authors' knowledge data on hydraulic expression of jatropha is completely lacking in literature. To aid in the optimisation of the process a model previously used for cocoa expression[25] is used to correlate the experimental data. Material properties obtained from this model enable quantification of the terms "hard" and "soft" seeds commonly used in literature. Furthermore, the influence of moisture content and temperature on material properties obtained from the experimental data is discussed, which is also lacking at present.

2.2 Modelling of oilseed expression

Mathematical models previously used in oilseed expression are either empirical[19], based on the nature of cell structures[26] or Terzagi type models[12,27]. The first type is limited to specific seeds and equipment on which the measurements were done. The second type of models is the fundamentally most correct, but requires knowledge of difficult to measure properties. The Terzagi-type models provide a good compromise between general applicability and parameters that are easy to measure. The Shirato model[27], which is an extended Terzagi type model originally developed for soil consolidation, has been shown to describe the expression of dry cocoa nibs quite well[25]. It was therefore decided to use it for other oilseeds as well in order to investigate the general applicability of the model. The Shirato model is given in equation 2-1, which describes the consolidation ratio as a function of time, pressure and material properties. The consolidation ratio (U_c) is defined as the ratio of cake thickness decrease at time t and the final cake thickness decrease. This ratio can be used to compare the rates of pressing of different seeds. The total consolidation is divided in two parts: primary and secondary consolidation (creep). The relative contribution of creep to the total consolidation is given by the parameter B.

$$U_c = \frac{l_0 - l(t)}{l_0 - l_\infty} = (1-B)\cdot\left(1-\exp\left(-\frac{\pi^2 i^2 C_e}{4\omega_0^2}\cdot t\right)\right) + B\cdot\left(1-\exp\left(-\frac{E}{G}\cdot t\right)\right)$$

Equation 2-1

with: $$Ce = \frac{P}{\mu_l \rho_s \alpha \, \partial e / \partial P}$$

with U_c = compression ratio (-)

l_0 = cake-thickness at the start of pressing (m)

$l(t)$ = cake-thickness at time t (m)

l_{end} = cake-thickness at end of experiment (m)

B = relative contribution secondary consolidation

i = number of drainage surfaces (-)

C_e = consolidation coefficient (m^2/s)

ω_0 = volume of solids per unit area (m^3/m^2)

t = time (s)

E/G = creep constant (s^{-1})

P = pressure (Pa)

μ_l = liquid viscosity (Pa.s)

ρ_s = solids density (kg/m^3)

α = filtration resistance (m/kg)

e = void ratio (-)

$$(1-\varepsilon) = (1-\varepsilon_0)\cdot\left(1+\frac{P}{P_a}\right)^n$$ ***Equation 2-2***

Equation 2-3

$$\alpha = \alpha_0 \cdot \left(1+\frac{P}{P_a}\right)^\beta$$

By fitting equation 2-1 to the experimentally obtained U_c's the filtration resistance (α), ratio of secondary consolidation to total consolidation (B) and creep constant (E/G) can be obtained. Furthermore the porosity (ε) can be obtained from the experimentally obtained yields. As is generally accepted in the field[28], filtration and porosity are functions of pressure as given in equation 2-2 and equation 2-3. Density and viscosity of the oil are necessary inputs for the model and therefore these were measured as well.

2.3 Experimental procedure and equipment

2.3.1 Materials

Sesame seed and linseed were donated by Dipasa B.V. (Enschede, The Netherlands), rapeseed was donated by Noord Nederlandse Oliemolen B.V. (Delfzijl, The Netherlands), Jatropha by Diligent Energy Systems B.V. (Eindhoven, the Netherlands) and palm kernel was obtained from a local market in Tangerang, Indonesia. Unless stated otherwise, seeds used in the pressing experiments were dried overnight in an oven at 103 °C. Preliminary experiments showed that sample weight did not decrease anymore after this period.

2.3.2 Physical properties

Density and viscosity

Density of the oils was measured at 10 °C intervals between 30 and 90 °C with a density meter (DMA5000, Anton Paar, Graz, Austria). 1 ml samples were automatically inserted in the measuring cell with the help of the SHx/SCx sample changer. Samples were equilibrated to within 0.01 °C of the desired temperature. Measurement uncertainty was $1 \cdot 10^{-2}$ kg/m^3. Reported values are an average of three measurements.

Viscosity was measured at 10 °C intervals between 30 and 90 °C with an Ubbelodhe Capillary (No.II). This capillary had a capillary constant of 0.1004 mm^2/s +/-0.65% and is suited for kinematic viscosities between 10 and 100 mm^2/s. These measurements were also done in triplicate and the average is reported. Maximum deviation between consecutive measurements was less than 0.2 mm^2/s.

Moisture conditioning

For the pressing experiments at different moisture contents, batches of seeds were equilibrated with a constant humidity atmosphere in a desiccator for at least a week. Constant humidity in the dessiccator was maintained by putting saturated solutions of different salts in with the seeds. No temperature adjustment was done, since no influence of temperature was reported on moisture content of the seeds within 15-35 °C[29]. Moisture content was determined according to Method B-I 4 of the German Standard Methods[30] by heating overnight at 103 °C. For low moisture contents (below 2 wt%) the same procedure was used, but zeolite A4 was used instead of salt solutions. The zeolite was dried overnight at 200 °C before use.

2.3.3 Hydraulic pressing

A schematic representation of the hydraulic press used is shown in figure 2-1 and discussed in detail elsewhere[4]. Seeds are placed on a sieve plate covered with fine wire mesh in a temperature controlled (30-100 ±1 °C) pressing chamber with a diameter of 30 mm. Pressures up to 100 MPa are exerted by a hydraulic plunger. The press is fitted with a thermocouple (±1 °C), pressure sensor and a position transducer (±0.01 mm), which measures the distance the plunger traveled. Measured values are automatically recorded every second.

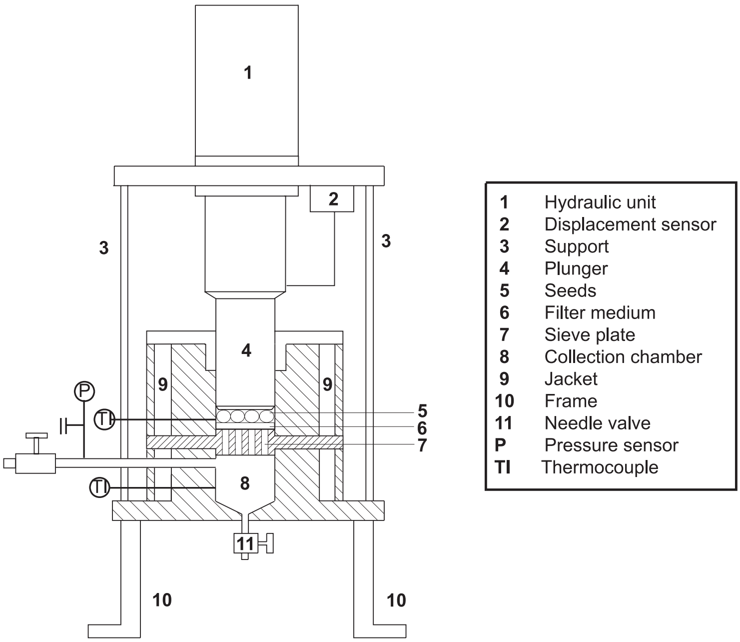


Figure 2-1 *Schematic representation of the hydraulic press*[31]

In a typical experiment, 10 gram of seeds was placed in the press-chamber, after which the piston was lowered on top of the seeds. The seeds were allowed to equilibrate to the pressing temperature for at least 30 minutes without mechanical pressure exerted on the seeds. After this, the mechanical pressure was raised up to 4 MPa for 10 seconds, providing a starting point for the compaction of the bed. Depending on the type of experiment, pressure was either increased in 2 seconds (to prevent pressure overshoot) to the desired value for the experiment or pressure was increased linearly at the desired speed (0.5, 1, 2 or 5 bar/s) until the final pressure was reached. For both types of experiment total pressing time was 10 minutes, except for the experiments to show the influence of pressing time.

2.3.4 Soxhlet analysis

Residual oil contents were determined by soxhlet extraction, based on method B-I 5 of the German standard methods[30]. Whenever necessary, samples were dried overnight at 103 °C before analysis. For each analysis, approximately 5 grams of sample was weighed with an accuracy of 0.0001 g. This was ground in a ball mill (Retsch, MM301, Haan, Germany) together with a small volume of petroleum benzene (boiling range 40 – 60 °C, VWR International B.V., Amsterdam, The Netherlands) for 20 seconds at 25 Hz. This was qualitatively transferred to a soxhlet thimble, covered with two wads of cotton wool and extracted with petroleum benzene for at least 4 hours (sesame, linseed) or overnight (jatropha, rapeseed, palm kernel). After evaporation of the solvent, samples were put in an oven at 103 °C overnight or until constant weight. The residual oil content is reported as gram oil per gram sample on a dry basis.

2.3.5 Data analysis

Yields and compression ratios (U_c) were calculated for all experiments. Yield is defined as the oil recovered from the seeds as percentage of the amount originally present in the seeds. The compression ratio is defined in equation 2-4 and is used as an indication for the rate of pressing. It is defined as the ratio between cake thickness decrease at time t and the final cake thickness decrease.

$$U_c = \frac{l_0 - l(t)}{l_0 - l_\infty} \qquad \textit{Equation 2-4}$$

2.3.6 Repeatability –analysis and press

In order to draw conclusions from the experiment, the repeatability of the experiments have to be tested. For the soxhlet extraction, the DGF-standard methods[30] report a repeatability for two analysis from one sample on the same day, by the same person to be within 0.4 wt% in oil content. For measurements on different days, this is reported to be within 1 wt%, which was confirmed by experiments.

To test the reproducibility of the complete procedure, duplicate experiments were done for sesame seed at 40 °C, with a linear increase in pressure of 0.1 MPa/s to 15 MPa and a total pressing time of 10 minutes. Yields were 40.7 and 40.3 wt%. Repeatability for cocoa was 1 wt% and therefore overall experimental error was taken as 1 wt% for all the seeds.

2.4 Results and discussion

2.4.1 Physical properties

Density

Density for sesame, linseed and rapeseed oil for temperatures ranging from 30 to 90 °C are given in figure 2-2.

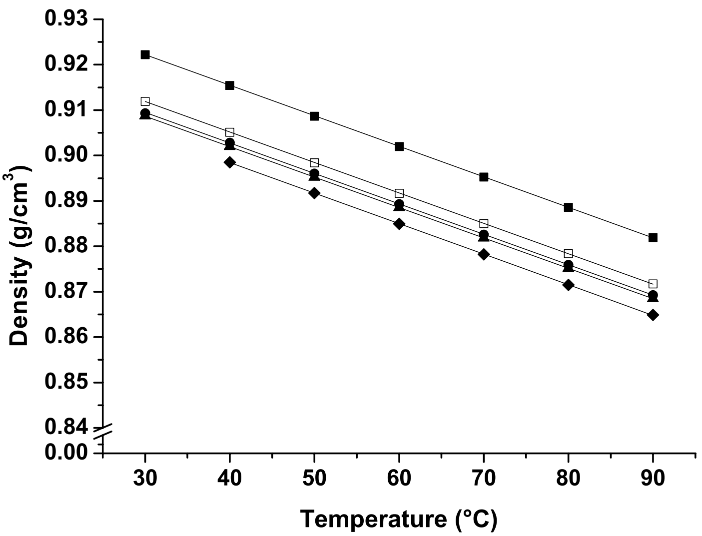


Figure 2-2 *Density of sesame (□), linseed (■), palm kernel (◆), jatropha (●) and rapeseed (▲) oil at different temperatures. Lines represent fits with equation 2-5 with values for parameters given in table 2-3*

Densities are well within the boundaries given by Bailey[6], as are the slopes of density vs. temperature ($6.7 \cdot 10^{-4}$ g/cm^3/°C experimentally for all oils vs. $6.4 \cdot 10^{-4}$ g/cm^3/°C from literature[6]). The slightly higher density of linseed oil compared to sesame and rapeseed can be explained by the fact that it has a high degree of unsaturation, which raises the density[6]. Densities were fitted using the linear equation given in equation

2-5, for which the fit values are given in table 2-3. Regression coefficients for all oils were 0.999 or better.

$$\rho = \rho_1 - \rho_0 \cdot T_1$$

Equation 2-5

with: ρ = density (g/cm^3)

T = temperature (°C)

ρ_0, ρ_1= fit parameters (g/cm^3/°C and g/cm^3)

Table 2-3 *Value of fit parameters in equation 2-5 and equation 2-6*

Oil	ρ_0 (g/cm^3/°C)	ρ_1 (g/cm^3)	μ_0 (mPa.s)	μ_1 (kJ/mol)
Sesame	$6.71 \cdot 10^{-4}$	1.115	1.55	25.8
Linseed	$6.73 \cdot 10^{-4}$	1.126	3.38	23.0
Rapeseed	$6.70 \cdot 10^{-4}$	1.112	1.40	26.0
Jatropha	$6.71 \cdot 10^{-4}$	1.113	1.56	25.7
Palm kernel	$6.73 \cdot 10^{-4}$	1.109	1.17	26.9

Viscosity

The viscosity of all oils, as shown in figure 2-3, is in agreement with the values specified in Bailey[6]. Viscosity can be described as a function of temperature by the modified Riedel equation, given in equation 2-6[32]. Regression coefficients for all oils were 0.997 or better. The μ_1-values obtained for sesame seed and rapeseed are similar (25.8 and 26.0 kJ/mol), whereas for linseed it is lower (23.0 kJ/mol). Agreement with literature values is excellent for rapeseed (lit: 26.3 kJ/mol[33]) and for linseed (lit: 26.1 kJ/mol[34]) and sesame (lit: 28.2 kJ/mol[33]) it is reasonable. Again the notable difference between linseed and the other oils is explained by its high degree of unsaturation[6].

$$\mu = \mu_0 \exp(\mu_1 /(kT))$$

Equation 2-6

with μ = dynamic viscosity (Pa.s)

μ_0, μ_1 = fit constants (mPa.s and kJ/mol)

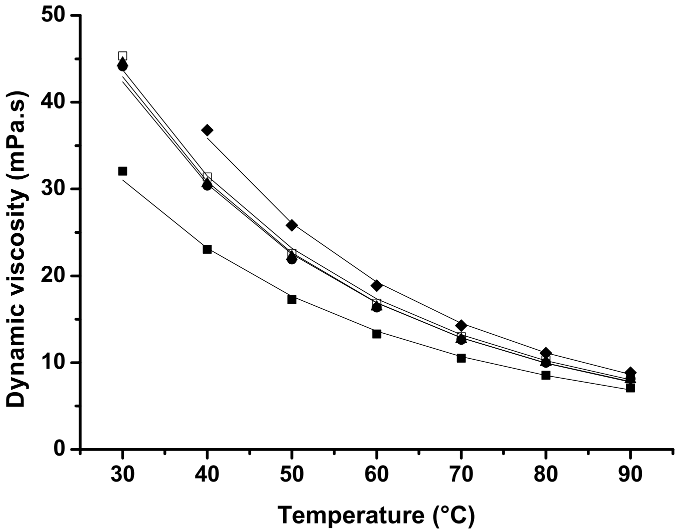


Figure 2-3 *Dynamic viscosity of sesame (□), linseed (■), palm kernel (◆), jatropha (●) and rapeseed (▲) oils as function of temperature. Lines represent fits of equation 2-6 with values from table 2-3*

Moisture sorption isotherms

The sorption isotherms of water for cocoa, sesame, linseed and jatropha are given in figure 2-4. As can be seen from the graph, the dehulled seeds (cocoa and sesame) have lower moisture contents than the seeds with hull. This suggests that moisture uptake in the hull is higher than in the kernel itself. To validate this, jatropha seeds were separated into hulls and kernels and these were dried separately. The measured moisture content of the kernel was 4.7 wt% (d.b.), whereas the hull contained 9.7 wt% (d.b.) moisture. The moisture content of the original seeds was 6.6 wt% (d.b.) at a relative humidity of 33 %. It can therefore be concluded that the majority of the moisture is located in the hull. The same was concluded by others for candle nut[35] and sesame[29].

The Guggenheim-Anderson-de Boer (equation 2-7) model was fitted to the sorption isotherms, parameter values for this fit are shown in table 2-4. This model was used, because it generally describes the sorption of seeds very well[35]. The higher monolayer factors (MC_0) for the hulled seeds clearly show the increased moisture uptake for linseed and jatropha.

$$\frac{MC}{MC_0} = \frac{MC_1 \cdot MC_2 \cdot RH}{(1 - MC_1 \cdot RH) \cdot (1 - MC_1 \cdot RH + MC_1 \cdot MC_2 \cdot RH)}$$ ***Equation 2-7***

with: MC = moisture content (wt%, d.b.)

RH = relative humidity (%)

MC_0, MC_1, MC_2 = fit parameters (wt%, 1/% and -)

Table 2-4 *Fit values for equation 2-7*

seed	MC_0 (wt%)	B (1000/%)	C (-)
Sesame	3.96	2.9	250
Linseed	5.55	4.6	137
Jatropha	5.83	4.5	250
Cocoa	2.52	4.5	524

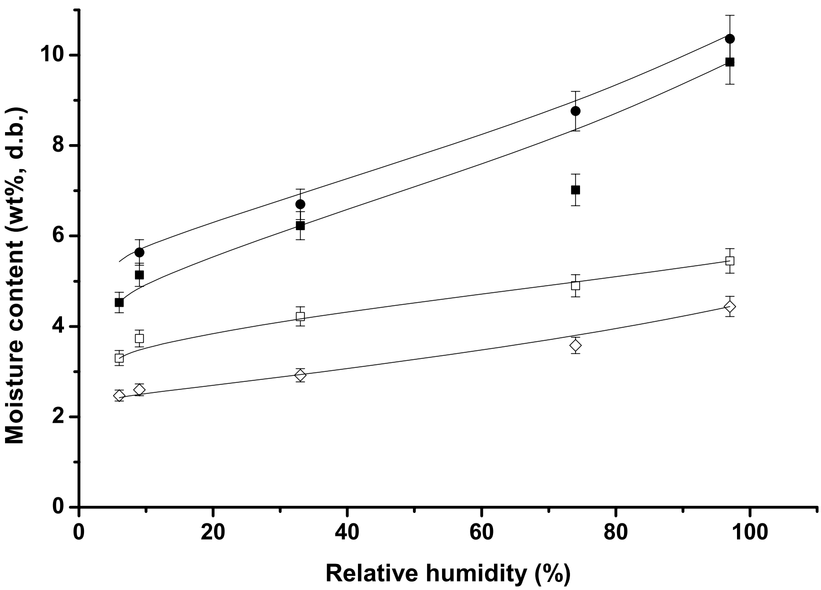


Figure 2-4 *Moisture content of sesame (□), linseed (■), cocoa (◇) and jatropha (●) as function of relative humidity at room temperature. Lines present fit by equation 2-7*

2.4.2 Pressing experiments

Default press settings

Several factors were identified to limit the experimental study by using standard parameters that were chosen for the majority of the experiments. First of all, it was shown previously that below a bed depth of 35 mm, the influence of press cake thickness on the oil yield was negligible for groundnut seeds[20] and cocoa[36]. Experiments were done with 5, 10 and 15 gram of both sesame seed and jatropha to test the validity of this statement for other seeds under the conditions used in this work. These amounts resulted in a maximum bed depth at the end of the experiment of roughly 15 mm, well below the limit reported in literature. These experiments showed no influence of the amount of seeds on the oil yield. Therefore the amount of material was fixed at 10 grams.

Secondly, it is reported in literature that the majority (>95%) of the oil is expressed in the first ten minutes of pressing[15,31]. Again, a limited series of experiments was done for sesame to validate this in the present situation. Indeed for the first ten minutes yield increased with time and thereafter remained approximately constant. Therefore 10 minutes was taken as a representative time for the rest of the experiments.

Furthermore, since oil quality is reported to be higher at lower temperatures, the major part of the experiments was done at 40 °C. Therefore, unless otherwise stated, all experiments were performed with approximately 10 grams of seed at 40 °C with a pressing time of 10 minutes. Data for cocoa were taken from a previous study[31].

Influence of pressure: constant pressure

As can be seen in figure 2-5, the yield increased for all seeds with increasing mechanical pressure, approaching a limit at higher pressures. The low yield for rapeseed at 10 MPa is due to operation near the reported oil-point for this seed (8.5 to 9.1 MPa)[7].

Furthermore, this figure shows that maximum yields are limited to 45-55 wt% for the hulled seeds (linseed, rapeseed and jatropha) and to about 70-75 wt% for the dehulled seeds (sesame and cocoa) in the pressure range investigated. It is assumed that this is caused by the fact that the hull does not contain significant amounts of oil[37] and the fiber in the hull absorbs oil during the expression, thereby lowering the overall yield. To support this assumption, jatropha seeds were manually dehulled and pressed under the same conditions as non-dehulled seeds. Mass fraction of hull was calculated (35.4 wt% d.b.) and the oil content of the hull was verified to be negligible by soxhlet extraction. Assuming that the press cake of non-dehulled jatropha has a uniform oil content, the amount of oil absorbed by the hulls can be calculated. Adding this amount to the determined yield for non-dehulled seeds should give a good correlation with experimental data for dehulled seeds. As is shown in figure 2-6, correspondence between the predicted and experimental yields is very good, supporting the assumption of oil absorption by the hulls.

The yields can be related to the porosity according to equation 2-8. By fitting this equation to the experimental data the material constants (ε_0 and n) in equation 2-2 can be obtained. The fits of porosity, shown as lines in figure 2-5, show that apart from the 10 MPa data, yields can be adequately described with equation 2-2. Values for the fit parameters are given in table 2-5. The variation of porosity with pressure for the dehulled seeds is significantly higher than for the hulled seeds, reflecting the higher compressibility of the dehulled seeds.

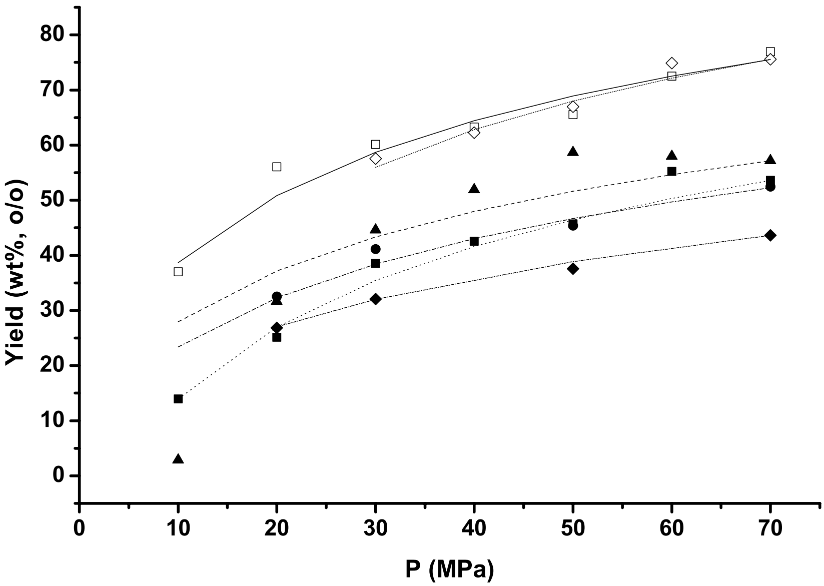


Figure 2-5 *Influence of constant pressure on yield for different seeds (T = 40 °C, time of pressing: 10 min, dry seeds), symbols are experimental, lines are fits with equation 2-2, sesame (□, —), linseed (■, ·····), rapeseed (▲, – –), jatropha (●, -··-), palm kernel (◆, -·-·-) and cocoa*[18] *(◇, ·····)*

$$Yield(wt\%, o/o) = \left(\frac{(1-F_0)\varepsilon\rho_0}{(1-\varepsilon)\rho_s F_0} - 1 \right) \cdot 100\% \qquad \textit{\textbf{Equation 2-8}}$$

With F_0 = original oil content (wt%, d.b.)

ρ_o = oil density (kg/m^3)

ρ_s = solids density (kg/m^3)

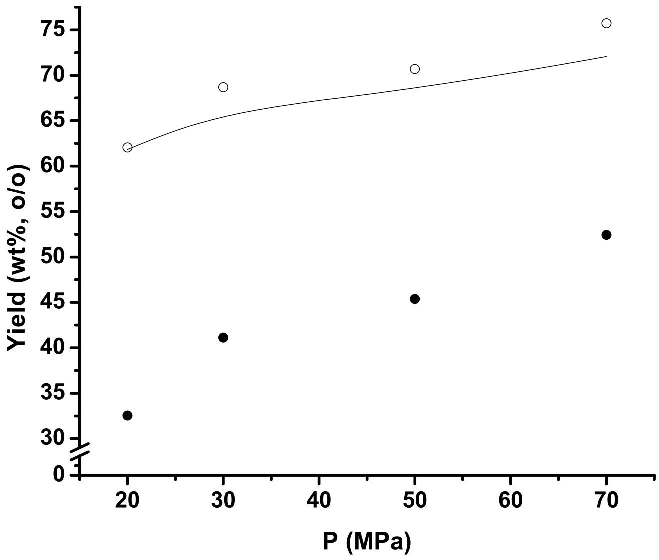


Figure 2-6 *Experimental yield and prediction for dehulled jatropha, hulled experimental (●), dehulled experimental (○) and dehulled predicted (—)*

Influence of pressure: pressure profile

In industry, the applied pressure profile is regarded as an important parameter in the expression of cocoa mass[38]. Figure 2-7 shows the yields for sesame and jatropha for a linear increase in pressure at different rates. For all experiments, the total pressing time was 10 minutes and the final pressure was 30 MPa. Yields increase with increasing rates, but do not exceed the yield for constant pressure (infinite rate of pressure increase). Since a slower rate results in a shorter time the seeds experience the final pressure (given a constant pressing time), yields are lower at these rates. Since cocoa showed similar results[31], the influence of pressure profile was not investigated further.

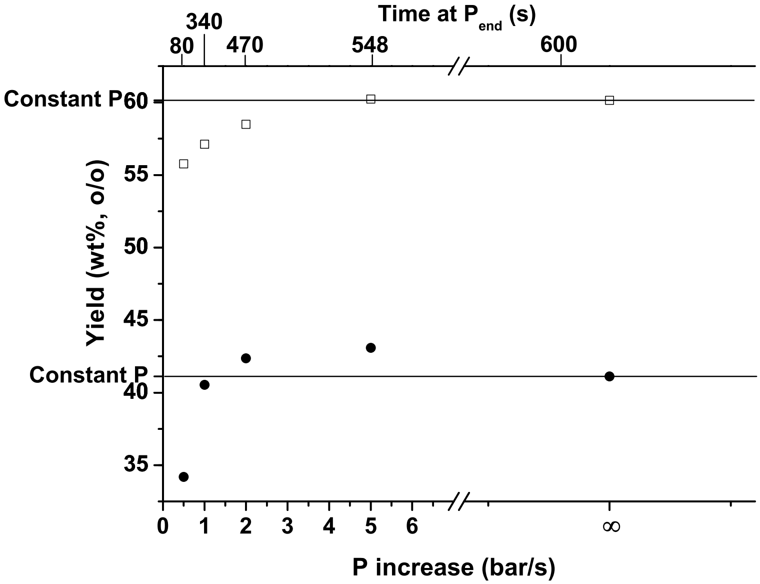


Figure 2-7 *Yields for sesame (□) and jatropha (●) for linear increase in pressure at different speeds (P_{end} = 30 MPa, T = 40°C, time of pressing: 10 min, 10 gram of dry seeds)*

Influence of temperature

Experiments were performed for all seeds at temperatures of 40, 80 and 100 °C and a constant mechanical pressure of 30 MPa. Yields for these experiments are shown in figure 2-8. As can be clearly seen from this graph, temperature only has a significant influence around 100 °C. Raising the temperature from 40 to 80 °C does not have a significant influence on the oil yield. Around 100 °C cooking takes place, which coagulates the protein and the oil globules[6]. These factors increase the yield. Temperature does have an influence on the rate of pressing for all seeds, linseed is shown as an example in figure 2-9. The influence of temperature can be caused by two effects: lowering of the viscosity of the oil or a change in the solid structure. As was previously shown[4], lowering the viscosity by dissolving of CO_2 at constant temperature resulted in the same displacement as a function of time as for the conventional experiments. It can therefore be concluded that the main factor of influence is the softening of the solids structure.

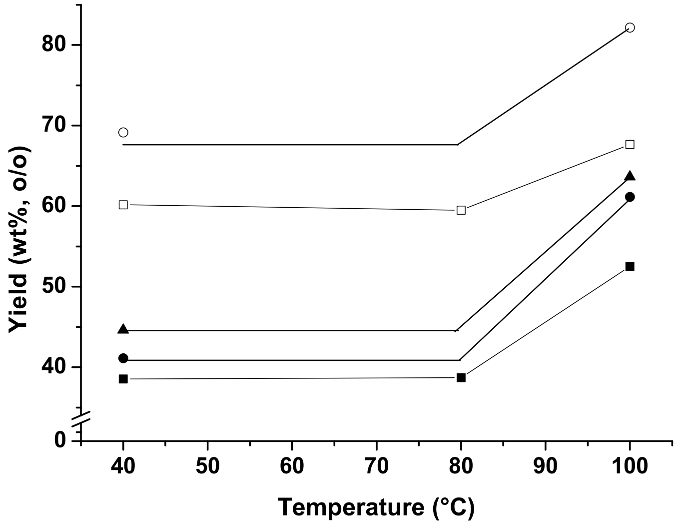


Figure 2-8 *Influence of temperature on oil yield for sesame (□), linseed (■), rapeseed (▲), jatropha (●) and jatropha dehulled (○) (P = 30 MPa, time of pressing: 10 min, 10 gram of dry seeds) Lines serve as visual aid only*

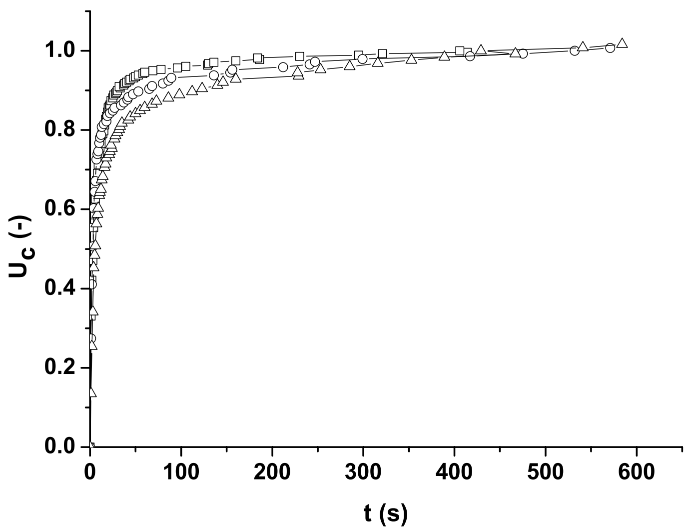


Figure 2-9 U_c *versus time for linseed at different temperatures: 40 °C (□), 80 °C (○) and 100 °C (△) (P=30 MPa, time of pressing: 10 min, 10 gram of dry seeds)*

Influence of moisture content

Preliminary experiments were done to check whether moisture was lost during the pressing experiments, either by evaporation or by expression. The ratio between water and solid (W/S) was taken as indicator. These experiments showed that moisture loss during the experiments (including thermal equilibration) at 40 °C was negligible (W/S reduced from 0.1143 to 0.1123 (linseed)), whereas at 100 °C moisture loss was significant (W/S reduced from 0.0723 to 0.0576 (sesame)). Therefore it can be concluded that moisture is not removed by expression, but losses are due to evaporation.

Results for sesame and linseed at different moisture contents are given in figure 2-10. The experimental values for sesame show a slight increase in yield compared to dry seeds, from 60.2 to 62.3 wt% at a moisture content of 2.1 wt% d.b.. It also showed that there is an optimum in the lower moisture content region as was reported earlier for cocoa and other seeds[11,31,39].

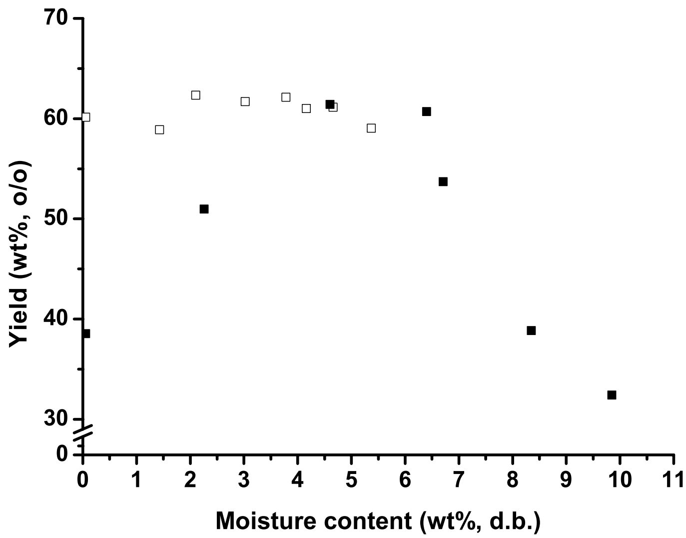


Figure 2-10 *Yield of sesame (□) and linseed (■) as function of moisture content (P = 30 MPa, T = 40 °C, time of pressing: 10 min)*

The yields for linseed show a similar dependency on moisture content to the sesame seeds. However, the increase in yield of the optimum yield compared to dry seeds is a lot larger: 22 wt% for linseed versus 2 wt% for sesame.

2.4.3 Qualification of material properties

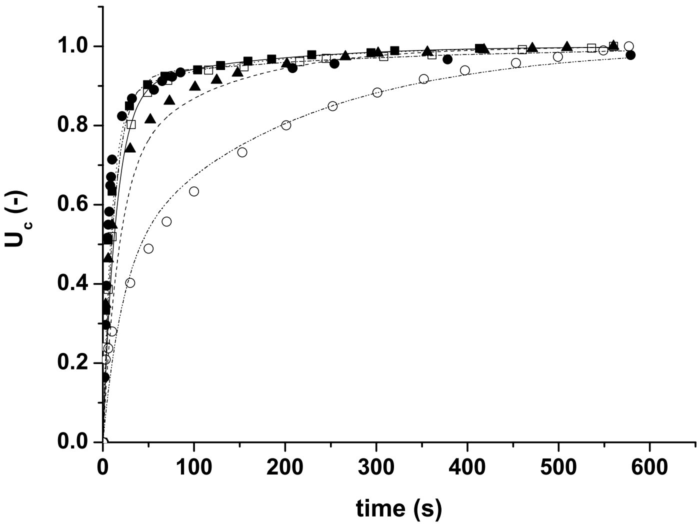


Figure 2-11 *U_c for different seeds: sesame (□, ━), linseed (■, ·····), rapeseed (▲, ----), jatropha (●, -·-) and dehulled jatropha (○, -··) (P = 30 MPa, T = 40 °C, 10 gram of dry seeds)*

The Shirato solution (equation 2-1) was fitted to the U_c-profiles for all seeds in the pressure range investigated by adjusting the α, B and E/G values. The values obtained for α were then correlated using equation 2-3. Results are given in table 2-5. The Shirato model describes the U_c profiles for all seeds reasonably well, as can be seen from figure 2-11.

Cocoa has a filtration resistance that increases strongly with increasing pressure, represented by a high value of β. This hardening phenomenon is well known in industry. Dehulled jatropha forms a very dense cake at all pressures investigated, which results in the relatively high filtration resistance. All other seeds show relatively low filtration resistances compared to dehulled jatropha and cocoa. The low correlation coefficient for palm kernel and dehulled jatropha is caused by the low number of experiments in these series.

Table 2-5 *Value of fit parameters for constitutive equation 2-2 and equation 2-3 for dry seeds at 40 °C P_a was taken as 10 MPa for each seed*

	ε_0 (-)	n (-)	R^2	α_0 (10^{10} m/kg)	β (-)	R^2	B_{avg} (-)	E/G (10^{-3}/s)
Sesame	0.57	0.25	0.96	0.37	1.36	0.98	0.11±0.04	6-8
Linseed	0.56	0.19	0.97	0.28	1.55	0.99	0.12±0.06	6-8
Rapeseed	0.54	0.16	0.92	1.04	1.05	0.95	0.36±0.09	4-8
Cocoa[25]	0.67	0.36		1.84	2.28		0.11±0.04	7
Jatropha	0.45	0.12	0.97	2.06	0.34	0.97	0.06±0.02	6-12
Jatropha dehulled	0.32	0.09	0.94	6.8	0.48	0.63	0.64±0.08	5-6
Palm kernel	0.39	0.08	0.99	1.24	1.0	0.83	0.16±0.04	4-8

The similar values for B show that the contribution of secondary consolidation to the total process for sesame, linseed and cocoa is similar and remains almost constant at different pressures, but for hulled jatropha it is smaller because of the hard and brittle hulls. Dehulled jatropha shows a large contribution of secondary consolidation, indicating very elastic solids. For rapeseed the results for secondary consolidation are inconsistent as can be seen from the larger error in the B-value. No clear distinction can be made between the E/G-values for the different seeds, especially considering that these values are obtained from a very small part of the U_c-graph. The values for n are higher for dehulled seeds (sesame, cocoa and dehulled jatropha) than for the hulled seeds (linseed, rapeseed and jatropha). This shows a stronger dependency of the porosity on pressure for the dehulled seed. When using hulled seeds, the hulls carry part of the pressure, whereas for dehulled seeds, all the energy is used to express the oil.

Moisture content

As can be seen from figure 2-12 increasing the moisture content for sesame does slow down the rate of compaction at 30 MPa and 40 °C. This indicates that the material shows more creep by the addition of moisture. Fitting of the Shirato solution to the experimental U_c-graphs (material properties are shown in figure 2-13) nicely illustrates this effect by an increase in the relative contribution of secondary consolidation (B, figure 2-13b), whereas the filtration resistance (α, figure 2-13a) and the creep constant (E/G, figure 2-13c) remain close to the value for dry seeds. The same was observed for the experiments at 50 MPa, showing that pressure dependency of the filtration resistance (exponent β in equation 2-3) is not affected by a change in moisture content.

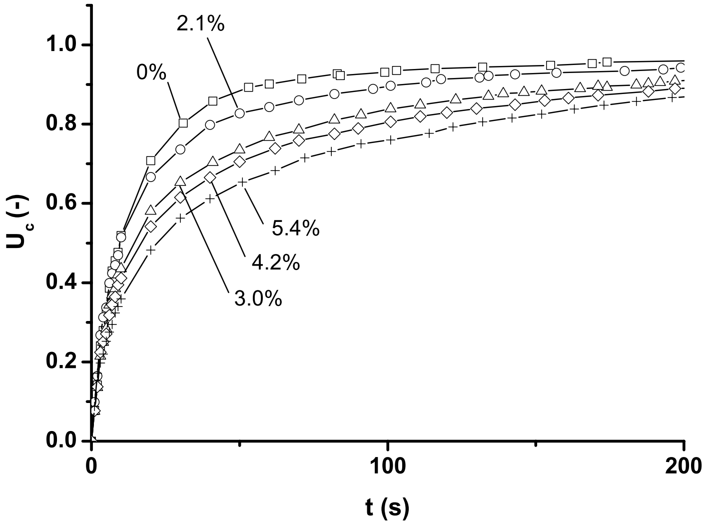
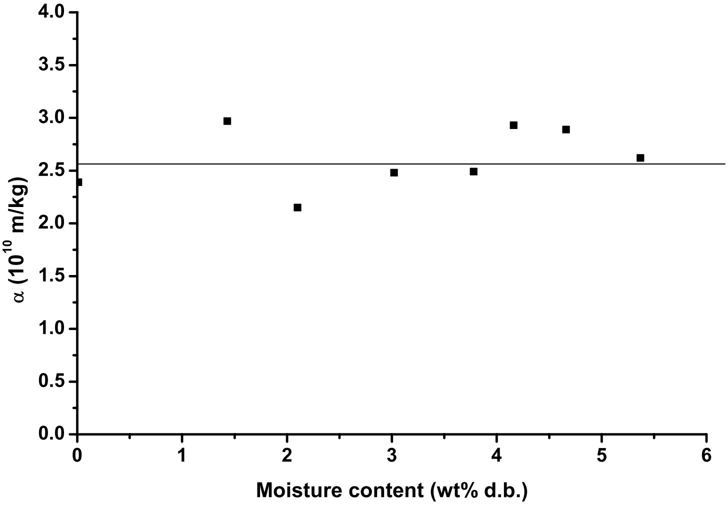
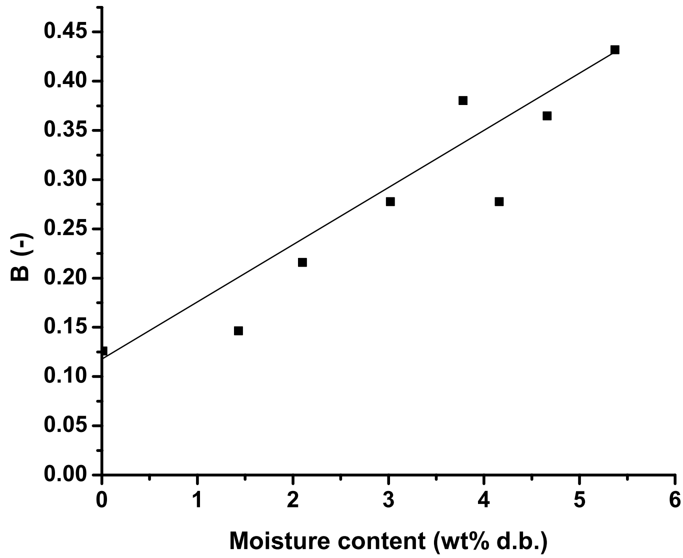


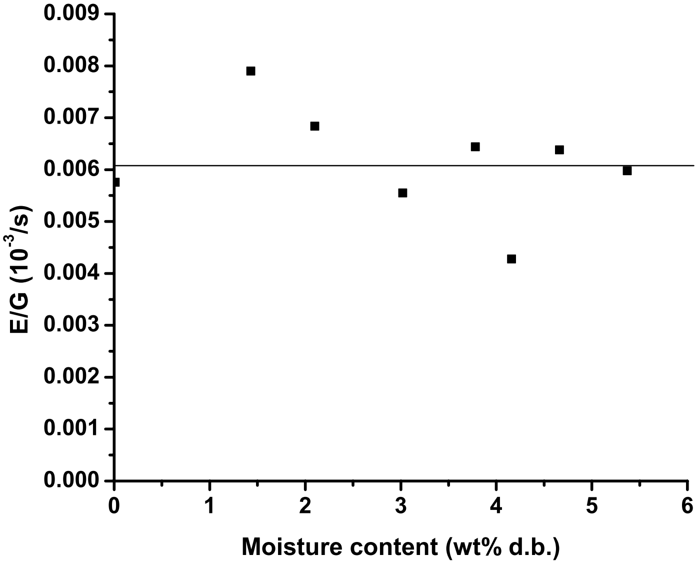
Figure 2-12 *U_c as function of time for sesame at different moisture contents: 0%(□), 2.1% (○), 3.0%(△), 4.2% (◇), 5.4% (+). (P = 30 MPa, T = 40 °C)*



(a)



(b)



(c)

Figure 2-13 *Material properties of sesame as function of moisture content (P = 30 MPa, T = 40 °C)*

2.5 Conclusions

This works shows the influence of pressure (-profile), temperature, cake thickness and moisture content on the oil yields and rate of pressing for a variety of seeds as determined in a laboratory press. Increasing the pressure, using a temperature of 100 °C and using the optimum moisture content increased the yield obtained for all seeds. Applying a pressure profile or changing the amount of seeds did not influence the yield significantly. The yields obtained for hulled seeds (linseed, rapeseed and jatropha) were limited to 45-55 wt%, for dehulled seeds (sesame, cocoa and dehulled jatropha) the limit was around 70-75 wt%. This difference could be attributed to the absorption of oil by the fibres in the hulled seeds. It shows that dehulling is crucial when high yields are desired in conventional expression. This work also shows that using a press capable of higher pressures (>45 MPa) does improve the oil yield by up to 15 wt% (oil/oil) compared to conventional presses. The limited yields obtained with conventional expression clearly show a need for an improved process.

The Shirato model describes the expression process reasonably well for all seeds tested, except rapeseed and can be used in practical applications. The pressure dependent filtration resistance and porosity show good agreement with the classification into soft (high n, low filtration resistance) and hard (low n, mostly high filtration resistance) seeds. For dry seeds, the contribution of secondary consolidation ranged from 10 to 20% and E/G-values did not show a significant difference between the seeds. The contribution of secondary consolidation increased with an increase in moisture content in sesame seed and cocoa, consistent with a more visco-plastic material.

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3 Gas Assisted Mechanical Expression of oilseeds

Gas assisted mechanical expression (GAME) utilises the solubility of supercritical CO_2 in vegetable oils to enhance the oil yields of mechanical expression of oilseeds. The general applicability of GAME was demonstrated with experiments with sesame, linseed, rapeseed, palm kernel and jatropha (hulled and dehulled) at 40 °C and varying mechanical pressures (10-70 MPa). Furthermore, the influence of moisture content, temperature and CO_2 pressure on yield and rate of pressing was investigated. Yields obtained with GAME were up to 30 wt% higher than for conventional expression at the same conditions (40 °C, 10-30 MPa effective mechanical pressure and 10 MPa CO_2 for GAME experiments). GAME yields for hulled and dehulled seeds were very similar, despite the lower yields for hulled seeds in conventional expression. The influence of moisture content and temperature on GAME was similar to their influence on conventional expression. Up to 10 MPa CO_2 yield increased significantly with CO_2 pressure. At higher pressures the improvement was minimal. The displacement of oil by dissolved CO_2 was identified as the major cause of increased oil yields for dehulled seeds. For hulled seeds the entrainment of oil by CO_2 during depressurisation increased the yields even further.

3.1 Introduction

Present day industrial technologies for the production of vegetable oils include hydraulic pressing, screw pressing and solvent extraction with hexane. Of these methods, solvent extraction has the highest yield, but results in a lower quality of the oil compared to the mechanical methods. The pressing methods produce higher quality oils, but lower yields. Today, consumers are getting more aware of the presence of potentially hazardous chemicals in foodstuff. It is therefore necessary to prevent the use of organic solvents in the production of vegetable oils. Two potential alternatives for the production of oil with high yields but without organic solvent residues are extraction with supercritical carbon dioxide (SCE) and a recently introduced process called Gas Assisted Mechanical Expression (GAME)[1]. In the SCE process, the oil is dissolved in CO_2 and thereby extracted from the plant material. However, the solubility of oil in CO_2 is limited to only a few weight percent at reasonable conditions[2,3]. This results in the use of huge amounts of CO_2, which makes the process uneconomical for commodity oils. The GAME process, however, exploits the solubility of CO_2 in the vegetable oils, which can be up to 50 wt% and thereby drastically reduces the amount of CO_2 required[3].

In the GAME process, CO_2 is dissolved in the oil contained in the seeds before pressing. It was shown for cocoa that the dissolved CO_2 displaces part of the oil during pressing[1] as shown in figure 3-1. It was concluded that at the same effective mechanical pressure (absolute mechanical pressure minus the actual CO_2 pressure) the *liquid* content is the same in both conventional and GAME press cakes. The liquid in the GAME press cake is saturated with CO_2 (typically 20-50 wt%), reducing the oil content compared to the conventional cake by the same amount. The contribution of this effect increases with increasing solubility of the CO_2 in the oil. Furthermore, the dissolved CO_2 reduces the viscosity of oil by about an order of magnitude[4], which increases the rate of pressing. After pressing, the CO_2 is easily removed from the cake and oil by depressurisation. During depressurisation of the cake, some additional oil is removed by entrainment in the gas flow as will be shown in this chapter.

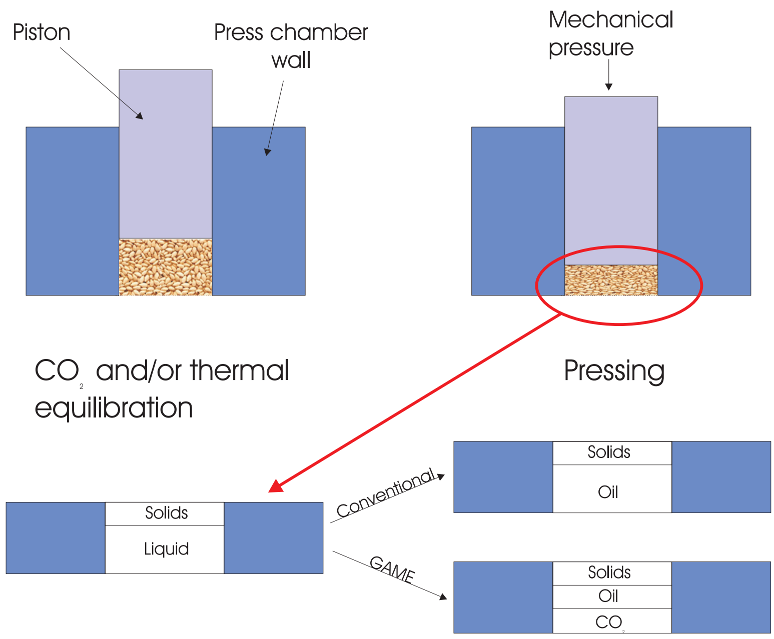


Figure 3-1 *Principle of Gas Assisted Mechanical Expression (GAME)*

The advantage of GAME compared to conventional pressing is the increased yield at lower mechanical pressure. Compared to supercritical extraction the required amount of CO_2 is reduced by two orders of magnitude from 100 kg of CO_2 per kilogram of seeds to typically 1 kg per kg. The second advantage compared to SCE is the low CO_2 pressure required for GAME, which is roughly 10 MPa, whereas for SCE extraction pressures of 40-70 MPa are not unusual[5,6]. These two effects present a significant reduction in the energy requirements for recycling and repressurising the CO_2. Furthermore several reports in literature suggest that the use of CO_2 at 7-20 MPa has a sterilising effect on the substrates[7,8], which may be a convenient side-effect of the GAME process.

To the best of the authors knowledge no information is available in open literature about the use of the GAME process, apart from a number of patents[9,10] (both on an extruder based process) and our previous work which considered obtaining cocoa butter from cocoa nibs[1]. Both patents claim that the oil yield can be increased when CO_2 is used during screw pressing of various seeds. In addition it was claimed to be possible to express oil from seeds at conditions where conventional expression was unable to express any oil at all because of the low oil content[9]. Actual data given in these patents is limited to a few examples and no systematic study into the effect of process parameters is given. In our previous work[1] cocoa was the major subject of the study and it was shown that yields can be increased by more than 20 wt%

compared to conventional expression at the same conditions. Preliminary results were shown for sesame and linseed with effective mechanical pressures of 30, 40 and 50 MPa and a CO_2 pressure of 10 MPa. Since these results showed an equally large increase in oil yield, the study was extended to verify the general applicability of the method for seeds with varying properties.

In this work a systematic study into the effect of mechanical and CO_2 pressure, temperature and moisture content of the seed on the yield and rate of pressing is presented. It presents an extension of the preliminary data on the use of GAME on sesame and linseed (below 30 MPa and above 50 MPa) and provides the first data on rapeseed, palm kernel and jatropha. These seeds were selected to present a variety of low market volume seed with a wide range of oil contents and hardness. Oil yields are provided for these seeds as function of mechanical pressure (10-70 MPa) and temperature (40-100 °C). For sesame and linseed, the influence of moisture content (0-9.8 wt% d.b.) on yield and rate of pressing is also reported. The influence of CO_2 pressure was also investigated for these two seeds to verify earlier findings for cocoa[1]. Secondly, this work demonstrates the effect of dehulling on both the yield and the rate of the process, using jatropha as an example. Finally more insight into the mechanism of the process is provided based on SEM-pictures and a set of mechanistic experiments.

3.2 Experimental procedure and equipment

3.2.1 Materials

Sesame seed and linseed were donated by Dipasa B.V. (Enschede, The Netherlands), rapeseed was donated by Noord Nederlandse Oliemolen B.V. (Delfzijl, The Netherlands), Jatropha by Diligent Energy Systems B.V. (Eindhoven, The Netherlands) and palm kernel was obtained from a local market in Tangerang, Indonesia. Unless stated otherwise, seeds used in the pressing experiments were dried overnight in an oven at 103 °C to remove all moisture. Preliminary experiments showed that sample weight did not decrease anymore after this period and the seeds were assumed completely dry.

For the pressing experiments at different moisture contents, batches of seeds were equilibrated with a constant humidity atmosphere in a desiccator for at least one week. Constant humidity in the desiccator was maintained by putting saturated solutions of different salts in the desiccator with the seeds. No temperature adjustment was done. Moisture content was determined according to method B-I 4 of the German Standard Methods[11] by heating overnight at 103 °C. For low moisture contents (below 2 wt%) the same procedure was used, but zeolite A4 (Tosoh Europe B.V., Amsterdam, The Netherlands) was used instead of salt solutions. The zeolite was dried overnight at 200 °C before use.

The CO_2 (purity >99.995%) used during the experiments was obtained from Hoek Loos (Schiedam, The Netherlands).

3.2.2 Experimental set-up and procedure

A schematic representation of the hydraulic press used during this project is shown in figure 3-2 and discussed in detail elsewhere[1]. Seeds are placed on a sieve plate covered with fine wire mesh in a temperature controlled (30-100 ± 1 °C) pressing chamber with a diameter of 30 mm. Mechanical pressures up to 100 MPa are exerted by a hydraulic plunger. The press is capable of withstanding CO_2 pressures up to 45 MPa. The CO_2 is supplied from a gas bottle and pressurized with a hand pump (Sitec Hand Pump 750.1060, Sitec Sieber Engineering, Zürich, Switzerland), The press is fitted with a thermocouple (± 1 °C), pressure sensor (± 0.5 MPa), a gas pressure sensor (± 0.1 MPa) and a position transducer (± 0.01 mm), which measures the distance the plunger has traveled. Measured values are automatically recorded every second.

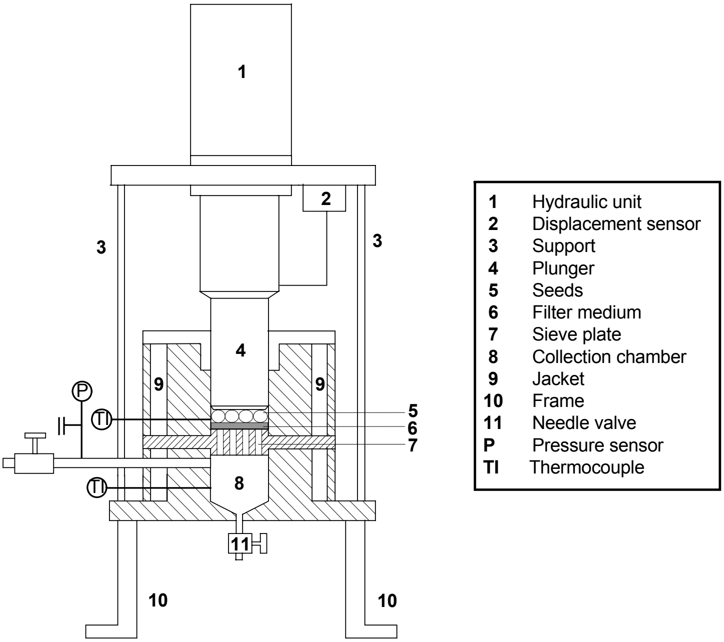


Figure 3-2 *Schematic representation of the hydraulic press*[1]

In a typical experiment, 10 grams of seeds were placed in the press-chamber, after which the piston was lowered on top of the seeds. Preliminary experiments showed no difference in yield in the range of 5-15 grams starting material and therefore 10 grams was chosen to provide sufficient press cake for the analysis. The seeds were allowed to equilibrate to the temperature of pressing for at least 30 minutes without mechanical pressure exerted on the seeds. During this period, CO_2 was allowed to dissolve in the seeds at the required pressure. If necessary, additional time was taken to reach equilibrium between the CO_2 and seeds.

After this, the mechanical pressure was raised up to 4 MPa for 10 seconds, providing a starting point for the compaction of the bed. Pressure was increased to the desired effective mechanical pressure for the experiment in 2 seconds to prevent pressure overshoot. The effective mechanical pressure (P_{eff}) is defined as the absolute mechanical pressure exerted by the piston minus the CO_2 pressure at the end of the experiment. For the GAME experiments this parameter has to be introduced since the CO_2 pressure will counteract the force exerted by the piston.

The oil yields are reported as the oil recovered from the seeds as a percentage of the oil originally present in the seeds. It was determined previously that the reproducibility of the oil yields is within 1 wt%[1].

For all experiments pressing time was 10 minutes, preliminary experiments showed that oil yield did not increase significantly after this period[12].

3.2.3 Analysis

Residual oil contents were determined by soxhlet extraction, based on method B-I 5 of the German Standard Methods[11]. Whenever necessary, samples were dried overnight at 103 °C before analysis except for linseed. Because of the drying properties of the linseed oil, these press cakes were analyzed while wet and residual oil content was recalculated. Preliminary experiments showed that during pressing at 40 °C moisture loss from the cake was negligible. For each analysis, approximately 5 grams of sample was weighed with an accuracy of 0.0001 g. This was ground in a ball mill (Retsch, MM301, Haan, Germany) together with a small volume of petroleum benzene (boiling range 40 – 60 °C, VWR International B.V., Amsterdam, the Netherlands) for 20 seconds at 25 Hz. This was qualitatively transferred to a soxhlet thimble, covered with two wads of cotton wool and extracted with petroleum benzene for at least 4 hours (sesame, linseed) or overnight (jatropha, rapeseed, palm kernel). After evaporation of the solvent, samples were put in an oven at 103 °C overnight or until constant weight. The residual oil content is reported as gram oil per gram sample on a dry basis.

3.3 Results

3.3.1 Equilibrium time

To determine the time necessary for the CO_2 to dissolve completely in the seeds, experiments were done at 30 MPa effective mechanical pressure and 10 MPa CO_2 pressure and equilibration times of 30, 60 and 90 minutes. The oil yields for sesame, linseed, jatropha and rapeseed are shown in figure 3-3.

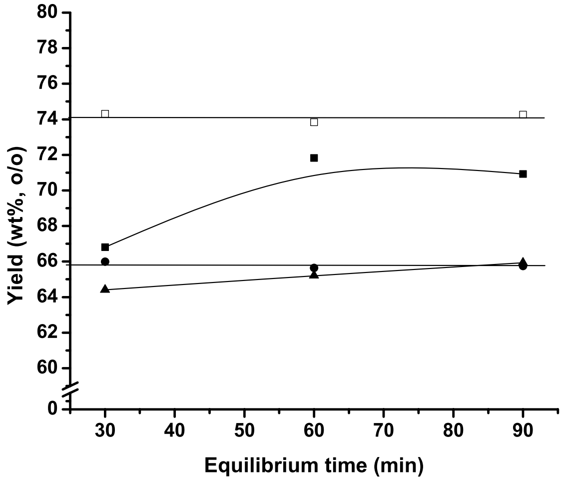
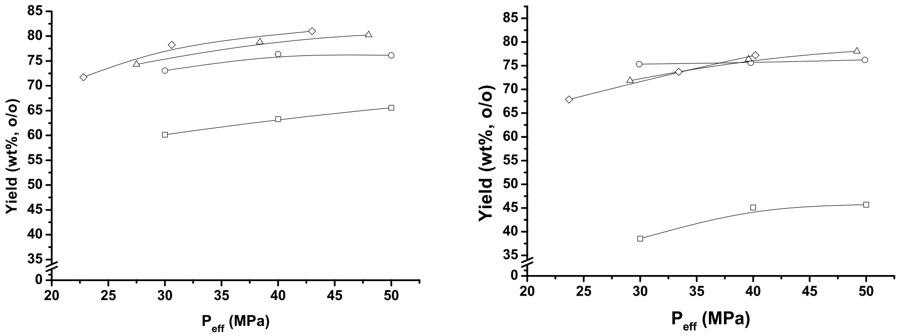


Figure 3-3 *Oil yield as function of equilibrium time for sesame (□), linseed (■), rapeseed (▲) and jatropha (●) (P_{eff} = 30 MPa, P_{CO2} = 10 MPa, T = 40 °C). Lines serve as visual aid only*

From these data it was concluded that for sesame and jatropha seeds 30 minutes was sufficient for equilibration, as yield did not increase with longer equilibration times. For the other seeds 60 minutes was required. These times were therefore used for all the other experiments. Based on the results for these seeds an equilibrium time of 60 minutes was used for palm kernel.

3.3.2 CO_2 pressure

The influence of CO_2 pressure on the yield was determined for sesame and linseed at effective mechanical pressures ranging from about 22 to 50 MPa and CO_2 pressures of 8, 10 and 15 MPa. As can be seen from figure 3-4, GAME always results in a large increase in yield compared to conventional expression. The yield obtained at 10 MPa CO_2 is considerably higher than for 8 MPa, but the increase in yield is limited when the pressure is further increased to 15 MPa. Therefore 10 MPa is considered a good trade-off between increased oil yield and additional energy input and was used in all further experiments.



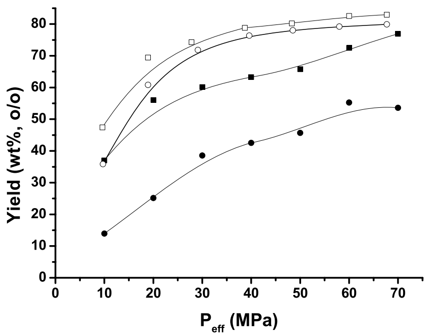
(a) (b)

Figure 3-4 *Oil yield as function of the effective mechanical pressures at 40 °C for different CO_2 pressures for (a) sesame and (b) linseed: P_{CO2} = 0 MPa (□), 8 MPa (○), 10 MPa (△) and 15 MPa (◇). Lines serve as visual aid only*

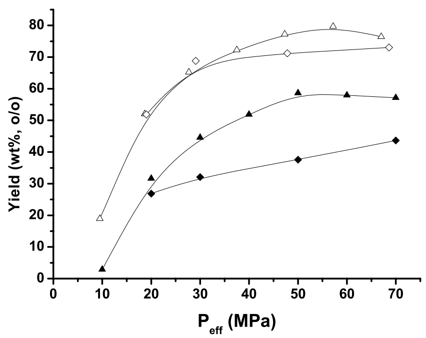
3.3.3 Effective mechanical pressure

The influence of effective mechanical pressure on the oil yield of sesame, linseed, rapeseed, palm kernel and hulled and dehulled jatropha is shown in figure 3-5 for 40 °C and 10 MPa CO_2. In each figure the oil yields for both conventional expression and GAME are shown for two seeds. The oil yield increases with an increase in (effective) mechanical pressure, as also observed in conventional mechanical expression. As was shown in the previous paragraph for sesame and linseed, GAME-yields are significantly higher than the corresponding conventional experiments for every seed investigated. This makes GAME a generally applicable method.

Whereas hulled seed (linseed, rapeseed, palm kernel and jatropha) gave significantly lower yields than dehulled seed (sesame, cocoa and dehulled jatropha) under conventional conditions, figure 3-5 shows that the GAME yields for hulled and dehulled seeds are much closer together. This effect is especially clear for hulled and dehulled jatropha in figure 3-5c. During a conventional pressing operation, oil is absorbed by the hulls. With GAME part of the absorbed oil is entrained in the CO_2 during depressurisation, because the absorption on the hulls is not very strong. The entrainment increases the oil yield for hulled seeds to the same level as the oil yields for the dehulled seeds. The effect of entrainment is less pronounced for the dehulled seeds because the majority of the residual oil is strongly contained in the oil cells. This opens up the opportunity to omit the dehulling step in the industrial production of the oils without a significant loss in oil yields.



(a)



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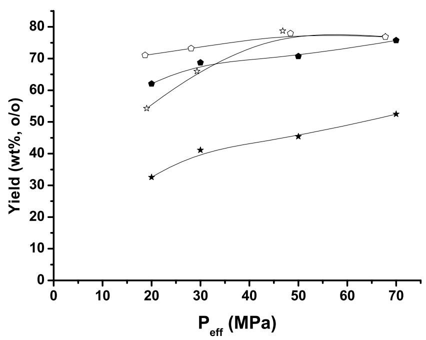


(c)

Figure 3-5 *Oil yield as function of effective mechanical pressure for (a) sesame (■, □) and linseed (●, ○), (b) rapeseed (▲, △) and palm kernel (◆, ◇) and (c) jatropha (★, ☆) and jatropha dehulled (⬟, ⬠) at 40 °C with 0 MPa CO_2 (closed) and 10 MPa CO_2 (open). Lines serve as visual aid only*

3.3.4 Temperature

The influence of temperature on the oil yield was determined for sesame, linseed and rapeseed (see figure 3-6). Yields obtained at 100 °C are always higher than at 40 °C, whereas the difference in oil yield for sesame and linseed between 40 °C and 80 °C is negligible. This effect is well known in literature for conventional expression[13,14] and attributed to increased cell wall permeability, coagulation of seed protein above 80 °C and decreased viscosity of the oil. It was previously reported that the flow of oil through the cake is not a limiting step in the process for cocoa[1]. Therefore the increase in yield is totally attributed to the effects of temperature on the solid structure. This effect is the same for conventional and GAME experiments. Therefore, the temperature influence is the same for the conventional and GAME process.

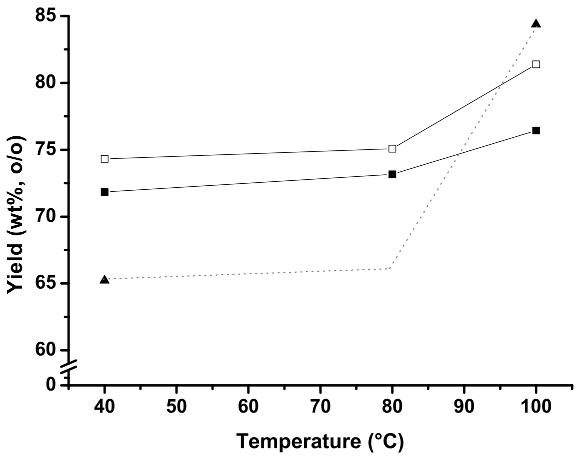


Figure 3-6 *Influence temperature on oil yield for sesame (□), linseed (■) and rapeseed (▲) (P_{eff} = 30 MPa, P_{CO2} = 10 MPa, time of pressing = 10 min, 10 grams of dry seeds). Lines serve as visual aid only*

3.3.5 Moisture content

The influence of moisture content was investigated for sesame and linseed at 40 °C, as shown in figure 3-7. Oil yield shows an optimum for sesame at 3-5 wt%, whereas for linseed the maximum yield is obtained with a moisture content below 6 wt% d.b.. At higher moisture contents, linseed shows a large decline in oil yield. Similar to the phenomena for conventional expression, the permeability of the cell wall and the elasticity of the solid phase increase with increasing moisture content. The increased permeability causes the increase in yield at the lower moisture contents, whereas the increased elasticity decreases the yield at higher moisture contents, because a larger part of the mechanical pressure is used to deform the solids instead of freeing the oil.

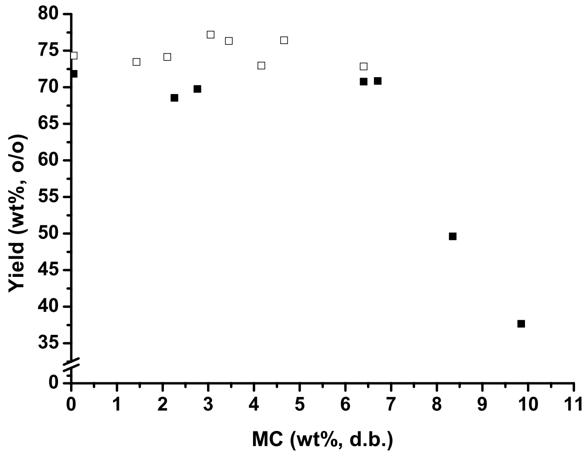


Figure 3-7 *Influence of moisture content on oil yield for sesame (□) and linseed (■) (P_{eff} = 30 MPa, P_{CO2} = 10 MPa, T = 40 °C)*

3.3.6 Mechanism

It was previously shown for cocoa that the decrease of oil viscosity and the entrainment of oil in the escaping CO_2 during depressurisation were of limited influence on the increase in yield[1]. To prove the general applicability of this statement, this was also investigated for sesame and linseed. Factors that can play a role in the increased yield for GAME are:

- Decreased viscosity of the oil due to dissolved CO_2
- Entrainment of oil by CO_2 when depressurising
- Rupture of cell walls by swelling due to CO_2 dissolved in the oil
- Displacement of oil by dissolved CO_2

The influence of the decreased oil viscosity by addition of CO_2 should be clearly visible in the displacement versus time graphs. A typical example for sesame at different temperatures is shown in figure 3-8, although the reasoning is valid for all seeds used in this study. As can be seen from this figure, the difference in displacement between GAME and conventional experiments is minimal. Since the viscosity of the oil-CO_2 mixture is an order of magnitude lower than for the pure oil, the difference should be much larger in case the oil flow rate was limiting. Therefore, it is concluded that the oil flow is not the rate-limiting step in the process for all seeds. The influence of temperature, which causes a smaller reduction in oil viscosity, however, is much larger, indicating that temperature acts mainly on the solid deformation characteristics, confirming once more that oil flow is not the limiting parameter.

Furthermore, the final displacement of GAME and conventional expressions at the same effective mechanical pressure is similar, indicating a similar liquid level at equal conditions. This confirms that final bed porosity, and thereby residual liquid content, is determined completely by the solid deformation characteristics

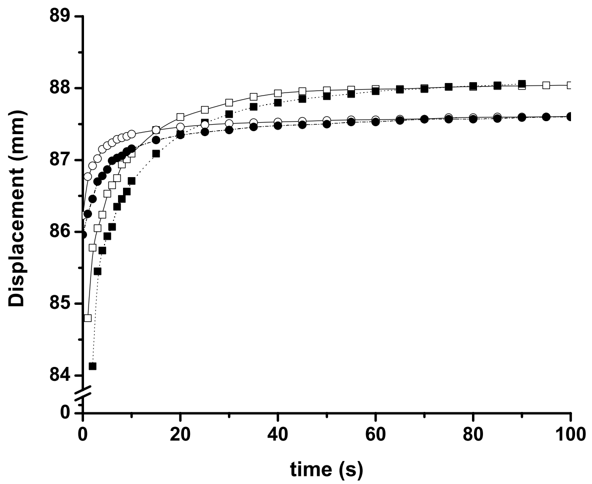


Figure 3-8 *Displacement of piston for sesame at 40 °C (conventional (■) and GAME (□)) and 80 °C (conventional (●) and GAME (○)) (P_{eff} = 30 MPa, P_{CO2} = 0 / 10 MPa CO_2)*

To determine the contribution of entrainment and rupture of the oil cells, the experimental procedure was modified to highlight these effects. The contribution of entrainment was determined by equilibrating the press cake with CO_2 after conventional expression at 30 MPa. Thereafter, the CO_2 was released and residual oil content of the press cake was determined by Soxhlet extraction. Any difference between this experiment and conventional pressing can be attributed to entrainment by the CO_2. By equilibrating the seeds with CO_2, releasing the CO_2 pressure and pressing these pre-treated seeds, the effect of cell rupture can be determined. If cells are ruptured by CO_2, the oil is freed and the oil yield should be higher. Figure 3-9 shows the yields determined for sesame and linseed for conventional, GAME, rupture and entrainment experiments. As can be seen from the graphs, for sesame the yield is increased neither by the rupture nor the entrainment experiments. To ensure that the cake and oil were fully saturated, the entrainment experiments was repeated for sesame with an equilibration time of 6 hours. If there were any diffusion limitations due to the compacted cake, the yield of this experiment would be higher. However, the oil yield for the 6 hour experiment was within experimental error of the 30 minute experiment (56.7 vs 57.4 wt% yield). For linseed however, the yield of the entrainment experiment is significantly higher than the conventional yield, showing that entrainment of the oil does play a role. The oil removed during depressurisation was mainly contained in the hulls, where the oil freed from the cells was absorbed. The oil remaining in dehulled seeds is for the most part contained in the cells itself, were it is more strongly bound. This explains why the effect of entrainment is larger for hulled seeds than for dehulled seeds.

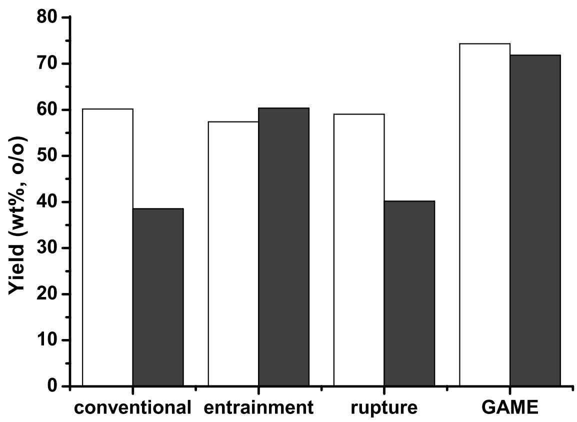


Figure 3-9 *Yields for conventional, GAME, rupture and entrainment experiments for sesame (light) and linseed (dark)*

To check for the occurrence of cell rupture during the experiments, SEM pictures were taken of a press cake after a GAME experiment (not shown) and of CO_2 saturated sesame seeds that were exposed to a sudden depressurisation (figure 3-10). This picture was compared to grape seeds after SCE, which showed massive cell rupture[15]. As can be seen from this picture, the damage to the cell walls done by SCE is more severe than the damage done by sudden depressurisation. No evidence of massive cell rupture was observed in the SEM images of both the depressurised seeds and the GAME press cake. It was therefore concluded that the CO_2 does not cause cell rupture and the mechanism of GAME is not based on the freeing of oil by rupturing the oil cells.

These observations rule out viscosity decrease, entrainment and cell wall rupture as causes for the increased oil yields for dehulled seeds. For hulled seeds, entrainment of the oil does play a role in increasing the yields. The only remaining cause is displacement of the oil by CO_2. This is supported by the similar final displacements for the conventional and GAME experiments at the same effective mechanical pressure.

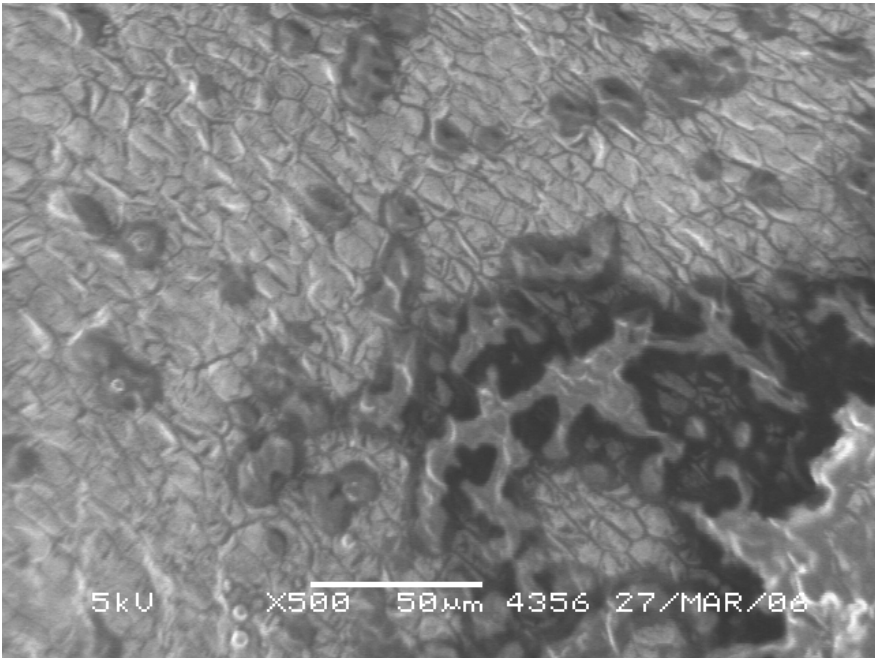
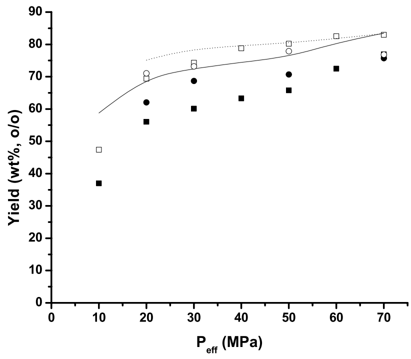
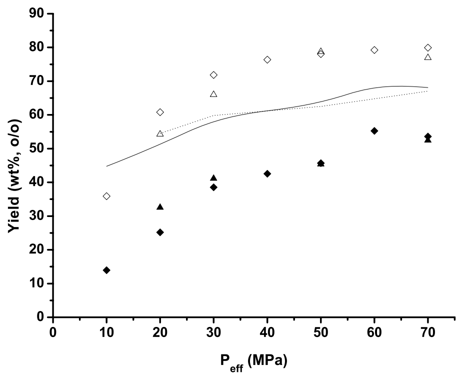


Figure 3-10 *SEM picture of CO_2 saturated sesame after sudden depressurisation*

After identifying the displacement of oil by CO_2 as the major cause of increased yield for dehulled seeds, an attempt was made to confirm this conclusion by predicting the GAME yields from the experimental values for conventional expression and the solubility of CO_2 in the oils for various seeds[3,16]. This was done by assuming the same liquid content in the cakes after pressing for both conventional and GAME experiments and calculating the residual CO_2 in the GAME press cake. After subtracting this from the residual oil content for the conventional experiment a prediction for the GAME experiment was obtained. Results are shown in figure 3-11. The predicted yields shown for sesame and dehulled jatropha (dehulled seeds) in figure 3-11a are almost within experimental error of the observed GAME yield. Considering that the seeds and oil are natural materials, with a certain variety between batches, the correspondence between prediction and experiment is exceptionally good. For hulled seeds, this prediction always underestimated the yields for GAME as confirmed for linseed and jatropha in figure 3-11b, because entrainment of oil from the hulls during depressurization is not taken into account.





(a) (b)

Figure 3-11 *Prediction of GAME yields (lines) based on conventional yields (closed symbols) and solubility of CO_2[3,16], experimental GAME yields are also shown. (a) Sesame (■, □, —) and dehulled jatropha (●, ○, ·····), (b) linseed (◆, ◇, —) and hulled jatropha (▲, △, ·····) (P_{eff} = 30 MPa, T = 40 °C, P_{CO2} = 10 MPa)*

3.4 Conclusions

The general applicability of the GAME process to enhance the oil recovery from oilseeds was demonstrated by pressing experiments for sesame, linseed, rapeseed, jatropha and palm kernel. It was shown that GAME is capable of reaching yields that are up to 30 wt% higher than conventional expression under the same conditions. GAME yields for hulled and dehulled seeds are very similar, despite the lower yields for hulled seeds in conventional expression. The oil yields obtained for GAME increased with increasing effective mechanical pressure and were the highest at a temperature of 100 °C. These effects are similar to conventional expression. The oil yield increased significantly with CO_2 pressure up to 10 MPa. Increasing the CO_2 pressure above 10 MPa did not increase the oil yield significantly compared to the oil yield at 10 MPa. Sesame showed a maximum oil yield at moisture contents of 3-5 wt% (d.b.), whereas for linseed the maximum oil yield was obtained below 6 wt% (d.b.) moisture.

The mechanism of GAME was shown to be mainly based on the displacement of oil by CO_2 during pressing, with entrainment of oil also playing a role for hulled seeds. The GAME oil yields for dehulled seeds could be predicted very well from the conventional oil yields at the same effective mechanical pressure and the solubility of the CO_2 in the oil at the given conditions. For dehulled seeds this prediction always underestimated the GAME yield.

3.5 References

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4 CO_2-saturated vegetable oils: CO_2 content, density and viscosity as function of pressure at 40 °C

The CO_2 content as well as the viscosity and density of CO_2-saturated oils of palm kernel, jatropha and linseed were measured between 2 and 30 MPa at 40 °C. The solubility of CO_2 in these oils was very similar, despite differences in average triglyceride length and degree of unsaturation. All oils showed a strong increase in solubility until approximately 10 MPa after which the increase was less strong reaching a limit of approximately 35 wt% CO_2 at 30 MPa. Viscosity of all CO_2/oil mixtures decreased sharply until about 5 mPa.s at 10 MPa, after which the decrease was more gradual. Above 10 MPa the viscosity of the three CO_2-saturated oils was very similar. The density showed an almost linear increase with pressure above 5 MPa, which was similar for the three oils.

4.1 Introduction

Increasing consumer awareness is stimulating the development of production processes for vegetable oils with high yields without the use of organic solvents. Supercritical extraction with CO_2 (SCE) and Gas Assisted Mechanical Expression (GAME) are two of such methods. In SCE the oils are extracted from seeds or flakes with CO_2. However, because of the limited solubility of the oils in the CO_2 (~1-2 wt%), large amounts of CO_2 are required (roughly 100 kg CO_2 per kg of oil)[1]. In the GAME process the seeds are saturated with CO_2 at around 10 MPa, after which the resulting CO_2-oil mixture is expressed from the seeds by mechanical expression[2]. In contrast to SCE, the GAME process uses the much higher solubility of the CO_2 in the oil, which is roughly 0.5 kg of CO_2 per kg of oil. This considerably reduces the costs for CO_2 recycling compared to SCE. The CO_2 enhances the oil yield by displacing part of the oil from the cake, to an extent that is related to the CO_2-solubility in the oil.

In order to understand and optimise the performance of the GAME process, the CO_2 solubility in the oils and the density and viscosity of the CO_2 saturated oils are required. Therefore an overview of data available in literature (given in table 4-1) was made. Sesame, linseed, rapeseed, palm kernel and jatropha are the object of our study into the GAME process and the properties of their respective oils were therefore of primary interest. Only the solubility of CO_2 in sesame[3], palm kernel[3] and rapeseed[4] was found in literature. Additional oils were included in table 4-1 to be able to draw a conclusion on the general applicability of the findings in this work. Apart our previous work on cocoa butter[5] and three data points for palm oil[6,7], no data set with composition, density and viscosity as function of pressure was found.

Since neither composition nor density nor viscosity was known for jatropha and linseed, these oils were studied first. To reduce the amount of experimental work, density and viscosity were correlated to the mixture composition, enabling a prediction of these properties for the other oils from the compositions found in literature.

It is expected that linseed oil will have the lowest capacity for CO_2 because of its high degree of unsaturation. Palm kernel oil (PKO) has a lower average molecular weight than the other oils and will therefore have a higher capacity for CO_2 on weight basis, assuming the solubility of CO_2 on a mole per mole basis is similar for all triglycerides. PKO was therefore included in this study to cover a broad range of CO_2 solubilities even though composition data is available[3]. The solubility of CO_2 in palm kernel, jatropha and linseed oil was measured with a static-analytical method at 40 °C and pressures ranging from 2 to 30 MPa. The density and viscosity of the CO_2 saturated oils were determined at the same conditions.

Table 4-1 *Overview of available CO_2 solubility in various oils, mixture density and viscosity (+ indicates data is available)*

Oil	P (MPa)	T (°C)	Compo-sition	Density	Viscosity
Sesame[3]	10-33	40-80	+	-	-
Linseed	-	-	-	-	-
Rapeseed[8]	10-85	40-100	+	-	-
Palm kernel[3]	10-32	40-80	+	-	-
Jatropha	-	-	-	-	-
Cocoa[5]	0.1-35	40-100	+	+	+
Brazil nut	15-30	50, 70	+	-	-
Castor[9]	2.1-25.5	13-70	+	-	-
Cocoa[10]	0.1-30	30-80	+	-	-
Corn germ[11,12]	0.1-30	-4-77	-	+	-
Palm[6,7]	20.8	50, 60, 80	+	+ (3 points)	+ (3 points)
Palm oil[11]	0.1-30	40, 59	-	+	-
Palm oil[13]	20, 30, 35	70	+	-	-
Soybean[9]	3.7-26.4	13-70	+	-	-
Soybean[14]	0.1-12	60-70	-	+	+
Soybean oil deodoriser condensate[15]	20-35	70	+	-	-

4.2 Experimental

4.2.1 Setup and procedure

The experimental set-up used in this work has been previously validated and described in detail elsewhere[5] and is only briefly discussed here. Figure 4-1 shows the autoclave with auxiliary equipment. The oil is placed in the autoclave and CO_2 is added to the desired pressure with the help of a hand pump (SITEC, Sitec Sieber Engineering, Zürich, Switzerland). The mixture is stirred with a magnetically coupled stirrer (Büchi AG, Uster, Switzerland) to speed up the equilibration process. After settling of the two phases and flushing of all the lines, viscosity can be measured with the viscosity sensor (Flucon, Clausthal-Zellerfeld, Germany, ± 0.2 mPa.s) in the autoclave itself. The density is measured with the external density sensor (DMA512P, Anton Paar, Austria) with an accuracy of 1 kg/m³. After this, the filled sample cell can be disconnected, weighed (yielding the total mixture weight) and emptied into a wash bottle. After thorough rinsing of the cell with hexane, the solvent is evaporated and the residual oil is determined gravimetrically. The CO_2 content of the mixture is calculated from the difference between the total mixture weight and the oil weight. For palm kernel the experimental procedure was the same as reported earlier[5]. For the measurements for jatropha and linseed oil, the sample cell was connected directly to the bottom of the autoclave. This increased measurement accuracy and reproducibility. Therefore only two measurements were done for every pressure for jatropha and linseed, unless the deviation between two measurements was more than 0.5 wt% CO_2, whereas for palm kernel oil three measurements were done unless the deviation between two measurements was more than 1 wt% CO_2. Composition data shown are the average of at least two measurements. All measurements were performed at 40 ± 1 °C.

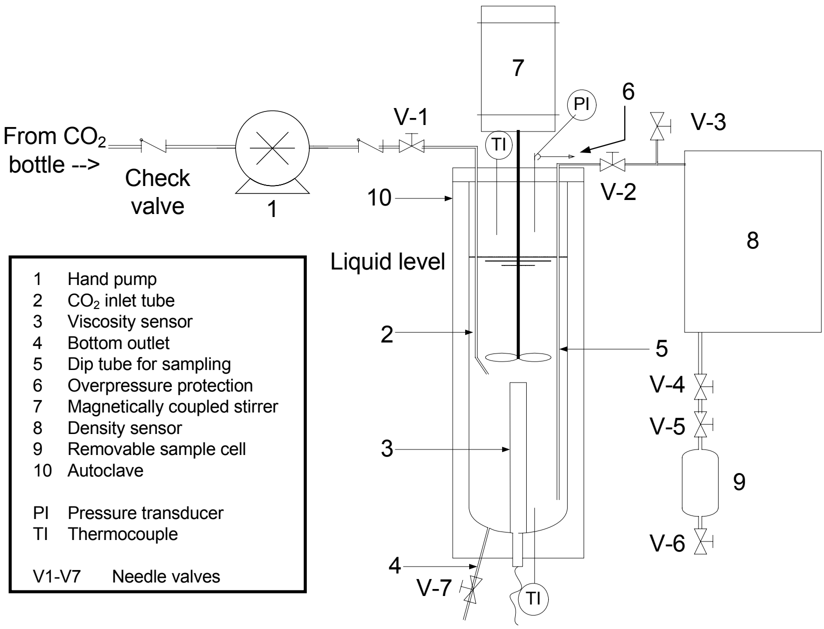

Figure 4-1 *Experimental setup*

4.2.2 Materials

Liquid CO_2 (purity >99.995%) was obtained from HoekLoos (Schiedam, The Netherlands). Palm kernel oil was obtained from De Lange B.V. (Belfeld, The Netherlands), Jatropha oil was obtained by screw pressing from seeds obtained at a local market in Tanzania and cold-pressed linseed oil was bought in a local shop.

Hexane (>99% purity) was obtained from Assink B.V. (Hengelo, The Netherlands).

4.3 Results

4.3.1 Composition

The measured compositions for palm kernel oil, jatropha oil and linseed oil at various CO_2-pressures are given in figure 4-2. The CO_2 solubility in the different oils is very similar. The solubility shows a strong increase with pressure up to about 10 MPa, after which the increase levels off. For all the oils, the maximum solubility of CO_2 is around 35 wt% at 30 MPa. The solubility of CO_2 in palm kernel oil is only marginally higher than in jatropha oil and linseed oil, despite its lower average molecular weight. This is in contrast to results reported in literature, probably due to a difference in triglyceride content. It is expected that all oils will have a similar CO_2-solubility on a mole per mole basis and a lower average molecular weight would therefore result in a higher CO_2-solubility on a weight per weight basis. Therefore, the triglycerides composition used in this work probably has a higher average molecular weight than the sample used in literature[3]. This is supported by the measured density, which is also higher than literature values as will be shown in further on. The solubility in linseed oil is slightly lower because of the high degree of unsaturation of the oil. The reported CO_2 solubility in sesame oil[3], rapeseed oil[8] and cocoa from previous work[5] is also very similar to the values presented in figure 4-2.

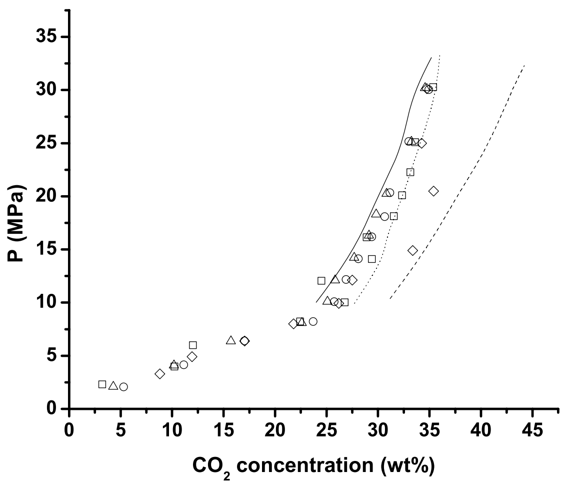

Figure 4-2 *CO_2 content at 40 °C at equilibrium for palm kernel (□), jatropha (○) and linseed (△) oil. Literature values for cocoa butter[5] (◇), sesame[3] (—), palm kernel[3] (- -) and rapeseed[8] (·····) oil are included for comparison*

4.3.2 Viscosity

Figure 4-3 shows the viscosity of the CO_2-saturated oils as function of pressure. The viscosity decreases dramatically with pressure increase until about 10 MPa. After this the viscosity decrease is limited, as the increase in CO_2 solubility is limited and the mixture viscosity approaches the pure CO_2 viscosity. The small differences between the viscosities of the oils at high CO_2 contents are caused by the reduced contribution of the oil viscosity to the mixture viscosity. Compared to the viscosity decrease seen with increasing temperature for the oils (given in figure 4-4), the decrease by the addition of CO_2 is much larger.

The Grünberg equation, given in equation 4-1, was fitted to the experimental data and fits are plotted in figure 4-3. The values for the interaction coefficient (G_{12}) are given in table 4-2, together with the Absolute Average Deviation (AAD %). The G_{12} values are negative for jatropha and palm kernel oil, indicating a less than expected interaction between the CO_2 and the oil. The interaction coefficient measured for cocoa in our previous work is an average value compared to palm kernel and jatropha. For linseed oil G_{12} has a slightly positive value, indicating a somewhat stronger interaction. This is consistent with the slightly lower solubility, indicating a higher activity of the CO_2.

$$\mu_{mix} = \mu_{oil}^{x_{oil}} \cdot \mu_{CO_2}^{x_{CO_2}} \cdot \exp(G_{12} \cdot x_{oil} \cdot x_{CO_2}) \qquad \textit{Equation 4-1}$$

Table 4-2 *Interaction coefficient (G_{12}) and Absolute Average Deviation (AAD) for palm kernel, jatropha, linseed oil and cocoa butter[5] at 40 °C*

Oil	Interaction coefficient G_{12} (-)	AAD (%)
Palm kernel	-2.3	18.5
Jatropha	-0.14	5.2
Linseed	0.14	8.3
Cocoa [5]	-0.8	13.8

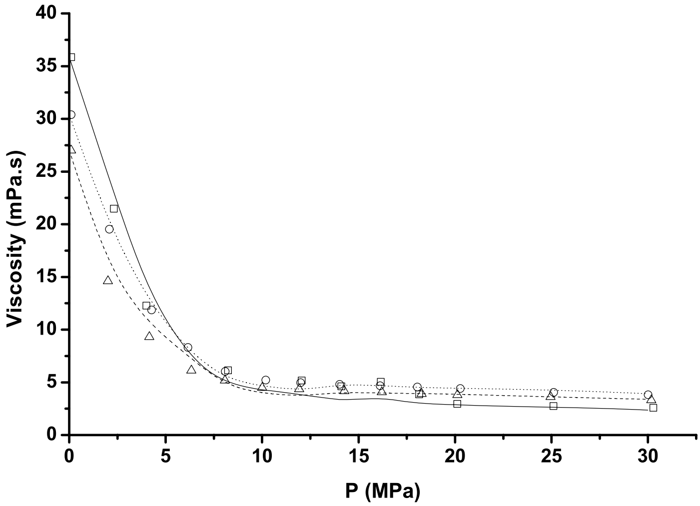

Figure 4-3 *Measured viscosity and fit using equation 4-1 for palm kernel (□, —), jatropha (○, ·····) and linseed (△, - -) oil at 40 °C as function of CO_2 pressure*

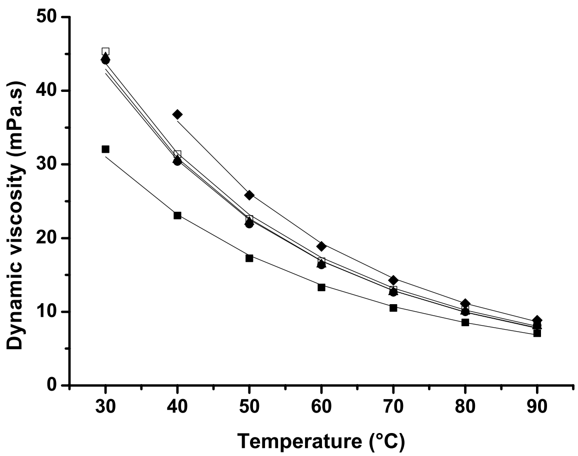

Figure 4-4 *Dynamic viscosity of sesame (□), linseed (■), palm kernel (◆), jatropha (●) and rapeseed (▲) oils at ambient pressure as function of temperature*

4.3.3 Density

The atmospheric density of the oils studied is given in figure 4-5 as function of temperature. The density decreases linearly for all oils with about 6.7 $\cdot 10^{-4}$ g/cm^3/°C as reported for other vegetable oils[16]. The slightly higher density of linseed oil compared to sesame and rapeseed can be explained by the higher degree of unsaturation, which raises the density[16].

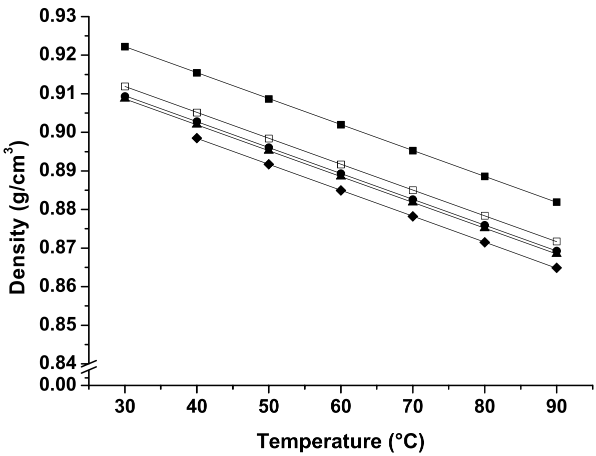

Figure 4-5 *Atmospheric density of sesame (□), linseed (■), palm kernel (◆), jatropha (●) and rapeseed (▲) oil as function of temperature*

The density of the oil/CO_2 mixtures increased with increasing CO_2 pressure, as shown in figure 4-6. Density increases almost linearly with pressure above 5 MPa, as was also reported for other oils[11]. Compared to the density as function of pressure for pure oils[17], the density of the CO_2-saturated oils shows a stronger increase with pressure. This was also observed by others[18,19]. The majority of the density increase can be attributed to the dissolution of the CO_2 and not to the compressibility of the oil[11]. The palm kernel oil density measured is much higher than the value reported in literature, which suggests a higher molecular weight of the triglycerides[16]. This is consistent with the difference between the measured CO_2 content and literature values.

$$\frac{1}{\rho_{mix}} = \frac{m_{CO_2}}{\rho_{CO_2}} + \frac{m_{oil}}{\rho_{oil}}$$ ***Equation 4-2***

The mixture densities were used to obtain an empirical density for the condensed

CO_2 in the oils. Densities were described as a function of composition using the simple mixing rule given in equation 4-2, in which the liquid density of the dissolved CO_2, ρ_{CO2}, was used as density dependent fit parameter. Density of the pure oil as function of pressure was either obtained from literature[17] or estimated using the experimental density at atmospheric pressure and the pressure dependency of the density of linseed oil from the same source. Since the CO_2 density was fitted for every pressure, the deviation between measured and calculated density was always less than 1.5 kg/m^3. Results are shown in figure 4-7. As shown in this figure, calculated CO_2 densities are very similar for all oils. Furthermore, there is a clear distinction between the pressure dependency below and above the critical pressure of CO_2 (7.3 MPa). Below the critical point, density decreases strongly with pressure. At low pressure, the CO_2 probably fills the free volume of the oil[18] at more or less constant volume of the mixture, which causes the strong increase in density and the high apparent density of the condensed CO_2. With increasing CO_2 content, the volume does increase and the apparent density of the CO_2 decreases. Above the critical point, density increases linear with pressure. In this region, the composition does not change dramatically and the density increase is caused mainly by simple compression of the mixture.

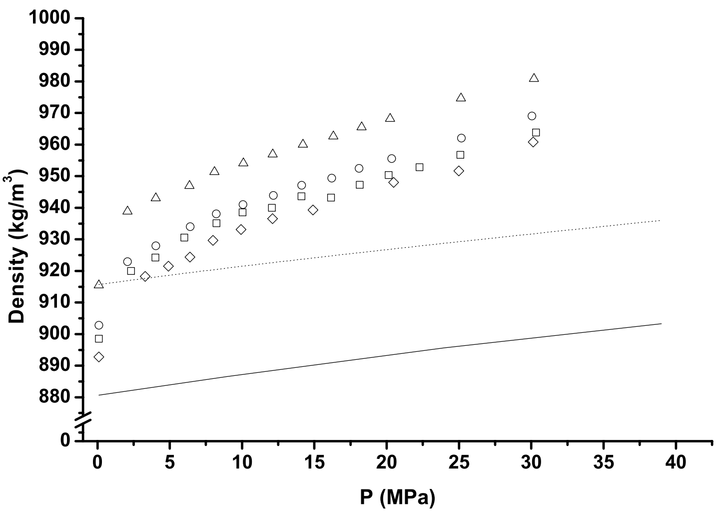

Figure 4-6 *Density of CO_2 saturated palm kernel (□), jatropha (○) and linseed (△) oil at 40 °C as function of CO_2 pressure and density of pure palm kernel[17] (—) and linseed oil[17] (·····) as function of pressure*

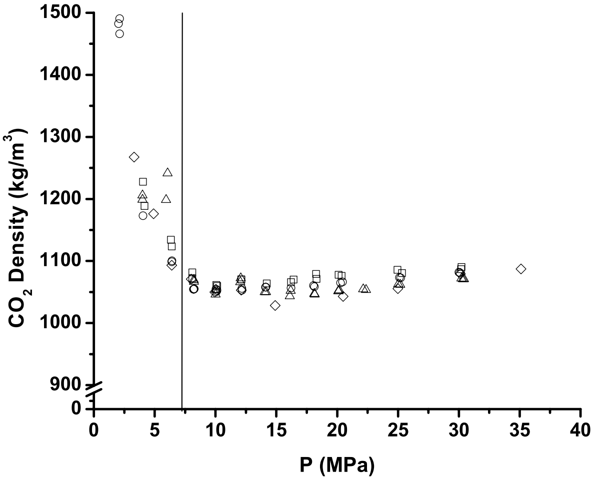

Figure 4-7 *Empirical condensed CO_2 density in various oils as function of pressure (T = 40 °C), the vertical line indicates the critical pressure of CO_2*

4.4 Implications for the GAME process

The data obtained during this study allow for some general conclusions for the GAME process. The similarity in CO_2 solubility in the various oils implies that for every type of seed a similar increase in oil yield can be obtained with the GAME process, because the CO_2 solubility is the major contribution to the higher oil yields. If the oil yield is available at conventional conditions for a given seed, it is possible to predict the GAME yields with reasonable accuracy based on the CO_2 contents measured in this study. Furthermore, the viscosity of the saturated oils can be predicted with reasonable accuracy based on the Grünberg equation and the CO_2 content of the saturated oil. Since the solubility of CO_2 does not differ significantly between the oils at the conditions applied in the GAME process, the viscosity of the saturated oils will not differ significantly either.

4.5 Conclusion

The composition of CO_2-saturated palm kernel, jatropha and linseed oil was measured at 40 °C between 2 and 30 MPa, as well as the mixture viscosity and density. The solubility of CO_2 in these oils was very similar, despite differences in average triglyceride length and degree of unsaturation. All oils showed a strong increase in solubility until roughly 10 MPa after which the increase was less strong reaching a limit of roughly 35 wt% CO_2 at 30 MPa. Viscosity of the mixtures decreased sharply until about 5 mPa.s at 10 MPa, after which the decrease was more gradual. Above 10 MPa the viscosity of the three CO_2-saturated oils was very similar.

The viscosity as function of CO_2 pressure could be described very well by the Grünberg equation. Density showed a linear increase with pressure above 5 MPa, which was similar for the three oils. The density increase with pressure was larger than the increase observed for pure oils[3]. The similarity in CO_2 solubility, viscosity and density as function of pressure despite the very different nature of the oils make the methods used generally applicable and the data can be used to predict these properties for other oils.

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5 A consolidation based extruder model to explore GAME process configurations

A mathematical model from literature was adapted to predict the pressure profile and oil yield for canola in a lab-scale extruder. Changing the description of the expression process from filtration to consolidation significantly improved the performance and physical meaning of the model. The model predicts the trends in pressure and residual oil content with varying screw rotational speed and choke opening very well, but the residual oils content is always overestimated. The model was unable to describe the influence of temperature on pressure and residual oil content.

With the developed model, four extruder designs were compared based on the resulting residual oil contents at the same process conditions: a single stage and a double stage conventional extruder, a single stage GAME extruder and an extruder with a conventional first stage and a second stage with GAME. The last layout was found to result in the lowest residual oil content (14.5 wt%) compared to a conventional residual oil content of 19 wt%.

5.1 Introduction

Increasing consumer awareness is stimulating the development of production processes for vegetable oils from oilseeds with high yields without the use of organic solvents. Recently, an organic solvent-free process called Gas Assisted Mechanical Expression (GAME) has been introduced[1-3]. In the GAME process the seeds are saturated with CO_2 at around 10 MPa, after which the resulting CO_2-oil mixture is expressed from the seeds by mechanical expression. The CO_2 displaces part of the oil from the cake, to an extent that is related to the solubility in the oil. To accomplish the full increase in yield, the oil in the seeds has to be completely saturated with CO_2, which requires 30-60 minutes either in a hydraulic press or in a pressure vessel with sufficient residence time[1]. This renders the use of such a press economically unviable and other processes have to be explored for industrial use of GAME. As suggested by the available patents[2,3], a screw press or extruder is a promising option for industrial application. These patents claim that it is possible to contain the CO_2 in (parts of) the extruder. It is also reported in literature that it is possible to maintain a CO_2 pressure of up to 12 MPa in an extruder in the case of supercritical extraction of hops[4] and even up to 20 MPa for rapeseed[5]. An extruder enables continuous operation and more importantly it allows for active mixing of the oilseed material and the CO_2. This dramatically reduces the time required to equilibrate the oil with the CO_2. Furthermore, the volume that contains high pressure CO_2 is significantly reduced. The last potential advantage of using an extruder over a hydraulic press is the higher yield that can be obtained with an extruder[6]. This is due to the maceration of the seeds (frees the oil from the cells), continuous mixing of the solids (reduces concentration gradients and breaks up the cake) and the smaller solid heights (shortens flow paths for the oil).

Despite the applications shown in the patents, it is still unclear which extruder configuration results in the lowest residual oil contents. Up to now, a single stage GAME extruder and a multistage GAME extruder have been used. In (large scale) conventional solvent extraction the oil content of the seeds is first reduced in a pre-pressing step in an extruder, because the first part of oil can be removed relatively easy allowing the extractor size and solvent requirements to be reduced. It could be advantageous to apply a similar principle in a GAME-extruder: remove part of the oil in a conventional stage first, followed by a GAME stage to remove the oil that is harder to obtain in a conventional way. This would also reduce the amount of CO_2 that is required in the process.

Before designing a GAME extruder, it is desirable to have an indication which configuration would be most promising. Therefore, it was decided to develop an isothermal steady state model that is capable to predict the performance of various configurations. This model should be able to predict throughput, pressure profile and residual oil content based on the extruder geometry, process conditions and material properties. Since the material properties vary significantly between batches and during the expression in the extruder, no detailed flow analysis inside the extruder is required.

As a number of models already exist for conventional extrusion/expression of oilseeds or other solid liquid mixtures, an overview was made of the available models (given in table 5-1).

Table 5-1 *Overview of mathematical models for expression in an extruder and oilseed extrusion. Q = throughput, P = pressure and F = residual oil content*

Designation	Material	Input[1]	Output	Limitations
Shirato (Kaolin)[7]	Kaolin	Q, P(x)	F	requires P-profile a priori
Wang[8]	Canola		P(x), Q	no expression
Shirato[9]	Sodium poly acrylate and carboxy methyl cellulose	Q	F, P	low concentration and pressure: constant properties
Vadke[10]	Canola		P(x), Q, F	

[1]Extruder geometry, process conditions and material properties serve as input for all models and are omitted in the table

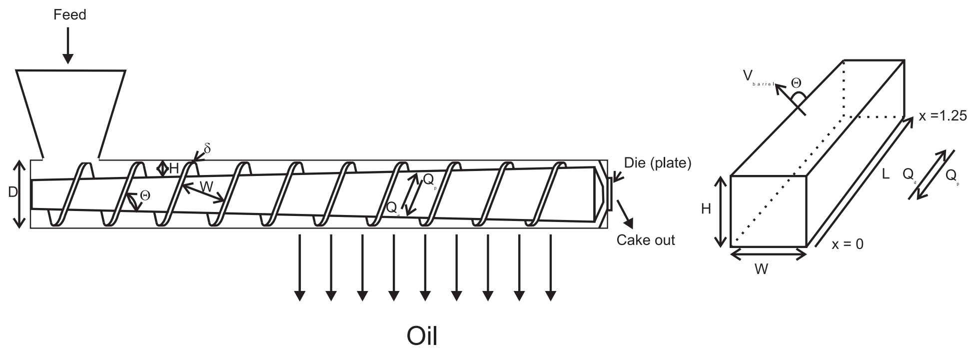
The Shirato (kaolin) model requires a priori knowledge of the pressure profile and the Wang model does not include expression. These models therefore do not meet the requirements set earlier and will not be used. The Shirato and Vadke model are both based on the Darnell and Mol model, which is a classical polymer extrusion model[11]. Shirato, however, used constant material properties because of the low concentrations and pressures involved. This is not the case in oilseed extrusion and therefore the Vadke model was chosen as the starting point. In the Vadke model, the expression of oil from the seeds is described as pure filtration. However, previous work has shown that in the case of hydraulic pressing of cocoa liquor (finely ground cocoa nibs) the flow of oil should be described as consolidation because filtration was virtually absent[12]. Therefore, it was decided to incorporate consolidation in the Vadke model.

The improved model was validated with literature data and the correct pressing characteristics are identified. Thereafter the consolidation model is used to study four extruder configurations to identify the most promising alternative for GAME in an extruder: single- and double-stage conventional extrusion, single-stage GAME extrusion and conventional extrusion followed by GAME.

5.2 Theory

5.2.1 Model structure and implementation

In an extruder (see figure 5-1a) oilseeds are transported and macerated by a rotating screw contained in a metal housing: the barrel. At the end of the screw the flow has to pass through a restriction, called the die. To overcome this resistance, pressure has to build up along the length of the screw. This pressure causes the oil to be expressed from the seed paste.



(a) *(b)*

Figure 5-1 *(a) Schematic representation of an extruder (b) unwrapped screw channel (Q_d = drag flow, Q_p = pressure flow)*

The mathematical description of the process can be simplified by assuming the screw to be stationary and the barrel to be rotating. To further simplify the mathematical treatment, the screw channel is unwrapped, an approach commonly adopted in (food) extrusion[13]. The flow through the screw channel can now be described as flow through a rectangular channel with a moving upper wall (shown in figure 5-1b).

The Vadke model[10] (and oilseed extrusion models in general) consists of three distinctive parts:

1. Description of material flow through the screw channel
2. Description of the expression process
3. Description of the pressure drop over the die

Each of these parts will be discussed in the following paragraphs. Figure 5-2 shows the mathematical connection between the three parts. The axial material flow and the expression parts are solved simultaneously at every position along the screw channel. Results of these calculations are pressure, throughput and residual oil content as a function of position. After reaching the end of the channel the material flow and properties are used to calculate the pressure drop over the die.

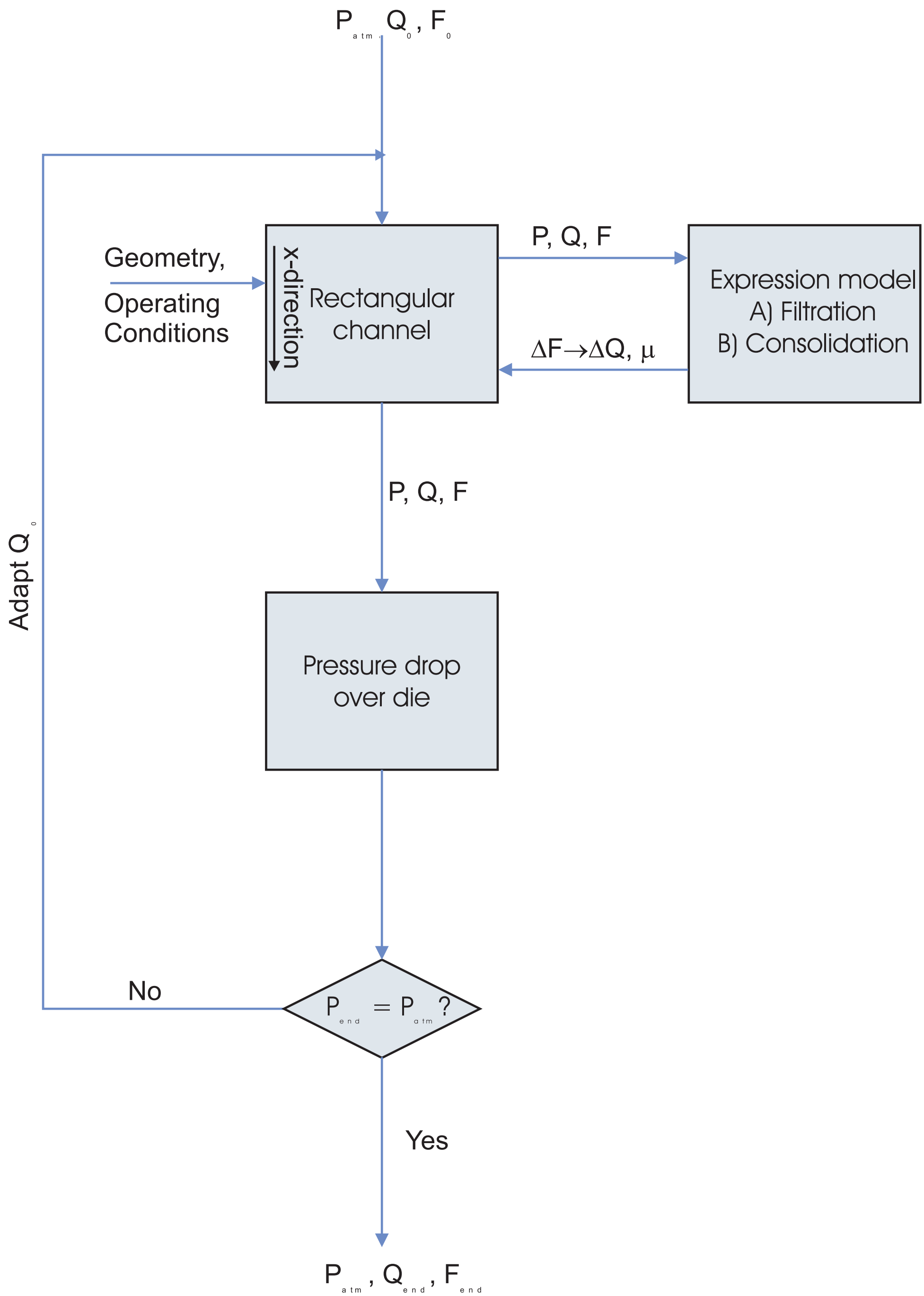


Figure 5-2 *Overview of the model structure*

Both the filtration and the consolidation model were implemented in gPROMS 3.0.2 (Process Systems Engineering Limited, London, UK). For the flow through the channel (eq. 5-1) and the die (eq. 5-2) a second order forward finite difference method was used. For the filtration (eq. 5-3) or consolidation (eq. 5-4) sub-models a second order centred finite difference method was applied. Throughput was iterated until the calculated pressure after the die was atmospheric.

5.2.2 Axial flow

The flow through the channel can be described as flow through a rectangular channel as given in equation 5-1. The first part of the right hand side of the equation describes the drag flow caused by the rotation of the screw, i.e. the maximum capacity for a given extruder design and screw speed. The second part describes the pressure flow caused by the pressure gradient in the channel. This flow is in the direction opposite to the transport direction of the screw and will therefore reduce the output of the extruder.

$$Q_x = Q_{drag-leakage} - Q_{pressure} = \frac{\pi D W (H-\delta) N f_d \cos\Theta}{2} - \frac{H^3 W f_{pd} f_{ps}}{12 n \mu_c} \cdot \frac{dP}{dX} \qquad \textbf{\textit{Equation 5-1}}$$

With: Q_x = axial volumetric flow rate (m^3/s)

$Q_{drag\text{-}leakage}$ = drag flow minus leak flow (m^3/s)

$Q_{pressure}$ = pressure flow (m^3/s)

D = barrel diameter (m)

W = channel width (m)

H = channel height (m)

δ = flight clearance (m)

N = screw rotational speed (1/s)

Θ = flight angle (rad)

f_d = shape factor for drag flow (-)

f_{pd} = correction factor for average viscosity in pressure flow (-)

f_{ps} = shape factor for pressure flow (-)

n = powerlaw index of seed paste (-)

μ_c = paste viscosity (Pa.s)

P = pressure (Pa)

X = position in channel (m)

It was assumed that the oilseeds were fully macerated and all air was removed at the beginning of the compression section of the screw at a position 0.5 m after the beginning of the screw channel[10]. This means that the extruder is completely filled from this point onwards towards the die (the so-called filled length) and this length was assumed to be constant. Furthermore, it was assumed that no pressure was built up before the compression section.

5.2.3 Die

The pressure drop over the die was calculated with equation 5-2, which describes the pressure drop of a powerlaw fluid in a circular tube[14]. This pressure drop is subtracted from the pressure at the end of the extruder channel. Since the extruder was operated as a choke-fed extruder, the throughput was determined by the choke opening (and the operating conditions) and no pre-feeding was used. When the correct throughput is used in the calculations, the pressure is reduced to atmospheric. If not, the feed flow is iterated until this is the case, see figure 5-2. When the pressure drop over the die is too high, the throughput is too high and has to be lowered. If the pressure drop over the die is too low, the throughput has to be increased.

$$\left(\frac{Q_x}{\pi \frac{n}{1+3n} \left(\frac{d_l}{2} \right)^{\frac{1+3n}{n}}} \right)^n = \frac{\Delta P_{die}}{2KL}$$

Equation 5-2

With: d_l = die diameter (m)

ΔP_{die} = Pressure drop over the die (Pa)

L = die length (m)

K = consistency index paste viscosity ($kg/(m.s^{2-n})$).

5.2.4 Expression

Expression of slurries generally consists of two main stages: filtration and consolidation. Whenever free-flowing particles are present, the operation is called filtration. From the point where all the solids form a solids bed onwards, the operation is called consolidation.

Filtration

In the original Vadke model, the flow of the oil through the cake is described as a simple Darcian filtration (equation 5-3). It was shown previously, that the filtration period for cocoa liquor (finely ground cocoa nibs) in a hydraulic filter press was virtually non-existent[12]. Since cocoa liquor closely resembles the macerated oilseed paste in the extruder, it is to be expected that the filtration period in an extruder will also be absent. Therefore, it was decided to investigate a modification of the Vadke model, in which filtration is replaced by consolidation.

$$\frac{dQ_X}{dX} = -\frac{\pi D P \rho_l}{\alpha \mu_l \omega_0 \rho_c}$$ **Equation 5-3**

With: ρ_l = liquid density (kg/m^3)

α = specific filter cake resistance (m/kg)

μ_l = liquid viscosity (Pa.s)

ω_0 = volume of solids per unit filtration area (m^3/m^2)

ρ_c = seed paste density (kg/m^3)

Consolidation

Previous work has shown that a two stage consolidation model described the expression of various oilseeds in a hydraulic press very well[12,15]. This model was therefore incorporated in the extruder model.

$$U_c(t) = \frac{l_0 - l(t)}{l_0 - l_\infty} = (1-B)\cdot\left(1-\exp\left(-\frac{\pi^2 Ce}{4\omega_0^2}\cdot t\right)\right) + B\cdot\left(1-\exp\left(-\frac{E}{G}\cdot t\right)\right)$$ **Equation 5-4**

with $Ce = \dfrac{P}{\mu_l \rho_s \alpha \, \partial e / \partial P}$ **Equation 5-5**

with: U_c = compression ratio (-)

l_0 = cake-thickness at the start of pressing (m)

$l(t)$ = cake-thickness at time t (m)

l_∞ = cake-thickness at end of experiment (m)

B = relative contribution secondary consolidation

C_e = consolidation coefficient (m^2/s)

t = time (s)

E/G = creep constant (s^{-1})

μ_l = liquid viscosity (Pa.s)

ρ_s = solids density (kg/m^3)

e = void ratio (-)

$$U_c(x) = \frac{(\varepsilon_{eq} - 1)\cdot(\varepsilon(x) - \varepsilon_0)}{(\varepsilon_{ea} - \varepsilon_0)\cdot(\varepsilon(x) - 1)}$$ ***Equation 5-6***

With: ε_{eq} = equilibrium porosity (-)

ε_0 = initial porosity (-)

$\varepsilon(x)$ = local porosity (-)

The consolidation ratio, given in equation 5-4, is the ratio between the filter cake thickness at time t and the final filter cake thickness. Both primary (rearrangement of solids bed and liquid removal) and secondary (creep and liquid removal) consolidation are included in the description. In an extruder the filter cake thickness is not determined by the material or the local pressure, but by the geometry of the extruder channel. The definition of U_c as the ratio of filter cake thickness at time t and equilibrium filter cake thicknesses therefore fails. Therefore the consolidation ratio has been interpreted as the deviation of the porosity (i.e. oil content) from the equilibrium oil content at the local pressure according to equation 5-6. The derivation of equation 5-6 is included in appendix A.

5.2.5 Material properties

The viscosity and density of the oilseed paste, the viscosity of the oil, the specific filtration resistance and the porosity of the cake as function of pressure are the material properties that are required for a complete description of the process. The paste viscosity (equation 5-7) and density as function of residual oil content (equation 5-8) were determined experimentally for canola/rapeseed by Vadke[10], the viscosity of the oil (equation 5-9) and filtration resistance (equation 5-10) were determined experimentally in a previous work[15]. Two options were pursued for the porosity: a relation obtained from experiments in a hydraulic press[15] (equation 5-11a) and a relation based on extruder data from Vadke[16] (equation 5-11b).

$$\mu_c = 2.49 \cdot 10^5 \cdot \gamma^{n-1} \cdot \exp(-18.39 \cdot F) \cdot \exp\left(\frac{1476}{T}\right)$$ ***Equation 5-7***

with $\gamma = \frac{\pi DN \cos(\Theta)}{h}$ ***Equation 5-8***

$$\rho_c = 1451 - 703F$$

$$\mu_l = 1.4 \cdot \exp\left(\frac{26 \cdot 10^3}{RT}\right)$$ ***Equation 5-9***

$$\alpha = 1.04 \cdot 10^{10} \cdot \left(1 + \frac{P}{10^7}\right)^{1.05}$$ ***Equation 5-10***

$$1 - \varepsilon = 0.54 \cdot \left(1 + \frac{P}{10^7}\right)^{0.16} \quad \text{(a)}$$

$$\varepsilon = 0.41 \cdot \exp\left(-3.9 \cdot 10^{-7} \cdot P\right) + 0.13 \quad \text{(b)}$$ ***Equation 5-11***

With: γ = shear rate (1/s)

F = fat content (wt %)

R = gas constant (J/mol.K)

T = temperature (K)

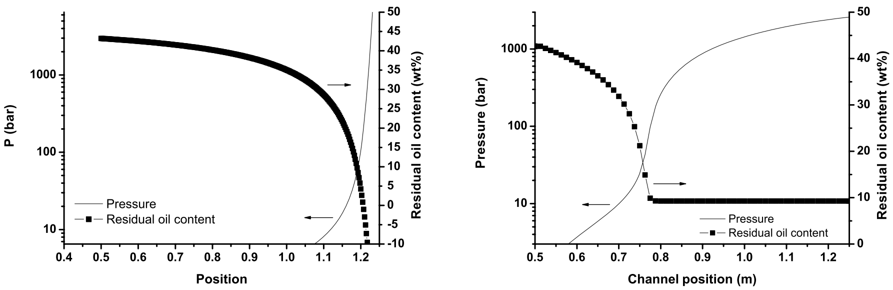
5.3 Model evaluation

Before the model is used to predict the performance of GAME in an extruder and compared to literature data, the correct description of the oil flow and the porosity as function of pressure have to be determined. In order to compare filtration and consolidation, the model was run at limiting cases to identify any problems. After identifying the correct description of the oil flow, the model was run with porosity-pressure relations from the hydraulic press[15] and experimental data from Vadke[16].

5.3.1 Filtration versus expression

Two problems were identified with the original Vadke model: the absence of a limit on the oil removal from the paste and the occurrence of multiple steady states. Both problems complicated the numerical simulation of the model.

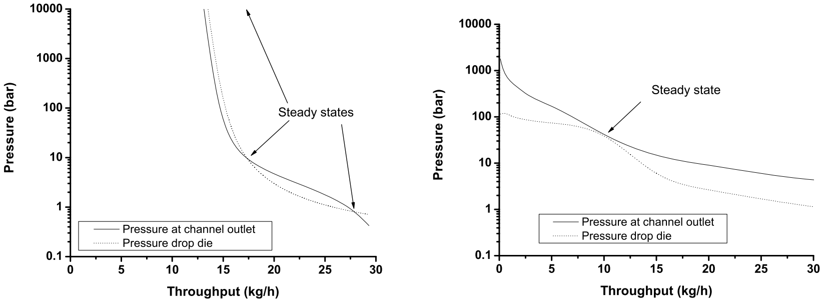
An example of pressure and residual oil content calculated as function of the position in the channel with the original Vadke model is given in figure 5-3a. The residual oil content decreases continuously along the channel and continues to decrease below zero. The original Vadke model does not have a mechanism that will limit the removal of oil and prevents the residual oil content to fall below zero. This is physically impossible and a correct model should not show this behaviour with extreme pressures. The modification to use equilibrium oil contents in the consolidation model prevents the occurrence of negative oil contents under high pressures. An example of this behaviour is shown in figure 5-3b: the pressure and the residual oil content level off towards the end of the extruder. The residual oil content even becomes constant because the function used for the equilibrium porosity has an asymptote at higher pressures.



(a) (b)

Figure 5-3 *Pressure and Residual oil content as function of position for 120 rpm and a specified throughput of 0.01 kg/h (a) the original Vadke model and (b) the consolidation model*

Although multiple steady states were reported in especially reactive extrusion[17], no evidence of multiple steady states in oilseed extrusion was found in literature. Therefore, the occurrence of multiple steady states in the original Vadke model is considered a flaw. The models were considered solved when a throughput was found for which the pressure drop over the die reduced the channel outlet pressure to atmospheric. With the original Vadke model, three steady states were observed (two are visible in figure 5-4a at the position where the lines intersect, the other is at a pressure $>10^5$ bar). For the same conditions, the consolidation model shows only one steady state (figure 5-4b). Most likely, the consolidation model only shows one solution because the residual oil content is limited. This induces a limit on the paste viscosity, which also limits the pressure drop over the die.



(a) (b)

Figure 5-4 *Pressure at channel outlet and pressure drop over the die as function of throughput for (a) the original filtration based Vadke model and (b) the consolidation model, steady states are visible where the lines intersect*

5.3.2 Porosity-pressure relation from hydraulic press (consolidation model)

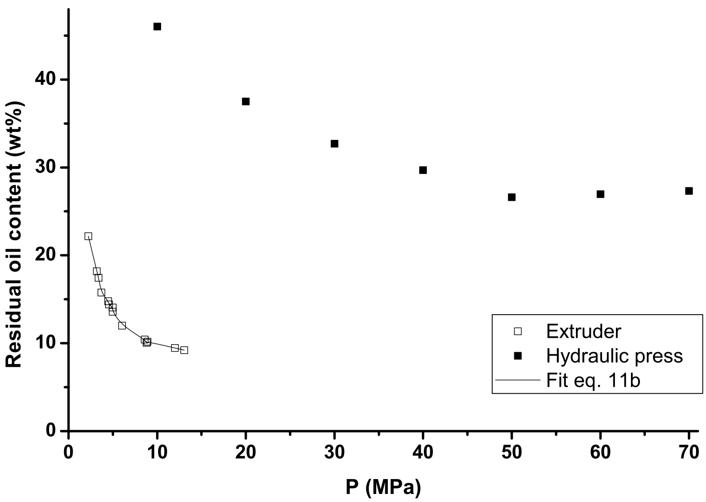


Figure 5-5 *Comparison of experimental data on residual oil content for canola/rapeseed in an extruder[16] and in a hydraulic press[15] as function of (end) pressure at 40 °C*

Where possible, the filter cake resistance and the porosity as function of pressure from hydraulic pressing experiments were used. figure 5-5 shows a comparison between residual oil contents obtained for canola in an extruder[16] and in a hydraulic press[15]. The residual oil contents obtained with an extruder are approximately 20 wt% lower than those obtained with the hydraulic press at the same pressure. Even at 70 MPa the press is unable to reach the oil contents obtained with the extruder.

This difference in yields is due to the maceration of the oilseeds in the extruder, which frees the oil from the cells, the continuous mixing in the extruder and the thinner solids layers obtained in the extruder[6]. Therefore, it is not possible to use the residual oil contents from the press in the extruder model and the experimental data from the extruder have to be used. When the data from the hydraulic press are used, the calculated pressure build-up in the extruder will be too low (see figure 5-6). For a given pressure the calculated residual oil content will be too high, which results in a calculated viscosity that is too low. This in turn limits the pressure build-up and the oil content will remain too high.

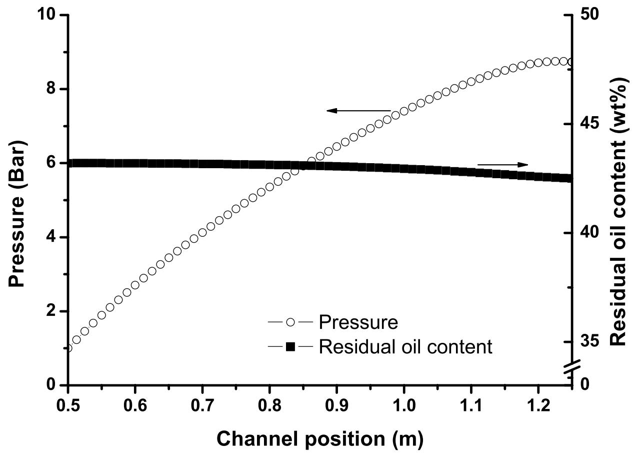


Figure 5-6 *Pressure (○) and residual oil content (■) as function of position in the extruder (70 rpm, feed temperature 40 °C) with residual oil-pressure relation from hydraulic press*

5.3.3 Comparison of the consolidation model to literature values

The consolidation model with the porosity-pressure relation from Vadke was further tested for its ability to describe experimental data from literature[16]. The model is able to predict the influence of screw speed on the pressure and residual oil content reasonably well, see figure 5-7. With increasing screw speed, the throughput increases and therefore the residence time decreases. Since less time is available for the oil to be removed from the cake, the residual oil content increases. This in turn ensures that the viscosity of the paste remains rather low and therefore pressure build-up is also low. This again causes the residual oil content to be relatively high.

The residual oil content is always overestimated by the model, because it was assumed that the cake has the equilibrium oil content for the pressure at the outlet of the extruder. However, calculated U_c values at the outlet of the extruder are in the range of 0.9 to 0.95 (equilibrium = 1) showing that equilibrium is not reached. The calculated oil contents will therefore always be higher than the experimental values.

Figure 5-8 shows the influence of the choke opening on pressure and residual oil content. Decreasing the choke opening increases the resistance to flow at the end of the extruder. The pressure required to overcome this resistance will also be higher, which causes the throughput to be lower. The higher pressure and the longer residence time cause a decrease in residual oil content at smaller choke openings. The model predicts the trends in pressure and oil content very well, but again the residual oil content is overestimated.

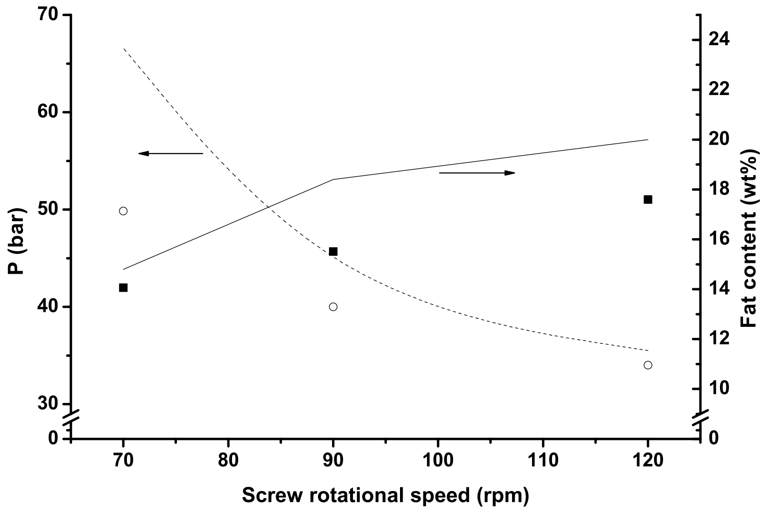


Figure 5-7 *Influence of screw rotational speed on pressure (○, ·····) and residual oil content (■, —) experimental data taken from Vadke*[16] *(feed temperature 40 °C)*

The model appeared not to be able to predict the influence of temperature on oil yield and pressure profile correctly. This is probably caused by the simplification that the paste viscosity is determined solely by the feed temperature and the oil viscosity exclusively by the outlet temperature.

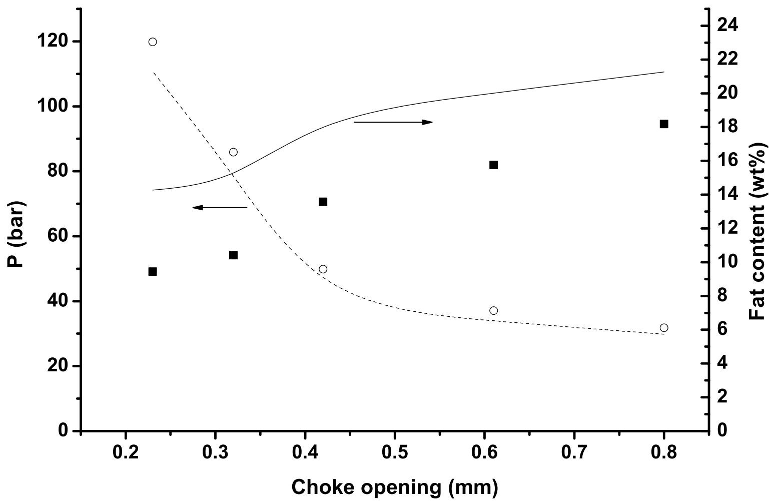


Figure 5-8 *Influence of choke opening on pressure (○, ·····) and residual oil content (■, —), experimental data taken from Vadke[16] (90 rpm, feed temperature 40 °C)*

5.4 Comparison of extruder layouts for GAME

After comparison of the model to literature data, four cases were studied to obtain an indication of the performance of this extruder for GAME. First the optimum mode of operation is determined in four case studies. After this, the influence of CO_2-pressure is investigated. In the case studies, it was assumed that the CO_2 can be contained in the extruder regardless of the (mechanical) pressure at the end of the extruder.

5.4.1 Mode of operation

Four cases were compared:

1. conventional extrusion (as before)
2. GAME extrusion, in which the paste is fully saturated with CO_2 before entering the extruder
3. two-step conventional extrusion, in which the cake from the first pass is fed to the extruder again and
4. conventional extrusion, after which the cake is saturated with CO_2 and fed to the extruder again

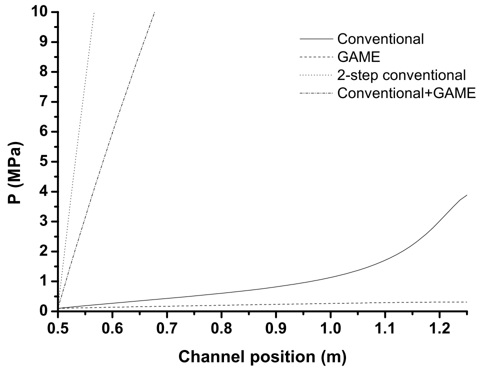
In all cases the extruder geometry and process conditions were kept constant. Screw rotational speed was 90 rpm and feed temperature 40 °C. In both GAME cases CO_2-pressure was 10 MPa.

Figure 5-9 shows the pressure and liquid content profiles for these four cases. In the conventional cases, the liquid content is equal to the residual oil content, in the GAME cases the liquid content is the CO_2-saturated oil content. For comparison the final *liquid* and *oil* contents are shown in table 5-2. For the two-step processes, only the second pass is shown. These are preceded by the profile calculated for the conventional case. The conventional case shows typical profiles: first pressure increases and liquid (oil) content decreases gradually. The decreased oil content causes an increase in paste viscosity and the pressure increase becomes larger. The stronger decrease in oil content towards the end of the extruder is consistent with industrial experience that the majority of the expression is done in the last part of the extruder[6].

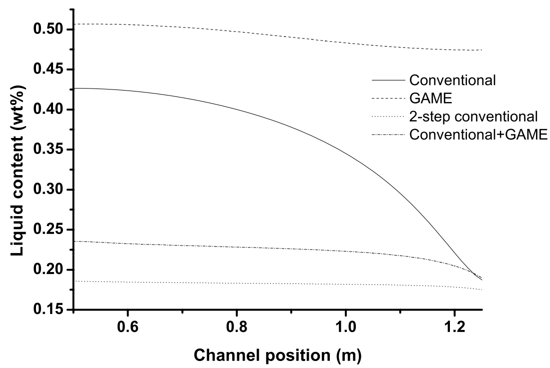
In case the seeds are saturated with CO_2 before entering the extruder, the residual oil content at the outlet is higher than in the conventional case. Because the paste is saturated with CO_2, the liquid content of the paste entering the extruder is increased by a factor 1.3. This lowers the paste viscosity significantly, which in turn prevents a large pressure build-up. The lower pressure in the extruder in turn results in a higher liquid *and* residual oil content.

When the cake produced by the conventional extruder is fed through the same extruder without the use of CO_2, the profile of the two-pass process is obtained in the second pass. The calculated pressure build-up is huge, in practice this extruder would have jammed. It is interesting to see that the oil content is only reduced by 1 wt%. Because of the very high pressures the filtration resistance is very high, which prevents the outflow of the oil.

The lowest oil content was achieved by subjecting the conventionally extruded cake to a pass through the extruder after saturation with CO_2. Although the pressure build-up is still large for the second pass, it is not too high to prevent some additional CO_2-saturated oil to be expressed from the cake. The liquid fraction slowly decreases and reaches a final value of 19 wt%, corresponding to a residual oil content of 14.5 wt%. These residual oil contents correspond to oil yields of 69 wt% oil/oil for conventional extrusion and 78 wt% oil/oil for the GAME extruder. This increase is similar to the increase observed in hydraulic pressing. This proves that with GAME the residual oil content can also be lowered significantly in an extruder and that the lowest oil content is obtained with a two-step process in which part of the oil is removed before CO_2 is introduced to the extruder. This has the additional benefit that the required amount of CO_2 is significantly reduced, since less oil has to be saturated. This in turn will also reduce the size of the CO_2-recyle loop in an industrial process.



(a)



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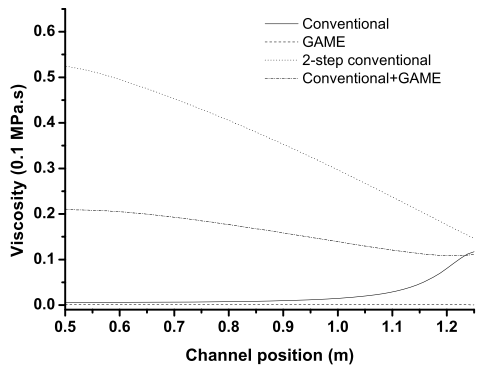

(c)

Figure 5-9 *Predicted pressure (a), liquid content (b) and viscosity (c) profiles for the cases studied (90 rpm)*

Table 5-2 *Final residual liquid and oil contents for the four systems investigated (90 rpm)*

Process	Residual liquid content (wt%)	Residual oil content (wt%)
Conventional	19	19
GAME	47	40
2-step conventional	17.5	17.5
Conv. followed by GAME		
- 8 MPa CO_2	19.0	15.2
- 10 MPa CO_2	19.0	14.9
- 15 MPa CO_2	18.9	14.3

5.4.2 Influence of CO_2-pressure

It was previously shown that the oil yield in a hydraulic press did increase significantly up to 10 MPa CO_2-pressure[1]. The use of higher pressure only marginally increased the yield. To find the optimum CO_2-pressure for GAME in an extruder, the CO_2-pressure was varied for the two-step conventional-GAME process. As with hydraulic pressing, CO_2-pressures of 8, 10 and 15 MPa were used. The residual oil content for these three pressures are within 1 wt% of each other, see table 5-2. The CO_2 solubility in the oil at these conditions are (with increasing pressure) approximately 24, 26 and 28 wt%[18]. The influence on the mixture viscosity is therefore similar for all three conditions and pressure profiles and die pressures are also similar. This results in very similar residual liquid contents and the residual oil content is therefore only determined by the difference in solubility.

5.5 Conclusions

A mathematical model from literature was adapted to predict the pressure profile and oil yield for canola in a lab-scale extruder. Changing the description of the expression process from filtration to consolidation significantly improved the performance and physical meaning of the model. The model predicts the trends in pressure and residual oil content with varying screw rotational speed and choke opening very well, but the residual oils content is always overestimated. The model was unable to describe the influence of temperature on pressure and residual oil content. With the developed model, four extruder designs were compared based on the resulting residual oil contents at the same process conditions: a single stage and a double stage conventional extruder, a single stage GAME extruder and an extruder with a conventional first stage and a second stage with GAME. The last layout was found to result in the lowest residual oil content (14.5 wt%) compared to a conventional residual oil content of 19 wt%.

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Appendix A

Assuming that the majority of the decrease in cake-thickness can be attributed to the removal of the oil from the cake, $U_c(x)$ can be described as:

$$U_c(t) = \frac{l_0 - l(t)}{l_0 - l_\infty} \Rightarrow U_c(x) = \frac{\Delta Q_{oil}(x)}{\Delta Q_{oil\ eq}} \qquad \textbf{\textit{Eq. A.1}}$$

With:

$$\Delta Q_{oil}(x) = Q_{oil}(0) - Q_{oil}(x) \qquad \textbf{\textit{Eq. A.2}}$$

$$\Delta Q_{oil\ eq} = Q_{oil}(0) - Q_{oil\ eq} \qquad \textbf{\textit{Eq. A.3}}$$

The oil flow can be related to the solids flow (constant throughout the extruder) and the porosity:

$$\varepsilon_0 = \frac{Q_{oil}(0)}{Q_{oil}(0) + Q_s} \Rightarrow Q_{oil}(0) = \frac{\varepsilon_0}{1-\varepsilon_0} \cdot Q_s \qquad \textbf{\textit{Eq. A.4}}$$

Similar equations can be derived for $\varepsilon(x)$, ε_{eq}, $Q_{oil}(x)$ and $Q_{oil\ eq}$. Combining eq. A.2-3 gives:

$$\Delta Q_{oil}(x) = \frac{\varepsilon_0}{1-\varepsilon_0} \cdot Q_s - \frac{\varepsilon(x)}{1-\varepsilon(x)} \cdot Q_s \qquad \textbf{\textit{Eq. A.5}}$$

$$\Delta Q_{oil\ eq} = \frac{\varepsilon_0}{1-\varepsilon_0} \cdot Q_s - \frac{\varepsilon_{eq}}{1-\varepsilon_{eq}} \cdot Q_s \qquad \textbf{\textit{Eq. A.6}}$$

Combining eq. A.1, 5 and 6 and eliminating Q_s:

$$U_c(x) = \frac{\dfrac{\varepsilon_0}{1-\varepsilon_0} \cdot Q_s - \dfrac{\varepsilon(x)}{1-\varepsilon(x)} \cdot Q_s}{\dfrac{\varepsilon_0}{1-\varepsilon_0} \cdot Q_s - \dfrac{\varepsilon_{eq}}{1-\varepsilon_{eq}} \cdot Q_s} = \frac{\dfrac{\varepsilon_0 \cdot (1-\varepsilon(x)) - \varepsilon(x) \cdot (1-\varepsilon_0)}{(1-\varepsilon_0) \cdot (1-\varepsilon(x))}}{\dfrac{\varepsilon_0 \cdot (1-\varepsilon_{eq}) - \varepsilon_{eq} \cdot (1-\varepsilon_0)}{(1-\varepsilon_0) \cdot (1-\varepsilon_{eq})}} \qquad \textbf{\textit{Eq. A.7}}$$

$$U_c(x)=\frac{\varepsilon_0\cdot(1-\varepsilon(x))-\varepsilon(x)\cdot(1-\varepsilon_0)}{(1-\varepsilon_0)\cdot(1-\varepsilon(x))}\cdot\frac{(1-\varepsilon_0)\cdot(1-\varepsilon_{eq})}{\varepsilon_0\cdot(1-\varepsilon_{eq})-\varepsilon_{eq}\cdot(1-\varepsilon_0)}$$ ***Eq. A.8***

Eliminate (1-ε(0)) and rearrange:

$$U_c(x)=\frac{\varepsilon_0\cdot(1-\varepsilon(x))-\varepsilon(x)\cdot(1-\varepsilon_0)}{\varepsilon_0\cdot(1-\varepsilon_{eq})-\varepsilon_{eq}\cdot(1-\varepsilon_0)}\cdot\frac{1-\varepsilon_{eq}}{1-\varepsilon(x)}=\frac{\varepsilon_0-\varepsilon(x)\cdot\varepsilon_0-\varepsilon(x)+\varepsilon_0\cdot\varepsilon(x)}{\varepsilon_0-\varepsilon_{eq}\cdot\varepsilon_0-\varepsilon_{eq}+\varepsilon_0\cdot\varepsilon_{eq}}\cdot\frac{1-\varepsilon_{eq}}{1-\varepsilon(x)}$$

Eq. A.9

Finally results in eq. A.10 / equation 5-6

$$U_c(x)=\frac{(\varepsilon_{eq}-1)\cdot(\varepsilon(x)-\varepsilon_0)}{(\varepsilon_{eq}-\varepsilon_0)\cdot(\varepsilon(x)-1)}$$ ***Eq. A.10***

6 Conclusions and outlook

6.1 Conclusions

The aim of this thesis was to show the general applicability of Gas Assisted Mechanical Expression (GAME) to recover oil from oilseeds with high yields. Furthermore, the development of GAME to an industrially applicable process was facilitated by predicting the performance of GAME in an extruder with a mathematical model.

Sesame, linseed, rapeseed, palm kernel and jatropha (both hulled and dehulled) were subjected to conventional expression in a laboratory hydraulic press to provide a benchmark for comparison with the GAME process. The conventional pressing experiments showed that the oil yields for the hulled seeds (45-55 wt% oil/oil) were significantly lower than the yields obtained for dehulled seeds (70-75 wt% oil/oil). This difference was attributed to the absorption of oil in the hull of the seeds during the expression process, as was proven by comparing the oil yields for hulled and dehulled jatropha. It was shown that increasing the mechanical pressure, using a temperature of 100 °C and using the optimum moisture content increased the yield obtained for all seeds. The conventional expression behaviour of all seeds was described very well by the Shirato model. In addition to the influence of pressure and temperature, the influence of moisture content was also incorporated in the model. With increasing moisture content the contribution of secondary consolidation to the process increased linearly, consistent with a more visco-elastic material.

The oil yields obtained for the GAME experiments were up to 30 wt% (oil/oil) higher than for the corresponding conventional oil yields for all seeds. This proves that GAME is a generally applicable method to improve oil yields. The difference in oil yields between hulled and dehulled seeds, which was clearly present in the conventional experiments, was absent in the GAME experiments. Therefore, dehulling prior to pressing is not necessary to obtain the highest possible oil yields and this step can be eliminated from the production process. Displacement of the oil by dissolved CO_2 was identified as the major cause of the increased oil yields, especially for dehulled seeds. It was shown that entrainment of the oil in the CO_2 during depressurisation increased the oil yields even further for hulled seeds. Oil yields increased significantly with an increase in CO_2 pressure up to 10 MPa. At higher pressures the increase was limited. The influence of pressure, temperature and moisture content on the oil yields and rate of expression was similar to their influence observed for conventional expression. The oil yield of dehulled seeds could be predicted very well from the conventional oil yields and the solubility of CO_2 in the oil. For hulled seeds this method systematically underestimated the oil yields, because the entrainment of oil in the CO_2 during depressurisation is not included in the calculation. Given the similarity of the CO_2 solubility in vegetable oils, as shown in this thesis, it is possible to predict the oil yield for GAME for any dehulled seeds from conventional expression yields and the solubility of CO_2 in the vegetable oils. Therefore, not only the GAME process is generally applicable, but also the method for predicting the oil yields.

A mathematical model from literature was adapted to predict the pressure profile and oil yield for canola in a lab-scale extruder. Changing the description of the expression process from filtration to consolidation significantly improved the performance and physical meaning of the model. The model predicts the trends in pressure and residual oil content with varying screw rotational speed and choke opening very well, but the residual oils content is always overestimated. The model was unable to describe the influence of temperature on pressure and residual oil content

With the developed model, four extruder designs were evaluated by comparing the resulting residual oil contents at the same process conditions: a single stage and a double stage conventional extruder, a single stage GAME extruder and an extruder with a conventional first stage and a second stage with GAME. The last layout was found to result in the lowest residual oil content (14.5 wt%) compared to a conventional residual oil content of 19 wt%. These residual oil contents correspond to oil yields of 69 wt% oil/oil for conventional extrusion and 78 wt% oil/oil for the GAME extruder. This increase is similar to the increase observed in hydraulic pressing.

6.2 Outlook

In this thesis the general applicability of GAME was shown and a start was made with the development of an extruder for GAME. To develop the process towards industrial implementation several hurdles still have to be taken, both in the GAME process itself and in the recovery of CO_2 from the oil.

6.2.1 Extruder modelling

In order to increase the ability of the model to describe the extrusion process, two modifications are recommended: making the filled length variable and incorporation of the temperature profile. In the present model the filled length is assumed to be constant, which in practice will not be the case. If this is included, the model will be better capable of handling variation in die resistance and screw speed. The developed model was unable to predict the influence of temperature on the pressure profile and residual oil content. It is expected that this is caused by the assumption that the paste viscosity is solely determined by the feed temperature, whereas the oil viscosity is determined by the temperature at the die. Incorporation of an energy balance into the model will enable a prediction of the temperature profile in the screw channel. This in turn can be used to adjust the paste and oil viscosity to the actual conditions.

6.2.2 Extruder experiments

Although an indication of the performance of GAME in an extruder was shown theoretically in chapter 5, the practical applicability of an extruder in the GAME process still has to be proven. Therefore, it is recommended to perform GAME experiments in an extruder adapted for this purpose. As the model calculations indicate that a two stage operation would provide the lowest residual oil content, this should be incorporated in the design. This would also provide a closed and limited volume in which the CO_2 can be contained at high pressure. Since the conditions in these two stages will differ quite a lot from each other, the screw design of the two parts should be well adjusted to reflect these changes in throughput, paste viscosity and required pressure.

6.2.3 Use of other gases

If even higher yields are required, other gases could be used instead of CO_2. Since displacement of the oil from the cake is a major cause of the increased oil yield, a solubility that is as high as possible is advantageous for the yield as shown in figure 6-1.

Propane or butane show complete miscibility with the oils at pressures above 0.3 MPa at 40 °C[1]. Therefore oil yield can be higher than with CO_2. Recovery of propane or butane from the oil will be easier than hexane, because the boiling points are lower and the required heat treatment is therefore less severe. However, this comes at the cost of the use of flammable organic solvents. Whether the increased yield is worth the increased risk is a consideration for the oilseed producers.

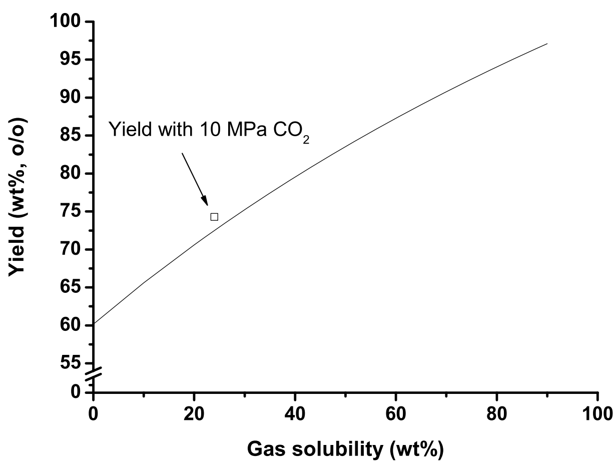

__Figure 6-1__ Predicted yields for sesame as function of gas solubility in the oil (—). The experimentally obtained yield with 10 MPa CO_2 is included as a reference (P_{eff} = 30 MPa, T = 40°C)

6.2.4 CO_2 recovery

Preliminary economic evaluations were done to get an indication of the economic feasibility of the process. In these calculations, it was assumed that the CO_2 was recovered in a series of separator vessels. These calculations showed that the recovery of CO_2 from the oil required approximately a third of the fixed capital investment and more than half of the energy requirements of the process. This was mainly caused by the compressors that were required to pressurise the CO_2 after separation from the oil. It is therefore worthwhile to investigate other methods to recover the CO_2 from the saturated oils. Given the large difference in molecular weight, removing the CO_2 from the oil with membranes should be possible with small pressure drops while still retaining high fluxes. This would lead to a relatively small membrane module that removes the majority of the CO_2 at high pressure. The remaining amount of CO_2 will have to be recovered at the cost of higher pressure drops. As (clean) CO_2 fluxes of close to 100 $kg/(m^2 \cdot h)$ have been reported for polyamide membranes with a pressure drop of only 0.3 MPa[2], this seems a feasible solution providing the polyamide membranes are resistant to these vegetable oils.

6.3 Literature

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