

**A New Concept in Layer-Based Fractional Crystallization Processes
for Fats**

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Kesarin Chaleepa

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1. Introduction

Edible fats and oils naturally own a big variety of triacylglycerides (TAGs) and fatty acid components. The diverse composition leads to broad melting point ranges and complex physical properties. The utilization of fats can be enhanced by a chemically or physically modified composition in order to be in the range of interest for applications. For example, the modification of confectionary fats to increase their melting points and solid fat contents provides a stability of fat containing products, like cookies or chocolate, where a lower melting temperature is fixed. Fractional crystallization or fractionation processes are a renowned physical-based fat modification technology. This technology is based on the crystallization of the high-melting triglycerides in the liquid oil and the separation of the solid crystals to obtain two fractions (a high-melting fraction and a low-melting fraction). Recently, this technology has received great attention over the conventional chemical processes like hydrogenation and interesterification processes. A big advantage of this technology is that there are no trans fat by-products, unlike the hydrogenation process. Moreover, the chemically modified fats from the interesterification process might not have the same metabolic impact as naturally-configured saturated oils.

The main problem of the fractionation process is governed by the incomplete phase separation of high and low melting fractions, the so-called entrainment. This problem plays a great role regarding the solid fat properties, especially, when the product of interest is the high-melting fraction. In general, the entrainment is caused by two main parameters. Firstly, the morphology of fat crystals from suspension typically leads to spherulites consisting of soft needles. Secondly, molten fats near to the melting point possess a high viscosity. Therefore, the separation of the solid crystals with a low amount of inclusions from the liquid fraction is a great difficulty. There is always a portion of liquid oil adhered in and between the solid crystals. This deteriorates the purity of the solid fraction. Organic solvents and detergents to reduce the oil viscosity in oil fractionation processes have been utilized in the past. However, the risk of the chemical contamination in food products is existing and the crystal morphology of fat still remains a problem.

As a consequence, the reduction of liquid entrainment in the oil fractionation process by optimizing both factors; crystal morphology and the viscosity of fats has become the main objective of this work. The optimization methods of these factors are aimed to avoid the use of conventional organic solvents or hazardous detergent. Confectionary fat from vegetable sources of refined, bleached, deodorized (RBD) coconut oil instead of oils from the animal sources was chosen as a fat model. This is due to the public health awareness and thus the growing market popularity of the vegetable oils. Coconut oil is widely used as an ingredient for chocolate coating, biscuit-filling cream and cooking. It is considered to be healthy oil containing rich sources of medium-chain fatty acids (MCFAs, C6-12) that promote human health and reduce the risk of atherogenic diseases.

To achieve this goal, this work is divided into 2 parts. The first part is to gain the insight of the crystallization behaviour of the coconut oil in the presence of additives. Food emulsifiers and fatty acids as additives are introduced as a key factor to morphologically modify the fat crystals. Apart from this, the effects of these additives on the viscosity, crystallization kinetics, polymorphic occurrence, metastable zone width and the thermal profile of coconut oil were examined. On the basis of this information, the additive which meets the requirement is further used for the fractionation of coconut oil.

The second part deals with the reduction of liquid oil entrainment by optimizing the fractionation process of coconut oil through the crystal morphology modification by selected food emulsifiers. In this part, a new fractionation process based on a low viscous oil emulsion crystallization of coconut oil, emulsifier and water, or the so-called emulsion fractionation, has been explored. The emulsions of coconut oil were prepared by 2 methods: a static mixer and a rotor stator system. The reduction of the viscosity effect on the oil emulsions was characterized by means of the dimensionless Ohnesorge number. The layer melt crystallization was examined via a cold-finger apparatus. The solid fractions are the interest product. The reduction of the entrainment was verified by a higher melting point and the solid fat content of the solid fractions. Finally, the separation efficiency in terms of a mass-related distribution coefficient of the new process was compared to the dry fractionation process.

2. Theoretical background and state of the arts

2.1 Coconut oil: a healthy source for confectionary

Coconut oil is one of the most widely used vegetable fats for confectionary which is gaining its popularity and growth in the market. It has been reported as valuable oil due to its health beneficial properties and no harmful by-products. Coconut oil can be produced via a wet process from coconut milk in which the emulsion of oil and water is destabilized through 3 mechanisms. The first stage is creaming phase separations via gravity forces resulting in the higher specific and the lower specific gravity phases. The second step is the flocculation of the oil phase without breaking the interfacial films of the globules. The last step is the coalescence of the oil globule due to the rupture of interfacial areas between the oil globules without the alteration of the oil nature. The coconut oil obtained from this process can be called virgin coconut oil [Mar09a]. In contrast, the coconut oil that is extracted via a dry method from copra or undergone further processes to remove the impurities and unpleasant aromas is called refined, bleached, deodorized (RBD) coconut oil [Can05]. This kind of coconut oil is more suitable for cooking, food processing, cosmetic and pharmaceutical industries.

Table 2.1: The fatty acid composition of RBD and virgin coconut oil [Mar09a].

Fatty acid	Codex standard for RBD coconut oil	APCC standard for Virgin coconut oil
C6	Nd-0.7	0.4-0.6
C8	4.60-10.00	5.00-10.00
C10	5.00-8.00	4.50-8.00
C12	45.10-53.20	43.00-53.00
C14	16.80-21.00	16.00-21.00
C16	7.50-10.20	7.50-10.00
C18	2.00-4.00	2.00-4.00
C18:1	5.00-10.00	5.00-10.00
C18:2	1.00-2.50	1.00-2.50
C18:3	Nd-0.20	<0.50

The common fatty acid composition of virgin coconut oil and RBD coconut oil is shown in Table 2.1. Unlike the other oils, the composition of coconut oil is simple which makes it well-known for its narrow melting temperature range. The main fatty acid components of coconut oil consist of 50% lauric acid (C12) and 15% of C6-C10 fatty acids which are classified as MCFAs (C6-C12) [Can05]. As a result, it is considered to be the richest source for MCFAs that has benefit to human health unlike the long-chain fatty acids (from C16). This explains that the MCFA is limited storable and follows the different digestion pathway in the human body [Bee03]. It

was reported that MCFA stimulates the metabolisms of the long-chain fatty acids and reduces the risk of atherogenic or heart diseases [Tak95]. Coconut oil exhibits a strong resistance character to the oxidative rancidity concerning its 90% saturated fatty acid components. It is also a rich source for natural phenolic antioxidants [Mar09b].

Coconut oil shows a simple polymorphic transformation with the β' -2 stable polymorph. An α -polymorph can occur at rapid cooling, but it easily transforms to the stable β' -2 form [Tim84]. Due to its distinctive composition and character, coconut oil has been used in several edible and non-edible purposes. It is widely used as a confectionary fat, a main ingredient for butter substitutes like margarine, shortening and non-dairy creamer/whiteners, biscuit cream and spray oil for crackers and cookies [Can05, Hal17, Pea85, You83]. It is also used in dietary, medical and infant food formulations [Day00]. For non-edible purposes, coconut oil is applied in cosmetics, pharmaceutical and biodiesel [Abe03, Abi00].

Coconut oil has a solid consistency at cool temperatures, but it melts nevertheless at a temperature above 25 °C due to its relative low melting point of 24.85 ± 0.15 °C. To enhance the solid stability of fat-based products, coconut oil is often treated chemically or physically leading to an increase of its melting point and its solid fat content or a restructuring of the TAG compositions [Lan85, Rao01, Ros85].

2.2 Modification processes of coconut oil

Nowadays, the best known modification processes can be divided into chemical and physical processes. The common chemical modification process is called **hydrogenation** where the double bonds of unsaturated fatty acids are filled with hydrogen [Ros85]. As a result, the physicochemical properties of fats are changed by reducing the degree of unsaturation of the acyl groups. However, this process always causes an isomeric alteration of the remaining unsaturated fatty acids from native cis-isomers into trans-isomers. The consumption of trans fats is more harmful than naturally occurring oil and increases the risk of cardiovascular heart diseases [Moz06].

Another type of chemical modification process is the **interesterification** which can be done chemically [Pea85, Lan85] or enzymatically [Ibr08, Rao01]. In most oils and fats, the 2-position of the TAG molecules is preferentially occupied by an unsaturated fatty acid which lowers the melting point of the fat. The interesterification process involves with the orientative rearrangement and randomization of the fatty acid within and between the TAG molecules. Afterwards, a change in the physical properties of the oil and fat like melting point and rancidity is gained. For instances, Rao [Rao01] applied the enzymatic interesterification process to replace myristic and palmitic acid of the coconut oil with stearic acid. However, the effect of the chemically modified fats on human health is still unclear since its metabolism is biologically different from naturally-configured oils [Hun06, Kri02].

Fractionation is the physical modification process of fats based on their physical properties and can be done by many techniques. Some were explained by Lüdecke [Lue03a]. The best-known and most convenient way for industrial application seems to be the fractional crystallization process [Tim05]. This process is generalized by the crystallization of the high-melting TAGs in the mother liquor and the separation of the solid crystals to obtain two fractions of a high-melting and a low-melting fraction or so-called stearin and olein, respectively.

Table 2.2: The melting point of coconut oil modified by various processes.

	Melting point [°C]	Reference
Coconut oil	24	[Ros85]
Interesterified coconut oil	28.2	[Lan85]
Coconut stearin	30	[Ros85]
Hydrogenated coconut oil	37.8	[Lan85]
Interesterified hydrogenated coconut oil	31.6	[Lan85]
Hydrogenated coconut stearin	32	[Ros85]

Table 2.2 is the summary of the melting points of coconut oil modified by various processes. The fractionation of coconut oil gives a solid stearin fraction possessing a higher melting point than a chemical process of interestification. Even though, the hydrogenation of coconut oil results in the highest melting point among the other processes, its usage is recently in decline due to the above mention reasons [Tim05]. Subsequently, the combination of the hydrogenation with the other processes like an interesterification and a fractionation was done to lower the trans-fat content. For instances, the use of interesterification and hydrogenation caused in the rearrangement and thus the increase of TAG species with a lower molecular weight of coconut oil. This results in a lower melting point of coconut oil than that of a hydrogenation process alone [Lan85]. The hydrogenation in-cooperation with a fractionation significantly increases the melting point of the coconut oil stearin up to the same level of the interestification-hydrogenation coprocess [Ros85].

In fact, both hydrogenation and interesterification including co-processes involving one of these are suffering from the chemical processing image which has environmental drawbacks. As a consequence the physical modification via fractionation has been developing to replace and compete with the chemical processes due to the health and environmental concerns [Tim05].

2.3 Fractional crystallization

Fractional crystallization refers to a repetition of a crystallization process performed in order to receive a further purified product. It can be conducted from the melt as well as from the solution. The difference between the crystallization from melt and

solution is expressed by the heat and mass transfer effects. Whenever heat transfer is dominating a process of solid-liquid phase change, it should be called melt crystallization while mass transfer is the dominant process in solution crystallization [Ulr03a].

In this work, the fractionation from melt crystallization or so-called dry fractionation is the main interest since it is a cost effective and environmental friendly process without addition of an organic solvent or detergent [Ulr04]. Fractionation has been used for many purposes [Tim05, Har99]. One of them is to increase the solid fat properties by narrowing the composition range and sharpening the melting profile for the confectionary purpose. The fractionation is also used to winterize the frying oil by removing the small quantity of high melting compounds. This provides the clarity to the frying oil even at the low temperature [Ham95].

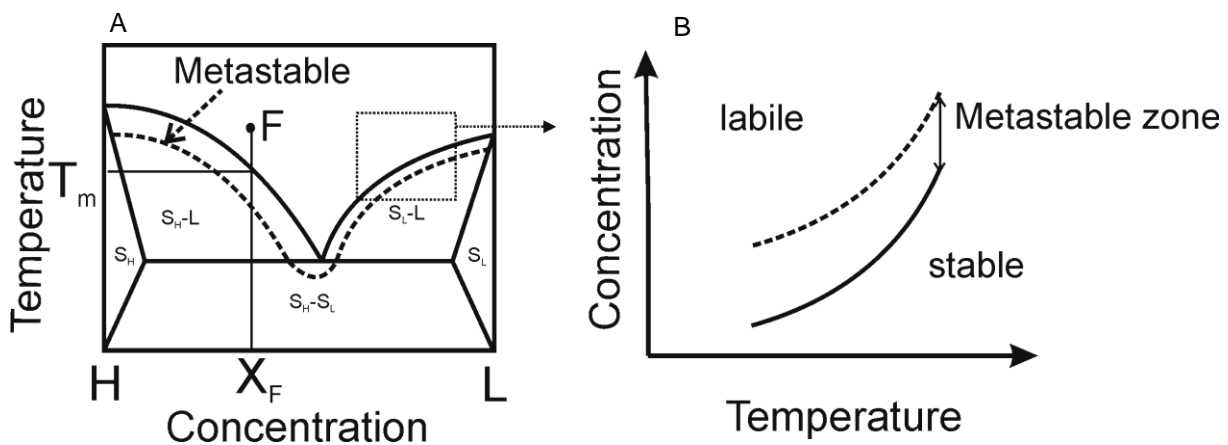


Figure 2.1: (A) phase diagram based on melting points and (B) the solubility curve of the binary system [Ulr03a].

For melt crystallization aspects, the fundamental knowledge in liquid-solid phase diagram are most important to characterize and control the crystallization systems [Koe03]. As above mentioned, fats and oils are considered as multicomponent mixtures of triglycerides in which the determination of their phase diagram requires a large number of variables and extensive experimental works. It is therefore clearly impossible to construct the phase diagram in a true situation. Instead, most studies consider an eutectic system of the binary TAG mixtures as depicted in Figure 2.1 [Tim84].

Figure 2.1A shows the most common phase diagram of a eutectic system. The TAGs of coconut oil can be roughly divided into the high-melting TAG component (H) and the low melting TAG component (L). Consequently, the TAG mixtures of coconut oil can be fitted to this eutectic type since the TAG components differ in molecular volume and shape of polymorph but not greatly in the melting point [Tim84].

In order to fractionate the high melting fraction (H), the crystallization should be done at the left side of the eutectic system. At the point F, the composition X_F is cooled slowly to the temperature T_m until the solid of the high melting fraction starts crystallizing in the liquid of the low melting fraction (L). During further cooling, the

solid-liquid compositions change according to the solidus line of H and the corresponding liquidus line until the temperature reaches the eutectic point where both fractions crystallize simultaneously. In real phase diagrams, an influence of kinetic parameters is involved and alters the crystallization behaviour. The characteristics of the solidus line were reported to depend on the growth rate. At higher growth rates, the solid crystals tend to form a multi crystallite structure with the inclusion of mother liquor and thus the solidus line was shifted closer to the liquidus line [Koe03].

In reality, the crystallization cannot occur at the liquidus line. A melt must be supersaturated (supercooled) in order for nucleation to occur and crystals to grow. The supercooling is achieved by cooling the melt to a temperature below the melting point. The temperature level of supercooling when nuclei are spontaneously formed is called metastable limit. In contrast to the saturation limit, the metastable zone is not thermodynamically defined and strongly depending on the process conditions such as cooling rate, agitation and impurities. Concludingly, the knowledge of the metastable zone width (MZW) is of great importance especially in suspension crystallization for both the design and the operation of crystallization processes or the final product properties [Ulr02].

2.3.1 Problems in fractionation

Fractional crystallization is the process based on the differences in melting or solubility of the high-melting TAGs and the low-melting TAGs which depend on their molecular weight and degree of unsaturation [Kel90]. This implies that the separation of the trisaturated TAGs from the unsaturated TAGs is more effective compared to that of the other TAG types [Ham95]. Hence, to fractionate TAGs mixtures which are not extreme dissimilar, this process possesses great drawbacks.

The difficulty in the complete phase separation of high and low melting fractions, the so-called entrainment is the main problem in dry fractionation as well as other fractionation processes. This problem plays a great role regarding the solid fat properties. The reduction of entrainment has been a major goal in the development of the fractionation process in the last decade and is still under development [Def00].

In general, the entrainment is caused by two main parameters. Firstly, the **crystal morphology** of vegetable oil as well as animal oil from suspension typically leads to spherulites consisting of soft needles as displayed in Figure 2.2. The morphology of a crystal is determined by the relative growth rates of the various faces of the crystals. Needle crystals are an example of the extreme non-faceted crystals. It was suggested that there are 2 reasons for it. The first explanation was given as a result of one or more crystal faces with low edge energy and the roughening of the faces occurred even at the low driving forces resulting in an unexpectedly high growth rates. This was expected when there are no relatively slow growing faces [Pry01]. Second, a concave or dendrite shape was suggested to result from the diffusion limited growth rather than the occurrence of kinetic roughening [Hol02]. More details

in the growth mechanism of TAG needle crystals are explained by e.g. Meekes [Mee03].

The formation of spherulites of needle crystals are not well explained but are linked in particular to solidification from viscous fluids. A spherulite, which is perpendicularly surrounded by the liquid molecule, is an aggregate of many crystalline lamellas that grow radially from the same central nucleus. Spherulites grow through a secondary nucleation mechanism for each lamellar surface. The spherulites of TAGs are considered to be fully crystalline since the molecules are all similar in size and hence perfectly integrate to the lamellas, unlike polymers [Rou02].

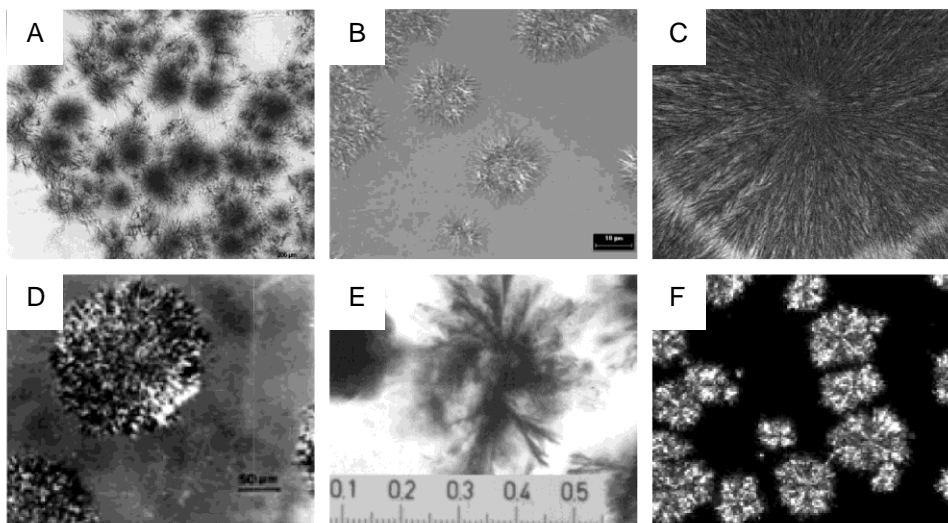


Figure 2.2: Crystal morphology of (A) coconut oil, (B) palm oil [Che02], (C) fractionated palm kernel oil [Sch01], (D) blend of palm stearin/sesame oil [Tor00], (E) polyunsaturated fatty acids [Lue03b] and (F) milk fat [Wri02].

In general, the crystals of fats and TAGs can occur in 3 basic forms of α (alpha)- the least stable and lowest melting, β' (beta-prime)-intermediate stable and β (beta)- the most stable and highest melting form. These polymorphisms are characterized into the monotropic system [Him06]. The recrystallization of crystals causes in the irreversible polymorphic transformation in the order from α to β' to β [Tim84]. In contrast to that, the formation of the crystals from the melt is a reversible process [Szy05]. The polymorphic form leads to different morphologies in fat crystals. The α -form exhibits loosely packed platelet crystals, while the β form exhibits dense long needle crystals. The intermediate form of β' is the most preference in food industries, especially margarine and shortening. Its morphology in fine needles makes it suitable for the optimal rheological and textural properties. However, such a needle crystal leads to high amount of liquid oil adhesion inside and between the crystals [Koe03]. It was suggested by Rossell [Ros85] that the optimal crystal characteristics for the fractionation should be large, compact and not needle-shaped. More details in polymorphic characteristics can be found by Lüdecke [Lue03a].

Another important parameter that influences greatly the entrainment is **the viscosity**, especially, in melt crystallization. The molten fats near the melting point always

possess a high viscosity. Viscosity functions reciprocal to the diffusion coefficient. The higher the viscosity is, the more difficult is the heat and mass transfer as well as the solid-liquid separation [Ulr03b]. It is reported as a rule of thumb that the preference of the viscosity of the melt should not exceed 20 mPa.s [Ulr03b], while the viscosity of coconut oil near to its melting point is about 50 mPa.s. Therefore, the separation of the solid crystals with a low amount of inclusions from the liquid fraction is difficult, especially, in the case of suspension-based melt crystallization processes. There is always a portion of liquid oil included in and between the solid crystals and hence lowered the melting point and the solid fat content of the solid fraction. As a consequence, the reduction of liquid entrainment by optimizing these parameters has been the major goal in the development of oil fractionation processes.

2.3.2 Development and optimization of the fractionation technologies

- **Viscosity reduction**

Conventionally, the reduction of the liquid entrainment by reducing the viscosity of the oil has been done by adding a wetting agent like sodium lauryl sulfate in cooperation with electrolytes of magnesium sulfate. Afterwards, oil is suspended in an aqueous phase. This process is called **detergent fractionation**. Nowadays, the interest for this process is lost due to the high costs and the contamination of the final products with the detergent [Kel07].

The use of organic solvents like hexane or acetone to dilute the oil phase has been performed in **solvent fractionation**. The advantages of this process are mainly the short crystallization time, easy filterability and hence the good separation efficiency and high yield of the final products. However, this process is becoming less interesting due to the residual solvent in the crystal lattices and the high costs of investment along with the risk of solvent inflammability [Lue03a].

So far, the melt-based fractional crystallization or **dry fractionation** has been intensively developing in order to overcome the entrainment problems and compete with the other processes. The application of solid layer techniques was recommended as an alternative in aiding the solid-liquid phase separation of dietary fats, milk fat and wax in comparison to suspension-based techniques due to lower crystal-melt interfacial area [Kus10, Lue03a, Pet99, Tie96]. In contrast, Lüdecke [Lue03a] recommended suspension-based melt crystallization for the fractionation of fatty acid mixtures respected to the quality and quantity of the olein fraction. The weak point of the solid layer process in comparison to the suspension process was suggested to be the limitation of the surface area for crystallization and a hence lower yield [Ulr03c]. The basic principle of layer melt crystallization can be found, for instances by Wynn [Wyn92], Peters-Erjawetz [Pet99] and Ulrich [Ulr03c].

After the crystallization, a sweating process based on a partial melting of crystal layers to remelt the adhering impurities and subsequently a washing step has been reported as the post-purification process. The operation of the sweating step must be sufficiently long to raise the purity and at the same time it must have less product

loss regarding an economical point of view [Ulr03c]. The control of crystallization conditions by introducing a long crystallization period, minimum shear agitating, multi fractionation stages and belt filters for an effective separation can improve the separation quality of the olein-stearin in palm oil fractionation. But the entrainment and the fat crystal morphology still remain problems [Ham95, Kel07].

•*Modification of crystal morphology*

It was found that the morphology of fat crystals and their aggregates was mainly dominated by the higher-melting lipid classes or the TAG saturation level [Shi05]. This implies that the morphological alteration of the fat crystals depends on the composition of the fats. Therefore, the variety of the TAG composition of the fats plays a significant role for their morphology.

Additives have been frequently used in crystallization to modify the crystal morphology where the chemical interactions like van der Waals, ionic and hydrogen bonding between the additive and the crystal surface are responsible for the change [Cod91, Ulr02]. In fat systems, such chemical interactions do not play a significant role as in ionic and inorganic systems [San07], while the van der Waals-London dispersion force and physical interactions are important.

Unlike solute-solvent crystallization, the studies on the morphological modification in bulk fat crystallization are rarely reported, especially, in coconut oil. It was only patented that the addition of 0.05-2 wt-% sucrose ester laurate (L-195) in the dry fractionation of lauric oil can modify the crystal morphology of coconut oil into large, dense spherulites without pores. Furthermore, the separation efficiency of 70% can be achieved [Van96]. However, the effect of this additive on the crystallization kinetics and the solid fat properties of the coconut oil have not been published. More studies are found in palm oil crystallization where emulsifier, surfactants like vinyl alcohol ester, dextrin derivatives and phospholipids are used as crystal habit modifiers [Smi00, van95].

Two main mechanisms have been reported to explain the effects of emulsifiers on crystal habits of bulk fats. First, the emulsifiers can act as heteronuclei, accelerating nucleation through the catalytic actions of such impurities. At the growing crystals, the emulsifiers are adsorbed at steps or kinks on the fat crystal interface and hence inhibit the crystal growth and modify crystal morphology [Cer03]. However, the effect of supersaturation (or supercooling in melt crystallization) must be taken into account. At a high supersaturation, the growth rates are high and hinder the additive adsorption, especially, when the adsorption kinetics is slow. For this reason changes of the crystal habit are difficult to obtain at high supersaturations. In other words, the impurities must be adsorbed rapidly to be effective crystal habit modifiers at high supersaturations. Or else, the impurity concentration can be increased to compensate this effect [Boi88].

The second mechanism was described as the effect of cocrystallization between a fat and an emulsifier due to the similar chemical structures. However, the structural

dissimilarities between TAGs and emulsifiers can delay nucleation and inhibit growth. The acceleration effect of hydrophobic emulsifiers (lower HLB value than 5) on the nucleation of the bulk fat system has not been observed as in emulsion systems. As a rule of thumb, high molecular weight emulsifiers with those mentioned characteristics have the potential to be good inhibitors in crystallization processes [Cer03].

It was reported that a certain additive can also stabilize the preferred polymorphic form. Sorbitan tristearate was added in margarine to inhibit the polymorphic transformation from β' to β [Mad87]. It was concluded that the transformation mechanism of β' to β involves a 180° rotation of chains in every second double layer. Thus, the effective surfactant was incorporated into the crystal lattice and blocked this rotation. In other words, the compound should have the ability to cocrystallize and be structural dissimilar with the fat so that it would not undergo polymorphic transformation [Gar01].

High power, low frequent ultrasound plays an important role in crystallization for food industries. The more even size distribution of ice crystals can be obtained via ultrasound irradiation [Mas96]. High power ultrasound also stimulates the nucleation kinetics in palm oil crystallization [Hig01]. However, the effect of ultrasound irradiation on crystal morphology in fat crystallization has not been reported.

2.3.3 Effects of additives on crystallization kinetics

As above mentioned, the introduction of foreign substances or additives in a crystallization process can affect strongly the crystallization kinetics as well as the crystal morphology. This explains that the modification of the crystallization kinetics refers to the change of the interaction between the additive and the crystal interface which is responsible for the growth morphology of crystals [San07].

In general, crystallization involves 2 kinetic steps. Firstly, nucleation, or the birth of crystals, which is probably the most important step for controlling crystallization in foods [Har01]. In order to initiate the nucleation, supercooling or supersaturation must be applied as a thermodynamic driving force [Gar87]. Once the nuclei are formed, they grow and develop into crystals. In fact, nucleation and crystal growth always occur simultaneously [Boi88]. The basic concept and mechanism of nucleation and crystal growth were summarized by Lüdecke [Lue03a]. According to Ulrich [Ulr02], the nucleation step has the strongest predetermining influence on product properties, such as purity of the crystalline product, solid fat content, crystal habit or crystal size and size distribution.

In order to perform kinetic studies on fat crystallization, the experimental technique must be sufficiently sensitive to detect nucleation and disregard crystal growth [Cer04]. The common techniques, which are frequently used for modeling studies to monitor the isothermal crystallization behavior of fats as a function of time, are differential scanning calorimetry (DSC) [Kel90, Tor02, Van02], nuclear magnetic resonance spectroscopy (NMR) [Klo00a, Ng94] and turbidimetry [Her99, Tor02]. These

techniques differ in their theoretical background, advantages and disadvantages depending on the fat systems and the experimental conditions.

The crystallization kinetics is evaluated by fitting mathematical models to the experimental data and the important parameters connected to nucleation and crystal growth are extracted. So far, a considerable number of models have been used to characterize the isothermal crystallization kinetics of fats, e.g. the Gompertz [Klo00a, Van02] and the Foubert model [Fou03, Fou02] or the most commonly used Avrami model [Her99]. The Gompertz model has been reported to show a better fit to the multiple crystallization peaks of fats than the Avrami model since the Avrami model is meant to fit only a single crystallization peak [Mac06]. The Foubert model is relatively new developed and contains kinetic parameters with, however, unclear explanations.

Sucrose esters are frequently used as additives in food, pharmaceuticals and cosmetics since they are nontoxic, tasteless, odorless and are digested to sucrose and fatty acid in the stomach [Mar04]. It is a nonionic emulsifier which has a wide range of hydrophilic-lipophilic balance (HLB) value. The sucrose ester laurate (L-195) which modifies the crystal habit of coconut oil inhibits the crystallization kinetic of the blend vegetable oils [Yuk90]. There are some reports on the effect of the other sucrose ester types on the crystallization kinetics of fats [Her00, Her96, Mar02, Nas01, Yuk90] where the results were varied and contradicted [Mar04].

The direct application of sucrose ester as well as other additives in crystallization of coconut oil has rarely been published. It was reported that the minor components like lauric acid and diacylglycerols at low concentrations retarded the crystallization kinetic of coconut oil. The quantification was done by using the Arrhenius equation where the effect of supercooling was excluded [Gor91]. The other examples of additives in fat crystallization; retardation effect of diacyl glycerols and phospholipids on the milk fat, palm oil and cocoa butter can be found by Smith, Vanhoutte, Wähnel, and Wright [Smi00, Van02, Wae91, Wri00a, Wri02].

The effect of additives on the nucleation of fat crystals has been explained by the adsorption kinetics of additives on the surface of the nucleus. It was discussed in Boistelle [Boi88] that when the adsorption of an impurity on the surface of the nucleus occurred, the interfacial energy decreases and consequently the nucleation rate should increase. However, it was suggested that impurities or additives also suppressed the growth sites of the nuclei since the amount of growth sites on the nuclei was limited. As a consequence, the development of these nuclei can be drastically reduced by only a few additive molecules even without a significant change in the interfacial free energy. Thus, impurities affect the nucleation rate through the kinetic factor more than through the thermodynamic factor. Accordingly, impurity adsorption always results in a decrease in the nucleation rate.

In addition, the chain length of the additive, nature, number, and position of chemical groups attached on the chain affects greatly the nucleation of fats. Regarding the chain length, it is often stated that the shortest molecules hinder nucleation due to

their higher adsorption rate, whereas the longest molecules hinder growth due to their large number of anchorage sites [Boi88].

Growth occurs in the metastable zone width (MZW) in which its definition and importance has been written in chapter 2.3. In fact, the supersaturation can be controlled more reliably when the metastable zone width is relatively wide [San07]. Consequently, the effect of additives on the metastable zone of fat crystallization must be also taken into account in parallel to the nucleation kinetics. In order to determine the MZW, on- and in-line techniques are needed that enable a fast detection of nucleation and exhibit direct applicability in slurry systems [Oma99, Smi05, Wri00b]. However, only limited knowledge is available on feasible practical techniques in bulk fat crystallization which can be attributed to the complexity of fat compositions and the difficulties in obtaining an accurate state estimation. It was discussed by Lüdecke [Lue03a] that the inline measuring technique of laser beam optical reflectance measurement (ORM) provides more reliable and sensitive information on the nucleation detection of fatty acid mixtures than ultrasound velocity technique. However, there was no information on the saturation point detection and MZW. Moreover, the experiments were carried out at low agitation speeds (<200 rpm). The measurements of both techniques in that study were not conducted and compared under the same conditions.

2.4 Motivation

It is thus a challenge to develop a fractionation process of fats by avoiding the use of hazardous solvents or detergents as written in the section 2.3.2. It is a question that a common solvent like water can be utilized to reduce the viscosity of the oil.

Emulsion crystallization was introduced as an alternative to bulk crystallization in order to improve the purity and the fractionation process of stearic acid and meta-chloronitrobenzene [Cor82, Dav95]. It was found that the emulsion crystallization enabled a melt forming a single crystal within the emulsion droplet so that homogeneous nucleation occurred at a lower rate than in a bulk melt. Thus, it is an advantage to perform this approach in the fractionation of coconut oil as well as the other oils since it requires no special equipments or solvents and hence lowers capital and operating costs in comparison to the other processes.

Emulsions: The dispersion of oil, water and emulsifiers can be produced by various methods. These methods including the formation of emulsions were described by Urban [Urb06a]. To apply the emulsion aspect in the field of fat fractionation effectively, the combination of water and emulsifier should have a significant role in reducing the viscosity of the oil. This concept has been utilized for the pipeline transportation of the high viscous crude oil where the viscosity of the crude oil was reduced by producing crude oil in the oil-in water emulsion state. For economical reasons, it is important to keep the oil concentration of the emulsion as high as possible, while the emulsion viscosity is maintained at a reasonable level [Rim92].

To achieve this, there are certain parameters that are needed to be optimized. It is believed that the more polydispersed the droplet-size distribution is, the lower is the emulsion viscosity for a given disperse phase concentration. The production of emulsion by high pressure results in the very fine and mono disperse droplets [Flo00]. The reduction of the drop size results in an increase in viscosity. This is explainable by several possible reasons, but it is mainly due to the increase of the hydrodynamic interaction and van der Waals interaction forces when the drop size decreases. Smaller droplets are more rigid [Pal96]. Sherman [She59] observed an increase in viscosity when a higher emulsifier concentration was added.

Beside the role of the emulsion on the viscosity, the selected emulsifier should also promote the morphological modification of fat crystals. However, it must be applicable in food and pharmaceutical industries. For this reason L-195 which can modify the crystal habit of coconut oil is a good example as an emulsifier in this work.

2.5 Objectives

The productions of high-melting solid fractions of natural oils or fats are of interest here. To achieve this, a new process was developed and tested for coconut oil. The optimization of the new process is focused on the insight of the crystallization step where the crystallization of fat occurs and how it can be controlled. For this purpose, the objectives of this work are:

1. To investigate the effect of emulsifiers; sucrose ester laurates (L-195) and (L-595) in comparison to the free lauric acid which is the main fatty components of coconut oil, and free stearic acid on the crystallization behaviour of coconut oil by means of:
 - Thermal profile
 - The crystallization kinetics which focuses on the nucleation kinetics
 - Metastable zone width (MZW)
 - Crystal morphology
 - Polymorphic occurrence
 - Shear viscosity
2. To develop the fractionation process in order to achieve the reduction of the liquid oil entrainment by introducing the emulsion crystallization to coconut oil fractionation. The process can be categorized into two steps, as followings:
 - 2.1 The production of coconut oil emulsions by using sucrose laurate L-195 as an emulsifier and water as a disperse phase. The preparation by a static mixer was compared to a rotor stator system. The effects of viscosity on coconut oil emulsions obtained from both techniques were characterized by means of the Ohnesorge number (showing the relation of the viscosity, droplet size, surface tension and density).

2.2 The fractionation of coconut oil emulsion by layer melt crystallization via the cold finger equipment. The solid fractions are the main interest where their properties were examined by means of:

- Melting point
- Solid fat content at 25 °C
- Fatty acid compositions
- Crystal morphology
- Polymorphic occurrence

Along with these factors, crystal growth rate and yields of the fractionation processes were also estimated. The separation efficiency of the emulsion fractionation in comparison to that of the dry fractionation was characterized by the distribution coefficient and mass-related distribution coefficient.

3. Materials, methods and kinetic modelings

3.1 Chemical and instrumental lists

Table 3.1: Chemical list.

Substance	Supplier
Refined, bleached, deodorized (RBD) coconut oil	Ostthüringer Nahrungsmittelwerk Gera, Gera, Germany
Sucrose ester laurate (L-195), HLB value = 1 Content: 1 wt-% monoester 4 wt-% diester 10 wt-% triester 13 wt-% tetraester 27 wt-% pentaester 24 wt-% hexaester 20 wt-% heptaester	Syntapharm Ges. F. Pharmachemie mbH, Mülheim an der Ruhr, Germany
Sucrose ester laurate (L-595), HLB value = 5 Content: 25-30 wt-% monoester 40-45 wt-% diester 22-27 wt-% triester 4-8 wt-% tetraester	Syntapharm Ges. F. Pharmachemie mbH, Mülheim an der Ruhr, Germany
Lauric acid (>98 wt-% purity)	Sigma-Aldrich Chemie GmbH, Munich, Germany
Stearic acid (>98 wt-% purity)	Sigma-Aldrich Chemie GmbH, Munich, Germany
Trimethylsulfonium Hydroxide in methanol (0.2 mol/L) (Methylating reagent for gas chromatography analysis)	TCI Europe, Zwijndrecht, Belgium
Methyl ter-butyl ether (>99% purity) (solvent for gas chromatography analysis)	TCI Europe, Zwijndrecht, Belgium
Standard fatty acid methyl esters mix GLC-10 (20 wt-% cis-9-oleic methyl ester, 20 wt-% methyl linoleate, 20 wt-% methyl linoleate, 20 wt-% methyl palmitate, 20 wt-% methyl stearate)	Sigma-Aldrich Chemie GmbH, Munich, Germany
Standard fatty acid methyl esters mix GLC-30 (20 wt-% methyl decanoate, 20 wt-% methyl laurate, 20 wt-% methyl myristate, 20 wt-% methyl octanoate, 20 wt-% methyl palmitate)	Sigma-Aldrich Chemie GmbH, Munich, Germany

Table 3.2: Instrumental list.

Instrument	Supplier
Differential scanning calorimetry (Mettler Toledo 12E)	Mettler Toledo, Giessen, Germany
Liquisonic30 immersion sensor (2 MHz, 0.1 W)	SensoTech GmbH, Magdeburg, Germany
Optical Reflectance Measurement (ORM)	Messtechnik Schwartz GmbH, Düsseldorf, Germany
Gas chromatography (CP9000)	Chrompack GmbH, Engstingen, Germany
GC column (WCOT, Fused silica 50 mx0.25 mm coating CP-select for FAME)	Varian Deutschland GmbH, Darmstadt, Germany
Light microscope (x100, VHX-500F)	Keyence, Neu-Isenburg, Germany
Light microscope (x16.5, BH2)	Olympus, Tokyo, Japan
X-ray powder diffractometer (D4 Endeavor)	Bruker AXS GmbH, Karlsruhe, Germany
Rotational viscometer (VT550)	Thermo Haake GmbH, Karlsruhe, Germany
Density meter (DE40)	Mettler Toledo, Giessen, Germany
Tensiometer (K10T)	A.KRÜSS Optronic GmbH, Hamburg, Germany
Mastersizer (Mastersizer 2000)	Malvern Instrument GmbH, Herrenberg, Germany
Gear rim disperser (T25 ULTRA-TURRAX®)	IKA® Werke GmbH & Co. KG, Staufen, Germany
Static mixer (Sulzer Quadro™)	Sulzer AG, Winterthur, Switzerland

3.2 Crystallization behaviour of coconut oil in the presence of additives

The model mixtures of RBD coconut oil in the presence of an additive (L-195, L-595, lauric acid and stearic acid) at various concentrations [wt-%] were prepared. Each mixture was molten at 80 °C for 30 minutes before experiments in order to destroy their crystal memories. The same batch of all substances was used throughout the experiments.

3.2.1 Thermal profile analysis

The thermal profile of fat mixtures was studied by differential scanning calorimeter (DSC). DSC is a technique to measure the heat flow difference between a sample and an inert reference as the two specimens are subjected to identical temperature throughout the whole experiment. This DSC is a heat flux DSC where the temperature of the sample and the reference, which are connected to the low-resistant metal disc, are controlled in the same furnace. The DSC was calibrated by using indium and lead (onset temperature 156.6 and 327.5 °C, respectively). Approximately 5.5 mg of each fat mixture was weighted and sealed in an aluminum pan. An empty pan was used as a reference throughout the experiments.

The thermal profile of fat samples was created in 4 steps. First, the sample was held at 80 °C for 10 minutes to destroy its crystal memories, then cooled to -10 °C at a rate of 2 K/min and held for 3 minutes at this temperature. It was then again heated from -10 to 80 °C at the same rate. The crystallization profile of the samples was taken from the cooling cycle. The **melting profile** of the samples was taken from the reheating cycle. The **melting point** of the samples was taken from the peak temperature of the reheating cycle.

3.2.2 Isothermal crystallization kinetics

• Isothermal temperature profile

The sample of each mixture underwent the isothermal run by holding it at 80 °C for 10 minutes to destroy the crystal memories. The melts were then rapidly cooled down to the crystallization temperature at a cooling rate of 10 K/min and isothermally held at this temperature for 30 minutes to observe the crystallization process. Afterwards, the melting thermogram was recorded by heating the sample at a rate of 2 K/min. The isothermal crystallization exothermic was taken for the kinetic modeling. Samples were reused for further experiments by repeating the same procedure before cooling again to the next isothermal temperature. Considering the fact that saturated fats are relatively unreactive and the continuous reheating of the samples have only little influence on their thermal behaviour [Mac06], the results related to a specific concentration were obtained by using the same sample.

• Isothermal crystallization analysis

Of each fat mixture, the complete exothermic peaks obtained from at least 5 isothermal crystallization temperatures were taken to quantify the isothermal crystallization kinetics by using the modified Gompertz equation (Equation 3.1). Figure 3.1A gives an example of exothermic peaks of the RBD coconut oil without additives. This model was originally used to predict bacterial growth. But it is claimable that there are several analogies between bacterial growth and crystal growth. The production of bacteria was comparable with the nucleation and growth of crystals and the consumption of nutrients were referred to the decrease of supersaturation [Klo00a]. The derivation from the original Gompertz equation to the reparameterized version was explained elsewhere [Fou03].

$$F(t) = Ae^{-e^{\frac{\mu(t-\tau)}{A}+1}} \quad (3.1)$$

Where $F(t)$ is the relative percent of the solid fraction crystallized at time t , A is the maximum fraction of solid fat in percent, μ is the maximum increase rate in crystallization (tangent to the inflection point of the crystallization curve) and τ is the induction time (interception of the tangent at the inflection point with the time-axis). The value of $F(t)$ was calculated by integrating the isothermal crystallization peak according to Equation 3.2:

$$F(t) = \frac{\Delta H_t}{\Delta H_{total}} * 100 \quad (3.2)$$

Where ΔH_t is the partial area under the crystallization peak at time t and ΔH_{total} is the total area under the crystallization curve. Normally, ΔH refers to the enthalpy and follows the definition of Equation 3.3:

$$\Delta H = \int_{T_0}^T C_p(T) dT \quad (3.3)$$

The cumulative solid fraction is plotted against time. The induction time of nucleation and the maximum crystal growth rate can be obtained by fitting the Gompertz model to the experimental data as exemplified in Figure 3.1(B):

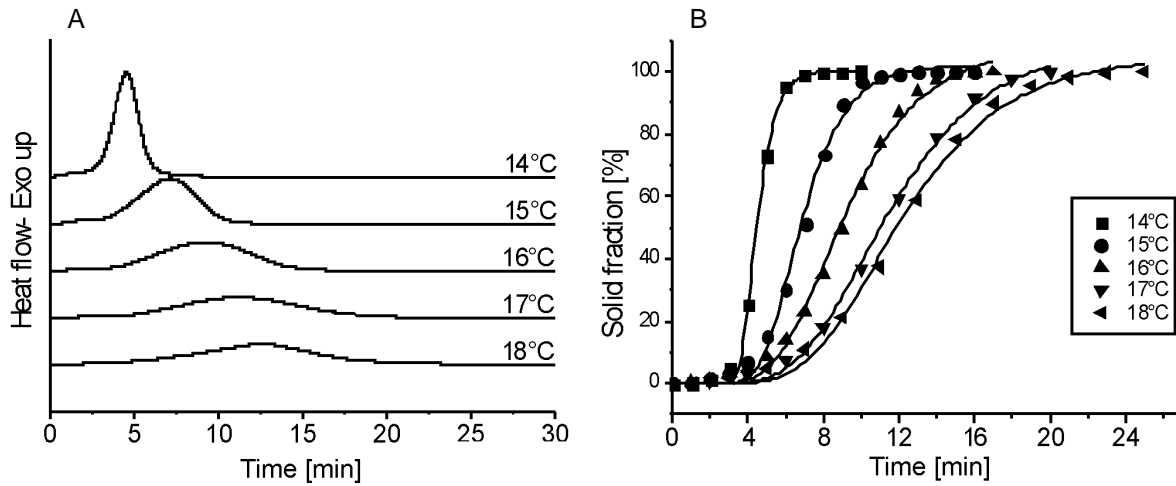


Figure 3.1: (A) isothermal crystallization peak (B) cumulative solid fraction curve of RBD coconut oil at different temperatures as an example system.

• Nucleation kinetics

The induction time of nucleation (τ) is generally taken as the reverse proportion of the nucleation rate (J) which can be used to calculate the activation energy of nucleation. This energy, which represents the energy barrier that a molecule has to overcome in order to develop a stable nucleus, can be evaluated by using the Fisher-Turnbull equation (Equation 3.4) [Ng90]. Nucleation kinetics in terms of the Gibbs free energy calculated from this equation is associated with the degree of supercooling and molecular diffusion. Although, this equation was originally derived for a single component [Tur49], it is applicable in multi-component systems of vegetable oils and milk fats [Che02, Mac06, Ng90, Tor00]:

$$J = \left(\frac{NkT}{h}\right) e^{\left(\frac{-\Delta G_d}{kT}\right)} e^{\left(\frac{-\Delta G_c}{kT}\right)} \quad (3.4)$$

Where J is the nucleation rate, N is the Avogadro number, k is the gas constant per molecule, h is the Planck constant and T is the temperature. ΔG_d is the Gibbs free energy of volume diffusion. For spherical nuclei, ΔG_c is Gibbs free energy of

nucleation which is related to the surface-free energy of the crystal-melt interface (π) and the degree of effective supercooling (ΔT) (Equation 3.5):

$$\Delta G_c = \left(\frac{16}{3}\right) \frac{\pi \Pi^3 (T_m^\circ)^2}{(\Delta H)^2 (\Delta T)^2} \quad (3.5)$$

Where ΔH is the heat of fusion. The effective supercooling (ΔT) which is defined as the difference of the equilibrium melting temperature (T_m°) and the crystallization temperature (T_c), is the driving force of crystallization. The equilibrium melting temperature has been widely used for the characterization of polymers which are also regarded as multi-component systems [Hir93]. It is the thermodynamic quantity defining the melting temperature of an equilibrium crystal with an infinite size. The direct measurement of T_m° is not possible. It can only be determined by extrapolation since polymers never reach a completely crystalline state [Alh02]. T_m° is the intersection of the so-called equilibrium line ($T_m = T_c$) and the apparent melting point (T_m) of the mixtures by using a remelting thermogram recorded after an isothermal crystallization cycle [Hof62] as shown in Figure 3.2. This method was introduced for fat systems [Tor00] since there are several analogies between fats and polymer molecules. Generally, the experimentally determined melting point of fats can be assumed as the melting point considering the fact that fats are crystalline substances and do not undergo glass transition [Cer04]. However, in the fat system containing additives such as sucrose esters, the effect of partial recrystallization and the partly amorphous structure have to be taken into account [Szu07]. As a result, to perform a kinetic study of such a system, the determination of the equilibrium melting temperature is essential.

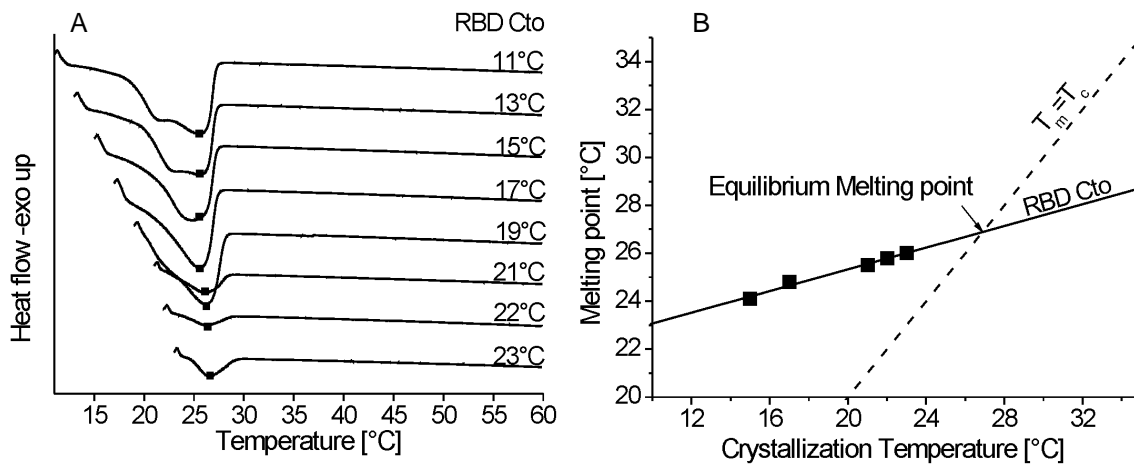


Figure 3.2: An example of the equilibrium melting point determination- (A) remelting thermogram of RBD coconut oil recorded after the isothermal step and (B) the determination of the equilibrium melting temperature of RBD coconut oil.

The main barrier to diffusion in TAG systems is proportional to the probability that a TAG molecule at the crystal surface is in the right conformation for the incorporation into the nucleus. Therefore, the diffusion term (ΔG_d) from Equation 3.4 can be replaced by $\alpha \Delta S/k$ where α is a fraction of molecules that should be in the right conformation for incorporation in a nucleus, ΔS is a decrease of entropy on

crystallization of 1 mole TAGs ($\Delta S = \Delta H/T$) [Klo00a]. Equation 3.4 can be rewritten as follows:

$$\tau^{-1} = J = \left(\frac{NkT}{h}\right) e^{\left(-\frac{\Delta S}{k}\right)} e^{\left(-\frac{16}{3}\right) \frac{\pi T^3 (T_m^\circ)^2}{(\Delta H)^2 kT(\Delta T)^2}} \quad (3.6)$$

After a mathematical rearranging and applying natural logarithm, the relation of induction time and temperature can be deduced as shown in Equation 3.7:

$$\ln \tau T = \ln \frac{h}{Nk} + \alpha \frac{\Delta S}{k} + \left(\frac{16}{3}\right) \frac{\pi T^3 (T_m^\circ)^2}{(\Delta H)^2 kT(\Delta T)^2} = \ln \frac{h}{Nk} + \alpha \frac{\Delta S}{k} + (\Delta G_c) \frac{1}{kT(\Delta T)^2} \quad (3.7)$$

According to Equation 3.7, the linear regression with a positive slope (s) can be obtained from the plot between $\ln \tau T$ and $1/T(\Delta T)^2$. The Gibb's free energy of nucleation is then calculated based on the slope by utilizing Equation 3.8:

$$\Delta G_c = \frac{sk}{\Delta T^2} \quad (3.8)$$

3.2.3 Metastable zone width

The MZW of coconut oil mixtures were determined by an ultrasound velocity detector and an optical light reflection measurement (ORM). These techniques were previously used to measure the nucleation occurrence of fatty acid mixtures as discussed in Chapter 2.3.3. In this present work, these techniques were extended in their applications to measure and compare the nucleation and saturation point of the metastable zone width of coconut oil, influencing by process parameters like agitation speeds, cooling rates and additives under non-isothermal crystallization conditions.

The ultrasound velocity measurement was introduced by Ulrich and Omar [Oma99] as a feasible online measuring device to detect the MZW of salt solutions by monitoring the ultrasound velocity as a function of temperature. According to Equation 3.9, the ultrasound velocity (v) is a function of the density (ρ) and the adiabatic compressibility of the medium (β_{ad}) [Str04].

$$v \approx \sqrt{\frac{1}{\rho \beta_{ad}}} \quad (3.9)$$

The density of oils was reported to show a reverse proportionality to temperature [Rod99], while the adiabatic compressibility is direct proportional to temperature [San05]. Ultrasonic velocity also varies with pressure and concentration.

ORM, similar to FBRM, is a commonly used method to determine particle size distributions. It enables both online and in-situ determinations even in systems exhibiting a high solid concentration [Bar99, Hei08, Kem08]. Its measurement is based on the laser light backscattering technique which determines chord length distributions (CLD). The laser light randomly travels through the measurement zone.

As the beam hits the surface of a particle (crystal), light is backscattered into the probe. Accordingly, the number of counts depends on the concentration of solid particles present in the suspension. So far, laser reflectance measurement has been used in various applications such as the determination of the aggregation and particle size in salt solutions and emulsion systems. This technique has rarely been reported in the context of fat crystallization and the MZW determination of fat. However, it possesses a great potential for detecting the MZW in fat systems due to the wide range of particle size detection from 0.14 up to 2400 microns.

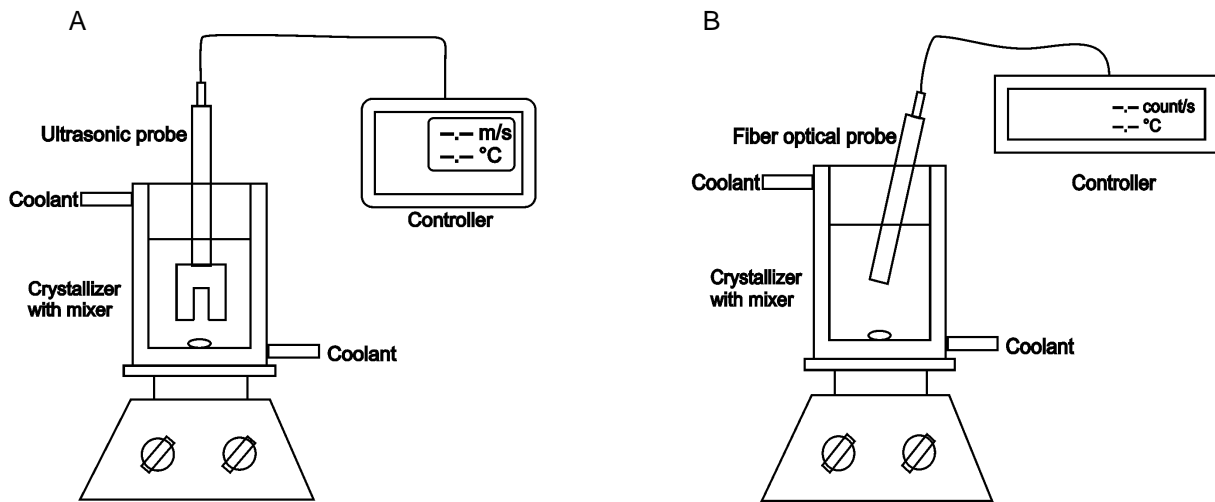


Figure 3.3: The experimental setup of (A) ultrasound velocity measurement and (B) ORM.

The experiments of both techniques were done under the same conditions and the setups were shown in Figure 3.3. An extra thermocouple was equipped with the ORM to detect the on-line temperature as a function of time and particle counts. In order to determine the MZW, 200 g mixture of coconut oil and an additive was filled into a crystallizer (400 ml double-wall beaker). The sensor was then immersed into the melt agitated by a magnetic stirrer. The temperature of the crystallizer was controlled by a programmable thermostat.

The experiment then began by conditioning the melt at 80 °C for 30 minutes. Later on, the melt was subsequently cooled down in a linear mode at 10 K/h with 500 rpm stirring speed until the first nuclei were formed. The melt was immediately heated up to the initial temperature at the same rate. The effect of process conditions like cooling rates on the MZW coconut oil was determined by varying the cooling rate of the programmable thermostat from 5 to 15 K/h at a constant agitation speed of 500 rpm. The effect of agitation speeds was studied by varying the agitation rate from 0 to 700 rpm while the cooling rate was set constant at 10 K/h.

Graphic interpretation of the experimental results

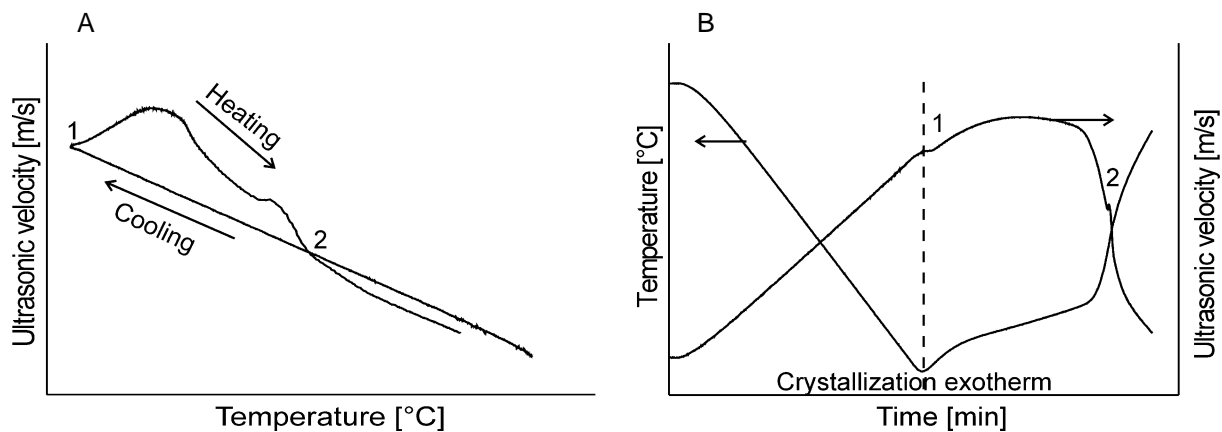


Figure 3.4: Ultrasound velocities as a function of (A) temperature and (B) time.

Figure 3.4 demonstrates the typical graphs of ultrasound velocity versus temperature (A) and time (B). The relation between ultrasound velocity and temperature is characterized by a curve exhibiting one shoulder (Figure 3.4A). The **nucleation temperature** was defined as the temperature value at which a sudden increase of ultrasonic velocity was detected in the cooling cycle (point 1). This point is in good agreement with the crystallization exotherm obtained from the temperature-time curve shown in Figure 3.4B. The temperature at the intersection of the ultrasonic velocity signal from the cooling and reheating cycle was defined as the **saturation point** of the systems (point 2). The maximum allowable supercooling (MZW) was determined as the temperature difference between the saturation and nucleation temperatures.

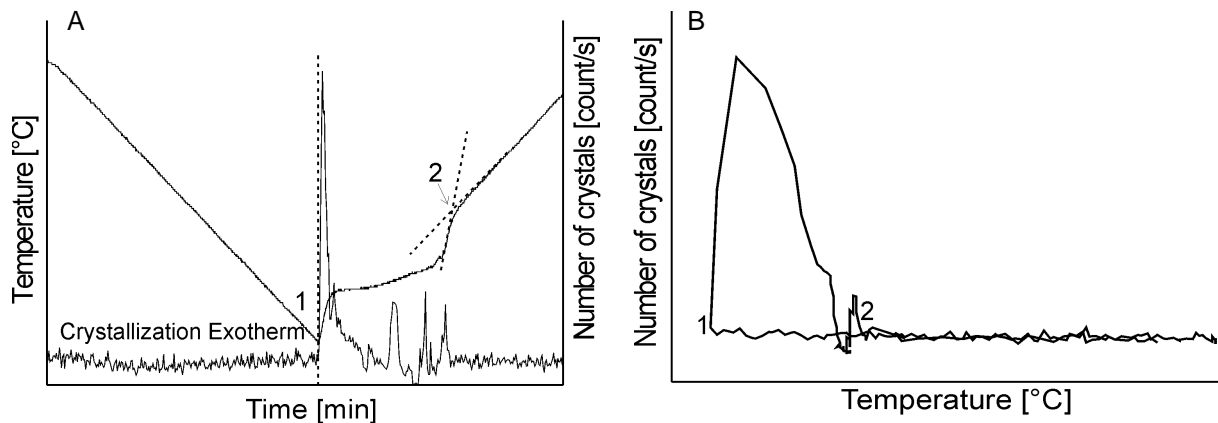


Figure 3.5: Crystal counts per second as a function of time (A) and temperature (B) determined by ORM measurements.

As shown in Figure 3.5A, temperature-time curves obtained from the ORM measurements exhibited the same character as detected via the ultrasound velocity measurements (Figure 3.5B) possessing a sharp crystallization exotherm where nucleation occurs. This point coincides with the last point of the particle-time curve before the great increase of particle numbers indicating that the sensitivity of ORM is sufficient to detect the first solid particles crystallized in the melt (*nucleation point, point 1*). The **saturation temperature** can be estimated by linear fitting of the

temperature-time curve (point 2). The saturation temperature (intersection obtained by linear fitting) is equal to the temperature where the number of the crystals decreases to the initial value. The MZW can also be determined from the curve of particle counts versus temperature (Figure 3.5B) presenting an oscillation at the end. The first point of the peak is related to the nucleation point, while the point where the signal of the reheating cycle is equal to that of the cooling cycle is the saturation point. In this experiment, the MZW is determined based on Figure 3.5A because of the great fluctuation of the crystal counts per second versus temperature curve presented in Figure 3.5B which leads to an inaccuracy of the measurements under certain experimental conditions.

3.2.4 Crystal morphology

To observe the effect of additives on crystal morphology of coconut oil under isothermal crystallization condition, approx. 3 ml of the mixtures was filled into a microscope cell (diameter 3.6 cm) equipped with a programmable thermostat. The temperature of the sample was set to 50 °C constantly for 15 minutes. Afterwards, the sample was cooled to a crystallization temperature with the cooling rate of 1 °C/min. When the crystallization temperature has been reached, the fat sample was kept isothermally. The crystal morphology of the sample after 60 minutes was visualized by a light microscope from Olympus (x 67).

For the fractionation experiments, the solid fractions were left at ambient temperature overnight until the crystals spontaneously grew. Afterwards, the crystal morphology was visualized by a light microscope from Keyence (x100).

3.2.5 Polymorphic occurrence

Table 3.3: The characterizations of α , β' and β polymorphic form based on the angle where the diffraction peak occurs according to Szydłowska-Czerniak [Szy05].

Polymorphic form	Angle [$^{\circ}2\theta$]
α	21.39
β'	21.13, 23.38
β	19.27, 18.97

The polymorphism of fat mixtures was characterized by X-ray powder diffractometer in reflection geometry using Cu $K\alpha_1$ ($\lambda=1.5406 \text{ \AA}$) radiation. The pattern was recorded in the range of 2-45 $^{\circ}2\theta$ for fat mixtures and 2-60 $^{\circ}2\theta$ for fatty acids with a step width of 0.05 $^{\circ}2\theta$ and an acquisition time of 1 s per step. The calibration was carried out with Al_2O_3 . The temperature of the sample holder during the measurement was approx. 30 °C. The fat mixtures were frozen prior to the measurement in order to avoid the remelting of the crystals. The characterizations of α , β' and β polymorphic forms are based on the 2θ diffraction peaks which are summarized in Table 3.3.

3.2.6 Shear viscosity

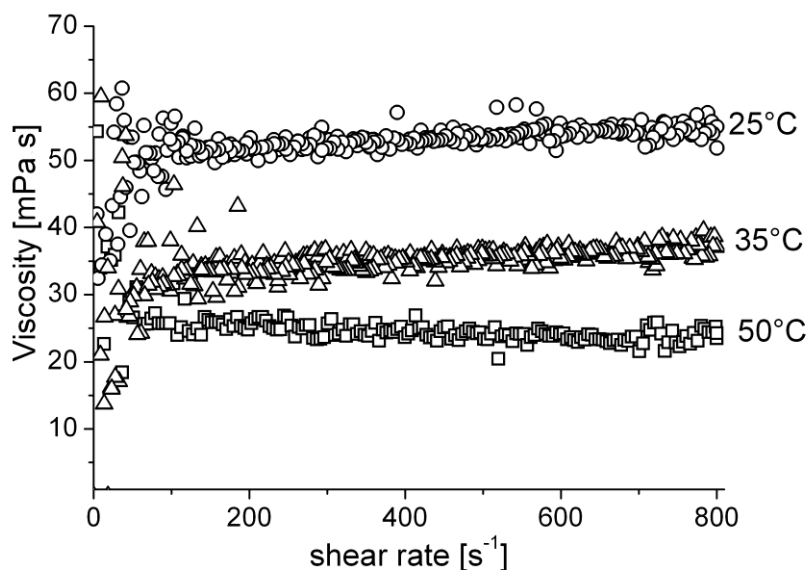


Figure 3.6: Dynamic viscosity of RBD coconut oil determined at 50 °C, 35 °C and 25 °C.

The viscosity of coconut oil is constant with the increasing shear rate from 200 s⁻¹, indicating Newtonian fluid behaviour at the temperature range from 25 to 50 °C (Figure 3.6). Therefore, the viscosity of coconut oil mixtures was measured at the shear rate of 200 s⁻¹. The sample, 50 ml was heated at 50 °C for 30 min in the sample holder of a viscometer. The temperature of the sample holder was cooled down to 25 °C with a cooling rate of 1 K/min. The fat sample was kept at 25 °C for 5 min and the shear viscosity was determined. The measurements were made in triplicate for each composition. Equation 3.10 shows the reciprocal relation between viscosity (η) and density (ρ) [Rod99]:

$$\rho = A + \frac{B}{\sqrt{\eta}} \quad (3.10)$$

3.3 Productions of coconut oil emulsions

60 g of the model emulsions containing RBD coconut oil, 1 wt-% sucrose laurate (L-195) were prepared with various water concentrations from 5 wt % to 35 wt-%. The same batch of coconut oil was used throughout the whole experiment. The oil phase containing L-195 and the water phase were prepared separately and conditioned at 60 °C for 30 minutes. The emulsions were prepared by two methods rotor stator via a gear rim disperser (Figure 3.7A) and a static mixer (Figure 3.7B).

3.3.1 Rotor stator

Emulsions were emulsified by a gear rim disperser at a rotation speed of 8000 rpm for 5 minutes. A gear rim disperser is a commercially emulsifier device. Figure 3.7A presents the scheme of a gear rim disperser. Here, the effective break-up energy is registered in the form of forces of inertia and shearing in turbulent flow. The product

throughput lies in the middle of the available range. The product stress can be classified as medium to high depending on the number of revolutions or the time of emulsifying and the geometry of the rotor-stator systems [Sch04]. More details in operating functions and application of gear rim dispersers can be found by Urban [Urb06b].

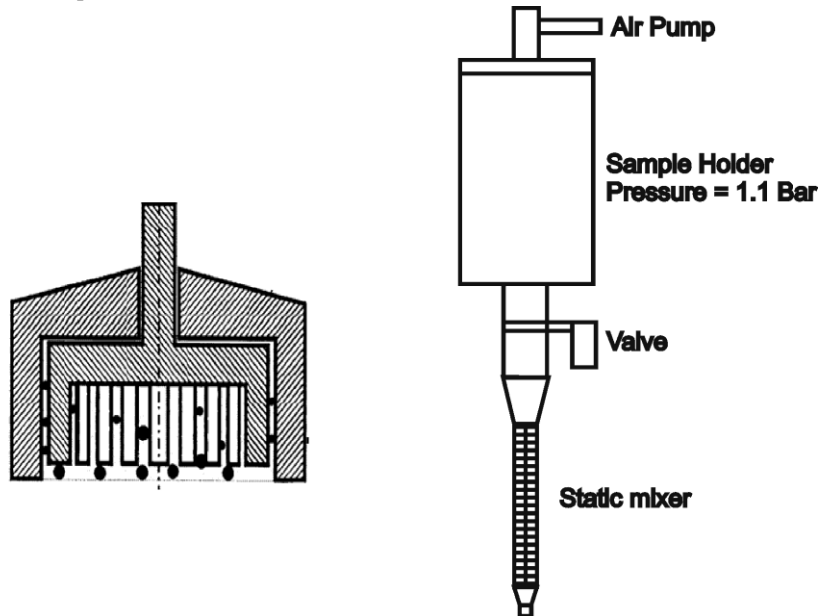


Figure 3.7: Scheme of (A) gear rim disperser [Urb06b] and (B) static mixer.

3.3.2 Static mixer

The mixture was pushed by pressure of about 0.2 bar through a static mixer (inner dimension of 5.3 x 5.3 mm, length of column = 127 mm) containing 24 series of mixed baffles (Figure 3.7B). They are geometrically designed to produce the simultaneously mixing pattern of flow divisions and radial mixings which result in a homogeneous dispersion of the water and oil phase. This process was repeated 15 times for each mixture until the mixture became a homogeneous emulsion.

3.3.3 Characterization of the emulsion process by Ohnesorge number

To characterize the free surface flow behaviour of complex fluids like emulsions, a large number of different forces interacted to the droplets, e.g. viscosity, inertia, gravity and as well as stress must be systematically taken into account. The Ohnesorge number (Equation 3.11) is the dimensionless parameter that predicts and relates the viscosity effect on the surface deformation of the droplets at the conditions of interest. In this work, the effect of emulsion producing techniques and water concentrations on the Ohnesorge number (Oh) of coconut oil emulsions was characterized. It was reported that a low viscous fluid is characterized by $Oh < 1$, at a free surface flow. In such flows, viscosity effects are not important. While at $Oh > 1$, the fluid exhibits a high viscous fluid type where the influence of surface tension and viscosity reacting on the flowing fluids are high [Rod05]:

$$Oh = \frac{\eta}{\sqrt{\rho\sigma L}} \quad (3.11)$$

From Equation 3.11, Oh refers to Ohnesorge number, η is the viscosity of the emulsion taken at 25 °C at the shear rate of 200 s⁻¹. ρ and σ is the density and surface tension of the emulsion measured at 25 °C by densitometer and tension meter, respectively. L is the characteristics length scales which refers to drop diameter in this case and was measured by a mastersizer (Malvern). The operations of these equipments can be found in the laboratory.

3.4 Fractionation of coconut oil emulsions

3.4.1 Cold finger apparatus

The prepared emulsion was subsequently fractionated based on the layer melt crystallization technique of a lab scale cold finger apparatus (Figure 3.8). The principle of this process is based on the temperature difference between the cold surface of the cold finger and the melt. The temperature difference refers to the degree of supercooling which is the driving force for the crystallization at the surface of the cold finger. The cold finger was dipped in a 100 ml beaker containing 60 g of coconut oil emulsion which was agitated by a special designed magnetic stirrer in order to provide the homogeneity of the emulsions. The temperature of the cold finger (diameter of 2.14 cm) was set according to the desired crystallization temperature range with the constant cooling rate of 0.2 K/h. The temperature of the melt and the agitation speed were set constantly at the optimal value of 36 °C and 500 rpm, respectively, throughout the whole experiments.

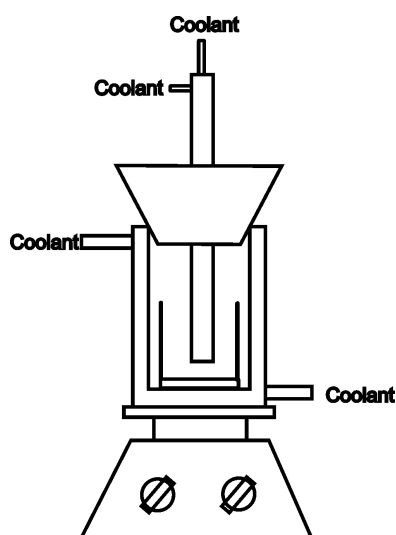


Figure 3.8: Scheme of the cold finger apparatus.

After 2 hours, the cold finger was removed from the melt. The crystalline layer underwent the sweating process for 2 minutes. Afterwards, it was totally removed and dried in an oven at 70 °C overnight to get rid of the water residue. The dried solid fraction was then weight and further analyzed. Its crystals were characterized by a light microscope and XRPD according to chapter 3.2.4 and 3.2.5, respectively.

3.4.2 Process characterizations

• Solid fat content and melting point

The purities and quality of the solid fractions was characterized by means of melting point, solid fat content and fatty acid compositions of the solid fractions. The determination of the *melting point* of fat samples was written in chapter 3.2.1. *Solid fat content* (SFC) is an empirical value which measures the ratio of fat in crystalline form to liquid at various specified temperatures which was as well determined by DSC. According to the temperature profile in chapter 3.2.1, the partial area under melting endotherms during the second heating segment (step 4) was integrated [Men00]. The area under the peak is reported to be proportional to the solid fat content at a selected temperature [Lop06]. The values of SFC given in this work are referred to the SFC at 25 °C.

• Fatty acid compositions

Fatty acid compositions of the solid fractions were analyzed by gas chromatography. 2 mg of fat sample was prepared in a sample holder with a septum lid. 200 µl of Ter-butyl methyl ether was added to the prepared fat sample as a solvent. The methylation of the fat sample was started by adding 100 µl Trimethylsulfonium hydroxide (TMSH). The sample was mixed in the ultrasonic bath at 30 °C prior to the analysis. The stationary phase was high polar column made of the cyanopropyl phase coating on fused silica capillary column. Nitrogen gas was used as the mobile phase. The analysis condition was set as follows: 0.7 µl of sample solution, temperature of injector 270 °C, split ratio of 1:60, temperature of the flame ionization detector (FID) 280 °C. The temperature program was set to be at 70 °C for 5 minutes and heat to 225 °C at the heating rate of 4 K/min. After each measurement, the column was heated to 250 °C for 15 minutes to get rid of impurities and residues. The measurement of each sample was repeated 3 times. The standard mixtures containing equal concentrations (20 wt-%) of saturated fatty acid methyl esters (FAMES) C8-C18 and unsaturated FAMES C18:1-3 were prepared to define the retention time. Table 3.4 shows the retention time and the relative percentages of FAMES in the GC standard mixture from which the correction factor of each FAME corresponding to the sensitivity of the detector was calculated according to Hlongwane [Hlo01] as shown in Equation 3.12:

$$F_i = \frac{A_{Palmitic acid}}{A_i} \quad (3.12)$$

Where the calculation of the correction factor (F_i) is based on the ratio of the peak area of the methyl ester of palmitic acid as a reference ($A_{Palmitic acid}$) and the peak area of the FAME (A_i) quantified from the chromatogram of the standard FAME mixtures.

The calculated correction factors were then used to normalize the GC peak areas in the analysis prior to relative percent calculation according to Equation 3.13:

$$\% A_i^{cr} = \frac{A_i^o F_i}{\sum_{i=1}^{i=n} A_i^o F_i} \times 100 \quad (3.13)$$

Where A_i^{cr} is the corrected relative percentage of FAME, A_i^o is the peak area of FAME and F_i is its correction factor.

Table 3.4: Retention time, relative percent from GC peaks of standard FAMEs.

F.A.M.E.	8	10	12	14	16	18	18:01	18:02	18:03
Retention time [min]	15.1±0.04	20.8±0.03	25.9±0.02	30.5±0.01	34.6±0.00	38.3±0.00	39.0±0.00	40.1±0.00	41.5±0.01
Relative percent [%]	19.0±0.47	19.7±0.12	20.0±0.21	20.6±0.20	20.6±0.35 ¹ , 19.9±0.61 ²	20.4±0.44	20.3±0.34	19.8±0.40	19.6±0.28
Correction factor	1.09	1.05	1.03	1	1	0.98	0.98	1.01	1.02

¹ For the calculation of correction factors of fatty acid C8-16. ² For the calculation of correction factors of fatty acid C16-18:03.

It must be noted that the lauric acid part of the sucrose laurate (L-195) can be methylized with the methyl agent resulting the lauric acid peak in the chromatogram as well as the lauric acid from the coconut oil. The peak area chromatogram of the pure sucrose lauric acid solution indicated that 1 g of sucrose laurate deliberated approximately 1.34 g of lauric acid. As a consequence, the content of lauric acid from sucrose laurate was subtracted from the lauric acid peak area of the samples containing sucrose laurate.

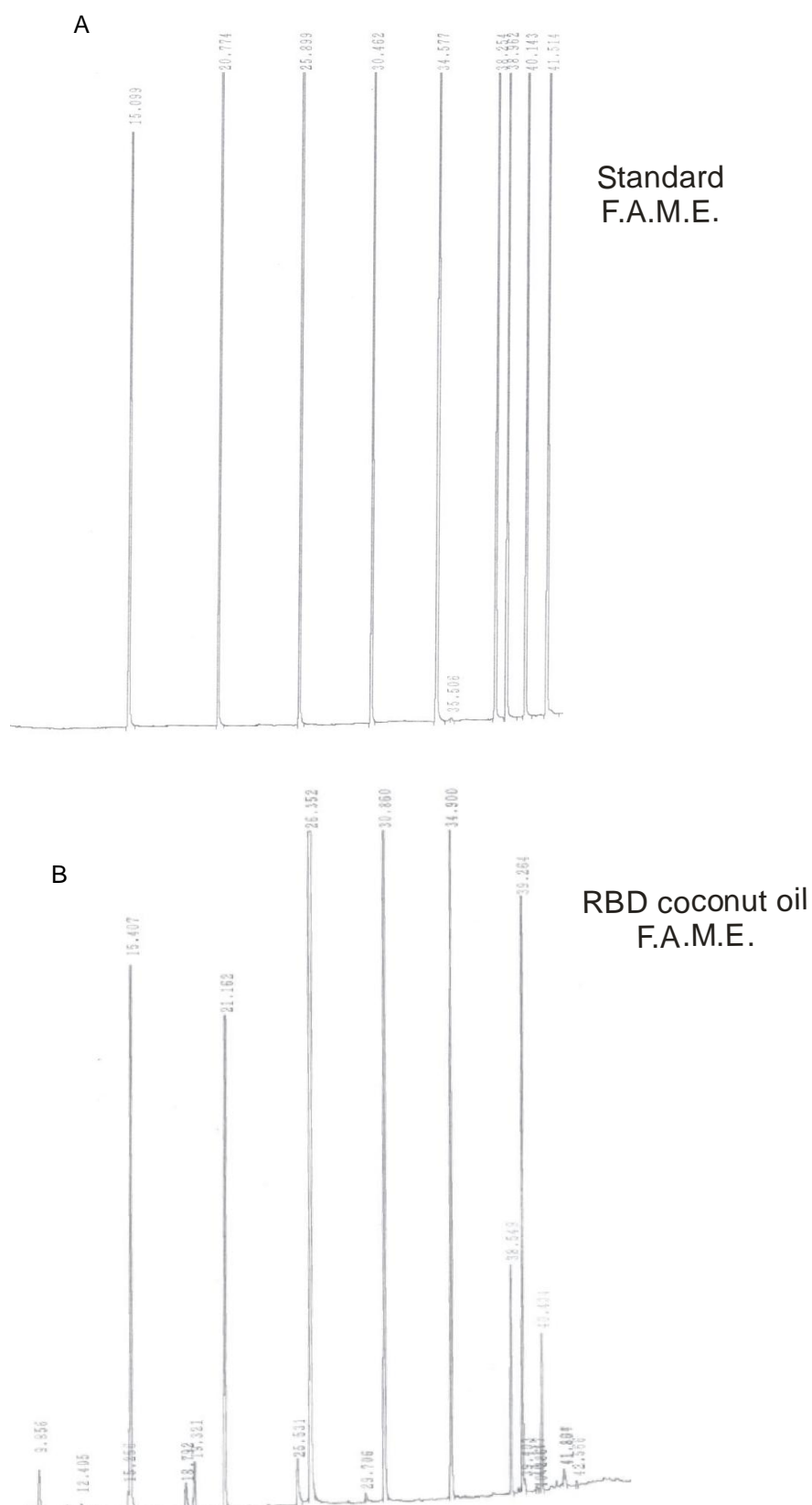


Figure 3.9: Chromatograms of (A) the standard fatty acid methyl esters (FAMES) and (B) RBD coconut oil.

• Crystal growth rate

The overall crystal growth rate [$\text{kg}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$] was calculated via Equation 3.14 [Chi03]:

$$R_G = \frac{dM_c}{A_c dt} \quad (3.14)$$

Where R_G is the crystal growth rate (assumed as a constant crystal growth rate), M_c is the mass of crystal deposited on the surface of the cold finger [kg], A_c is the surface area of the cold finger [m^2] ($A_c = 2\pi rL + \pi r^2$) and t is the crystallization time [s].

• Yield of crystallization

The crystallization *yield* [%] was calculated via Equation 3.15:

$$Yield = \frac{M_{solid}}{M_{oilfeed}} \times 100 \quad (3.15)$$

Where M_{solid} is the mass of the dried solid fraction [g] and $M_{oilfeed}$ is the mass of the oil phase of the initial feed [g].

• Effective distribution coefficient

For industrial crystallization, the effective distribution coefficient (K_{eff}) is a common-used parameter to evaluate and indicate the separation efficiency of the process referring to the purity of the solid products. The derivation of this parameter was written by Lüdecke [Lue03a]. It was defined as the ratio of the total impurity content in the solid crystals (C_l^S) to the total impurity content in the initial feed (C_l^F) according to Equation 3.16:

$$K_{eff} = \frac{C_l^S}{C_l^F} \quad (3.16)$$

The impurity in this work refers to saturated fatty acids C8 to C10 and unsaturated fatty acids C18: 1 to C18:3 regarding their low melting point. The concentration in this part was measured by GC according to chapter 3.4.2.

• Mass-related effective distribution coefficient

To compare the separation efficiency of different processes and conditions, the yield of the process as well as purity must be taken into consideration. The mass related distribution coefficient (K_{m-eff}) has been introduced by Lüdecke [Lue03a] and applied here:

$$K_{m-eff} = \frac{K_{eff}}{Yield} \quad (3.17)$$

4. Results

4.1 Effects of additives on crystallization behaviour of coconut oil

4.1.1 Melting profile

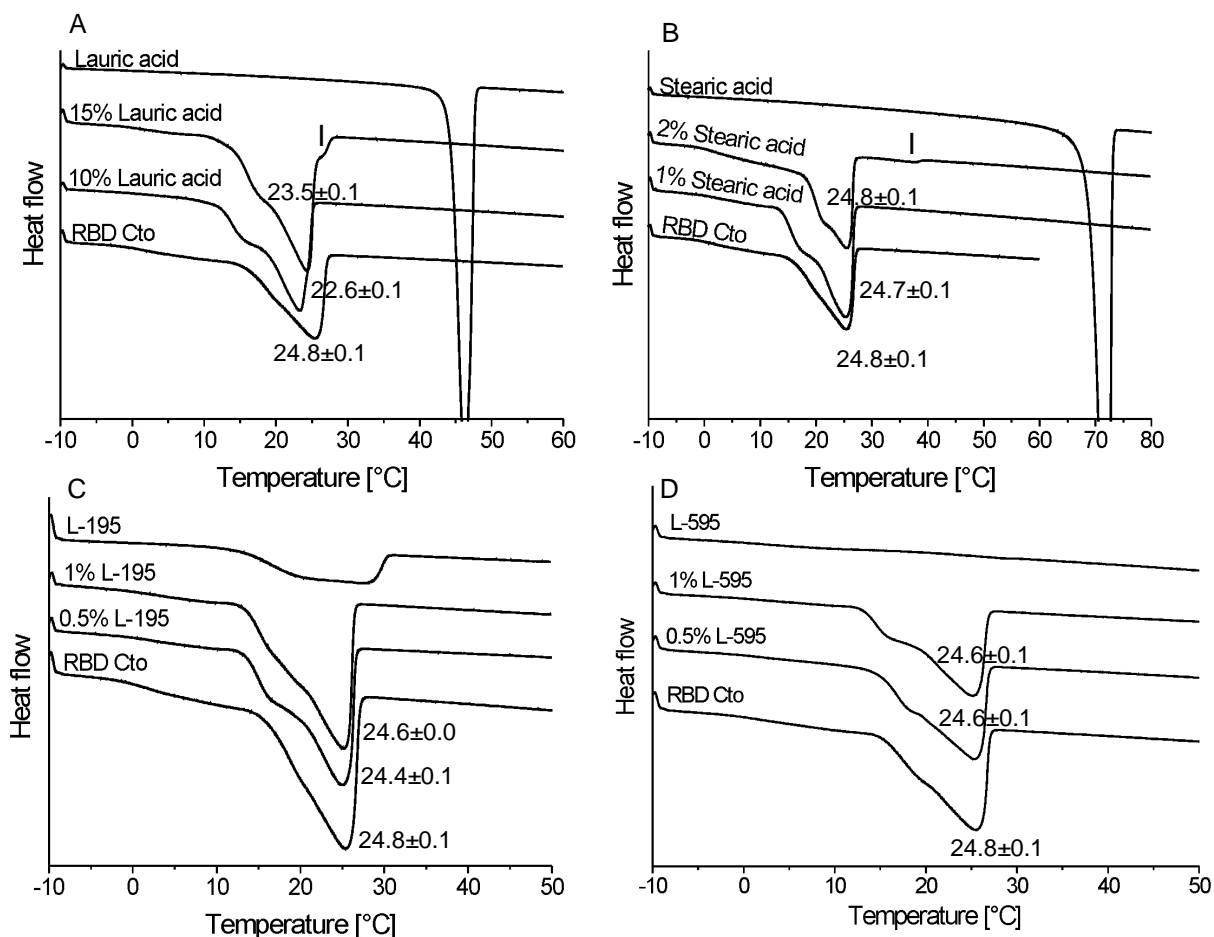


Figure 4.1: Melting profiles of (A) RBD coconut oil in the presence of lauric acid, (B) stearic acid, (C) L-195 and (D) L-595.

In general, the melting curve of coconut oil is relatively simple with one major endotherm at 24.83 °C and a small shoulder on the lower temperature side. The melting curves of coconut oil in the presence of two concentrations of lauric acid (Figure 4.1A) and stearic acid (Figure 4.1B) are compared to the melting profile of the pure coconut oil and the pure fatty acids. Both fatty acids have higher melting points than coconut oil. The melting profiles of coconut oil in the presence of these fatty acids exhibit one major peak similar to that of the pure coconut oil. But the endothermic peak of the coconut oil systems containing lauric acid slightly shifts to the lower temperature, while no significant change is found in the stearic acid systems. However, a small peak (I) can be noticed on the right side of major endotherm for 15 wt-% lauric acid and at 38 °C for 2 wt-% stearic acid system. This peak is believed to be the fatty acid endotherms.

The melting profiles of coconut oil in the presence of a sucrose laurate with HLB value of 1 (L-195) and 5 (L-595) in comparison to that of the pure coconut oil and the pure sucrose Laurates are shown in Figure 4.1C and D, respectively. The addition of

L-195 and L-595 in coconut oil at these concentrations did not affect the melting behaviour of coconut oil unlike the fatty acid additives. The concentration of sucrose ester in this study is not exceeding the maximum level of 2 wt-% according to the European Parliament and Council Directive 95/2/EC [Uni95]. It is noted that the melting profile of both sucrose laurate types do not exhibit a clear endothermic peak. Especially, there is no melting transition occurred the case of L-595. The main difference between both sucrose laurate is the monolauric acid ester content (Table 3.1, Chapter 3.1) in the composition that determines the HLB value.

In general, the sucrose esters of the low melting fatty acid like lauric acid exhibit unclear melting behaviour unlike sucrose esters of the longer chain fatty acid. Since the lauric acid molecule is much smaller than the polar side of the sucrose molecule, the penetration of the lauric acid chain increases the space available for the polar head groups. This causes in a large distance and hence a weak force between the polar head groups [Lar92]. Therefore, the molecular orientation for the crystallization is relatively complicated due to the hydrophobic shielding effect. More endothermic peaks should be observed in the case of sucrose ester with low HLB values due to the higher variety of esterification degree [Szu07]. The low degree of esterification in L-595 results in a larger number of positional isomers of the OH- group of the sucrose molecules and hence a more unclear melting behaviour than L-195.

4.1.2 Isothermal crystallization kinetics

Equilibrium melting temperature

Equilibrium melting temperature of the fat mixtures evaluated according to the Hoffman-Weeks method (Figure 4.2) shows a very good linearity of the data plots ($R^2 > 0.85$). In this work, the equilibrium melting temperature (T_m°) of the fat mixtures is always higher than the melting point obtained from the experiments (T_m , see Chapter 4.1.1). This can be explained by the fact that T_m° is based on the calculation referring to perfect crystalline state, while T_m is related to the formed crystals under the applied experimental conditions.

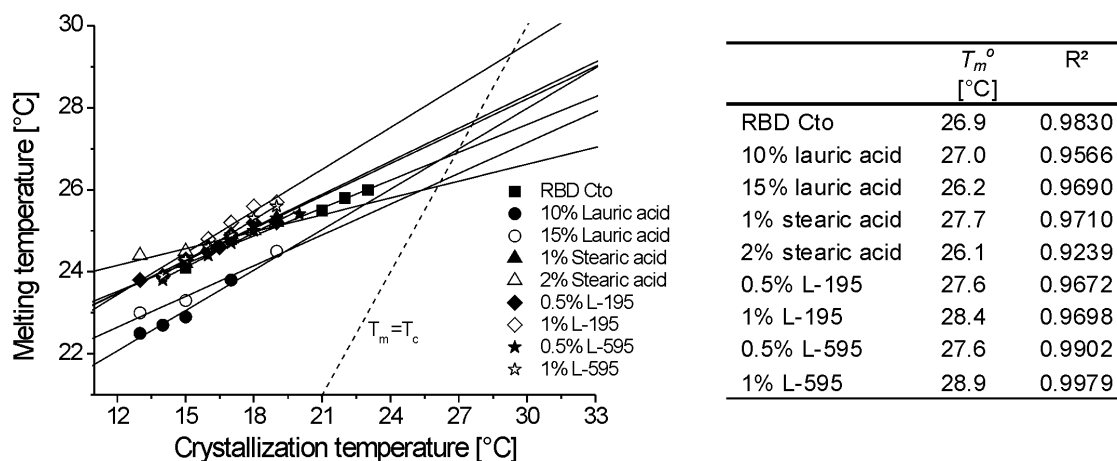


Figure 4.2: Determination of equilibrium melting temperature according to the Hoffman-Weeks method (T_m : melting point obtained from experiments; T_m° : equilibrium melting temperature).

The equilibrium melting point of coconut oil mixed with lauric acid and stearic acid did not significantly alter from that of the pure coconut oil system. In contrast, the equilibrium melting point elevation of coconut oil was observed with the addition of both sucrose laurate types. In addition, the T_m° of coconut oil slightly increased as a function of the sucrose laurate concentrations.

Isothermal crystallization kinetics

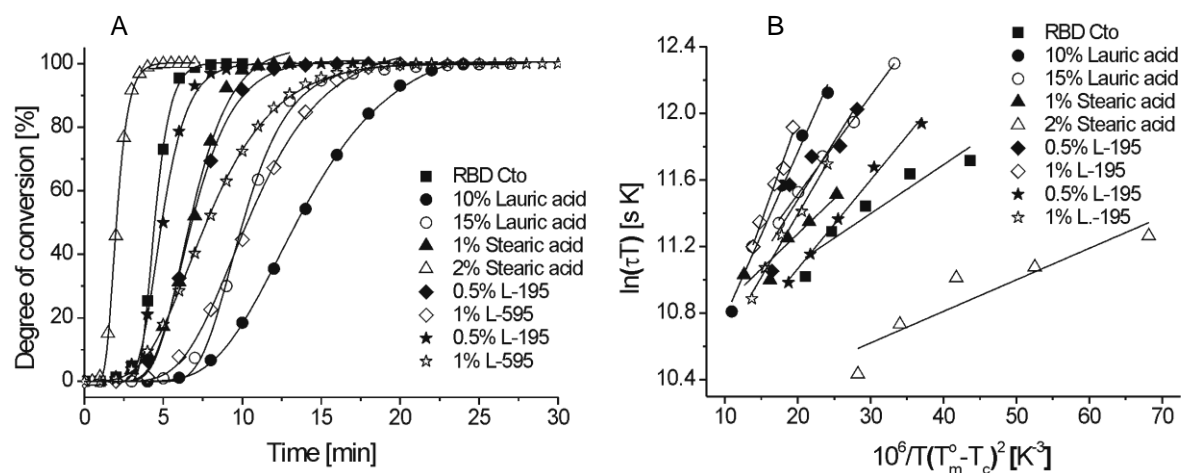


Figure 4.3: Model fittings of the crystallization data of coconut oil in the presence of different additive concentrations. (A) Gompertz model fitted to the crystallization data of the mixtures at 14 °C. (B) Fisher-Turnbull model fitted to the nucleation data of the same fat systems.

Figure 4.3 shows the kinetic model fittings to the crystallization data of coconut oil in the presence of additives. The correlation coefficients of the plots in Figure 4.3A indicate that the Gompertz model fits perfectly to the crystallization data of these fat mixtures. A fairly good linearity of the plots of the Fisher-Turnbull equation reveals that the nucleation kinetics of the fat systems containing additives can be predicted by the Fisher-Turnbull equation (Figure 4.3B). The kinetic parameters and the correlation coefficients of the kinetic model fittings are summarized in Table 4.1.

Table 4.1: Kinetic parameters quantified by the Gompertz and Fisher-Turnbull equations according to Figure 4.3.

Fat mixture	A^a	μ^a	τ^a	ΔG_c^a	R^2	R^2
	[%]	[%/min]	[min]	[kJ.mol ⁻¹]	Gompertz ^a	Fisher ^a
RBD Cto	100.36	55.35	3.55	1.48	0.9987	0.8925
10 wt-% lauric acid	107.10	9.69	8.27	4.87	0.9996	1.0000
15 wt-% lauric acid	99.79	18.29	7.29	3.31	0.9990	0.9973
1 wt-% stearic acid	105.33	55.32	4.47	1.87	0.9942	0.8983
2 wt-% stearic acid	100.26	72.59	1.34	1.08	1.0000	0.8570
0.5 wt-% L-195	102.11	28.09	6.15	3.15	0.9930	0.8442
1 wt-% L-195	105.65	12.11	6.18	4.93	0.9991	0.9861
0.5 wt-% L-595	100.06	33.73	3.42	2.38	0.9992	0.9930
1 wt-% L-595	100.61	12.57	3.73	2.80	0.9998	0.9903

^a Abbreviations- A : the maximum fraction of solid fat; μ : the crystallization rate; τ : the induction time of nucleation; ΔG_c : the Gibb's free energy of nucleation; R^2 : the correlation coefficient.

The quantification of crystallization kinetics using the Gompertz model yielded the kinetic parameters in terms of the maximum fraction of solid fats (A), induction time of nucleation (τ) and the crystallization rate (μ). The maximum fraction of solid fats (A) quantified by Gompertz model has no significant meaning to the kinetic studies. It represents the maximum fractions that solid crystals can be crystallized at a certain temperature resulting from the model fitting. The induction time of the nucleation is an important parameter which is generally connected to the nucleation kinetics.

As summarized in Table 4.1, the induction time (τ) of nucleation of coconut oil increased with the addition of all additives. The addition of lauric acid resulted in the longest induction time of coconut oil nucleation, following by L-195, L-595. The addition of the lauric acid and stearic acid at higher concentrations (15 wt-% and 2 wt-%, respectively) caused the reduction of induction time. Especially, the induction time of the coconut oil mixed with 2 wt-% stearic acid is shorter than that of the pure coconut oil. The addition of both sucrose laurate types influenced the induction time of coconut oil nucleation in the similar way. The increasing of sucrose laurate concentration did not further affect the induction time of coconut oil. The information on induction time of nucleation was further taken, together with equilibrium melting point, to evaluate the Gibb's energy of the nucleation by Fisher-Turnbull equation.

Gibb's free energy (ΔG_c) calculated based on the induction time and equilibrium melting point of the fat mixtures gave results in the similar fashion to the induction time of nucleation but more meaningful. The elevation of ΔG_c value of the coconut oil by the additives was observed, excepted the fat system containing 2 wt-% stearic acid. It can be seen that the fat systems containing lauric acid and L-195 exhibited relatively the largest value of Gibb's energy and following by L-595 and stearic acid. The larger value of Gibb's energy implies that the energy barrier that the molecules need to overcome and achieve the nucleation is higher and hence the nucleation process occurs slower in a system containing additives compared to a pure melt. This allows the conclusion that all additives have inhibition effects on the nucleation of coconut oil. This effect also depends on the concentration of additives in the fat system. Increasing of both fatty acid concentrations resulted in the decrease of Gibb's energy of coconut oil, especially in the case of 2 wt-% stearic acid addition whose Gibb's energy was lower than that of the pure coconut oil. In contrast to the induction time of nucleation, Gibb's energy of coconut oil in the presence of L-195 and L-595 was larger when both sucrose laurate types were presented at the higher concentration in coconut oil.

The maximum crystallization rate (μ) which was quantified by the Gompertz model is the kinetic parameter showing a reverse tendency to the induction time (τ) and Gibb's energy. This is due to the crystallization rate being dependent on the number of nuclei available for crystal growth. The longer the induction time is, the slower is the crystallization rate. As a result, the crystallization rate of the coconut oil was suppressed by the presence of additives, except stearic acid. The dependency of the

crystallization rate on the Gibb's energy and concentration of the additives can be clearly seen in the system containing L-195 and L-595.

4.1.3 Metastable zone width

The detection of nucleation and saturation temperature referring to the metastable zone width (MZW) of fats is essential to define effects of composition, additives as well as process parameters like cooling rate and agitation on the fractionation process as written in Chapter 2.3. In this study, the effects of process parameters and additives on the metastable zone width of coconut oil were determined by ultrasound velocity measurement and ORM according to Chapter 3.2.3. The results of both techniques were compared.

• Influence of cooling rate

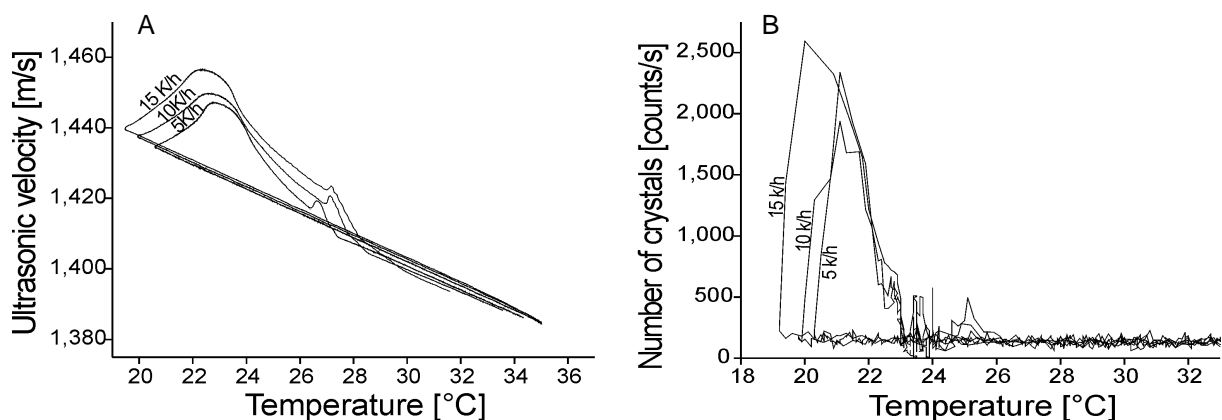


Figure 4.4: Effect of cooling rate on the MZW of coconut oil detected by (A) the ultrasound technique and (B) by ORM.

Ultrasound velocity increases linearly through the melt with decreasing temperature until the nuclei are formed (Figure 4.4A). It can be explained by the fact that nucleation leads to a decrease in the density or the adiabatic compressibility of both of the liquid phases [Klo00b]. Figure 4.4B depicted the number of the crystals counted as a function of temperature by ORM. The sharp increase of the peak refers to the presence of crystals, while the signal intensity falls back to the baseline value when all particles are molten in the reheating cycle.

Figure 4.4 clearly demonstrates the shift of the nucleation point to lower temperatures when increasing the cooling rate for both measuring techniques. This tendency, however, is better visualized by the ultrasonic curves (Figure 4.4A), while Figure 4.4B reveals a high disturbance of the ORM signal. In general, the nucleation point of a binary system can be shifted by varying the process parameters such as cooling rate. Whereas, process conditions have no impact on the saturation point in case of aqueous solutions [Chi03]. The experimental results revealed that a cooling rate of 15 K/h increased the saturation point of the model system.

Table 4.2: Effect of cooling rate on the MZW of coconut oil.

Nominal cooling rate [K/h] [†]	T _n [°C] [‡]		T _s [°C] [‡]		MZW [‡]	
	Ultrasound	ORM	Ultrasound	ORM	Ultrasound	ORM
5	20.51 ± 0.18	20.30 ± 0.00	27.12 ± 0.03	27.07 ± 0.02	6.61	6.77
10	20.00 ± 0.21	19.73 ± 0.06	27.75 ± 0.11	27.66 ± 0.05	7.76	7.93
15	19.53 ± 0.06	18.87 ± 0.35	28.21 ± 0.09	28.79 ± 0.37	8.68	9.92

[†] Nominal cooling rate were set on the programmable thermostat

[‡] T_n = nucleation temperature; T_s = saturation temperature; MZW = T_s-T_n

The ultrasonic sensor detects the nucleation point at higher temperatures than ORM which can be attributed to higher sensitivity of the ultrasonic probe (Table 4.2). As a consequence, the MZW of coconut oil detected by the ultrasound velocity sensor is significantly more narrow compared to the data obtained by ORM. The results summarized in Table 4.2 indicate that both of the applied measuring techniques detected a broadening of the MZW with increasing cooling rate. This is in good agreement with the findings of Ulrich and Strege [Ulr02].

• Influence of agitation speed

Table 4.3: Effect of agitation speed on the MZW of coconut oil.

Agitation Speed [rpm]	T _n [°C]		T _s [°C]		MZW	
	Ultrasound	ORM	Ultrasound	ORM	Ultrasound	ORM
0	18.31 ± 0.01	18.97 ± 0.06	28.89 ± 0.01	27.1 ± 0.94	10.57	8.14
200	20.53 ± 0.18	19.70 ± 0.17	28.83 ± 0.06	28.2 ± 0.15	8.31	8.46
500	20.00 ± 0.21	19.73 ± 0.06	27.75 ± 0.11	27.7 ± 0.05	7.76	7.93
700	20.07 ± 0.12	19.57 ± 0.06	27.70 ± 0.04	27.9 ± 0.16	7.63	8.30

The results included in Table 4.3 indicate that both techniques detect nucleation at higher temperatures in an agitated melt. This can be explained by the fact that agitation provides a rapid and hence more efficient heat and mass transfer. Therefore, nucleation also occurs faster in an agitated system. On the other hand, it is well-known that the first nuclei crystallize near to the wall and the bottom of the reactor. As a consequence, a static supercooled melt is not homogeneous. The nuclei can easily settle without agitating the melt. Considering that the ORM sensor has a measuring zone of 1 mm, it is reasonable to assume that there are some particles located out of this zone which cannot be detected by the sensor in a static system. The evaluation of the experimental results reveals that the ultrasound velocity measurements detected a significant increase of the nucleation temperature and a more narrow metastable zone when applying an agitation rate of 200 rpm, while increasing the agitation rate above this value has no considerable effect on the nucleation point.

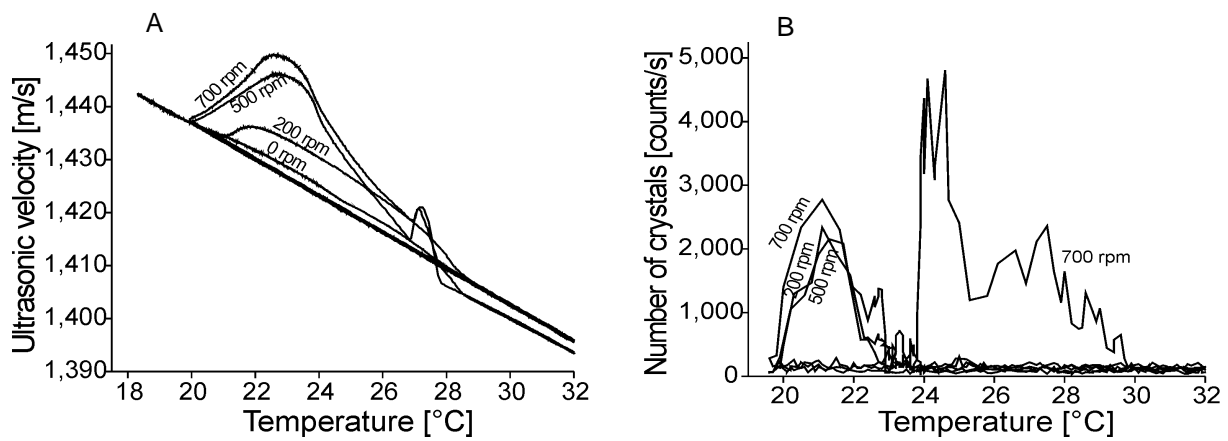


Figure 4.5: Effect of agitation on the MZW of coconut oil detected by (A) ultrasound velocity technique and by (B) ORM.

Figure 4.5A demonstrates that the nucleation temperature detected by both techniques increases when applying agitation during the crystallization process. The graph indicates that the ultrasound velocity signals of the cooling and heating cycles of the system without agitation are only slightly different. The graphic interpretation of the data also confirms that the variation of the agitation rate (500 or 700 rpm) has no significant effect on the nucleation point. Figure 4.5B, however, shows a sequence of large peaks at the agitation rate of 700 rpm. The descent of saturation point with the increment of agitation speed could be detected by the ultrasound technique, while ORM provided an unclear trend due to a scattered signal.

• Influence of lauric acid

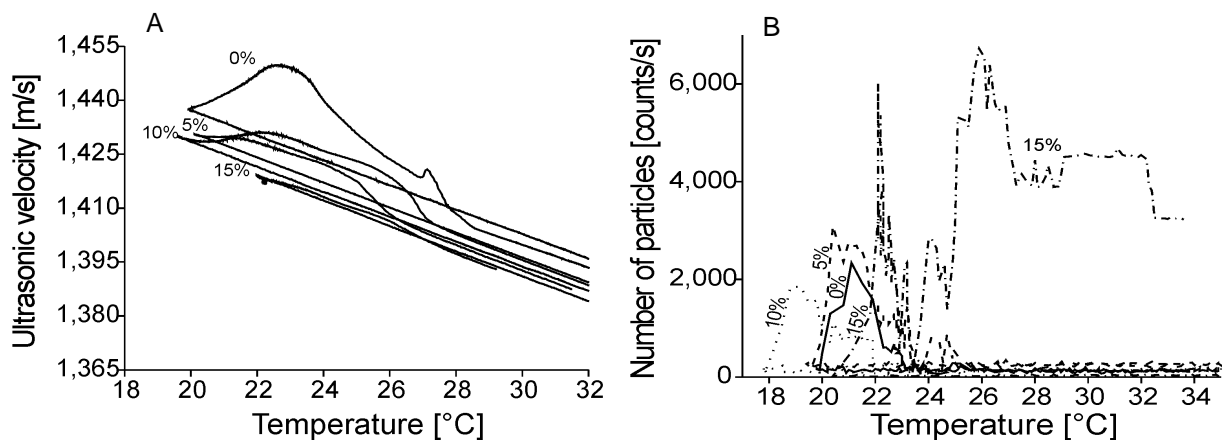


Figure 4.6: Influence of lauric acid on the MZW of coconut oil determined by (A) ultrasound technique and (B) ORM.

Figure 4.6A demonstrates higher values of ultrasound velocity in a pure melt compared to those containing lauric acid. The effect is more pronounced when increasing the lauric acid concentration. In addition, the shoulder becomes smoother when increasing the lauric acid content. The data obtained by the ORM technique displays a similar tendency (Figure 4.6B). The particle curve generated at 15 wt-% lauric acid concentration shows a great fluctuation in the particle number and the intersection of the signal obtained from the heating and cooling cycles cannot be identified (Figure 4.6B). The ultrasound velocity measurements performed at the

highest additive concentration (15 wt-%) also provided a curve displaying a different character than at lower concentrations.

According to Table 4.4, both methods detected similar values for the nucleation and saturation temperatures of the mixtures. However, the ultrasound technique still detected the temperature change earlier than the ORM method. Increasing the concentration of lauric acid to 10 wt-% resulted in the depression of the nucleation point. An addition of lauric acid affects the saturation temperature of the melt in the same manner as described for the nucleation temperature. The saturation temperature decreases as the amount of lauric acid is increased up to 10 wt-% in concentration. When more than 15 wt-% lauric acid is present, the saturation temperature increases but less dramatically than the nucleation temperature.

Table 4.4: Effect of lauric acid concentration on MZW of coconut oil.

Lauric acid [wt-%]	T_n [°C]		T_s [°C]		MZW	
	Ultrasound	ORM	Ultrasound	ORM	Ultrasound	ORM
0	20.00 ± 0.21	19.73 ± 0.06	27.75 ± 0.11	27.66 ± 0.05	7.76	7.93
5	20.21 ± 0.10	19.43 ± 0.06	27.36 ± 0.06	27.26 ± 0.02	7.15	7.83
10	19.37 ± 0.31	17.77 ± 0.06	26.35 ± 0.06	26.21 ± 0.17	6.98	8.45
15	22.51 ± 0.05	20.43 ± 0.25	26.80 ± 0.10	26.79 ± 0.08	4.29	6.36

It was observed that there were colloid-like particles suspended in the mixture during the cooling cycle that caused a sudden decrease in the ultrasound velocity signal at the temperature of 22.51 °C. However, the further cooling of the mixture resulted in a second stage of nucleation at a temperature of about 19 °C. The nucleation at this temperature is similar to the one of the coconut oil mixture in the presence of low lauric acid concentrations. Therefore, the nucleation point matching this mixture in Table 4.4 results from the temperature where the change of ultrasound velocity signal can be detected.

Up to this point, it can be clearly seen from the materials and instrumentation used here that the ultrasound velocity technique yielded better graphical reproducibility and more sensitive to the solid-liquid state change than ORM. As a consequence, the determination of MZW of coconut oil in the presence of the other additives was done by the ultrasound velocity measurement technique only. The effects of different additives on MZW of coconut oil detected by ultrasound velocity measurement were evaluated.

• Influence of stearic acid

The addition of stearic acid at 1 wt-% concentration in coconut oil lowers the ultrasound velocity signal of the coconut oil as can be seen from Figure 4.7. But a further increase of the stearic acid concentration has no significant influence on the ultrasound velocity. The detected nucleation point and also saturation point of this fat mixture slightly shifts to higher temperatures. The ultrasound curve of the coconut oil mixed with stearic acid exhibits a similar behaviour to that of lauric acid addition

showing the smooth curve at a low additive concentration. The curve of 2 wt-% stearic acid concentration displays a different character than that at lower concentrations with a very small loop. Moreover, both detected nucleation and saturation points greatly shift to the higher temperatures.

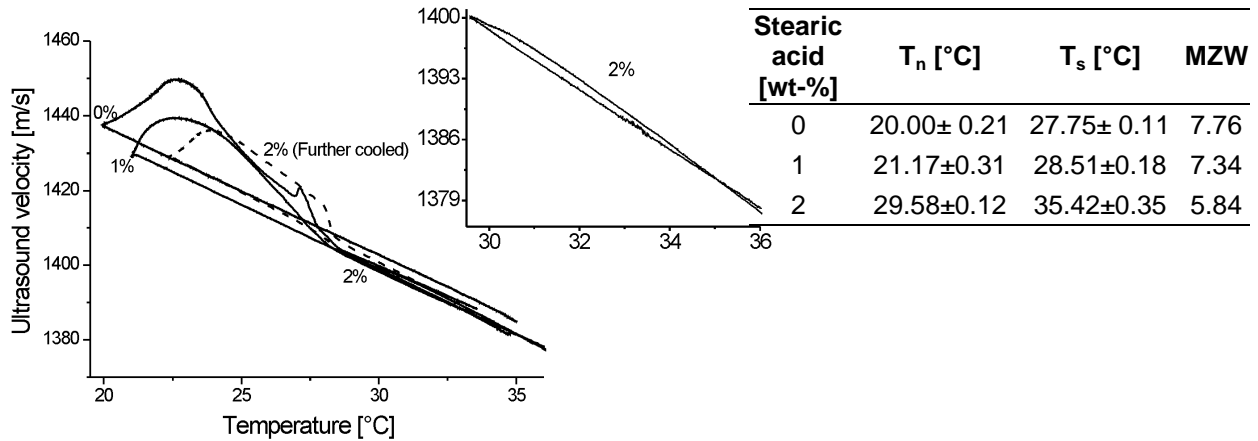


Figure 4.7: Influence of stearic acid on MZW of coconut oil.

At 2 wt-% stearic acid addition, it was evident that there were particles suspended in the mixture during the cooling cycle that caused in a sudden decrease in the ultrasound velocity signal at this temperature (29.58 °C). Further cooling of the mixture resulted in the shift of ultrasound velocity signal to the same values of the pure coconut oil and a second stage of nucleation occurred at about 22 °C, where the change of the ultrasound velocity can be detected again (dashed curve in Figure 4.7). The reheating process caused the rise in the ultrasonic signal as a function of the temperature and falls to intersect with the ultrasound signal of the cooling cycle of the pure coconut oil. Due to this phenomenon, the real MZW of the coconut oil in the presence of stearic acid at 2 wt-% concentration cannot be defined.

• Influence of L-195

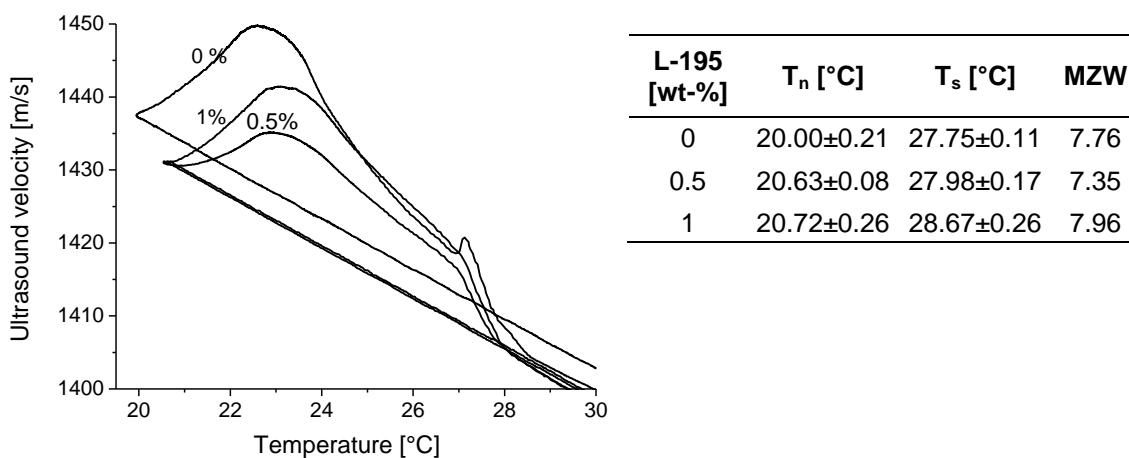


Figure 4.8: Influence of L-195 on the MZW of coconut oil.

The regular curve shape can be found in this system (Figure 4.8). The ultrasound velocity signals of coconut oil in the presence of both L-195 concentrations were detected at the lower values than that of the pure coconut oil melt. The addition of L-

195 at both concentrations slightly elevated the nucleation temperature of the coconut oil at the same level. In this system, the dependency of saturation temperature on the concentration of the additive can still be seen. The saturation temperature of the coconut oil was detected at the higher temperature as the concentration of L-195 increased.

• Influence of L-595

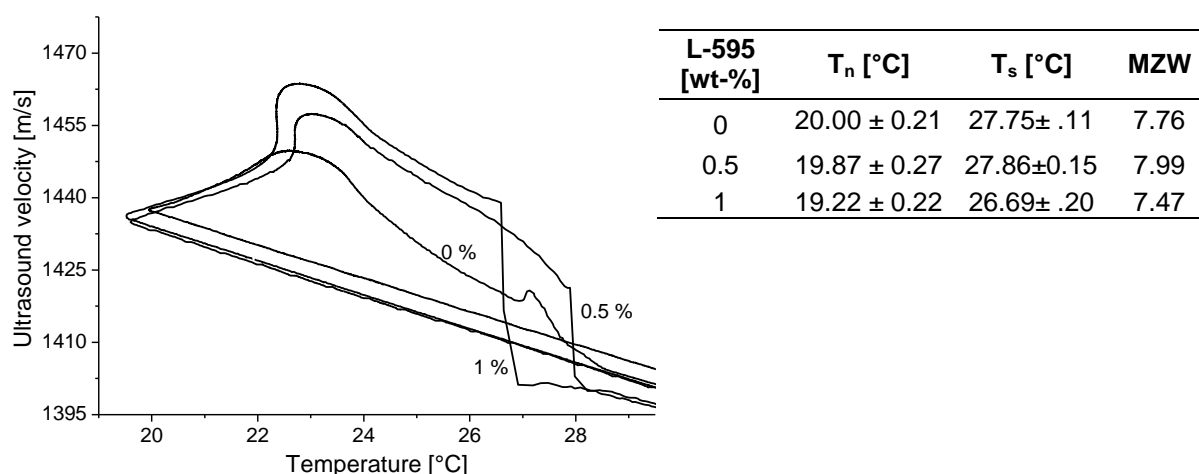


Figure 4.9: Influence of L-595 on the MZW of coconut oil.

The ultrasound velocity signals of the coconut oil containing L-595 as a function of temperature are shown in Figure 4.9. In the coconut oil system containing L-595, both nucleation and saturation point of coconut oil decreased as a function of L-595 concentration unlike the system of L-195 addition.

4.1.4 Crystal morphology

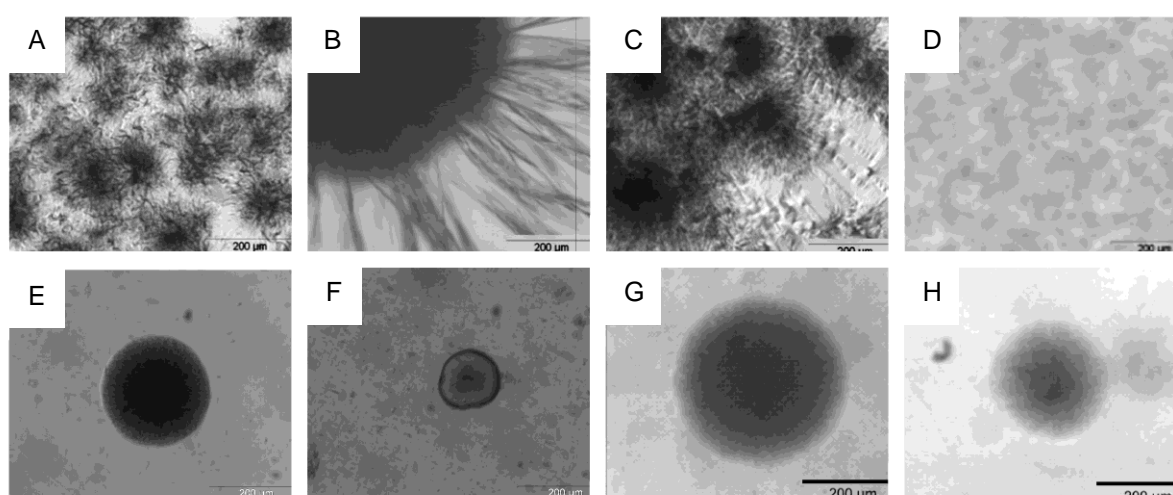


Figure 4.10: Crystal morphology of coconut oil in the presence of (A) 10 wt-% lauric acid, (B) 15 wt-% lauric acid, (C) 1 wt-% stearic acid, (D) 2 wt-% stearic acid, (E) 0.5 wt-% L-195, (F) 1 wt-% L-195, (G) 0.5 wt-% L-595, (H) 1 wt-% L-595.

The native crystal morphology of coconut oil is a spherulite consisting of needle crystals as depicted in Figure 2.2A. The concentration of additives was reported to affect the morphological characteristics and the final microstructures of the crystals [Shi05]. Figure 4.10 shows the micrograph of coconut oil crystals in the presence of additives taken after 60 minutes at 21 °C, except the crystals of coconut oil in the presence of 15 wt-% lauric acid which were taken at 18 °C. The spherulites of needle crystals similar to the crystals of the pure coconut oil were observed in the mixture of coconut oil and 10 wt-% lauric acid (Figure 4.10A). At 15 wt-% lauric acid concentration, plate crystals were observed on the surface of the melt without the formation of spherulites (Figure 9.1A, Appendix).

At this concentration, two stage of crystallization resulting in mixed crystals of needle spherulites surrounded by plate crystals were observed at a crystallization temperature of 18 °C (Figure 4.10B). During the first 20 min of the crystallization process, plate crystals were present on the surface of the melt. Afterwards, the typical spherulites of needle crystals of coconut oil were formed in the melt. At the same time, the plate crystals were observed to grow at the edge and surface of the spherulites, allowing the simultaneous crystallization of coconut oil and lauric acid.

The spherulites of needle crystals were still observed in the case of coconut oil containing stearic acid at 1 wt-% (Figure 4.10C). However, at 2 wt-% concentration, the crystallization process occurred already at the temperature around 28 °C (Figure 9.2, Appendix). Further cooling resulted in the sudden crystallization of the fat mixtures with undefined fat networks (Figure 4.10D). The addition of L-195 at 0.5 wt-% in coconut oil caused in the rounder and smaller spherulites in comparison to the crystals of pure coconut oil (Figure 4.10E). Interestingly, the morphological alteration of the coconut oil crystals into round and non-porous crystals was obviously observed when the concentration of L-195 increased to 1 wt-% (Figure 4.10F). In contrast, the alteration of crystal morphology of the coconut oil crystals was not observed in the system of coconut oil containing L-595 (Figure 4.10G). The addition of L-595 at 1 wt-% only led to the smaller and less dense spherulites, comparing to the coconut oil crystals (Figure 4.10H). This indicates that only L-195 is an effective crystal habit modifier of the coconut oil crystals among the other studied additives.

4.1.5 Polymorphic occurrence

The polymorphisms of coconut oil mixtures in the presence of additives were analyzed by X-ray powder diffraction and their diffractograms are shown in Figure 4.11. The diffractogram of coconut oil in the presence of lauric acid is slightly different from that of the pure coconut oil (Figure 4.11A). An extra peak at $2\theta = 9.8^\circ$ (I) was found in the diffractogram of the coconut oil containing 10 wt-% lauric acid. The same peak but stronger intensity and at $2\theta = 23.8^\circ$ (II) were found in the case of coconut oil mixed with lauric acid at 15 wt-% concentration. These two peaks refer to the lauric acid fraction in the mixture as confirmed by their presence in the diffractogram of the pure lauric acid. The diffractograms of coconut oil in the presence of other additives

exhibit the same pattern as that of the pure coconut oil without extra peaks from the pure additive. This is because the limit of detection by using X-ray diffraction is generally about 10 wt-% [Sal94]. The concentration of stearic acid, L-195 and L-595 presenting in the coconut oil is very low (0.5-2 wt-%). Therefore, it is not possible to see the peaks of these additives in the coconut oil mixtures.

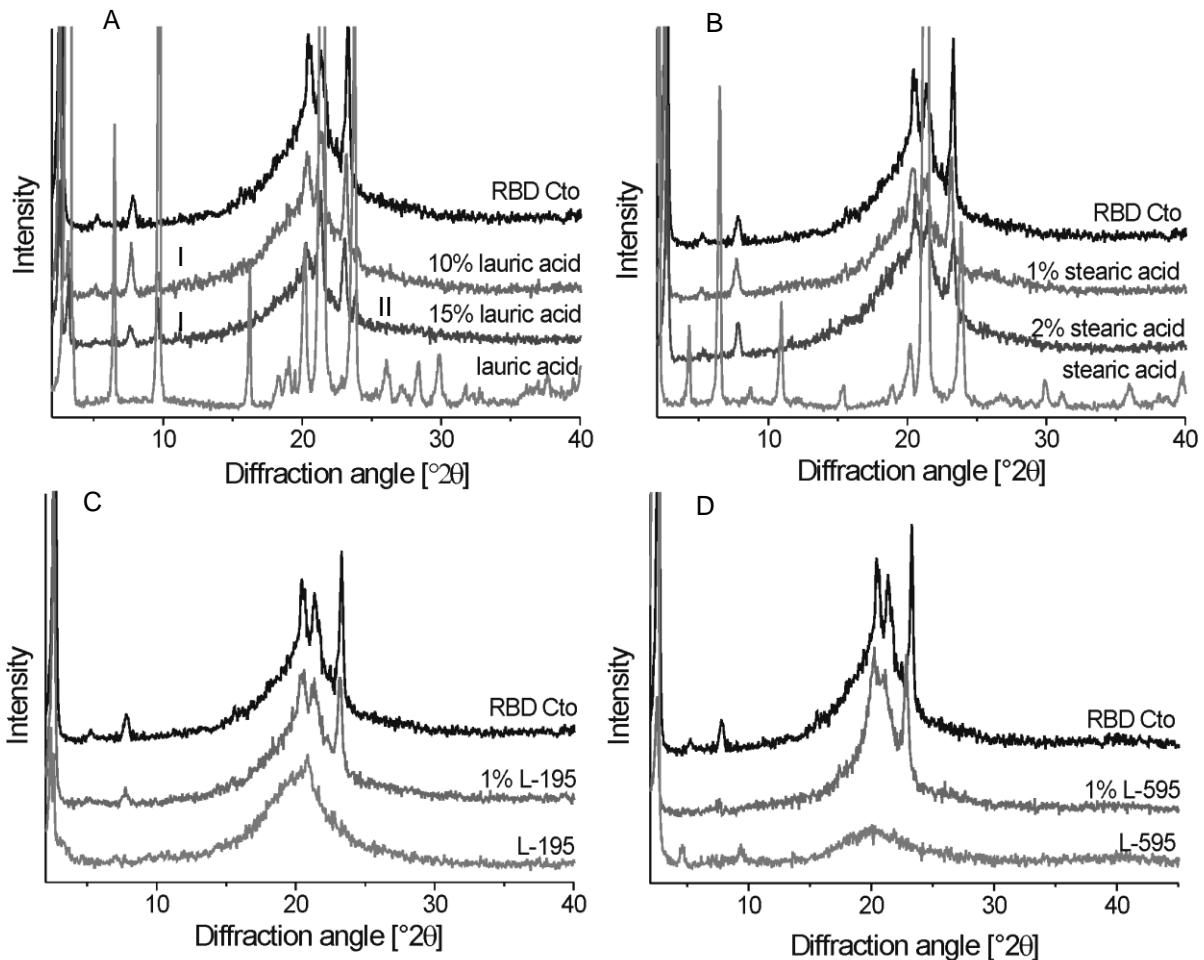


Figure 4.11: XRPD pattern of coconut oil mixtures in the presence of (A) lauric acid, (B) stearic acid, (C) L-195 and (D) L-595.

The polymorphism of TAGs refers to the ability of molecules to arrange themselves in a crystal lattice in a number of different packing forms. The diffractograms of the pure coconut oil and the coconut oil in the presence of all additives exhibit peaks at $2\theta = 20.5^\circ$ and 23.25° indicating the β' polymorph (Figure 4.12A). The strong peak at $2\theta = 21.35^\circ$ corresponds to the occurrence of the α form. According to the literature, coconut oil exhibits a simple polymorphic form of β' [Tim84]. However, at the rapid cooling condition, α form can occur but it quickly transforms to the β' form. It must be addressed here that the fat crystals were frozen prior to the XRPD analysis. This might be the reason for the occurrence of the α form in the diffractograms.

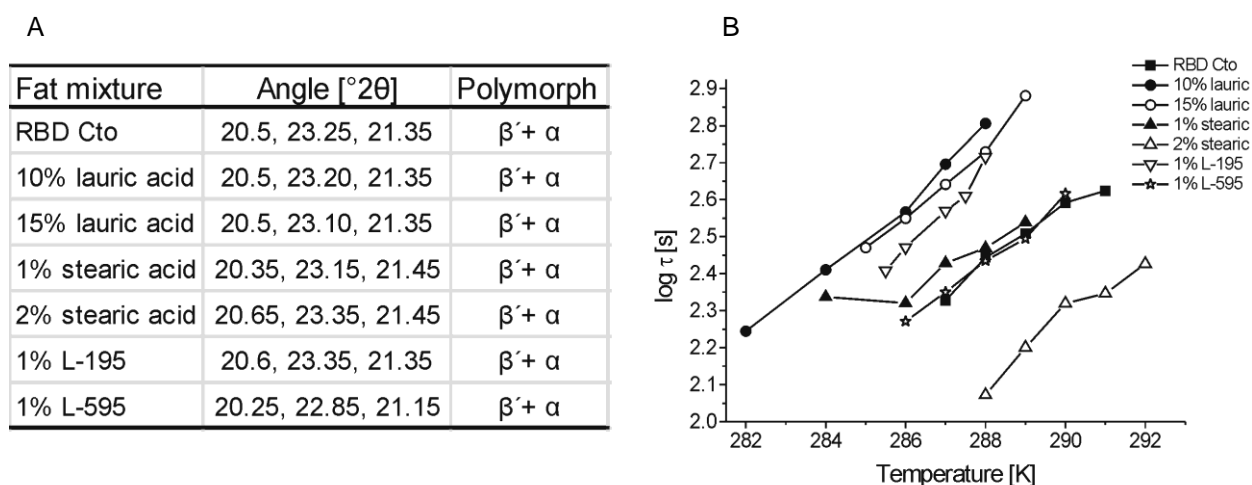


Figure 4.12: Polymorphic occurrence of the coconut oil mixtures by means of (A) diffraction peaks summarized from Figure 4.11 and (B) nucleation curves.

The plot of log induction time as a function of crystallization temperature or so-called the nucleation curve could be used to predict the polymorphic occurrence of palm oil and its derivatives [Che02, Ng90]. In this work, the nucleation curve was applied to predict the effect of additives on the polymorphic occurrence of coconut oil (Figure 4.12B). The induction time of nucleation was obtained from the Gompertz model fitting (Table 4.1, Chapter 4.1.2).

Figure 4.12B shows a continuous nucleation curve of the RBD coconut oil without the jump of the induction time. This behaviour can be interpreted that one polymorph crystallized in the applied temperature range. The nucleation behaviour of the coconut oil in the presence of additive is similar to that of the pure coconut oil showing continuous curves with the similar tendency. This polymorphic form is suggested to be the β' form. As investigated by XRPD analysis, crystals of coconut oil in the presence of these additives as well as the pure coconut oil occurred in the stable β' and unstable α form referring to the fast cooling. The absence of an α form in the nucleation curve is because the fat mixtures were crystallized at the smaller supercooling in comparison to the XRPD experiment, where the samples were suddenly frozen at -20°C .

However, the nucleation curves of the coconut oil in the presence of additives are shifted toward the lower temperature range, except the 2 wt-% stearic acid. This reveals that the nucleation of coconut oil in the presence of additives is slower than that of the RBD coconut oil at every observed temperature. This is because the nuclei of coconut oil are suppressed by additives and hence need more time to initiate the nucleation. But in the presence of 2 wt-% stearic acid, the nucleation of coconut oil is stimulated.

4.1.6 Shear viscosity

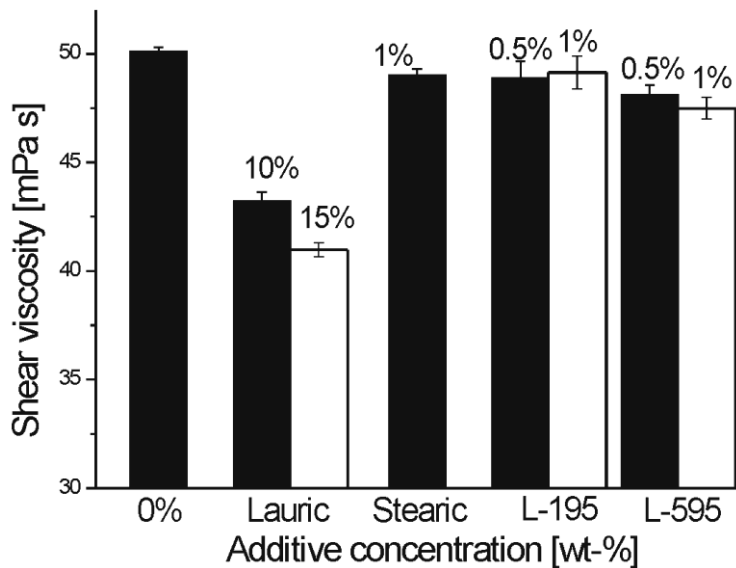


Figure 4.13: Shear viscosity of the coconut oil in the presence of additives (25 °C, 200 s⁻¹).

Figure 4.13 shows the viscosity of the coconut oil in the presence of additives measured at 25 °C, 200 s⁻¹. The diagram presents only that of the additive concentrations where the melt still remains a homogeneous liquid at this temperature. Therefore, the viscosity of coconut oil containing 2 wt-% stearic acid is not included in the diagram due to the presence of solid phase before the temperature reaches 25 °C as informed in Chapter 4.1.3. It can be seen that the addition of lauric acid strongly reduced the viscosity of coconut oil, while stearic acid and L-595 significantly less lowered the viscosity of coconut oil (P-value < 0.05). Moreover, L-195 did not significantly affect the viscosity of coconut oil and tended to increase the viscosity of coconut oil at the higher concentrations. This might be due to the fact that lauric acid was used in the higher concentration in comparison to the other additives.

4.2 Screening of the additives

The studied results of crystallization behaviours of coconut oil in the presence of different additives are summarized in Table 4.5. The additive concentration shown in the Table 4.5 was selected based on the highest additive concentration that can be added in the coconut oil system without causing the additional nucleation. It was found that all additive types retarded nucleation and crystal growth kinetics of coconut oil. Even though, they significantly affected the melting point and MZW, but the effects were very small and could be negligible. Moreover, all additives could still maintain the β' polymorphic form of coconut oil. But the addition of 1 wt-% L-195 significantly modified the crystal habit of coconut oil from needle spherulites into round crystals. However, 1 wt-% L-195 did not reduce the viscosity of coconut oil and the viscosity was tended to increase at the higher concentration. Instead, the other

additives possessed the ability to reduce the coconut oil viscosity. This information is very useful for the fractionation process of coconut oil.

Table 4.5: Summary of the crystallization parameters of coconut oil in the presence of additive.

Coconut oil mixture Parameter	+10 wt-% Lauric	+1 wt-% Stearic	+1 wt-% L-195	+1 wt-% L-595	Remark
Melting point	decrease	no change	no change	no change	negligible
Nucleation kinetics	retard	retard	retard	retard	
Crystal growth rate	retard	retard	retard	retard	
MZW	decrease	decrease	no change	no change	negligible
Polymorphic occurrence	β'	β'	β'	β'	
Crystal habit	needles	needles	round crystals	needles	
Viscosity at 25 °C	decrease	decrease	no change	decrease	

Concerning the fractionation process, two main parameters determining the separation efficiency of the solid-liquid phase are the needle spherulites of coconut oil crystals and high viscosity of the fat melt. The aim of applying additives is to modify the crystal morphology of coconut oil crystals and reduce the viscosity effect of the melt. Up to this point, L-195 appeared to be the best candidate as a crystal habit modifier without changing the polymorph resulting from the coconut oil. The fractionation process of coconut oil in the presence of L-195 should be easily designed. This is because L-195 did not significantly affect the important parameters like melting point and MZW of coconut oil, even though it retarded the nucleation of coconut oil. L-195 was therefore used as the additive in the fractionation of coconut oil. Due to the relative narrow MZW and high viscosity of the coconut oil, the fractionation process was performed based on the layer crystallization. However, the high viscosity of coconut oil still remains the problem and is not reduced by L-195 addition. As a consequence, the further developments were done in order to overcome the viscosity effect of the fat melt in the fractionation process.

4.3 Emulsion productions

According to the conclusion in Chapter 4.2, L-195 possessed ability as a crystal habit modifier for coconut oil without altering the polymorphic occurrence. But the addition of L-195 in coconut oil subsequently increased the shear viscosity of the coconut oil mixture which is not preferred for the fractionation process. In this part, the problem in high viscosity of the coconut oil was optimized before subjecting the coconut oil mixtures to the fractionation process. It was known from the previous chapters that L-195 is a food emulsifier. Therefore, it would be possible to reduce the viscosity effect by producing the coconut oil in the low viscous emulsion with the help of L-195 and

water. The concentration of the L-195 was used at 1 wt-% based on the oil phase. The concentration of water was varied from 5 to 35 wt-%. The production of coconut oil emulsion was done by a rotor stator and a static mixer. The operation of these processes was written in Chapter 3.3.

4.3.1 Emulsion Characteristics

The coconut oil emulsions produced by the rotor stator and the static mixer are water in oil emulsions due to the low HLB of L-195. At all water concentrations, homogeneous emulsions were obtained by the production via the static mixer process (Figure 4.14A). In contrast, the emulsions produced by the gear rim disperser exhibited large amounts of bubbles leading to foam formation and agglomerated drops which formed solid-like flocs and aggregation at a water concentration from 10 wt-% (Figure 4.14B showing the emulsion mixture containing 20 wt-% water content). This results in an inhomogeneity of the emulsion mixtures. It was, however, observed that the amount of these solid-like flocs reduce after an undefinable time period which makes the system even more inconstantly. The occurrence of such a phenomenon should be due to air involved in the process of the rotor stator system, while there is less air contact of the mixture during the emulsification via the static mixer.

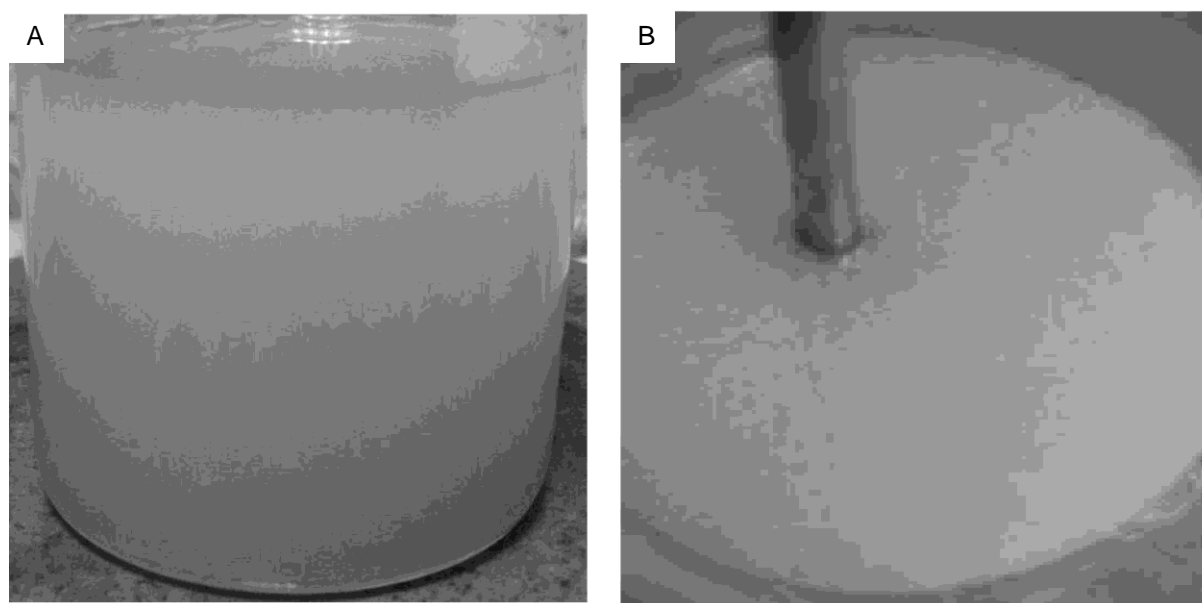


Figure 4.14: Appearance of the emulsion (20% water/ 1% L-195/ 79% oil) produced by (A) a static mixer and (B) a rotor stator.

The solid-like flocculation in the case of the rotor stator system causes drastic errors in viscosity measurements as can be seen in Figure 4.15, while the production of emulsions via the static mixer system indicates good reproducibility of the measurements. The production of emulsion by the latter system leads to a significant reduction in the viscosity and even to the lower viscosities than that of the coconut oil as the water concentration increased (p -value <0.05).

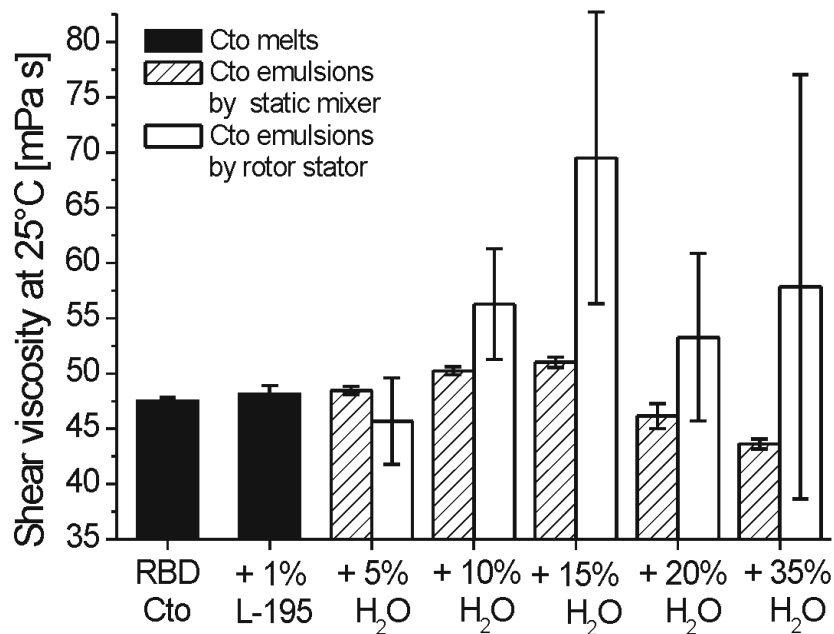


Figure 4.15: Shear viscosity of the coconut oil emulsions as a function of water concentration [wt-%] produced by (A) the static mixer and (B) the rotor stator.

It must be noted here that the coconut oil used in the production of emulsions containing 10 wt-% and 15 wt-% water was not from the same batch as the others. As a consequence, the results exhibit different characteristics and should not be compared to those of the other water concentrations.

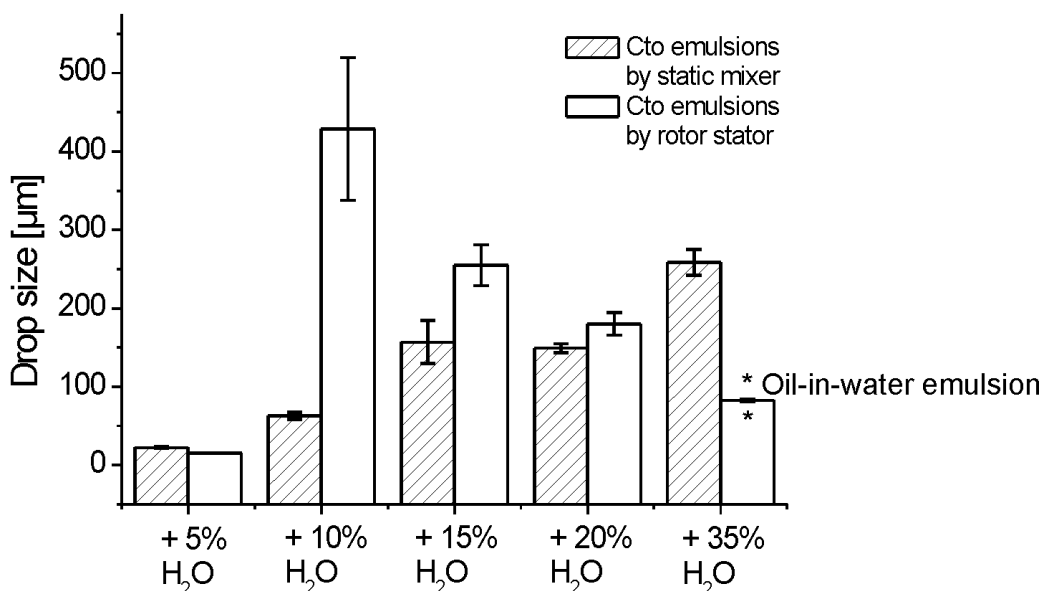


Figure 4.16: Drop size of the emulsions produced by the static mixer and the rotor stator as a function of water concentration [wt-%] in comparison to that of the pure coconut oil and coconut oil with 1 wt-% L-195.

The results in the viscosity of the emulsion mixtures are in correlation to the drop size and size distribution of the emulsion as shown in Figure 4.16. It can be seen that the

emulsions containing 5 wt-% water content produced by both techniques have small average drop sizes with a very low deviation. The correlation between the drop size and the water concentration of the emulsions produced by the static mixer was found. The emulsion drops enlarge their sizes when the water concentration increases. This is in agreement with the results in viscosity and the report from Pal [Pal96]. The smaller the droplet size is, the higher is the viscosity. The small deviation indicates a very good reproducibility of the results of this system.

In contrast to the results above, in those cases when the water concentration increases to 10 wt-% and above, enormously large average drop sizes of the emulsion produced by the rotor stator were detected. The high deviation of the results implies that a high rate of flocculation and coalescence of the drops causes random and various detected drop sizes in each measurement. For this reason, the true drop diameter of the emulsions containing water contents above 10 wt-% could not be measured any more.

Surprisingly, phase inversion of emulsions from water-in-oil to oil-in-water was observed in the emulsions containing 35 wt-% water concentration produced only by the rotor stator. The phase inversion process leads to the homogeneous milky and water miscible emulsions with significant smaller drop sizes than the emulsions containing lower water concentrations. The occurrence of the phase inversion in the emulsion in this case is still unclear since the HLB value of sucrose ester is generally stable and does not change with temperature as reported by Bolzinger-Thevanin [Bol99].

However, a small experiment was done to observe the phase inversion temperature of the 35 wt-% water emulsion produced by the rotor stator. The temperature of the emulsion was online detected by a thermo couple from the start of the emulsification process at 60 °C. At every 5 °C temperature reduction level, the emulsification process was repeated and a small amount of the emulsion was taken to test the water or oil miscibility. This is because water-in-oil and oil-in-water emulsions are simply differentiated by their appearance and water or oil miscibility. At the temperature range of 45-40 °C, it was found that the emulsion suddenly changed its appearance from a milky emulsion to the flocculation of the white particles which were water immiscible. This indicates the phase inversion to the regular water-in-oil emulsion.

It must be noted here that the determination of the drop and drop size distribution was done immediately after emulsification process (emulsified approx. at 60 °C). Moreover, the temperatures during the measurement could not be controlled and are based on the temperature of the samples. Therefore, the temperature during the drop size measurement in this case was approx. 60 °C which was above the phase inversion temperature. As a result, the drop sizes of the emulsions containing 35 wt-% water presented in Figure 4.16 belong to the oil-in-water emulsions.

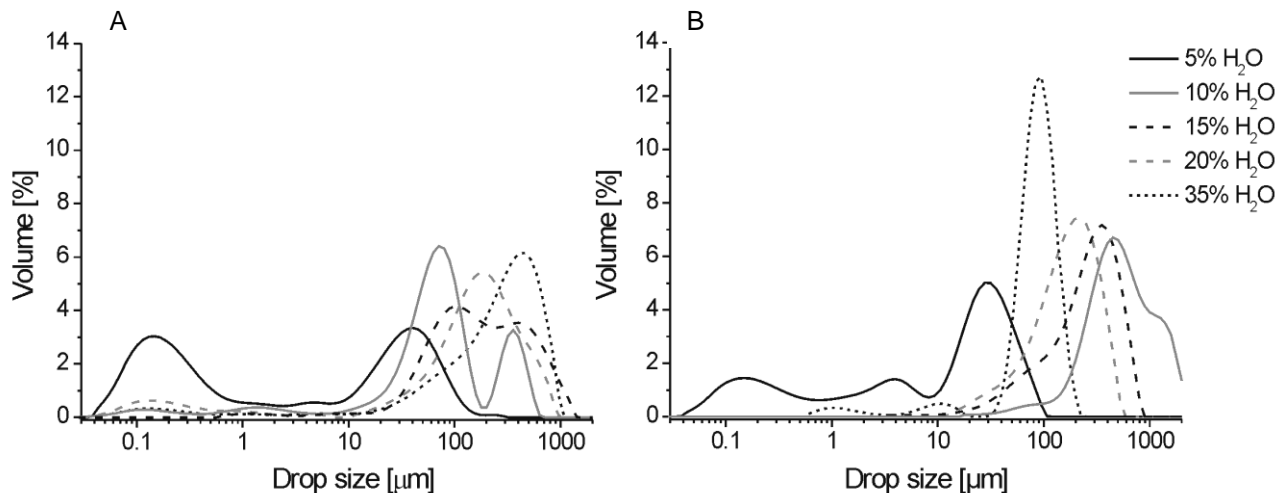


Figure 4.17: Drop size distribution of the emulsions produced by (A) the static mixer and (B) the rotor stator as a function of water concentration in comparison to that of the pure coconut oil and coconut oil with 1 wt-% L-195.

The drop size distributions of the emulsions produced by these techniques are shown in Figure 4.17. In the production via the static mixer system (Figure 4.17A), the emulsion containing 5 wt-% water exhibits a relatively wide range of the drop sizes which are distributed mainly between the very small drops of $1\ \mu\text{m}$ and the small drops of $20\ \mu\text{m}$. The emulsification of the emulsions containing higher water concentrations significantly widened the range of the drop sizes as the very fine emulsion drops were still present. But the amount of the very small drops decrease and the drop sizes were shifted more towards the larger size region up to $1000\ \mu\text{m}$ as the water concentrations increase, indicating a wider size distribution range. It was suggested that the more drop size distribution is polydispersed, the lower is the emulsion viscosity [Pal96]. Therefore, the lowering of the emulsion viscosity with increasing water concentrations can be also related to the more polydispersed drop size distribution of the emulsions produced by the static mixer.

The emulsions containing 5 wt-% water produced by the rotor stator system (Figure 4.17B) exhibit wide ranges of the drop sizes from $0.1\ \mu\text{m}$ to $100\ \mu\text{m}$, which are similar to those produced via the static mixer. At higher water concentrations (from 10 to 20 wt-%), the emulsification via the rotor stator causes flocculation of very small drops into white solid-like flocs as shown in Figure 4.14. The flocculation of drops are supported by the detected larger drop sizes which are distributed among 50 to above $1000\ \mu\text{m}$ and the disappearance of the very small drops according to Figure 4.17B. The emulsion containing 35 wt-% water produced by the rotor stator system is the oil-in-water emulsion as explained above. The drop size distribution of this emulsion mixture is therefore not compared to that of the other emulsion mixtures.

4.3.2 Ohnesorge number

In this part, the main goal is the reduction of the viscosity effect via the production of emulsions. As can be seen from Chapter 4.3.1, the emulsion production via the static mixer system leads to the homogeneous and low viscous emulsions in comparison to

the pure melt of coconut oil. In fact, emulsions are considered to be a complex fluid of 2 dispersed phases which is different to the one phase of the pure oil. The flow behaviour of such a fluid is affected by a large number of different forces not only the viscosity, but also surface tension, gravity and stress resulting in the formation of various droplet sizes and size distributions. The Ohnesorge number as a dimensionless parameter is therefore introduced to systematically predict and relate the viscosity effect on the surface deformation of the droplets at the conditions of interests.

In this chapter, only the Ohnesorge number of the emulsions produced via the static mixer was calculated. This is because high rates of flocculation occurred in the case of the emulsions produced by the rotor stator system which did lead to a severe error in the results. The calculation of the Ohnesorge number of the emulsions produced by the static mixer as a function of the water concentration is based on the parameters summarized in Table 4.6.

Table 4.6: Surface tension, density, viscosity measured at 25 °C and the droplet size of the emulsions produced by the static mixer method as a function of water content.

C_{H_2O} wt-%	Surface tension mN/m	Density g/cm ³	Droplet size μm	Viscosity mPa s
5	27.15 ± 0.71	0.9215 ± 0.0003	22.24 ± 1.12	48.48 ± 0.37
10	26.71 ± 0.1	0.9242 ± 0.0002	63.09 ± 4.50	50.25 ± 0.35
15	28.78 ± 0.28	0.9262 ± 0.0004	157.03 ± 27.54	51.029 ± 0.47
20	28.40 ± 0.17	0.9306 ± 0.0009	149.03 ± 5.75	46.17 ± 1.14
35	28.47 ± 0.29	0.9370 ± 0.0004	258.50 ± 16.50	43.64 ± 0.44

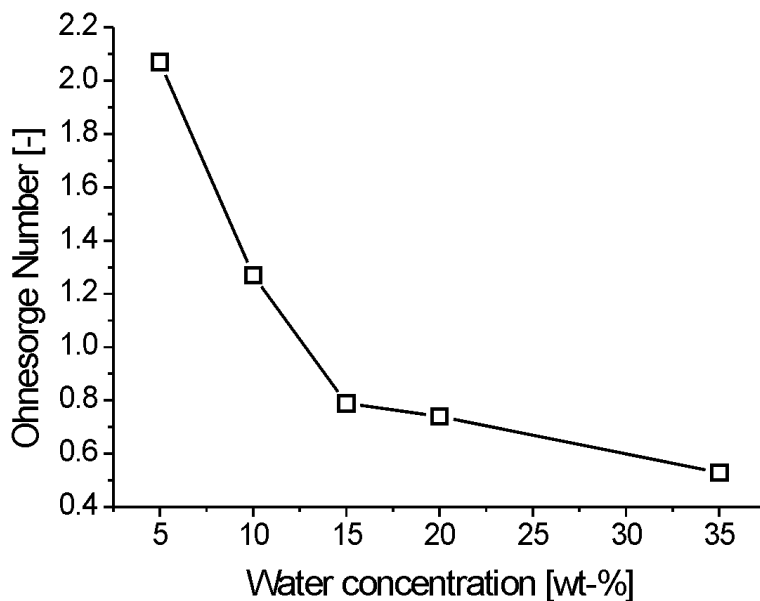


Figure 4.18: The Ohnesorge number of the coconut oil emulsion produced by the static mixer as a function of the water concentration.

The Ohnesorge number of the coconut oil emulsion produced by the static mixer decreased as the water content increased (Figure 4.18). Above 15 wt-% water concentration, the Ohnesorge number is already below 1. This verifies that above this water concentration the viscosity effect has no influence on the flowing emulsions. The coconut oil emulsion above this water concentration is consequently characterized as a low viscous fluid. Based on the evaluation of the Ohnesorge number, the static mixer is an effective tool for the production of the low viscous coconut oil emulsions. Therefore, the low viscous coconut oil emulsion can be prepared by the static mixer prior to the fractionation step.

4.4 Fractionation of the coconut oil emulsions

Coconut oil emulsions produced by the static mixer were further fractionated based on layer melt crystallization via a cold finger technique focusing on the high-melting solid fractions. In this process, layers of the higher-melting solid fractions are formed on a cold surface of a steel tube which is dipped in the warm coconut oil emulsion. In this case, its key crystallization parameters (such as cold finger temperature, temperature of the mother liquor, agitation speed and cooling rate) must be controlled and optimized in order to achieve the desired products. Considering these process parameters, it was found here that the cold finger temperature has the highest impact on the quality of the higher melting fractions [Cha10]. Therefore, the cold finger experiments were done under the optimal condition with the various cold finger temperatures as written in Chapter 3.4.1. The fractionation of coconut oil emulsions with 3 water concentrations was done and compared with the dry fractionation of coconut oil without water addition. The high-melting solid fractions obtained from these processes were analyzed and the results are shown in the following.

4.4.1 Characteristics of the solid fractions

4.4.1.1 Solid fat properties

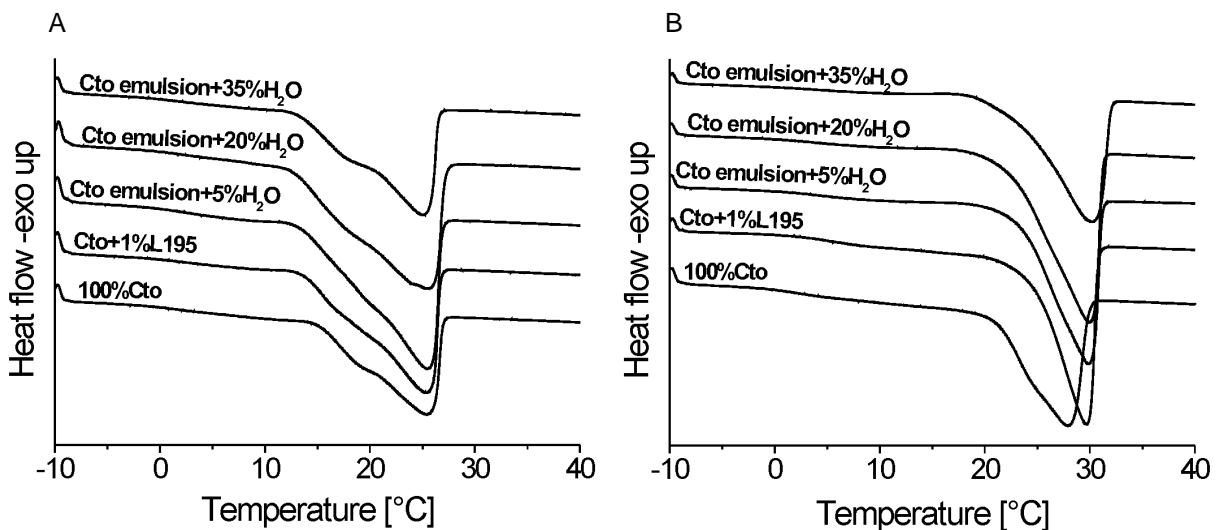


Figure 4.19: Melting profile of (A) initial coconut oil feeds and (B) the high-melting solid fractions (coconut stearin) from different fractionation processes.

Solid fat properties of the fractionated high melting products indicate the efficiency of the fractionation process. The achievement of the fractionation can be preliminary evaluated by comparing the melting profiles of the initial oil feeds (Figure 4.19A) to that of the coconut stearins (Figure 4.19B). The melting profiles of the initial pure coconut oil feed including the coconut oil emulsion feed are very similar in their characteristics. After the fractionation of these feeds, it can be clearly seen that the melting profiles of the coconut stearins, especially from the emulsion fractionation, are more narrow and sharper than their initial feeds. Moreover, the melting curves shift to the higher temperature ranges. This indicates that the coconut stearins contain less TAG species than that of the initial RBD coconut oil and the remaining TAG species are constituted of higher melting fatty acids.

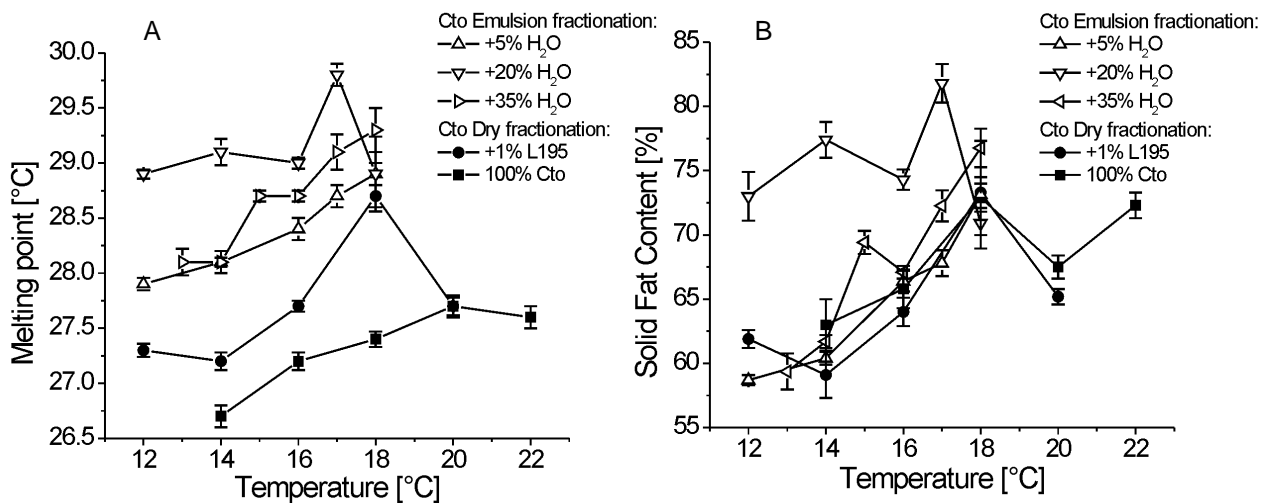


Figure 4.20: solid fat properties (A) Melting point and (B) solid fat content at 25 °C of the coconut stearins obtained from emulsion fractionation in comparison to that of the dry fractionation as a function of crystallization temperature.

The melting point and solid fat content (SFC) at 25 °C of the coconut stearins obtained by the fractionation of coconut oil emulsions with 3 different water concentrations in comparison to the dry fractionation of pure coconut oil and coconut oil in the presence of L-195 are shown in Figure 4.20A and 4.20B, respectively. The solid fat properties (the melting point and SFC of the solid fractions) and the cold finger temperature have a direct proportional correlation. Decreasing of the cold finger temperature caused in the lower melting point and solid fat content of the coconut stearins. Coconut stearins obtained by the dry fractionation of the pure coconut oil melt possess the lowest solid fat properties among the other processes at all cold finger temperatures. The addition of L-195 aides the dry fractionation of coconut oil, indicated by the higher solid fat properties of the coconut stearins at all cold finger temperatures. Nevertheless, the coconut stearins from the dry fractionation without L-195 in this work possess relatively lower solid fat than previous results [Cha10]. This is, however, due to the different batches of coconut oil. Since coconut oil is a natural product, its TAGs can vary and strongly affect the fractionation process.

Comparing to the dry fractionation, the fractionation of coconut oil in an emulsion state prepared with all water concentrations improves the fractionation efficiency and leads

to a higher melting point and SFC of the coconut stearins. Besides, higher melting points and SFCs of coconut stearins can be obtained when the water concentration of the emulsion increases up to 20 wt-%. One reason apart from the viscosity reduction is that water has a better flowability than oil which promotes the draining efficiency of liquid oil surrounded solid crystals during the sweating process. As a result, there is less entrainment of the low melting TAGs resulting in the higher SFC and melting point of the coconut stearins obtained by an emulsion fractionation than a dry fractionation. However, the modification of coconut stearin properties can only be done up to a certain extent of water. At concentration of 35 wt-% water and above, the melting point of coconut stearins will not be significantly modified and particularly decreased in the case of SFC.

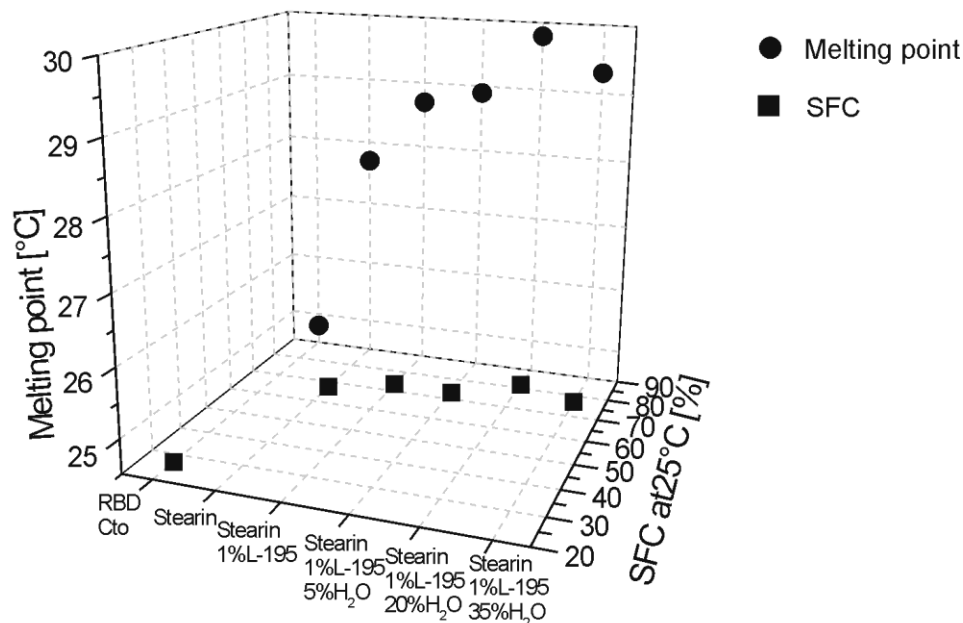


Figure 4.21: The highest solid fat properties of the coconut stearins obtained from emulsion fractionation in comparison to that of the dry fractionation and the original RBD coconut oil.

The highest melting point and SFC of the coconut stearins obtained by these fractionation processes were summarized in Figure 4.21. RBD coconut oil has a melting point of 24.8 °C and a SFC at 25 °C of 27%. Among the others, the fractionation of coconut oil via the emulsion fractionation gives the coconut stearin possessing a highest melting point of approx. 30 °C and a SFC of about 80%. These values are in the same range as those obtained by a solvent or a detergent fractionation [Ros85]. In addition, the most effective water concentration for the emulsion fractionation is at 20 wt-% water. To point out that the fractionation efficiency of the emulsion fractionation process is relatively higher than that of the dry fractionation 8 wt-% in terms of the melting point and 25 wt-% in terms of the SFC.

4.4.1.2 Fatty acid compositions

Fatty acid compositions of the coconut stearins obtained from the emulsion fractionation and dry fractionation processes were analyzed by GC. Figure 4.22

presents the fatty acid compositions of the highest melting coconut stearin obtained from these fractionation processes.

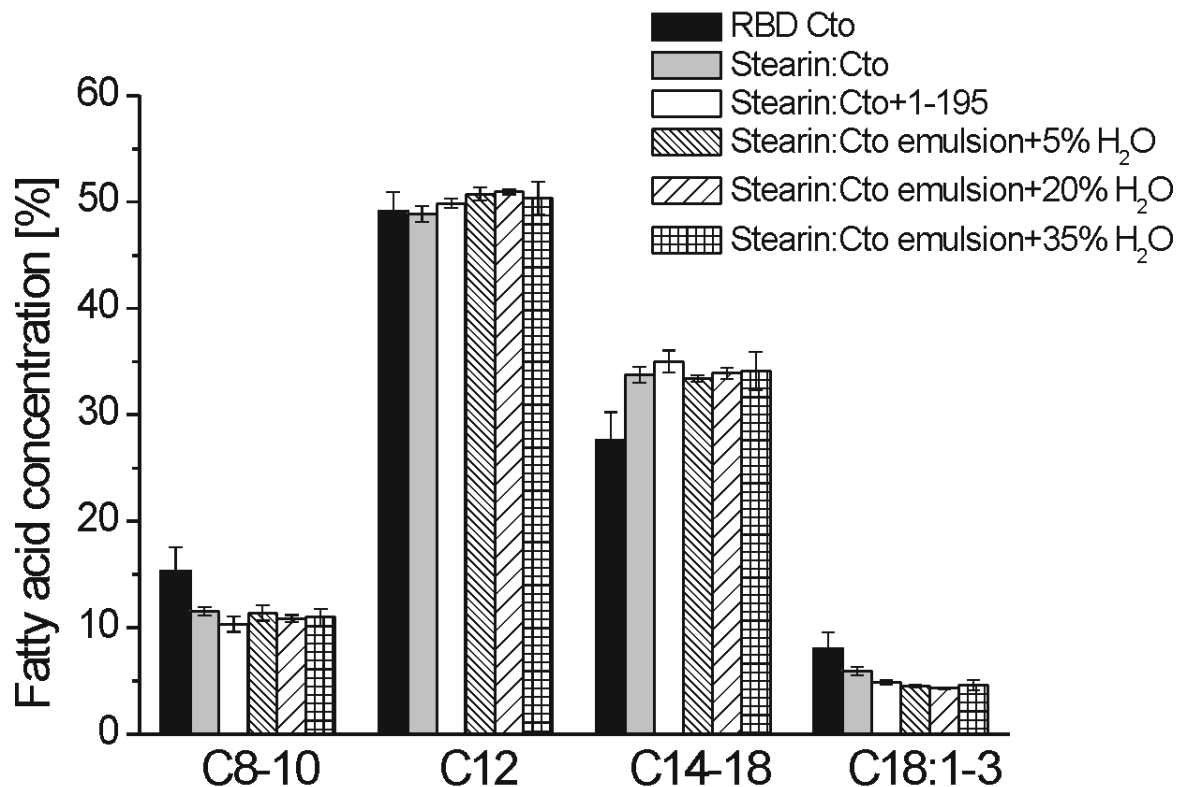


Figure 4.22 Fatty acid concentrations of coconut stearins possessing the highest melting points from different fractionation processes.

Coconut stearins obtained from all fractionation processes contain significant higher concentrations of the saturated fatty acids from C12 to C18 and less amount of the medium chain fatty acids of C8 and 10 and the unsaturated fatty acids than the RBD coconut oil. This effect is especially strong in the coconut stearin obtained from the emulsion fractionation. These results support the increase of the melting point of the coconut stearins. On the basis of these results, the high melting fatty acid group corresponding to the melting point elevation refers to the saturated long chain fatty acids of C12 to 18. The low melting fatty acid group that lowers the melting point of coconut oil refers to shorter chain saturated fatty acids of C8 to 10 and the unsaturated fatty acids. The goal of the fractionation is that the coconut stearin should contain the high melting fatty acids as much as possible and at the same time contain as less as possible the low melting fatty acids. The relation of the low melting fatty acid and the high melting fatty acid contents of the coconut stearin TAGs as a function of their melting point are plotted and shown in Figure 4.23.

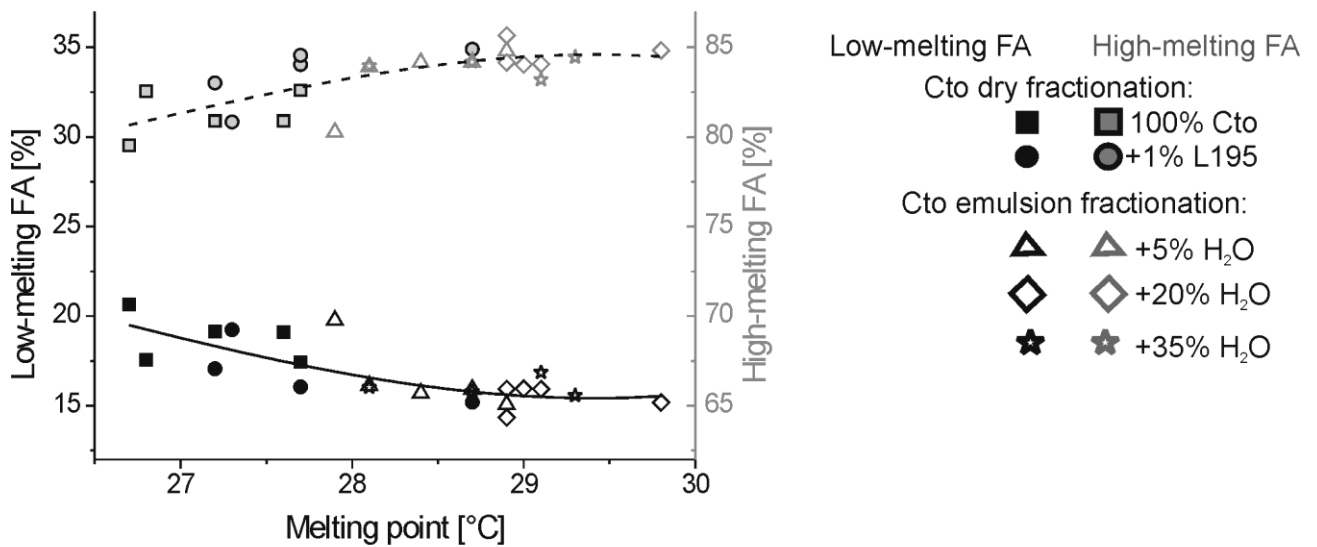


Figure 4.23: Relation between the melting point and the high melting fatty acid and the low melting fatty acid groups of the coconut stearin.

The initial RBD coconut oil consists of about 23 % low melting fatty acids and 77 % high melting fatty acids. It can be seen from Figure 4.23 that the fractionation of coconut oil leads to reduced amounts of the low melting fatty acids and an increased amount of the high melting fatty acids. The limit of the separation is realized at the melting point of 30 °C where the low melting fatty acids remain entrapped at 15 % and a further increase of high melting fatty acid above 85 % cannot be reached. This is achieved by emulsion fractionation at 20 wt-% of the water addition.

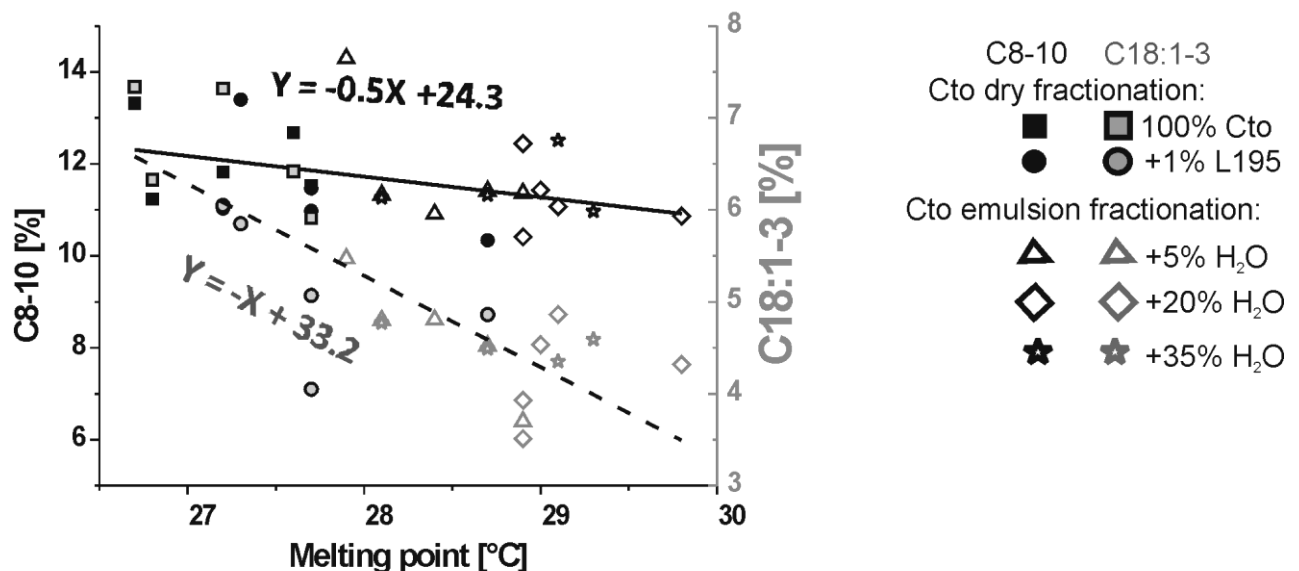


Figure 4.24: Melting point, medium chain saturated fatty acid contents (C8-10) and the unsaturated fatty acid contents of the coconut stearins.

Figures 4.24 and 4.25 provide more information on the effect of fatty acid composition on the melting point of coconut stearins. The low melting fatty acid group is subdivided into the medium chain fatty acid class (C8-10) and the unsaturated fatty acid class

(C18:1-3). Their relations to the melting point of the coconut stearin are shown in Figure 4.24. As the melting point of the coconut stearins increases, the unsaturated fatty acid content decrease with the higher reduction ratio than the medium chain saturated fatty acid as can be seen from the steeper slope. This indicates that the higher content of unsaturated fatty acids can be removed than that of the medium chain saturated fatty acids. This implies that the selectivity of the fractionation based on the dissimilarity of the molecular structures. Since 90 % of the coconut oil composition is saturated fatty acids, therefore, separation of the unsaturated TAGs from the saturated TAG matrix is easier to achieve, comparing to the separation of the medium chain saturated TAGs from the long chain saturated TAGs matrix.

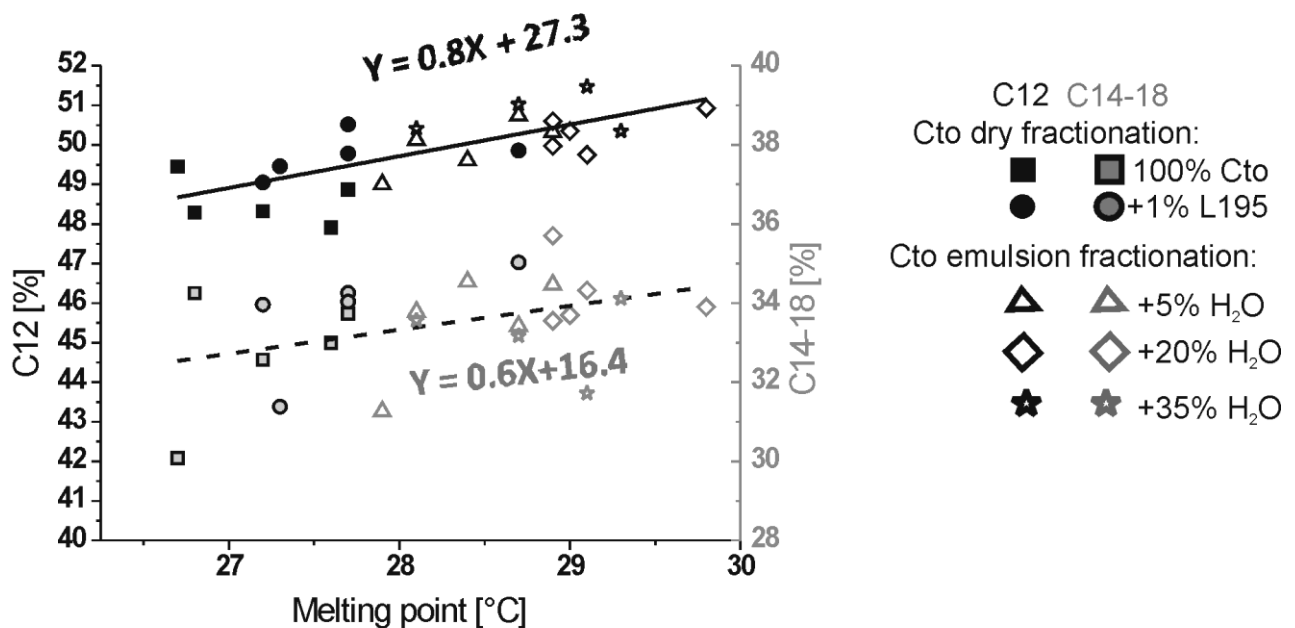


Figure 4.25: melting point, the lauric acid contents (C12) and the longer chain fatty acid contents (C14-18) of the coconut stearin.

To indicate which kind of high melting fatty acid groups play a significant role on the melting point of the coconut stearins, the effect of lauric acids and the longer chain saturated fatty acids on the melting point of coconut stearins are compared. Figure 4.25 indicates that the increased amount of both lauric acid contents and the longer chain fatty acid contents are in the similar ratio as the melting point of the coconut stearin increased. The plot of the C14-18 is wide scattered that the determined tendency may be erroneous. However, Table 9.1 (see Appendix) shows that the coconut stearins actually contain longer chain fatty acids (C14-18) relatively 6 % higher than the RBD coconut oil, while their lauric acid concentrations are relatively 2 % higher than that of the RBD coconut oil. This implies that the increase of the melting point of coconut oil is due to the reduction of the unsaturated fatty acids and the increasing amount of longer chain fatty acids. But the longer chain fatty acids of the coconut stearin are still relatively lower in concentration than lauric acid which belongs to the medium chain fatty acid group. It has therefore a lower melting point than the longer chain fatty acids. This probably explains why the melting point of coconut

stearin is slightly increased to the maximum of 30 °C compared to the initial RBD coconut oil of 25 °C.

4.4.1.3 Crystal morphology

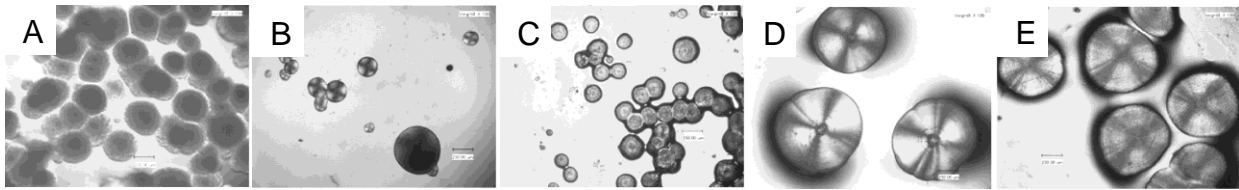


Figure 4.26: Crystal morphology of coconut stearin obtained from (A) dry fractionation without L-195 and (B) with 1 wt-% L-195 and emulsion fractionation with (C) 5 wt-% water, (D) 20 wt-% water and (E) 35 wt-% water.

The crystal morphology of coconut stearin obtained by dry fractionation without emulsifier addition exhibits typical spherulites of needle crystals (Figure 4.26A). The addition of the emulsifier L-195 in the dry fractionation of coconut oil altered the crystal morphology of the coconut stearin into non-porous crystalline round particles (Figure 4.26B). This is in agreement with the results from Chapter 4.1.4. Such a form also occurred in coconut stearin obtained from an emulsion fractionation (Figure 4.26C-E). The crystal size is also increased with increasing the water concentrations. Since the modified crystals are non-porous, there is less amount of liquid oil inclusions between the crystals. Due to this aspect, the efficiency of the solid-liquid separation is improved which consequently leads to higher SFCs and melting points of coconut stearins as to be seen in the previous chapter.

4.4.1.4 Polymorphic occurrence

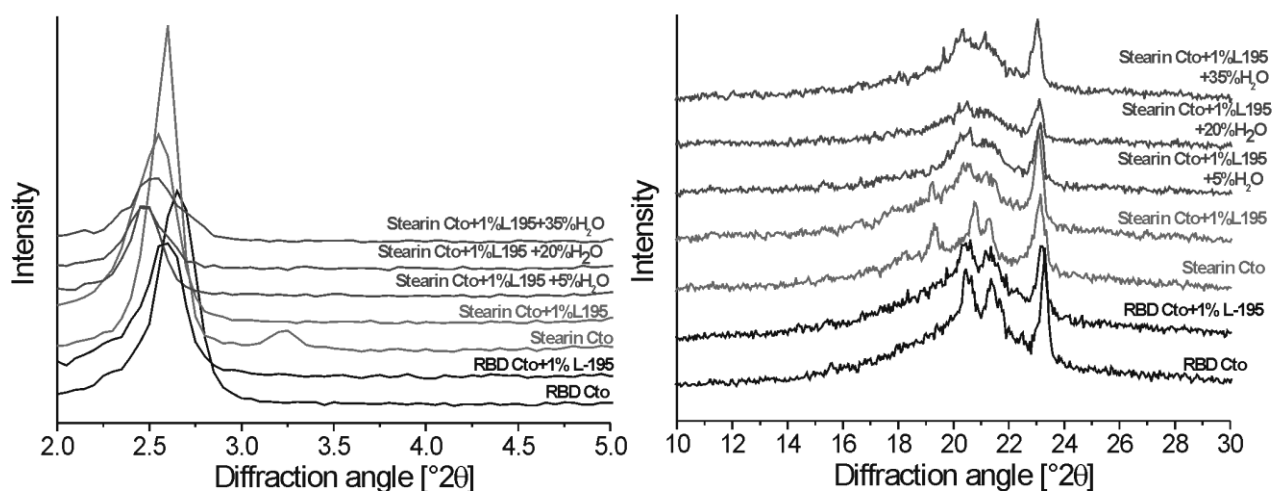


Figure 4.27: XRPD diffractogram showing polymorphic existence of coconut stearins obtained from different processes.

The XRPD pattern of the coconut stearins obtained from different fractionation processes in comparison to the RBD coconut oil is illustrated in Figure 4.27. All substances exhibited a peak at $2\theta = 2.6^\circ$ (34 Å) indicating the double layer packing structure of the TAGs [Smi06]. The polymorphic forms of these fractionated coconut

oils in comparison to the original RBD coconut oil are summarized in Table 4.7. The fractionated coconut oil obtained by a dry fractionation process without L-195 addition has a similar diffractogram to the original RBD coconut oil, showing the β' and α forms. But a significant extra peak at $2\theta = 19.3^\circ$ occurred indicating the β polymorph. The XRPD diffractogram of the coconut stearin obtained from the dry fractionation process of coconut oil containing 1 wt-% L-195 exhibits reduced peak signals at $2\theta = 21.15^\circ$ of the α polymorph and at 19.2° of the β form. The reduction of these peak signals is more significant in the case of the coconut stearins obtained from the emulsion fractionation.

Table 4.7: Summary of the polymorphic forms of the coconut stearins in comparison to that of the initial oil feeds.

Sample	Angle [$^\circ 2\theta$]	Polymorph
RBD Cto	20.5, 23.25, 21.35	β' , α , double layer packing
1% L-195	20.25, 22.85, 21.15	β' , α , double layer packing
Stearin: Cto	20.8, 23.2, 21.35, 19.3	β' , α , β , double layer packing
Stearin: Cto+1%L-195	20.5, 23.05, 21.15, 19.2	β' , β , double layer packing
Stearin: Cto emulsion+5% H ₂ O	20.55, 23.05, 19.8	β' , β^* , double layer packing
Stearin: Cto emulsion+20% H ₂ O	20.5, 23.05, 20.0	β' , β^* , double layer packing
Stearin: Cto emulsion+35% H ₂ O	20.35, 23.05, 21.1, 19.65	β' , α , β^* , double layer packing

* Low to no detectable peak signal.

The results imply that the fractionation leads to the modification in the polymorphic form of the coconut oil. The coconut stearin obtained from dry fractionation of the pure coconut oil is more susceptible to the polymorphic transformation from the β' to β form. It is known from the results of Chapter 4.1.5 that the fat samples were frozen prior to the XRPD analysis which results in the occurrence of the α form.

It is surprising that the α form does not exist in the coconut stearins obtained from the fractionation processes where the initial oil containing L-195, even though they were frozen like the other samples. In addition, the peak indicating the β form of the coconut stearins from emulsion fractionation is much smaller than the coconut stearin from the dry fractionation. Based on this information, it seems to be that L-195 is not only effective as a crystal habit modifier to the coconut oil, but also functions as a polymorphic stabilizer. The addition of L-195 stabilizes the β' form of coconut oil and prevents; more or less, the transformation to the β form as well as to the α form after the fractionation. This β form prevention is of great desire for the confectionary products since the texture of the β form fat crystals is different from the β' form giving an unpleasant mouth feeling [Ham95].

4.4.2 Evaluation of the fractionation processes

4.4.2.1 Crystal growth rate

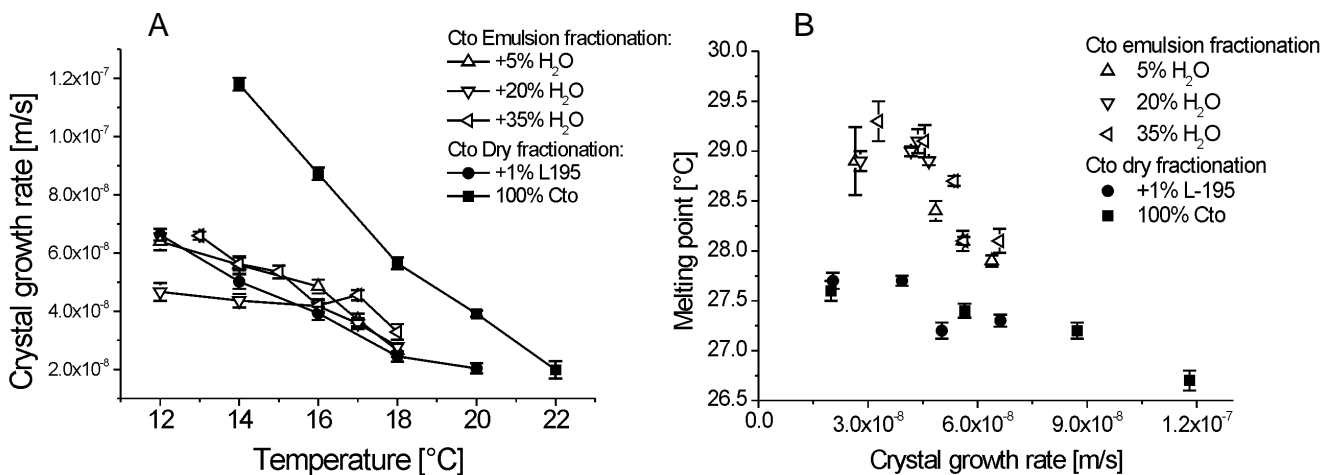


Figure 4.28: Crystal growth rate of coconut stearins as a function of (A) cold finger temperature and (B) melting points.

The overall growth rates of coconut stearin crystals calculated based on Equation 3.14 from emulsion fractionation are compared to that of the dry fractionation process (Figure 4.28A). From all fractionation processes, it can be seen that the operation of the fractionation must be done at slow crystal growth rates in the range of 10^{-8} to 10^{-7} m/s in order to achieve the fractionation of the high melting coconut stearins. The crystal growth rate of the coconut stearins decreased with increasing the cold finger temperature. The addition of the emulsifier (L-195) in the coconut oil fractionations either with or without water results in the retardation of the crystal growth rate in comparison to the process without L-195 at all cold finger temperatures. This can be explained by a kinetic study of L-195 on the crystallization of coconut oil. L-195 inhibited the crystallization kinetics of coconut oil (see Chapter 4.1.2). And the crystal growth rates of the emulsion fractionation process regardless water concentration are relatively in the same range as the dry fractionation of coconut oil containing L-195. This gives a hint that an increase in the supercooling value might not be significantly needed for the crystallization of the water-in-oil emulsion drops since the continuous phase is the oil phase, unlike oil-in-water emulsion systems [Huc09].

Faster growth rates in the range of 10^{-7} m/s leads to the low melting point of the coconut stearin indicating low separation efficiency (Figure 4.28B). The results at the slow growth rate range of 10^{-8} m/s reveal that the coconut stearins obtained from emulsion fractionation process have significantly higher melting points than that of the dry fractionation process. This implies that in order to produce coconut stearin via a dry fractionation with the same purity as that of the emulsion fractionation, extremely slow growth rate probably in the magnitude of 10^{-10} m/s, which is time and energy consuming, is needed. The reduction of the viscosity effects via the emulsion production and the modification of coconut oil crystal habit via L-195 addition enhance the solid-liquid separation by lowering the content of low melting liquid inclusions.

4.4.2.2 Yield

Yields of the coconut stearin obtained from the emulsion fractionation processes in comparison to that of the dry fractionation processes are plot against the cold finger temperatures as shown in Figure 4.29.

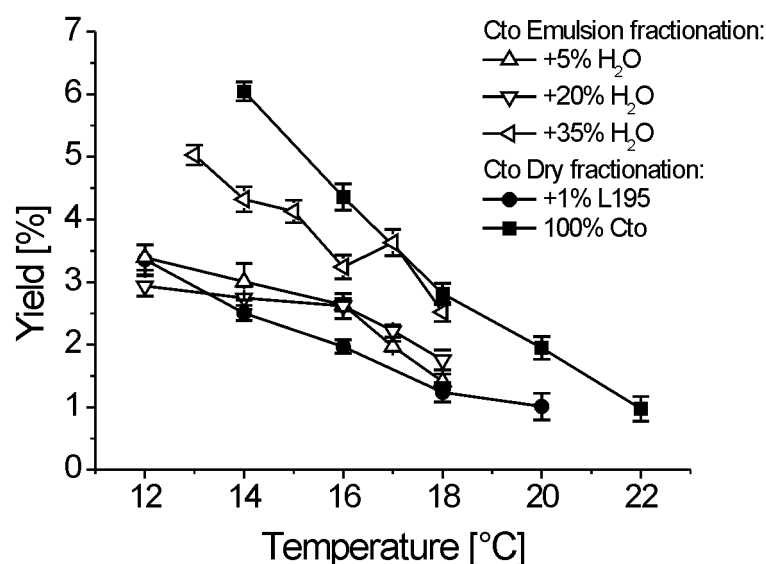


Figure 4.29: Yield of the coconut stearins obtained from different fractionation processes.

In consequence to the crystal growth rate, the coconut stearins of the fractionation process involving with L-195 addition are lower than those from the fractionation of the pure RBD coconut oil. However, the stearin yields of the emulsion fractionations increase with the increasing water concentration. This is due to the fact that the stearin yield based on the relation of the solid fraction to the initial oil amount (Equation 3.15). Increasing water concentration in the emulsion refers to the reduction of the oil phase. Consequently, the stearin yield from the emulsion fractionations increased with the increasing water concentration. Especially, the stearin yield of the fractionation of coconut emulsion containing 35 wt-% water can be produced at the similar ranges of the yield obtained from the dry fractionation of the pure RBD coconut oil.

4.4.2.3 Effective distribution coefficient

The effective distribution coefficient (K_{eff}) is introduced as a measure to evaluate the separation efficiency of the fractionation process in terms of the purities of the fractionated products. In this case, the coconut stearin fraction is the main product. As defined in the previous chapter, the low melting fatty acid group of medium chain fatty acids and unsaturated fatty acids is considered to be the impurities which lower the SFC and the melting point of the coconut stearins. To obtain high melting coconut stearins, the low melting fatty acid group must be retained in the coconut stearin composition as low as possible, indicating a good separation of the process. The effective distribution coefficient is calculated based on the ratio of the impurities of the coconut stearin to the impurities of the initial feed oil. Therefore, K_{eff} is a

dimensionless parameter where the lower K_{eff} is, the higher is the purities as well as the separation efficiency of the fractionation process. In this case, K_{eff} of both emulsion fractionation and dry fractionation processes were examined and used to evaluate the separation efficiency.

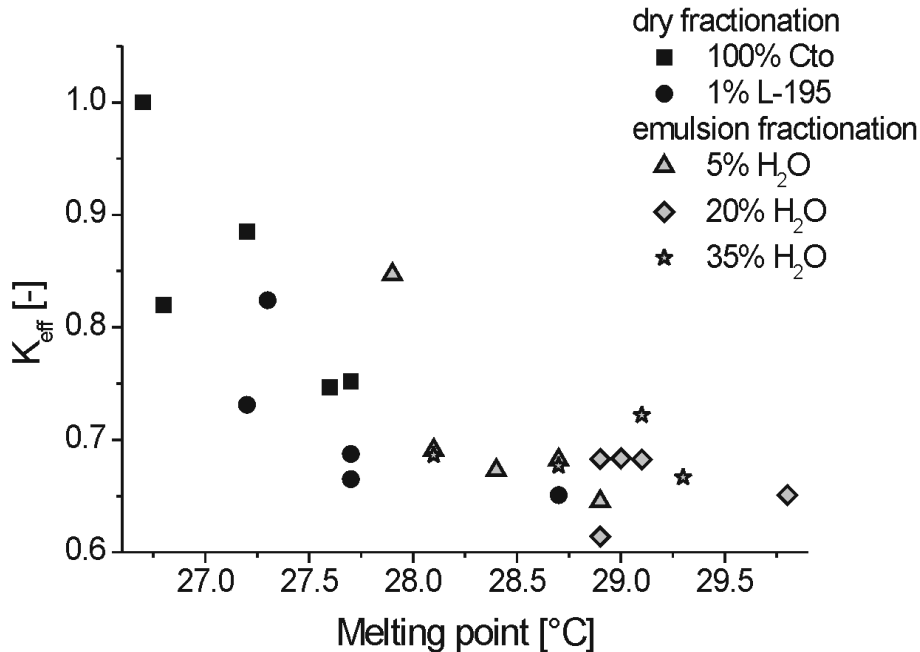


Figure 4.30: Effective distribution coefficient of the emulsion fractionation process with 3 water concentrations and the dry fractionation of RBD coconut oil and in the presence of L-195 as a function of the melting point of coconut stearins.

The effective distribution coefficients of the fractionation process of coconut oil emulsion with 3 water concentrations and the dry fractionation of coconut oil melt as a function of the melting point of coconut stearins are shown in Figure 4.30. The diagram clearly indicates that the K_{eff} of the fractionation process decreases as the melting point of the coconut stearin increases. Furthermore, K_{eff} of the emulsion fractionation is lower than that of the dry fractionation process with the higher melting point of the coconut stearins. As a consequence, the emulsion fractionation has a better separation efficiency than the dry fractionation process in terms of product quality.

Considering only the emulsion fractionation systems, K_{eff} of the process decreases as a water concentration increases. However, increasing of the water concentration above 20 wt-% has no further effect on the K_{eff} since the K_{eff} of the emulsion fractionation of both 20 wt-% and 35 wt-% water concentration are in the same ranges.

4.4.2.4 Mass-related distribution coefficient

From an economical point of view, not only the product quality, but also the product quantity must be taken into account. In order to define if the emulsion fractionation process is more cost effective than the conventional dry fractionation, the concept of the mass-related distribution coefficient (K_{m-eff}) is further extended from K_{eff} . This dimensionless K_{m-eff} parameter is therefore calculated by relating coconut stearin yields of these fractionation processes to the product purity according to Equation 3.17.

Figure 4.31 is the diagram showing the K_{m-eff} of the emulsion fractionation process comparing to that of the dry fractionation process as a function of melting point of the coconut stearins.

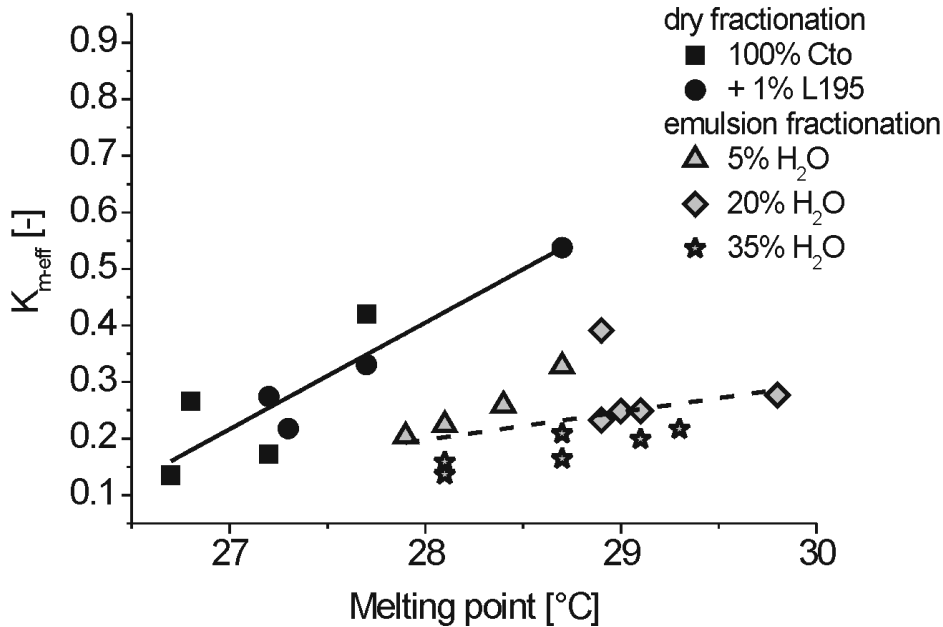


Figure 4.31: Mass related distribution coefficient of the emulsion fractionation in comparison to the dry fractionation as a function of the melting point of coconut stearins.

The evaluation of this diagram can be made by comparing the K_{m-eff} of emulsion fractionation and the dry fractionation process. K_{m-eff} of the emulsion fractionation is lower than that of dry fractionation process indicating a higher efficiency. It is clear that the emulsion fractionation meets the requirement as the better cost effective process. To point out, at the same purity of the coconut stearin, higher amount of yield can be obtained from the emulsion fractionation process. The melting point of the coconut stearins from the emulsion fractionation is approached 30 °C, at the same time; the amount of the stearin yield is acceptable. For the emulsion fractionation, the increasing of water content of an emulsion mixture resulted in a slight reduction of the K_{m-eff} . This is because higher amounts of the coconut stearin were obtained as explained in chapter 4.4.2.2. For this reason, it can be concluded that an emulsion fraction process is the more cost effective process compared to a dry fractionation process from the economical point of view by taking the purity as well as yield of the product into account.

5. Discussion

5.1 Effects of additives on crystallization behaviour of coconut oil

5.1.1 Melting behaviour

In this study, the experiments concerning melting behaviour by DSC was conducted at the scanning rate of 2 K/min. It was known from Tan [Tan01] that the thermal profiles of fat depend on the scanning rates. In the case of coconut oil, the melting profiles at all heating rates exhibit similar characters with one sharp major peak and a shoulder at the lower temperature side. This behaviour indicates cooperative nature of the TAG composition. The major peak is suggested to be the main saturated TAGs composed of capric acids, lauric acids and myristic acids according to Tan [Tan01]. However, at high scanning rates (10-20 K/min), the distance between the main peak and the shoulder increases with larger peak enthalpy since there is no time for the substance to response to the transmitted heat. At the slower scanning rate of 1 K/min, there is in fact more accurate information, but the experiments are time-consuming. Therefore, the scanning rate of 2 K/min which provided sufficient information was selected as an optimum rate for the analysis of coconut oil.

Additives in this work are defined as the amount of the foreign substance that adds to the coconut oil and does not thermodynamically affect phase diagram of coconut oil TAGs, but it has definitively a kinetic effect. The addition of free lauric and stearic acids at the concentrations upto 10 wt-% and 1 wt-%, respectively did not interfere with the melting profile of coconut oil. But, the addition of lauric acid and stearic acid at concentrations of 15 wt-% and 2 wt-%, respectively into coconut oil caused in the occurrence of the extra peak of the free fatty acid (peak I, Figure 4.7A and B), indicating thermodynamic intervention. In this case, the system of coconut oil TAGs in the presence of these free fatty acid concentrations is not a binary system any more, but involving the third component which is the free fatty acid. Hence, lauric acid and stearic acid at these concentrations cannot be considered an additive in the coconut oil system.

It is noticed that the concentration of lauric acid that can be added to the system without affecting the melting behaviour of coconut is higher than with stearic acid. This indicates the stronger interaction and dilution when mixing coconut oil with lauric acid compared to stearic acid since lauric acid is the main fatty acid of coconut oil TAGs. This behaviour is suggested to strongly depend on the similarity in molecular characteristics between low and high melting components.

However, the study in both sucrose laurate types based on melting behaviour cannot be included in this hypothesis due to the very low studied concentration in comparison to fatty acid. Moreover, it is probably due to the overlapping of the L-195 peak in the major peak since L-195 has similar melting range like coconut oil.

Toro-Vazquez [Tor02] reported that the equilibrium melting temperature of the blends of palm stearin and sesame oil was independent from the blend concentration and

the cooling rate to reach the isothermal condition but it rather depended on the heating rate for remelting. Therefore, the nucleation kinetic was quantified based on one equilibrium melting temperature for all blend compositions. This is partially true in the case of fatty acid additions in coconut oil here but not in the case of the sucrose ester addition where the T_m° of coconut oil mixtures significantly increases as a function of sucrose ester contents even at a much lower concentration comparing to fatty acid additives. The increase in T_m° by sucrose ester addition might be explained according to the polymer study since there are several analogies between fats and polymers and the T_m° theory was actually derived from polymer applications. The crystallization of a crystalline polymer mixed with a compatible amorphous one resulted in the larger lamellar thickness than the pure crystalline polymer. This is due to the fact that the lower supercooling can be supplied for the crystallization of the blend. The increase in lamellar thickness subsequently originates the melting point elevation of the blend [Run84]. Comparing to this study, L-195 and L-595 can be considered as the materials possessing amorphous parts concerning their melting behaviour and coconut oil as the crystalline substance.

For polymers, the blends of two compatible/crystallizable polymers generally lead to the melting point depression since this is potentially related to degree of intermolecular interaction between these molecules [Rim84]. In fact, the mixtures of coconut oil and fatty acids can be categorized into this group since coconut oil and fatty acids are crystalline substances according to their melting profile. However, the significant equilibrium melting point reduction of coconut oil by fatty acid has not been observed, especially in the lauric acid even though coconut oil and lauric acid has strong molecular interactions. This is probably due to the concentrations of the fatty acid mixed in the fat system are relatively low in comparison to the blends of referent polymers.

5.1.2 Isothermal crystallization kinetics

The very well-fit crystallization data of the coconut oil system in the presence of additives in this work indicates the reliability of kinetic parameters quantified by the Gompertz model. As a consequence, a further analysis based on these kinetic parameters is dependable. In fact, the induction time of nucleation can be used as a primary indicator for nucleation kinetics. However, this parameter is varied and depends on experimental conditions and the sensitivity of the detecting equipment [Tor02]. In this work, the nucleation kinetics was interpreted rather by means of Gibb's free energy where the induction time of nucleation and equilibrium melting point referring to the crystalline properties were taken into account. Therefore, it is more senseful to interpret the nucleation kinetics by mean of Gibb's energy rather than only the induction time for the fat systems in the presence of additives.

The results in nucleation kinetics in this work are in agreement with previous studies [Gor91, Mar04]. It must be noted that the Gibb's free energy of nucleation calculated in this work is significantly lower than those published in a previous work of Gordon [Gor91]. This can be explained by the shortcoming of the Arrhenius model that does

not include the degree of supercooling as stated in Chapter 2.3.3 and resulting in higher values. The values of Gibb's free energy calculated in this work are in the similar number range comparing to other fats as reported by many authors, e.g. Ng and Toro-Vazquez [Ng90, Tor02].

As written in Chapter 4.1.2, the addition of lauric acid has the strongest inhibition effect on the nucleation kinetics of coconut oil, followed by L-195, L-595 and stearic acid at the low concentration of each additive. This effect could be related to the dissimilarity in the molecular shape of the additives and the triglycerides of coconut oil. Since lauric acid is the main fatty-acid component of coconut oil, it has higher possibilities to integrate into the nucleus due to the similar molecular structure and hence retards the nucleation [Gor91].

According to the lauric ester content of L-195 and L-595, the sucrose of L-195 was esterified with the higher contents of lauric acid than L-595. As a consequence, the chance that lauric sides of sucrose ester molecule of L-195 can be integrated and adsorbed on the crystal interface of coconut oil TAGs due to the physical interaction is higher than for L-595. For this reason, the stronger inhibition effect of L-195 was observed than in the case of L-595.

In the case of stearic acid, it is unclear to interpret its real effect on the nucleation kinetics of coconut oil. This is because first, the fitting of Fisher-Turnbull equation in the fat system containing stearic acid showed a less fitability at lower 0.85 in comparison to the other additive systems whose lauric acid is the main constituent. This might be referred to the great difference in molecular structures between stearic acid and TAGs of coconut oil since coconut oil contains stearic acid approx. 3-4 % in its TAGs compositions. Moreover, the addition of stearic acid at 2 wt-% in coconut oil system affects the thermodynamic of coconut oil as described in Chapter 5.1.1. At this condition, it is likely that stearic acid started crystallizing during cooling before coconut oil and served as seeding materials, initiating the heterogeneous nucleation which significantly lowered the Gibb's energy of coconut oil. This is also in accordance with the faster crystallization rates (μ) of coconut oil in the presence of stearic acid which were quantified by the Gompertz model (Table 4.1).

It was reported that the Fisher-Turnbull equation could be applied in the multi-component system, e.g. palm oil and sesame oil [Ng90, Tor00] to predict the occurrence of polymorphs, even though it was derived from the homogeneous nucleation of a single component system [Him06, Tor01]. In this work, this concept was proven to be a useful and practical tool for the nucleation study of pure melt coconut oil. It was also extended here for the prediction of the effect of additives on nucleation kinetics of fats. It is found here that this equation is suitable to apply in fat systems containing an additive where the molecular structure of the additive is similar to that of the main fatty acid component of fat TAGs. If it is not this case, this equation is not likely to be fitable and may lead to dismiss kinetic information.

5.1.3 Metastable zone width

The nucleation point of the coconut oil was earlier detected by ultrasound velocity measurement than by the ORM technique, where the saturation point detected by the former technique is higher than the latter under all experimental conditions. As a consequence, the MZW detected by the ultrasound velocity measurements was more narrow compared to those obtained by the ORM method. This can be attributed to a higher sensitivity of the ultrasonic technique for these substance combinations, which is due to the fact that a direct evaluation of the ultrasound curves is possible. Furthermore, the ultrasound measurements exhibited a better graphical reproducibility.

The experimental results in MZW determination of multi-component systems using coconut oil as a fat model in this present work are contradictory to the previous work of Lüdecke [Lue03a]. This is because the experiments in this work were done at the high agitation speed where mass and heat transfer is sufficiently provided the homogeneous suspension density throughout the experimental periods. As a result, the ultrasound detecting sensor can detect the density change during the nucleation. The evaluation of the results in this work leads to the conclusion that the determination of MZW by ultrasound velocity technique as well as ORM is reliable and sensitive when the sufficient agitation is provided.

The ORM curves, on the other hand, enable a simple determination of the nucleation temperature while the saturation point can be estimated via a linear fitting giving the possible inaccuracy. It must be addressed that the ultrasound measurements are based on density determination while ORM detects particles possessing a minimum size within the measuring zone of the optical sensor. If the nuclei grow very slow, this can also be considered as a limiting factor concerning sensibility. For this reason, the effect of process parameters on the MZW of coconut oil was evaluated only by means of ultrasound technique.

The experiments concerning the determination of the MZW of coconut oil in this present work is in line with the previous reports that the nucleation temperature depends on the process parameters like cooling rates, agitation speeds, additives [Oma99, Chi03]. The changes in the nucleation temperature result in the variation of the MZW of the crystalline substances. The reverse dependency of the ultrasound velocity and the temperature in this work is supported by the observation of Sankarappa [San05]. As the temperature decreases, the density of coconut oil increases while the adiabatic compressibility decreases. This implies that the effect of adiabatic compressibility reduction is relatively higher than the increment of density and therefore causes in the increasing of the ultrasound velocity with decreasing temperature. It is also evident that the ultrasound velocity of coconut oil depends on the concentration of the additives. This is in agreement with the work of Omar [Oma99].

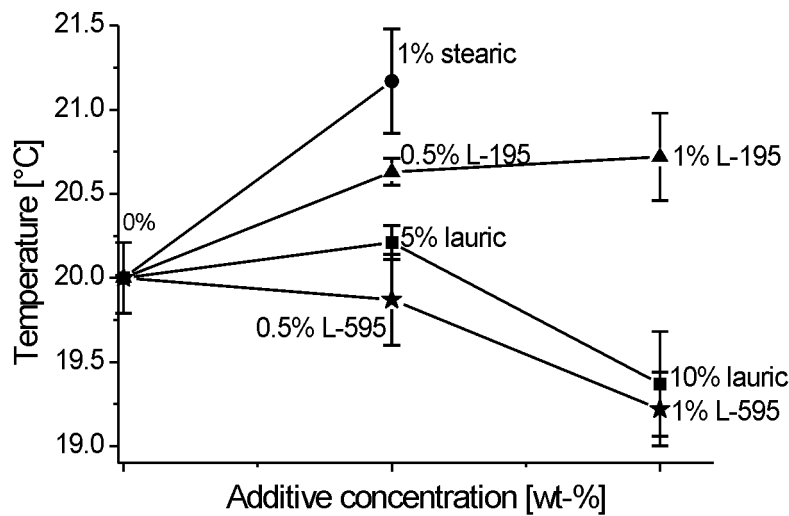


Figure 5.1: Nucleation temperature of the coconut oil in the presence of additives.

Figure 5.1 shows only the first detectable nucleation point of coconut oil in the presence of an additive. In this case, the results of coconut oil in the presence of 15 wt-% lauric acid and 2 wt-% stearic acid are not included. In this work, slightly change of the nucleation point as induced by additive can be detected, the maximum value of 1 °C significantly differed from that of the pure coconut oil (p -value <0.05). The effect of additives on the MZW of coconut oil in this work can be consequently negligible. It was reported that the ionic system of KDP crystals, the addition of trivalent cations Cr (III) suppressed the nucleation temperature of KDP crystals 20 to 30 °C below the solubility temperature [Shi89]. It must be noted that in such a system, chemical interactions like ionic bonding between additive and the crystals play a great role and thus strongly suppress the nucleation. In contrast, the nucleation of coconut oil was mainly suppressed by additives due to the van der Waals and physical interactions between the fatty additive and TAGs which are weaker than the ionic interaction. As a result, the retardation of nucleation by physical interaction might not be as great as that in the ionic systems.

Concerning the results in nucleation kinetic studies, even though the nucleation kinetics of coconut oil was proven to be inhibited by these additives, but it was not significant in the case of nucleation temperature and MZW. One reason might be the different experimental conditions and techniques. The determination of MZW was involved with many process parameters, while the nucleation kinetic was studied under, more or less, ideal crystallization conditions. This information is useful for the fractionation process of coconut oil. Additives can be applied to such a process without significantly affecting the process parameters of the fractionation, especially in suspension-based crystallization. Therefore, the fractionation process of coconut oil in the presence of these additives can be carried out at the same process parameters as pure coconut oil melt. There is no need of the further optimization.

It was reported that the crystallization via layer technique would be more beneficial than the suspension technique for a substance which has a narrow MZWs ($<1\text{ }^{\circ}\text{C}$) since the operation is not limited by MZW [Ulr03b]. In fact, the MZW of coconut oil in the presence of an additive (approx $8\text{ }^{\circ}\text{C}$) is in the operation range that is possible for both suspension and the layer crystallization technique. However, the suspension-based crystallization might be difficult for the coconut oil system due to the effects of high viscosity and unwanted crystal habit of the coconut oil. The layer-based fractionation was found to be a proper method.

It is interesting that in the system of coconut oil and fatty acids, the ultrasound velocity signals responded to both nucleation of the fatty acid and coconut oil. This can be specially observed in the case of the stearic acid system. Previously, the ultrasound technique was applied only in the systems containing a solute and a solvent to detect the MZW and define the concentration. Many publications also discussed about the application of the ultrasound velocity technique on the crystallization kinetic studies of fats and emulsions [Duk05, Klo00b, Mas96]. In this work, it was proven that ultrasound can also detect saturation point referring to the melting point in melt crystallization. Therefore, it might be possible to apply the ultrasound technique for the determination of phase diagram of a binary system in melt crystallization. This is because the ultrasound velocity depends on the adiabatic compressibility and density of the medium (Equation 3.9) which are specific parameters depending on the materials.

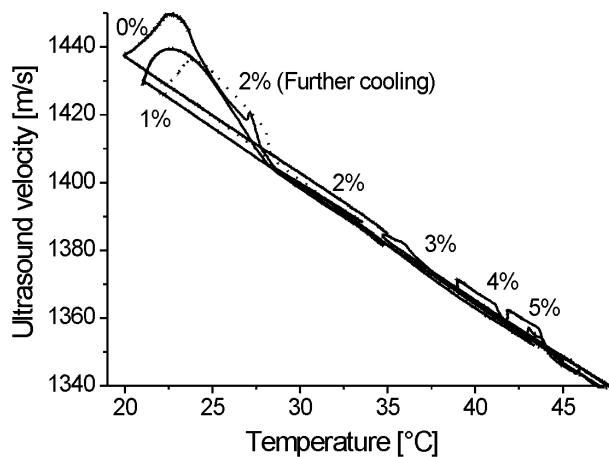


Figure 5.2 Ultrasound velocity signal as a function of the binary system of coconut oil and stearic acid.

Figure 5.2 is an example assuming coconut oil and stearic acid are a binary system. The nucleation of stearic acid can be detected at the concentration from 2 wt-% as explained in Chapter 4.1.3. Further cooling of this mixture results in the nucleation of coconut oil, indicated by the similar curve shape and the value of the ultrasound velocity to that of the pure coconut oil. The reheating signal of this mixture intersected the cooling signal of pure coconut oil at the temperature close to the saturation point of the pure coconut oil. Finally, the reheating signal of this mixture falls back to the cooling signal of this mixture at the temperature of $35\text{ }^{\circ}\text{C}$ which is

identical to the saturation point of stearic acid as shown in Figure 4.7. Increasing of the stearic acid concentration leads to a higher detectable nucleation and saturation temperature. If this concept is further extended with a sensible equation, the ultrasound velocity technique possesses a high potential to define the phase diagram and at the same time define the metastable zone width of the crystalline substances in the real crystallization conditions.

5.1.4 Crystal morphology, polymorphic occurrence and viscosity

The characterization of crystal morphology performed by light microscopy supported the hypothesis stated in the nucleation kinetics. The effect of additives on nucleation is assumed to be related to the strength of the molecular interactions between the TAGs of coconut oil and the additive, which strongly depends on concentration. In the case of lauric acid, it is well known that lauric acid is the main fatty acid component of coconut oil TAGs. Therefore, when present in relatively small concentrations, lauric acid can form strong physical bonds with the coconut oil TAGs. Figure 4.10B in Chapter 4.1.4 is a good example showing the growing lauric acid crystals out of the coconut oil spherulites as well as its own formed crystals at the 15 wt-% concentration. Unlike the case of stearic acid addition, such a double growing crystal was not observed at the 2 wt-% stearic acid addition. At this concentration, stearic acid caused in the crystallization around 28 °C and induced the crystallization of coconut oil when more supercooling was applied.

Smith [Smi05] reported that the higher melting additive may act as a seeding material and initiated early nucleation. This is in accordance to the case of stearic acid addition. But the results in lauric acid study allow the hypothesis that lauric acid does not act as a seeding material, even though it is applied in high concentrations, since it operates in the nucleus and retards the true nucleation of coconut oil. The excess amount of lauric acid seems to result in separate crystallization of the two components without inducing the nucleation of the coconut oil.

The modification of coconut oil crystals from needle spherulites into round crystals by the addition of L-195 at 1 wt-% concentration is still not fully understood. However, the adsorption mechanism and cocrystallization of L-195 on coconut oil crystals is assumed here based on the study of fatty acid additives. The lipophilic part of L-195 which is esterified lauric acid is adsorbed and integrate in the preselected coconut oil TAGs due to the strong intermolecular van der Waal interaction forces between the lauric acid parts of sucrose ester and the TAGs. Further details will be discussed in Chapter 5.3.1.3.

Interestingly, only L-195 can modify the crystal morphology of coconut oil, while L-595 only caused in the less dense spherulites. In fact, L-595 exhibit higher polarity than L-195 due to higher number of hydroxyl groups attached to the sucrose rings. This implies that the hydroxyl group referring to hydrogen bonding does not play a significant role in the crystallization of TAGs systems as described in Chapter 2.3.2. One possible reason for this might be because L-595 consists of less amounts of

estered lauric acids. As a consequence, the possibility that the molecule of L-595 can integrate with the TAGs of coconut oil is less than L-195. The hypothesis in this part is also supported by the elevation of the equilibrium melting temperature and the kinetic studies.

The polymorphic form of coconut oil was not modified by the additives in this work, even though L-195 lead to the morphological modification of coconut oil crystals. The results in this part is in accordance to Ng [Ng90]. The nucleation curve seems to be a practical tool providing the information both on nucleation kinetics as well as the polymorphic occurrence. Its application has been extended here in this work for the prediction of the polymorphic occurrence of coconut oil in the presence of additives.

In this part, XRPD did not provide the concrete information on the role of additives in the polymorphism of coconut oil due to the detection limit of the XRPD technique when the substance concentration present in the system is lower than 10 wt-%. Therefore, the extra diffraction peaks belonging to lauric acid in the coconut oil mixed with both lauric acid concentrations (Figure 4.11A) cannot be concretely identified if they are resulted from the cocrystallization or separate crystals of the lauric acid part and coconut oil molecules.

The intention to apply additives besides for the morphology modification is to reduce the viscosity of coconut oil which is the major problem in phase separation for oil fractionation based on melt crystallization. It was found that even though lauric acid strongly reduced the viscosity of coconut oil compared to the other additives, but it did not modify the crystal morphology of coconut oil. Previous studies reported that viscosity reduction (e.g. by using additives) accelerates nucleation. However, systems are known where viscosity of the bulk solution may be modified by additives without a significant influence on nucleation [Har01]. Moreover, it must be used in relatively high concentration that its natural character exhibits unpleasant odor. L-195 which promotes the alteration of crystal morphology appears to be an ineffective reducing agent of oil viscosity and tends to increase the coconut oil viscosity when its concentration in coconut oil increases. All in all, L-195 appears to be the most effective additive as a crystal habit modifier, even though it does not influence the viscosity of coconut oil.

5.2 Emulsion productions

The production of low viscous coconut oil emulsions in this part is aimed as a green technique to reduce the viscosity effect of the pure oil (melt) by using water and the food emulsifier of L-195. This is to replace the use of conventional organic solvents and detergents as describe in Chapter 2.3.2. It was found in Chapter 4.3.1 that the emulsion production via the static mixer system led to the reduction effect in viscosity as the water concentration increased. In addition, their viscosity is considerable lower than that of the pure coconut oil which meets the requirements. The reduction of the viscosity is supported by the large detected mean drop diameter and wide drop size distribution of the emulsion as the water concentration increased indicating a high

coalescence rate. In this work only sufficient pressure was needed to produce emulsion drops, since the drop size is the reverse proportion to the pressure [Flo00].

In this work, drops of coconut oil emulsions can be regarded as soft spheres [Pal 96]. Coalescence is the process referred to the drop deformation due to the rupture of interfacial film when two or more drops approaching each other resulting in a large single drop. In this operating system, the force that attracts two approaching drops and leads to the coalescence is assumed to be mainly London dispersion energy [Vin84]. Since sucrose ester is a non-ionic emulsifier, therefore the electrical double layer interaction which takes place in the case of ionic surfactants can be ignored [Vin84]. The London dispersion force (F_d) is given in Equation 5.1:

$$F_d = \frac{-Ar}{12d} \quad (5.1)$$

Where A is the net Hamaker constant, r is the droplet radius and d is the distance between two droplets. At the low water concentration, the system is considered to be the dilute emulsion where the distance of the drops are far apart. Therefore, the attractive force which brings drops close together is very low and hence it has a low coalescence rate. In this case, the coalescence rate is found to be independence of the drop size [Nan06].

Increasing of the water concentration in the emulsions related to an increasing in the volume fraction of the dispersed phase. In this case, the system can be considered as the dense emulsion where the distance of the drops is closer and the attractive force is driven higher. Smoluchowski [Smo17] simplified a theory that explains the relation between the coalescences rate and the number of drops in which the coalescence results from shearing effect. This theory is based on the assumption that all drops move along streamlines and every collision results in coalescence rate according to Equation 5.2:

$$C_s(v, v') = \frac{\gamma}{\pi} [(v)^{1/3} + (v')^{1/3}]^3 n(v)n(v') \quad (5.2)$$

Where γ is the shear rate and $n(v)$ is the number density of drops having volumes between v and $(v+dv)$. From this equation, the number density of drops ($n(v)$) is direct proportional to the volume fraction of the dispersed phase (water concentration). The volume (v) is related to the drop radius where the drop is assumed to be in spherical shape ($v = \frac{4}{3}\pi r^3$). The production of the emulsions by a static mixer at all emulsion mixtures was carried out at the same experimental conditions and thus the shear rate is constant for all emulsion mixtures. Therefore, the coalescence rate is direct proportional to the volume fraction of water and the sizes of the drops.

Beside the shear effect, the coalescence of drops can also result from the Brownian motion and specific gravity induced creaming or sedimentation. These effects will be important when drop diameters are smaller than 1 μm and specific gravity of the

continuous phase and the dispersed phase is significant different [Nan01, Pal96]. At high water concentrations, the drop sizes are large (Figure 4.16). Moreover, the specific gravity of the coconut oil and water is relatively similar (0.937 and 1 for coconut oil and water, respectively). Therefore, the effects of Brownian motion and specific gravity on the coalescence of the coconut oil emulsion at high water concentrations are small.

The coarsening of drop size as the water concentrations increase is believe to be one of the reasons for the reduction of the viscosity which is in agreement with Pal [Pal96]. At high water concentration, the dispersed phase of coconut oil emulsion is dense and above the maximum packing concentration where the viscosity becomes infinite. In this case, the pack sphere is not in the spherical but in polyhedral shape in which its rheology is governed by the thin film of continuous phase between the drops. The rheological properties including viscosity of the emulsions follow the ratio of σ/r , where σ is surface tension and r is the drop radius [Pal96]. As a result, increasing the drop radius leads to the reduction of surface tension, viscosity, stress and rheological properties [Pal96]. At a low water concentration (5 wt-%), the system is diluted and has soft dispersed spheres of very small drops ($< 1\mu\text{m}$) as well as small drops (about $15\mu\text{m}$). In this case, the effect of Brownian motion may be partly involved and raises the viscosity.

In contrast to the results of the static mixer, strong flocculation of the emulsion drops occurred in the case of coconut oil emulsion produced by the rotor stator system when the water content of the emulsion is above 10 wt-%. The flocculation of emulsions results from the Brownian motion might not be the main reason since relative large drop sizes of the emulsions were obtained even at a low water content (Figure 4.17B). This phenomenon is suggested to be directly related to the air involved in the process of the rotor stator in which inertia and shear forces are high in turbulent flows [Urb06b]. Systems are known where the agglomeration rate of the concentrated suspension is promoted by air and the increase of high inertia force related to torque [Whe95].

It was reported that the oxygen permeability of the high viscous oil is lower than in water [Mac90]. In this case, an increasing water content improves the oxygen permeability in the emulsion mixtures and at the same time the amount of emulsion drops increase, indicating larger susceptible interfacial area for gas. During the high shear input of the emulsification process, bubbles are strongly mixed and transferred through the boundary layers of oil as well as water pathways. This assumption is based on the fact that at a high volume fraction of water, the amount of water is sufficient to form liquid films and at the same time being trapped within the drop by coconut oil during the emulsification. Therefore, the bubble absorption on the interface of the drops is also enhanced by a water liquid film. The gas absorption mechanism in gas-oil-water system was reviewed by Dumont [Dum03]. Figure 5.3 simulates the flocculation of the coconut oil drops enhanced by a bubble which occurred in a rotor stator system. This model is supported by the observation in the gradual disappearance of these solid-like flocs due to the coalescence of drops and bubbles after some time.

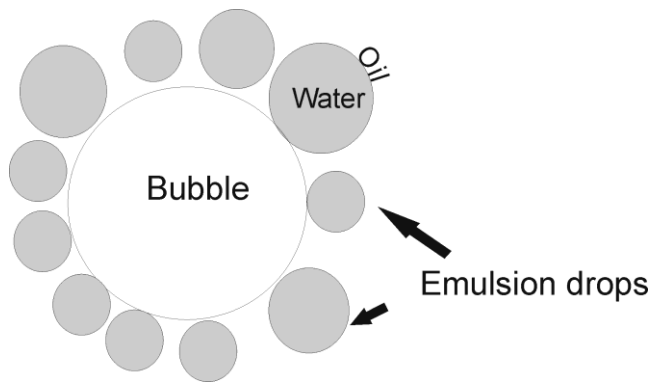


Figure 5.3: Flocculation of the emulsion drops enhanced by bubbles in the rotor stator systems at high water concentrations.

The occurrence of the phase inversion into oil-in-water emulsion of the emulsion mixture containing 35 wt-% by the production of rotor stator is still unclear since the HLB value of sucrose ester is generally stable and does not change with temperature as reported by Bolzinger-Thevanin [Bol99]. It was reported that the phase inversion of the emulsion can occur by the change of temperature or the emulsion composition [Vin84]. It is clear in this case that the phase inversion composition (PIC) of the coconut oil emulsion is at the ratio of 65 wt-% coconut oil and 35 wt-% water phase. It is, however, still a question why coconut oil produced by the static mixer at this concentration ratio did not exhibit the oil-in-water phase inversion like in the case of the rotor stator. The effect of the shear induced and gas/bubble cooperation on the phase inversion phenomenon should be further investigated.

In fact, the production of oil-in-water emulsions is very useful for the fractionation process since the viscosity of the oil-in-water emulsion is very low like that of milk. But in this case, the temperature of the emulsion must be kept above 45 °C during the fractionation in order to maintain the oil-in-water emulsion state. This temperature range is too high to drive the crystallization process on the surface of the cold finger. In consequence, it was not possible to perform the experiment to fractionate the coconut oil emulsion in the oil-in-water emulsion. Therefore, the fractionation of the coconut oil emulsions in the water-in-oil emulsion state produced by the static mixer was carried out. The effect of the viscosity reduction by emulsion production of coconut oil in terms of Ohnesorge number on properties of the fractionated product focusing on the solid fraction will be discussed and compared to the dry fractionation of pure coconut oil melt in the following sections.

5.3 Emulsion fractionation

All fractionation processes of coconut oil in which the feed contained L-195 via the cold finger equipment were done at a slightly lower crystallization temperature range as the dry fractionation of the pure coconut oil melt. This implies that the nucleation temperature controlled by nucleation and crystal growth kinetics of the coconut oil by the addition of L-195 is only slightly suppressed as discussed in Chapter 5.1.3. A Higher melting point and solid fat content of the coconut stearin was obtained at a crystallization temperature closer to the melting point of the coconut oil. This is in

accordance with the rule of thumb that the higher purities in the products will be obtained at low supercoolings, while high supercoolings cause low product purities.

As criteria to perform the emulsion fractionation, the agitation during the experiment must be sufficient to provide homogeneity throughout the whole reactor unlike that of the dry fractionation [Lue03a]. It is not possible to use the typical horizontal magnetic stirrer since this emulsion mixture is not so stable. The oil-water phase separation occurred rapidly resulting in inhomogeneous mixtures and the difference of the feed at the bottom region and the side region of the reactor can be clearly seen. For this reason, a specially designed stirrer which provides agitation horizontally at the bottom and vertically surrounding the cold finger was used to enhance the homogeneity of the emulsion feed as shown in Figure 3.8. This stirrer was also applied in the dry fractionation in order to keep the experimental conditions constantly. However, this kind of stirrer might affect product qualities since the heat transfer rate at the interfacial area of crystal layer and the melt differs from the case of a common horizontal magnetic stirrer.

5.3.1 Characteristics of the solid fractions

5.3.1.1 Solid fat properties

Low viscous oil emulsions of coconut oil, water and L-195 were successfully produced by the static mixer and the viscosity of the emulsion decreased upon the increasing of water contents. Consequently, it was hypothesized that the fractionation of these low coconut oil emulsions would lead to the higher purities (melting point and solid fat content) of the coconut oil stearin than that of the dry fractionation. For this reason, the purities focusing on melting point of the coconut stearin obtained from the emulsion fractionation are compared to that of the dry fractionation as shown in Figure 5.4. These points are related to the other parameters that govern the fractionation process like crystal habit, viscosity, as well as drop size and Ohnesorge number for the emulsion fractionation.

According to Figure 5.4 the coconut stearin obtained from all fractionation processes generally have distinctive higher solid fat properties than the initial RBD coconut oil. In the case of dry fractionation, even though the addition of L-195 slightly increased the viscosity of coconut oil, but the coconut stearin of this process has a significant higher melting point than the coconut stearin from dry fractionation without L-195. This indicates that the viscosity maybe not the only parameter determining the product purities, but also contributes to the modification of crystal habit of coconut oil by the addition of L-195. The dense non-porous round shape of coconut crystals helped in the fractionation by preventing and lowering the inclusion of the low melting TAGs in and between the crystals of the high melting TAGs. Due to this aspect, the efficiency of the solid-liquid separation is improved which consequently leads to the higher solid fat properties of coconut stearin. It can be therefore concluded that the crystal habit modification is the predominant factor determining product purities in the dry fractionation rather than the viscosity effect.

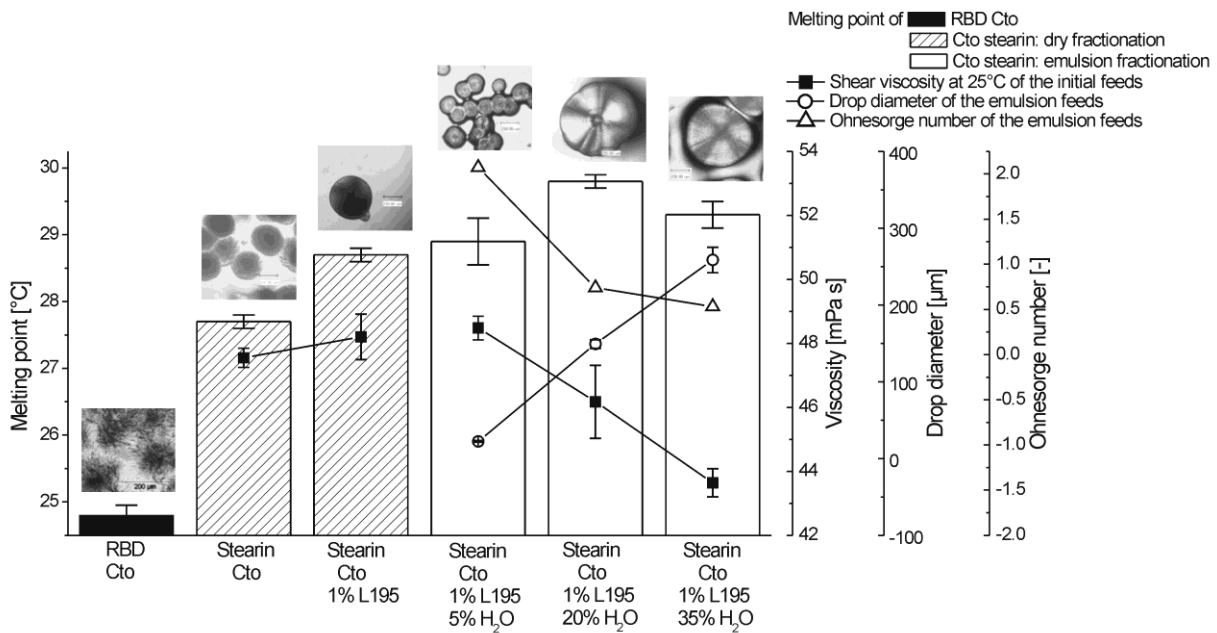


Figure 5.4: The highest melting point and crystal habit of the coconut stearin obtained from the emulsion fractionation in a relation to viscosity, drop diameter and Ohnesorge number of their emulsion feeds compared to that of the dry fractionation.

The melting point of the coconut stearin obtained from the emulsion fractionation is significantly higher than those from the dry fractionation. This can be related to the modified crystal habit and the lower viscosity of the coconut oil emulsions than the native pure coconut oil melt which is in accordance to the hypotheses stated above. Concerning only the emulsion fractionation process, the concept in viscosity reduction by water addition to improve product purities is possible only up to a certain water extent of 20 wt-%. Above this water concentration, there is no significant improvement of the product purities even though the viscosity of the emulsion feed still decreases and the emulsion drop diameter coarsens with increasing water content. In the consequence, viscosity or drop size of the emulsion feeds do not provide a reasonable explanation. This is probably because an emulsion is a complex fluid. In this case, interpretation by the Ohnesorge number which includes all the important factors that characterize the drop formation seems to be more sensible.

The Ohnesorge number of the coconut oil emulsion as a function of the water content is correlated to the melting point of their coconut stearins. Increasing of water content up to 20 wt-%, the Ohnesorge number decreased to the value below 1, indicating a low viscous fluid where the viscosity effect is not any more important and the melting point of coconut stearin increases. A further increase of the water content above 20 wt-% has no influence on the Ohnesorge number of the emulsion as well as on the melting point of the coconut stearin since the Ohnesorge number stays almost constant below 1. Strictly speaking, the Ohnesorge number reaches and stays constant at this value since the water is added from 15 wt-% according to Figure 4.18. The product purities is related to the water content by emulsion fractionation and can be predicted by means of the Ohnesorge number. The evaluation of the emulsion production by the Ohnesorge number is in accordance to Pal [Pal96]. In

order to be economic, the water content should be kept as low as possible and the oil content should be kept as high as possible. As a rule of thumb, the water concentration should be where the Ohnesorge number of the emulsion is below 1. This is the most effective concentration for the emulsion fractionation and leads to the highest product purities. The effective water content of the coconut oil emulsion mixture that helped the solid-liquid separation starts from 15 wt-%. The lower the water content is, the lower the energy is needed for the post crystallization process of water removal.

It must be noted here that the round, non-porous crystal habit of coconut stearin is independent on the water concentration of the emulsion since such a form identically occurred in all water concentrations. Moreover, the concentration of emulsifier is 1 wt-% constant, based on the oil phase. The size of the crystals is not discussed in this work since the visualized crystals were taken at the ambient temperature.

5.3.1.2 Fatty acid compositions

Coconut oil is one of the simplest fats referring to the TAG composition. It consists of only 8 % unsaturated fatty acids and 92 % saturated fatty acids whose majority are lauric acid and medium chain saturated fatty acids (see Chapter 4.4.1.2) which have strong physical interactions due to molecular similarity. For this reason and the relative low TAG type variations which are also described by Tan [Tan01], coconut oil has a narrow melting range with a small shoulder of the coconut oil (Figure 4.19A). In the consequence, the fractionation of the coconut oil TAGs containing unsaturated fatty acids from the fat matrix of saturated TAGs is easier to achieve. But it is difficult to fractionate the low melting saturated fatty acids from the high melting saturated fatty acids. To do so, the slow crystal growth rates are needed which can be reached by an emulsion fractionation with a considerable yield. Therefore, the purities of the coconut stearin are mainly governed by the content of unsaturated fatty acids.

This is evident by Figure 4.24 where the reduction of unsaturated fatty acid groups is at the higher ratio than the low melting saturated fatty acid components (MCFA from C8-10). The observation is in agreement with Ham [Ham95] who discussed the limitation of the physical-based fractionation due to the molecular structure of TAGs. Moreover, the removal of unsaturated fatty acid groups of coconut oil was more effective and enhanced by the emulsion fractionation than the dry fractionation (Figure 4.22). This is supported by the reduction in the viscosity effect and the crystal habit modification that aid the separation in the emulsion fractionation process as discussed in the previous chapter. On the basis of this, the limitation of the separation is realized at the melting point of 30 °C of the coconut stearins from the emulsion fractionation, which is approx. only 5 °C higher than the original RBD coconut oil.

5.3.1.3 Crystal morphology

The crystal habit of coconut stearin obtained from dry fractionation without the addition of L-195 exhibits spherulites of needles. The crystals of coconut stearin

obtained from all fractionation processes in which the oil feed contains L-195 exhibits round-non porous crystals. These results are in agreement with the results in Chapter 4.1.4. However, the round crystals of the coconut stearin are more obvious than that of the RBD coconut oil crystals. In Chapter 5.1.2 are discussed the occurrence of this round crystals of the two components of coconut oil and L-195 where the adsorption mechanism is corresponding due to the Van der Waals interaction between lauric acid parts of the L-195 and coconut oil TAGs. The 1 wt-% concentration of L-195 in coconut oil is above the critical micelles concentration [Ber93] and thus the reverse micelles due to the low HLB value of L-195 can be formed (Figure 5.5A). The crystallization of such a system results in round crystal formation.

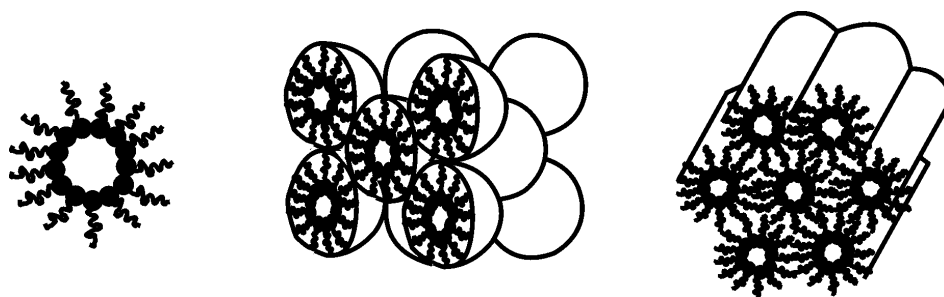


Figure 5.5: Assumed structures of (A) reverse micelles of the binary system of coconut oil and 1 wt-% L-195, (B) viscous isotropic phase and (C) hexagonal phase of the emulsion system of coconut oil, L-195 and water at a water concentration above 20 wt-% [Ott84].

When the water is added to the emulsification system, water is surrounded by the emulsifier and TAGs (water in oil type) and divided into a number of drops, allowing heteronuclei to be isolated in a certain drop. In the dilute emulsion (5 wt-%), the micelles are randomly distributed throughout the continuous phase of oil. As the water concentration increases (20 wt-% and above), the water concentration should be sufficiently high so that organized structures in the drops are able to form. The drop packings of the coconut oil emulsion in this case is assumed to be either in the shape of a viscous isotropic (cubic) or a hexagonal phase since the temperature is relatively high (Figure 5.5B and C respectively). The report from Larsson [Lar92] supports the occurrence of these packings. The existence of drop packing structures depends on the composition and the temperature range from the lowest of lamellar to the intermediate viscous isotropic and to the highest of hexagonal phase. Moreover, the emulsions occurred in the lamellar phase mostly lead to gel formation. The crystallization of the well-ordered packings of viscous isotropic or hexagonal phase of emulsion drops enhances the distinctively round crystals. However, further investigations should be done to verify the real packings of the emulsion drops. In this case, a temperature controllable short angle X-ray diffractometer is needed [Huc09].

5.3.1.4 Polymorphic occurrence

It was found in Chapter 4.4.1.4 that the coconut stearins from dry fractionation without L-195 addition are more susceptible to the phase transition from β' to β modification. It was suggested by Szyłowska-Czerniak [Szy05] that the formation of β' was attributed

to the presence of a high concentration of trisaturated TAGs. This is confirmed with the more enriched saturated fatty acid components of the coconut stearins after fractionating RBD coconut oil. According to Himawan [Him06], both β' and β forms can exist in either double or triple chain length structure. The diffractograms (Figure 4.27) reveal the existence of the double layer packing structure of the TAGs (Figure 5.6), referring to the very similar or the same natural character of their three fatty acid components [Him06]. This supports the fact that the saturated TAGs of the coconut oil are very similar in nature and hence the fractionation between saturated TAGs of coconut oil is extremely difficult.

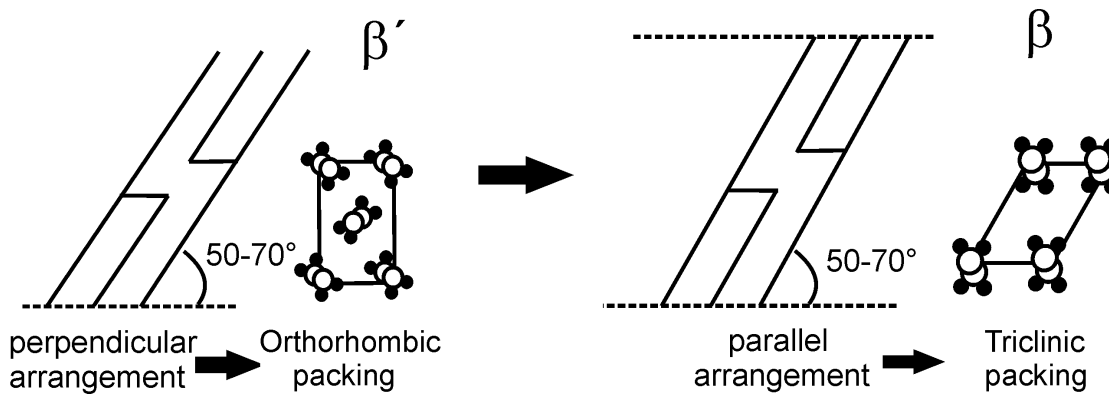


Figure 5.6: β' - β phase transformation mechanisms via the double layer rotation from perpendicular to parallel arrangement proposed for coconut stearin TAGs resulted in the change of the packing forms from orthorhombic to triclinic packing.

As described in Chapter 2.3.1, β' is the most preferred form for food industries. The occurrence of the β form causes an unpleasant sand mouth feeling in margarine for an example. Moreover, the polymorphic transitions from β' to β phase is accompanied by the formation of fat bloom in the production of chocolates [Smi06]. The addition of L-195 in the coconut oil feed stabilized the β' polymorph concerning the coconut stearin to the less extent of β transformation, indicating that L-195 is an effective polymorphic stabilizer. It was suggested by Garti [Gar01] that the effective polymorphic stabilizer should be able to cocrystallize and be structural dissimilar to the TAGs of coconut oil TAGs. The finding in this work indicates that L-195 possesses this ability. This information is in correlation to kinetic studies, in which the nucleation and crystal growth kinetics of coconut oil were retarded by L-195 addition due to this mechanism (discussed in Chapter 5.1.4).

Figure 5.6 predicts the different arrangement of the double chain structured β' and β forms of coconut stearin TAGs according to Himawan and Madsen [Him06, Mad87]. The β' form is in perpendicular arrangement with the tilt angle of 50-70° resulting in the orthorhombic packing. The rotation of the second double layer to 180° results in the parallel arrangement with the triclinic packing form, indicating the β form. It is assumed here that L-195 is incorporated into the crystal lattice of coconut oil and blocks this chain rotation. Hence the fat is not undergone the β polymorphic transformation. In order to prevent the polymorphic transformation, tempering of the fat product at a certain temperature is also possible to control the preferred polymorphic form [All03].

This process is commonly used in chocolate production whose polymorphisms are very complicated [Mac02]. So far, this tempering process has been rarely used for coconut oil. Further investigation on this might be interesting.

5.3.2 Evaluation of the processes

5.3.2.1 Crystal growth rate and yield

In general, the production rate for melt crystallization processes mainly depends on two parameters of the surface area for crystallization and the growth rate [Ulr03b]. For the static layer melt crystallization system, the typical interfacial crystal-melt area and the crystal growth rate is in the range of 10-100 m²/m³ and 10⁻⁷-10⁻⁸ m/s, respectively. This crystal growth rate range is in the same order as that of a melt suspension system. Much faster growth rates can be used by the dynamic layer melt system. In this work, the relative crystal-melt interface and the crystal growth rate were approx. 73 m²/m³ and 10⁻⁸ m/s, respectively, which is in the typical range of the static layer technique. It is noticed that the fractionation of fats via the layer crystallization technique is mostly carried out at this crystal growth rate range [Pet01], even in a lab-scale dynamic layer system [Tie97]. This implies that this crystal growth rate range is a suitable range for the fractionation of fats in order to enable the crystallization of the high melting TAG fraction in the liquid of low melting TAG fractions. For layer crystallization, the growth rate can be as high as the purity of the crystal layer, which is mainly governed by constitutional supercooling, allows it. In this work, it is assumed that the chosen operation range of growth rate is slow enough that the effect of the constitutional supercooling can be neglected.

To speed up the crystal growth rate, increasing the cooling rate above 0.2 K/h is not possible in the static layer system here since the solid fat properties of the coconut stearins are greatly deteriorated [Cha10]. Moreover, slow growth rates are required, especially, to enhance the adsorption kinetics of the additive on interfacial area of coconut oil TAGs according to Boistell [Boi88].

It is to denote that the suspension method seems to be not appropriate for fat fractionation since this process mostly requires slower growth rate than layer crystallization. In fat system, the growth rate of crystal layer is already extremely slow in order to achieve the fractionation. Via the suspension technique, the crystallization rate may be operated even at a range below 10⁻¹⁰ m/s in order to crystallize the high-melting fraction, which is too time- and energy- consuming. Moreover, the post process of solid-liquid separation after suspension crystallization is much more difficult than layer technique due to much larger and uncontrollable liquid-crystal interfacial area [Ulr03b]. This last point leads to the clear decision in favour of the solid layer process. Therefore, layer crystallization technique is proven to be the proper technique for the fractionation of fat and hence performed in this work.

According to the classical crystallization theory, the factors limiting growth rate are mainly shear viscosity (reciprocal to the diffusion coefficient) and the nucleation rate [Nga00]. This is especially true in melt crystallization. It has been shown in this work

that the addition of L-195 in the coconut oil system increased significantly the viscosity and retarded the nucleation rate of the coconut oil. Therefore, the crystal growth rate of the coconut oil is greatly suppressed. The crystal growth rate of the dry fractionation of coconut oil without the addition of L-195 is significantly faster than those in the presence of L-195 in both dry and emulsion fractionation (Figure 4.28). For this reason, the highest coconut stearin yield quantity was obtained from the dry fractionation process without L-195. However, the stearin yield from the emulsion fractionation is increasing with the increasing water content in emulsion feeds since yield was commonly calculated from the initial oil phase [Ham95]. Increasing water concentration in the emulsion feed refers to the reduction of the oil phase. Consequently, the stearin yield of the emulsion fractionation is increased.

The amount of stearin yields from all processes is relatively low in comparison to the other works. One reason is because the short crystallization period of 2 hours at the slow growth rate. In order to improve the yield quantity, the following modifications in this lab-scale experiment may be made by:

- *Longer crystallization period.* In this case, the crystallization duration must be correlated to the ending point where the further crystallization cannot take place any more since the relation of the crystal yield and the growth rate does not follow a linear but rather polynomial relation. Prolong the crystallization duration after the ending point will only waste the energy and time.
- *Using a seed layer.* The selection of seeding material is important. For coconut oil, a seed layer is suggested to be the layer of coconut stearin. However, using a seed layer has the disadvantage that the higher energy is required to cool the cold finger through the seed layer in order to reach the crystallization temperature at the surface boundary of the seed layer and the melt. Moreover, as written above, increasing the cooling rate above 0.2 K/h to compensate the energy loss due to the growing crystal layers greatly deteriorates the product qualities.
- *Increasing the melt-crystal interfacial area* since the upper limit for the available melt-crystal area for crystallization is in the order of $10^2 \text{ m}^2/\text{m}^3$. This can be done by changing the design of the cold finger and the reactor. For example, firstly, the diameter of the cold finger can be larger to increase the surface area. In this case, the volume of the melt feed will be automatically decreased if the experiment is done at the same reactor. Secondly, to perform the experiment at the same volume of the melt fed (60 g), the diameter and the height of the double wall beaker can be reduced and increased, respectively. In both cases, the distance between the surface of the cold finger and the wall of the beaker is shorter and hence the temperature gradient is changed. For this reason, the heat and mass transfer rate should be optimized. Another possibility is to increase the surface roughness of the cold finger in a well-defined structure. The over-all surface area will be consequently increased without changing the set up of the experiment.

It was reported that post crystallization processes like a sweating process improves the purity of the fractionated products [Lue03a, Pet01, Tie97]. In this work, the sweating process was conducted for only 2 minutes. It is denoted that the sweating time and the crystal layer thickness must be optimized. The layer thickness around the cold finger in this experiment is about 0.5-1.5 mm. Hence, the increasing heat from the cold finger surface to the over-all crystal layers is transferred relatively fast. At a longer sweating time, the thin crystal layers become unstable and slip off of the cold finger, especially, in the case of the dry fractionation. This problem has been experienced by Kuszlik [Kus10] who suggested that such a behaviour might result from the low volume of high-melting solid crystals compared to that of the surrounded low-melting liquids. Hence, the contact area between solid crystals which mechanically stabilize the crystal network is depressed. During sweating where the liquid inclusion is softening, the insufficient stability would lead to the releasing and draining off of the crystals with the low-melting oil. To improve, the sweating process from the product side might be an option to partially melt only the outer layer surface where the contaminants and the inclusions of most of the low melting TAGs fraction (impurities) are located [Pet01].

5.3.2.2 Distribution coefficients

In fact, the distribution coefficients can be used to predict and optimize the effect of impurities in the initial feed on the separation efficiency [Ste03]. In this work, the initial feed is commercial coconut oil in which its composition was fixed from the manufacture. The impurity or low melting TAGs of coconut oil is, therefore, relatively constant. In consequence, the evaluation of the process by distribution coefficients was based on the melting point of the fractionated product (coconut stearin).

The evaluation of the process by both effective and mass-related distribution coefficients (Figures 4.30 and 4.31) indicates that emulsion fractionation is the more effective process compared to dry fractionation concerning both product quantity and quality. According to Table 2.2, the highest melting point of coconut stearin that can be achieved by physical-based fractionation is at 30 °C. It was shown in the results that it's not possible to achieve this target value by using the dry fractionation process alone, even when the process parameters were optimized [Cha10]. In the past, this target melting point could only be reached by using an organic solvent or a detergent or so-called solvent and detergent fractionation process, respectively [Ros85]. It is known that these processes are involved with hazardous chemicals which are not preferred for food industries and hence not performed in this work. It has been shown here that this product purity is achievable with an acceptable yield quantity by the new developed emulsion fractionation process. This process is based only on one common solvent "water" and a food emulsifier to reduce the viscosity effect unlike in the former processes. In this case, the emulsion fractionation can be considered as an environmental-friendly and suitable process for food applications.

In terms of construction, the dry fractionation process is well-known as the most cost effective process among the others [Kel07]. However, more than one crystallizer or

crystallization stage may be needed in order to increase the yield and product purities. The emulsion fractionation process seems to be more costly than the dry fractionation process since an extra unit for emulsion production and a post unit for water removal are needed. However, this is still less expensive in comparison to the solvent and detergent fractionation processes. Figure 5.7 summarizes the optimization steps of the way from the dry fractionation to the emulsion fractionation process as a useful scheme for further works. In order to extend the concept of the emulsion fractionation, further studies with more complex oils like palm oil and milk fat which can be separated into more distinctive different fractions can be done according to this flow chart. The pre-screening of the food emulsifier as a crystal habit modifier for each fat is of great importance. In this case, the fatty acid component of fat TAGs should be known since the structural molecular similarity and dissimilarity of the additive and the main TAG component of fat is the key factor determining this property as proven in this work.

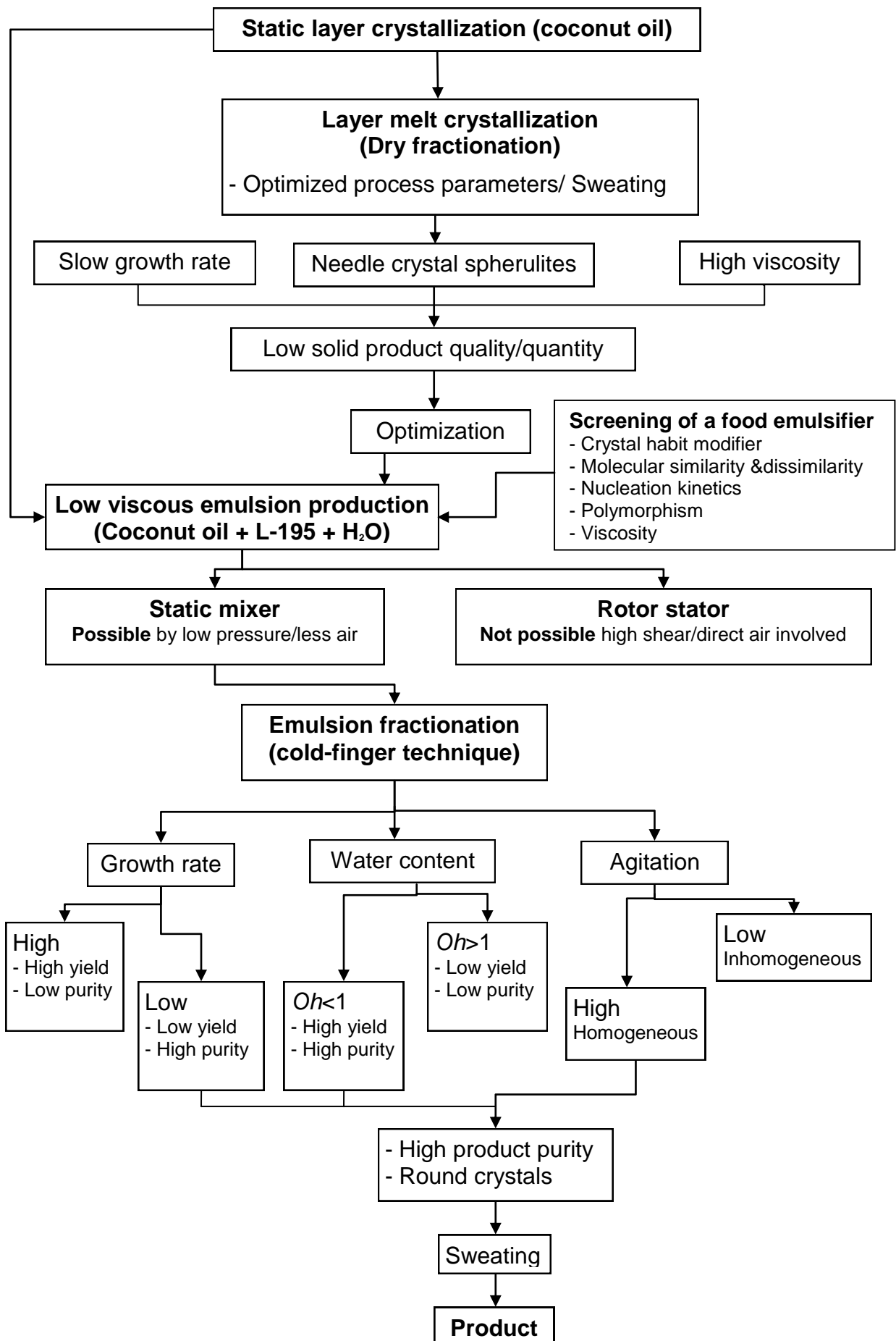


Figure 5.7: Optimization step from the dry fractionation to the emulsion fractionation.

5.4 Conclusions

On the basis of the results and discussions, it can be concluded as follows:

- Food emulsifier: sucrose laurate (L-195) is found to be the effective crystal habit modifier of the coconut oil by altering the needle spherulites into the round and non-porous crystals without changing the polymorphism of coconut oil.
- The mechanisms of crystal habit modification are assumed to depend on the emulsifier character which forms reverse micelles due to low HLB value of L-195. L-195 is adsorbed and integrated with the TAG molecules of coconut oil via the physical interaction due to molecular similarity between the lauric acid parts of L-195 and coconut oil TAGs. Moreover, the dissimilar part between the molecule of L-195 and coconut oil interfere the integration of the additive molecule into the TAG molecule.
- Hence, the addition of the L-195 as well as other additives in this work results in the inhibition of the nucleation and crystallization kinetics of coconut oil. However, the nucleation point relating to the MZW of coconut oil was slightly affected by these additives.
- The determination of MZW of coconut oil indicates that the fractionation of the coconut oil in the presence of L-195 is possible by both suspension crystallization and layer crystallization. However, the shear viscosity of the pure melt of coconut oil is naturally high and tends to increase with the addition of L-195. In consequence, a layer-based crystallization via cold finger equipment was chosen as the fractionation technique since layer crystallization is more suitable for higher viscous melts.
- It has been shown here that the application of ultrasound velocity measurement for the determination of MZW in fat system is possible. Moreover, this technique has a potential to be a promising technique enabling the construction of the phase diagram which provides the MZW information in the real crystallization conditions.
- In order to reduce the viscosity effect of the coconut oil melt, the low viscous emulsion of coconut oil, water and L-195 was successfully produced by the static mixer system. It was found that when the water concentration of the emulsion mixture increases, the viscosity of coconut oil emulsion is reduced with coarsening of drops and a more polydispersed size distribution. The Ohnesorge number of coconut oil emulsions at a water content above 15 wt-% is below 1, indicating a low viscous fluid in which the viscosity has no influence on the flow properties.
- For this reason, the new concept of the fractionation, so-called emulsion fractionation, was developed in order to overcome the main problem in solid-liquid separation of the dry fractionation process. It has been found that the use of water in cooperation with L-195 to produce low viscous emulsions enhanced the solid-liquid separation. This results in a higher melting point and higher solid fat

contents of the coconut stearin than that of the dry fractionation process, even at the same crystal growth rate. The product qualities of coconut stearin obtained by the emulsion fractionation are comparable to those of the solvent or detergent fractionation process.

- The fatty acid composition of coconut stearins was analyzed. It is well known that 90% of the fatty acid components of coconut oil belong to saturated fatty acid. It was found that the increase of the melting point of the coconut stearins results from the removal the low melting fatty acid groups of the unsaturated fatty acids rather than the medium chain fatty acids. The fractionation process is most effective for the system in which the molecular structure of multi-components are greatly different, e.g. unsaturated TAGs and saturated TAGs.
- The coconut stearins obtained from emulsion fractionation processes exhibit round and non-porous crystals as proven and explained above. Moreover, they are less phase transformation (β' to β), unlike the coconut stearin from dry fractionation process. This implies that not only L-195 is the effective crystal habit modifier, but also the effective β' polymorphic stabilizer which is a big advantage for applying L-195 in the fractionation of coconut oil for food industries. The polymorphic stabilizer property of L-195 is due to the cocrystallization ability and structural dissimilarity of the L-195 and the TAGs of coconut oil according to Garti [Gar01]. This was also supported by the kinetic study as explained above.
- The optimal condition for the emulsion fractionation concerning the solid product in quantity and in quality was found as follows:
 - A slow growth rate of 10^{-8} m/s is needed to crystallize only the high melting TAGs as well as to enhance the adsorption kinetics of the L-195 into the TAGs of coconut oil.
 - The emulsion feed composition must have an Ohnesorge number below 1.
 - A sufficient agitation is necessary to produce a homogeneous mixture thoroughly and throughout the whole experiment.
- However, yields of coconut stearin obtained from both dry and emulsion fractionation processes in this work are relatively low. Further work should be done to improve the yield. Changing of the geometrical design of the cold finger and the reactor to increase the crystallization surface area could be a possible example.
- The evaluation of mass-related distribution coefficients indicates that the emulsion fractionation process is more effective than the dry fractionation process from an economic point of view by considering both product purity and quantity. Since the emulsion fractionation process requires only water and food emulsifier, unlike a solvent or detergent fractionation, it could be considered an environmental friendly process. All in all, the emulsion fractionation process possesses the potential to be the promising alternative technique to existing edible oil and fat fractionation technologies.

6. Summary

Fractionation technologies via a fractional crystallization have been commonly used to modify the physical properties of confectionary fats in order to extend their utilizations. Fractionation of fat to obtain a higher melting solid fraction provides stability of fat products, like cookies or chocolate is the main focus in this work. The 'dry' fractionation based on crystallization of a pure fat melt without the addition of any solvents or detergent is by far the most preferable process for food industries. Such a process would be considered as a cost-effective and environmental-friendly process. However, it is well-known that the main problem in the dry fractionation of fats determining the final product purities is the incomplete solid-liquid phase separation. This is mainly contributed to *the native crystal morphology* in needle spherulites and *the high viscosities* of fats. In consequence, the fractionated products possess only low qualities.

So far, this process has been extensively developed and optimized to overcome the problem, e.g. improving the separation techniques or crystallization conditions. Nevertheless, there are always portions of liquid inclusions which limit the separation since the 2 key factors: crystal morphology and viscosity where the entrainment problem is originated, has not been optimized and understood. It has been shown here that the entrainment problem in the fractionation technology of fats can be overcome by optimizing and controlling these 2 key factors. Coconut oil was chosen as a fat model due to its functional properties and health aspect. Food additives were introduced as a key factor controlling the crystallization behaviour of the coconut oil. Consequently, the new concept in fractionation of coconut oil has been proven and developed.

The first part of this work dealt with the effects of fatty acid and food emulsifier additives on the crystallization behaviour of coconut oil. The aim was to screen the additive that effectively modified the crystal habit of coconut oil and to understand the mechanism. It has been found here that sucrose laurate with HLB value of 1 (L-195) was the effective crystal habit modifier and β' polymorph stabilizer of coconut oil. By altering the needle spherulites into round and non-porous crystals, the progress was achieved. These properties were hypothesized to be result from the emulsifier character of L-195 and the adsorption mechanism based on the similarity and dissimilarity of molecular structures between the additive and the main TAGs of coconut oil. This hypothesis was supported by the retardation of the nucleation and crystallization kinetics which were quantified by the Gompertz model and the Fisher-Turnbull equation.

High viscosity of coconut oil as well as other oils is the second key factor that governs the product purity in oil fractionation. The addition of L-195 in the coconut oil system also tends to raise the viscosity of coconut oil. Therefore, the second part of this work was to reduce the viscosity of the coconut oil by producing a low viscous emulsion of coconut oil, water and L-195 as a food emulsifier. The results revealed that the viscosity of coconut oil emulsions produced by a static mixer decreased with

increasing the water concentration, whereas a gear rim disperser produced high viscous emulsions and flocs. The viscosity effect of emulsions produced via the static mixer system was evaluated by using a dimensionless Ohnesorge number. Low viscous fluids of emulsions which the effect of viscosity is not important on the flowing fluid are indicated by an Ohnesorge number below 1. This was found at the coconut oil emulsion consisting of water content above 15 wt-%.

Both limiting key factors of the fractionation process were successfully optimized. The last part of this work dealt with a new concept in the fractionation based on the layer crystallization of a low viscous oil emulsion called “emulsion fractionation process”. This concept was proven by using a model emulsion of coconut oil, water and L-195 prepared by the static mixer and subsequently fractionated via layer-based technique. Afterwards, their fractionated solid fraction or coconut stearins were compared with those of the dry fractionation process of the pure oil melt. It has been proven that the combination of L-195 and water to reduce the viscosity effects and modify the crystal habit of the coconut oil in this new process helped in the solid-liquid separation. This resulted in higher melting point and SFC of the coconut stearin than that of the dry fractionation. The coconut stearins from this process are also less susceptible to transformation from β' to β due to the stability effect of L-195. Concerning the product quality/quantity, the emulsion fractionation process is more effective than the dry fractionation. The product qualities of coconut stearin obtained by the emulsion fractionation are comparable to those of the solvent or detergent fractionation processes. The key factors controlling the efficiency of emulsion fractionation are mainly: a slow crystal growth rate (10^{-8} m/s), an Ohnesorge number of the emulsion feed composition below 1, and a sufficient agitation.

Since the emulsion fractionation process involves only water and food emulsifier, it is considered an environmental-friendly process, unlike solvent and detergent fractionations. However, there are still some weak points of the emulsion fractionation that are needed to be improved, e.g. yield, better additional post crystallization treatments. Further experiments with more complex oils like palm oil or milk fat should also be conducted to prove and extend this concept. After all, there is a chance for the emulsion fractionation process to be a promising alternative in oil and fat fractionation technologies.

7. Notations

A	Maximum fraction of solid fat	[%]
A_c	Surface area of the cold finger	[m ²]
A_i	Peak area under of each standard FAME chromatogram	[%]
A_i^{cr}	Corrected relative percentage of FAME chromatogram	[%]
A_i°	Peak area of each FAME chromatogram	[%]
C_i^F	Impurity content in the initial oil feed	[%]
C_i^S	Impurity content in the solid crystals	[%]
$C_s(v, v')$	Coalescence rate	[m/s]
C_p	Heat capacity at a constant pressure	[J/K]
d	Distance between two droplets	[m]
F_d	London dispersion force	[J]
F_i	Correction factor	[-]
$F(t)$	Solid fraction crystallized at time t	[%]
ΔG_c	Gibb's free energy of nucleation	[J/mol]
ΔG_d	Gibb's free energy of volume diffusion	[J/mol]
h	Planck constant	6.6×10^{-34} J.s
ΔH	Heat of fusion	[J/g]
J	Nucleation rate	(1/min)
k	Gas constant per molecule	$8.3 \text{ JK}^{-1} \text{ mol}^{-1}$
K_{eff}	Effective distribution coefficient	[-]
K_{m-eff}	Mass-related effective distribution coefficient	[-]
L	Characteristic length scale	[m]
M	Mass	[kg]
N	Avogadro number	$6.02 \times 10^{23} \text{ mol}^{-1}$
$n(v)$	Number of drop	[-]
Oh	Ohnesorge number	[-]
r	Droplet radius	[m]
R^2	Correlation coefficient	[-]
R_G	Overall crystal growth rate	[kg.m ⁻² .s ⁻¹]
ΔS	Entropy	[J/K]
T	Temperature	[°C]
ΔT	Supercooling	[°C]
T_c	Temperature of the crystallization	[°C]
T_m	Melting point	[°C]
T_m°	Equilibrium melting point	[°C]
T_n	Nucleation temperature	[°C]
T_o	Initial temperature	[°C]
T_s	Saturation temperature	[°C]
v	volume	[m ³]
wt-%	Weight percent	[%]

Greek symbols

α	Fraction of molecules that in the right conformation	[-]
β_{ad}	Adiabatic compressibility	[m.s ² /kg]
γ	Shear rate	[1/s]
η	Shear viscosity	[mPa.s]
π	Surface-free energy of the crystal-melt interface	[N/m]
σ	Surface tension	[mN/m]

ρ	Density	[kg/m ³]
τ	Induction time	[min]
ν	Ultrasound velocity	[m/s]
μ	Maximum crystallization rate	[%/s]

Subscripts

<i>c</i>	crystals
<i>Oilfeed</i>	Initial oil feed
<i>solid</i>	Dried solid crystals
<i>t</i>	time
<i>total</i>	total time

Abbreviations

APCC	The association of professional compliance consultants
C:-	Number of Carbon atom : double bonds in a fatty acid chain
Codex	Codex Alimentarius commission
Cto	Coconut oil
CLD	Chord length distribution
DSC	Differential scanning calorimeter
FAME	Fatty acid methyl ester
FID	Flame ionization detector
GC	Gas chromatography
HLB	Hydrophilic-lipophilic-balance
L-195	Sucrose laurate, HLB value 1
L-595	Sucrose laurate, HLB value 5
MFCA	Medium-chain fatty acid
MZW	Metastable zone width
ORM	Optical light reflectance measurement
RBD	Refined, bleached, deodorized
SFC	Solid fat content
TAG	Triacylglyceride
TMSH	Trimethylsulfonium hydroxide
XRPD	X-ray powder diffraction

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9. Appendix

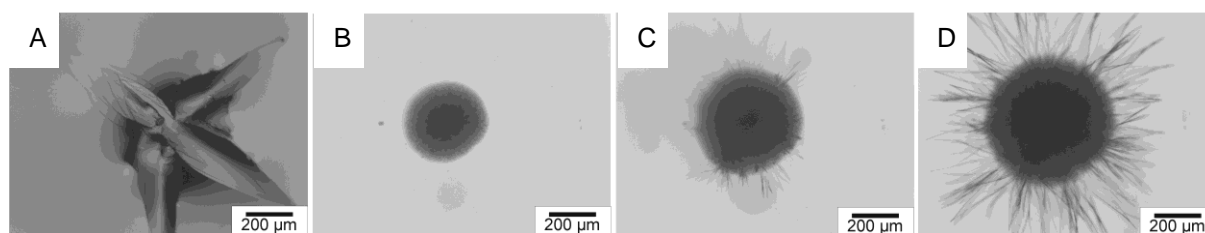


Figure 9.1: Crystal morphology of coconut oil and plate needle-like crystals of the coconut oil +15% lauric acid (A) crystallized after 60 min at 21°C, (B) crystallized at 18°C after 30 mins, (C) 48 min, (D) 50 min.

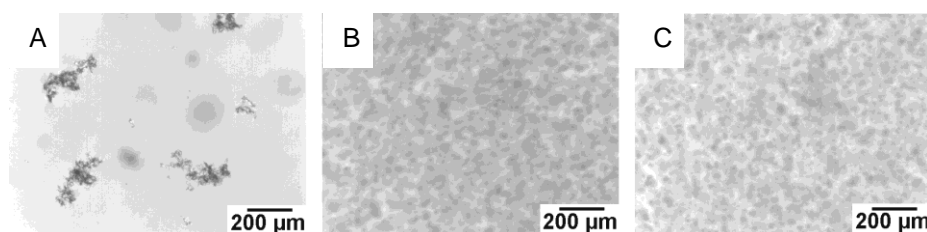


Figure 9.2: Crystal morphology of coconut oil in the presence of 2 wt-% stearic acid crystallized at (A) 28 °C, (B) 21 °C, (C) at 18 °C.

Table 9.1: Fatty acid composition of coconut stearins obtained at different crystallization temperatures from the dry fractionation process and the emulsion fractionation process.

Coconut stearin	T _c [°C]	C8	C10	C12	C14	C16	C18	C18:1	C18:2	C18:3
<i>Dry fractionation</i>										
Cto	14	7.2 ± 0.2	6.1 ± 0.0	49.5 ± 0.6	18.5 ± 0.3	9.1 ± 0.2	2.5 ± 0.2	5.9 ± 0.4	1.3 ± 0.1	0.1 ± 0.0
Cto	16	6.2 ± 0.3	5.6 ± 0.2	48.3 ± 0.2	19.9 ± 0.5	9.9 ± 0.2	2.7 ± 0.1	5.8 ± 0.2	1.4 ± 0.0	0.1 ± 0.0
Cto	18	5.8 ± 0.2	5.4 ± 0.0	48.3 ± 0.0	20.7 ± 0.1	10.5 ± 0.0	3.0 ± 0.1	5.6 ± 0.1	0.6 ± 0.0	0.2 ± 0.0
Cto	20	5.9 ± 0.3	5.6 ± 0.1	48.9 ± 0.8	20.6 ± 0.2	10.3 ± 0.4	2.8 ± 0.2	5.0 ± 0.3	0.8 ± 0.1	0.1 ± 0.0
Cto	22	7.0 ± 1.9	5.7 ± 0.4	47.9 ± 0.3	19.9 ± 1.2	9.9 ± 0.5	3.2 ± 0.7	5.2 ± 0.6	1.1 ± 0.1	0.2 ± 0.1
Cto+L195	12	7.1 ± 1.2	6.3 ± 0.7	49.3 ± 1.5	19.5 ± 1.2	9.3 ± 1.0	2.5 ± 0.3	4.6 ± 0.6	1.2 ± 0.1	0.1 ± 0.0
Cto+L196	14	5.5 ± 0.0	5.5 ± 0.1	49.0 ± 0.5	21.0 ± 0.2	10.2 ± 0.2	2.8 ± 0.1	4.8 ± 0.1	1.2 ± 0.0	0.1 ± 0.0
Cto+L197	16	5.4 ± 0.4	5.5 ± 0.2	49.7 ± 0.7	21.5 ± 0.2	10.0 ± 0.2	2.8 ± 0.5	4.0 ± 0.4	0.9 ± 0.1	0.1 ± 0.0
Cto+L198	18	4.9 ± 0.5	5.4 ± 0.3	49.8 ± 0.4	21.9 ± 0.6	10.4 ± 0.3	2.8 ± 0.1	3.8 ± 0.1	0.9 ± 0.0	0.1 ± 0.0
Cto+L199	20	5.8 ± 0.1	5.7 ± 0.0	50.4 ± 0.5	21.1 ± 0.0	10.2 ± 0.1	2.7 ± 0.0	3.6 ± 0.1	0.4 ± 0.3	0.1 ± 0.0
<i>Emulsion fractionation</i>										
Cto+L-195+5% water	12	8.0 ± 1.7	6.3 ± 0.3	48.9 ± 2.4	19.1 ± 0.7	9.2 ± 0.3	3.0 ± 0.8	4.4 ± 0.7	1.0 ± 0.1	0.1 ± 0.0
Cto+L-195+5% water	14	5.6 ± 0.5	5.7 ± 0.4	50.1 ± 0.1	21.1 ± 0.7	10.0 ± 0.2	2.7 ± 0.0	4.0 ± 0.0	0.7 ± 0.0	0.1 ± 0.0
Cto+L-195+5% water	16	5.4 ± 0.6	5.6 ± 0.4	49.5 ± 0.8	21.4 ± 0.7	10.4 ± 0.5	2.8 ± 0.1	4.1 ± 0.1	0.6 ± 0.0	0.1 ± 0.0
Cto+L-195+5% water	17	5.7 ± 0.4	5.7 ± 0.4	50.7 ± 0.6	21.0 ± 0.2	9.9 ± 0.0	2.5 ± 0.0	3.7 ± 0.0	0.8 ± 0.0	0.0 ± 0.0
Cto+L-195+5% water	18	5.4 ± 0.4	6.0 ± 0.6	50.3 ± 0.5	21.0 ± 0.3	10.7 ± 0.2	2.8 ± 0.1	3.0 ± 0.2	0.7 ± 0.0	0.0 ± 0.0
Cto+L-195+20% water	12	6.3 ± 0.4	6.2 ± 0.3	50.6 ± 0.2	20.8 ± 0.4	10.0 ± 0.2	2.8 ± 0.0	3.2 ± 0.0	0.1 ± 0.0	0.2 ± 0.0
Cto+L-195+20% water	14	5.5 ± 0.1	5.6 ± 0.1	49.8 ± 0.5	21.2 ± 0.2	10.3 ± 0.2	2.8 ± 0.1	4.1 ± 0.1	0.7 ± 0.0	0.1 ± 0.0
Cto+L-195+20% water	16	5.7 ± 0.3	5.7 ± 0.3	50.3 ± 0.7	21.1 ± 0.4	10.0 ± 0.5	2.7 ± 0.2	3.8 ± 0.2	0.7 ± 0.0	0.1 ± 0.0
Cto+L-195+20% water	17	5.2 ± 0.2	5.6 ± 0.1	50.9 ± 0.2	21.5 ± 0.4	9.8 ± 0.2	2.6 ± 0.0	3.5 ± 0.1	0.8 ± 0.0	0.1 ± 0.1
Cto+L-195+20% water	18	5.0 ± 0.1	5.4 ± 0.0	50.0 ± 0.1	22.2 ± 0.0	10.7 ± 0.1	2.8 ± 0.0	3.6 ± 0.0	0.2 ± 0.0	0.1 ± 0.0
Cto+L195+35% water	13	5.6 ± 0.2	5.7 ± 0.3	50.4 ± 0.2	20.8 ± 0.7	10.0 ± 0.3	2.8 ± 0.1	3.8 ± 0.0	0.8 ± 0.1	0.2 ± 0.0
Cto+L195+35% water	14	5.3 ± 0.5	6.0 ± 0.3	50.4 ± 0.4	21.1 ± 0.7	9.6 ± 0.2	2.9 ± 0.1	4.0 ± 0.1	0.6 ± 0.0	0.2 ± 0.0
Cto+L195+35% water	15	5.5 ± 0.3	5.8 ± 0.2	51.0 ± 0.5	20.0 ± 0.3	10.4 ± 0.3	2.8 ± 0.1	3.7 ± 0.2	0.7 ± 0.0	0.1 ± 0.1
Cto+L195+35% water	16	5.0 ± 0.4	6.3 ± 0.4	51.0 ± 0.2	19.8 ± 0.6	10.7 ± 0.1	2.7 ± 0.2	3.7 ± 0.1	0.8 ± 0.0	0.0 ± 0.0
Cto+L195+35% water	17	6.4 ± 0.2	6.2 ± 0.4	51.1 ± 0.3	20.4 ± 0.8	9.2 ± 0.8	2.4 ± 0.2	2.8 ± 0.4	0.7 ± 0.1	0.1 ± 0.0
Cto+L195+35% water	18	5.0 ± 0.4	6.0 ± 0.2	50.3 ± 0.1	21.2 ± 0.2	10.3 ± 0.2	2.6 ± 0.0	4.6 ± 0.3	0.9 ± 0.0	0.1 ± 0.0

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