Solidification of Emulsions:

Formation of Spherical Particles – A New Concept -

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1. INTRODUCTION

Vegetable oils and fats are naturally occurring triglycerides (TAGs) and fatty acids that contribute an appropriate oil phase for the production of most of the food items and as well as in the manufacturing of cosmetic and pharmaceutical products. Generally, edible fats composed of more than hundred different TAGs and their physical properties strongly depend upon the fatty acid composition. The phase behavior of water-natural triglyceride-surfactant systems got little attention because of the low solubilization of these TAGs by common surfactants at ambient conditions. The application of fats in diverse areas can be increased by improving their composition through physical or chemical processes. The modifications of fat contents of higher melting points make it possible for versatile utilization of it in the manufacturing of cookies, chocolate, margarines and shortenings. The use of fats in the form of emulsions fine particles for dressing of food items and as a drug delivery carrier system are of much interest in application for the emulsified fat particles. Hence, the idea of particles formation from emulsion for their use in the mentioning areas drew an attention and needed to be addressed.

The drop formation of individual materials has been studies exclusively in a number of chemical processes and application and their solidification behavior were observed thoroughly. They can be produced by different processes like the use of an orifice or capillary, atomization and in granulation formation e.g. in the fertilizer industry. However, the drop formation of emulsified fats has not been addressed significantly so far. Also, numerous studies are available on the isothermal crystallization kinetics of pure fats as well as mixture of fats and effects of different additives that influence the fat crystallization in the bulk system. But, solidification or crystallization of emulsified fats in the form of fine drops in a direct contact coolant at temperatures below the freezing point is rare been addressed and attempted. Therefore, this work emphases the drop formation of emulsified fats in a direct contact coolant water system. The main problem in the bulk crystallization system is that it is very difficult to control according to the desired requirements. The advantage of emulsion drop to particle technology in comparison with the bulk solidification or crystallization is, that it is easy to handle, store, and transport, and produce particles of desired size or it can easily be modified according to the application of interest.

The significance of the process is that the particles of the emulsified fats were produced taking into account of the size and the shape of the particles obtained in the coolant. The operating parameters of the process were optimized in order to obtain the particles of smaller size range in the window of current operating conditions. Refined palm oil was chosen as a model emulsified fat and span 20 as an emulsifier for the generation of drops to particles from the emulsified fat. The selection of palm oil was done due to interest of human health and the world market. Nearly 90% of palm oil produced in the world is used as an ingredient in the production of margarine, deep fat frying, shortening, ice creams, chocolate and rest 10% is employed in soap and oleo-chemical manufacturing like, fatty acids, methyl esters, fatty nitrogenous derivates, surfactants and detergents [Idr93].

The main objective and motive behind this work is to achieve spherical emulsion particles in a direct contact cooling system. To achieve this goal, work is categorized into two parts. The first part is comprises the observations obtained during the emulsification process of the fat by a magnetic stirrer and a rotor stator system. The stability, characterization, viscosity effects in the form of water concentration, and effect of different energy input were examined. In the second part, the formation or generation of emulsion drops to particles were observed based on the information and knowledge gathered in the first part. The effects of different capillary size, reduction in the interfacial tension between the coolant and an emulsion drops, effect of emulsion temperature on the particle size was measured. In this part, the generation of emulsion drops that turn to solid particles compared with the conventional fat crystallization was explored and examined. The process was then modified by reducing the interfacial tension of working materials in order to obtain the smaller particles. Finally, the crystallization mechanism within the solid particles was discussed with the literature.

2. BACKGROUND

2.1 Phase change materials

2.1.1 Theory of phase change materials

The materials used for the storage of thermal energy at short span of temperature are called phase change materials (PCM). These materials absorb and release the thermal energy in the form of heat during the loading and unloading of PCM storage, respectively. The phase of these materials shifts from solid to liquid with the slight gradient of temperature. The PCMs are commonly used for the transportation of temperature control boxes, prevention and protection from thermal shocks, storage and usage of solar energy and the thermal comfort in the buildings. The smaller temperature interval influences the loading and unloading capacity of PCMs significantly; hence, the properties of the PCM play an important role for the proper design of the system. The storage energy is termed as phase change enthalpy. Keeping in view the application of the system, the performance of the PCM may affected considerably even at small subcooling change [Gün07].

Phase change materials have been extensively studied for the number of applications in the past few decades. Inaba et al. [Ina96, Ina99] studied the tetradecane droplets behavior in the ethylene glycol solution and also meso-erythritol droplets were investigated in the silicone oil for their solidification. Nakao et al. [Nak04] observed the solidification of hexadecane droplets in the water and the water-ethylene glycol systems while Iqbal and Ulrich [Iqb10] reported the palm oil emulsion mechanism in the water coolant system. Although PCM have a wide range of potential applications in different fields but still their use in the form of emulsion is limited, especially in the area of pharmaceutical industries. Hence, the palm oil which is widely used in the food industry is considered as a PCM and its solidification behavior and droplets formation was observed.

Palm oil is a lipid extracted from the fleshy orange red mesocarp of the fruits of the oil palm tree which contains 45% to 55% oil. Two distinct oils are produced by oil palms namely: palm kernel oil (PKO) and palm oil, both of which are important in the world trade [Pur83]. Palm kernel oil is the minor oil obtained from the seed of the palm fruit which contains about

50% oil. It is a hard, light yellow in color and having similar taste of coconut oil. It is widely use in edible fats, confectionaries and baked goods, ice creams, mayonnaise, manufacture of toilet soaps, soap powders and detergents [Oye68]. Palm oil may be fractionated into two major fractions: liquid oil (65– 70%) palm olein (m.p. 18–20 ◦C) and a solid fraction (30–35%) stearin (m.p. 48–50 ◦C). The other fractions such as mid-fraction and the double fractionated palm olein (super olein) are obtained with more sophisticated oil processing. Palm mid-fraction, which has properties somewhere in between olein and stearin, contains 60% palmitic and 40% oleic acid, and is used as a cocoa-butter equivalent [Gun83, Tan81, Tan89]. Palm olein and super olein are more unsaturated and are obtained from refining, bleaching and deodorization of palm oil. The fractionation of palm oil increases the monounsaturated oleic acid with the reduction of palmitic acid as well as the quantities of oleic and linoleic acids [Gun86].

Table 2.1 Physicochemical properties of palm oil and its fractions [Has88].

Properties	Palm oil	Palm olein	Palm stearin
Melting point (^{o}C)	34.2	21.6	44.5-56.2
Relative density 50^{o}C/water at 25^{o}C	0.89- 0.92	0.91- 0.92	0.88- 0.89
Refractive index	1.46	1.47	1.45
Moisture and Impurities (%)	0.1	0.1	0- 0.15
Iodine value	47- 55.83	55.0- 61.54	21.6- 49.4
Saponification value (mg KOH/g)	196- 208.2	189- 198	193- 206
Unsaponifiable matter (%)	0.01- 0.5	0.001- 0.5	0.1- 1.0

Around the globe, 90% of palm oil is used for edible purposes e.g., margarine, deep fat frying, shortening, ice creams, cocoa butter substitutes in chocolate; the remaining 10% is used for soap and oleo-chemical manufacturing like, fatty acids, methyl esters, fatty nitrogenous derivates, surfactants and detergents [Idr93]. The physicochemical properties of palm oil and its fractions are given in the Table 2.1. Palm olein, super olein and red palm oil have similar major fatty acids e.g. palmitic, oleic and linoleic acids as outlined in the Table 2.2. But the palm olein and super olein have more oleic and linoleic acids than that of palm stearin. In fact, palm olein and super olein are more unsaturated. Hydrogenation is not necessary due to the semisolid texture of palm oil at room temperature.

Table 2.2 Fatty acid composition of palm oil and its fractions [Gun86, Kin84].

Fatty acid	Red palm oil	Palm olein	Super olein	Palm stearin
Lauric (12:0)	0-0.2	0.1-0.2	0.4	0.1-0.2
Myristic (14:0)	0.8-1.3	0.9-1.0	1.4	1.0-1.3
Palmitic (16:0)	43.1-46.3	39.5-40.8	31.5	46.5-68.9
Stearic (18:0)	4.0-5.5	3.9-4.4	3.2	4.4-5.5
Oleic (18:1)	36.7-40.8	42.7-43.9	49.2	19.9-38.4
Linoleic (18:2)	9.4-11.9	10.6-11.4	13.7	4.1-9.3
Linolenic (18:3)	0.1-0.4	0-0.4	0.3	0.1-0.2
Arachidic (20:0)	0.1-0.4	0.1-0.3	0.4	0.1-0.3
Saturates	50.2	45.8	36.6	52.1-76.2
Monounsaturates	39.2	42.5	49.2	19.9-38.6
Polyunsaturates	10.5	11.6	14.0	4.2-9.5

Margarines and shortenings comprises both of liquid oil and solid fat products which are semisolids. Palm oil is an excellent choice for the production of margarines and shortening due to naturally semi-solid property at ambient temperature. Palm oil has the distinct property among other vegetable oils and fats due to its balanced fatty acid composition. Both palm oil and palm kernel oil have large number of TAG molecules. The high melting TAG molecules influences the crystal habit and determine the crystal form.

2.1.2 Emulsions of the phase change materials

Emulsions comprise the systems in which droplets of one liquid dispersed in another liquid which is completely immiscible. They are generally classified into two types, namely: w/o and o/w emulsions. In the first type emulsions, water droplets dispersed in the oil phase, and in the second type oil droplets distributed in the water medium. Food emulsions lies in the first type while water in the crude oil in the petroleum industry belong to the second category [Cla05]. Emulsions can also be further classified into more complex forms like w/o/w or o/w/o emulsions. These complex emulsions referred as double emulsions. The PCMs have been studied exclusively in general and their emulsions were investigated in particular. Kousksou et al. [Kou09] reported the thermal analysis of different PCMs. They investigated the emulsions of hexadecane, octadecane, distilled water and NH_4CL-H_2O binary eutectic systems. The thermal and physical properties of phase change emulsions based on n-tetradecane were studied by a number of researchers [Ina95, Ina96a, and Zhe00]. The other parameters like preparation method, suitable surfactant, mass ratio, microstructure etc. of n-tetradecane based phase change emulsions were monitored by Hui et al. [Hui05].

As described earlier in the Chapter 2.1.1, palm oil is also considered as one of the PCM material among others. The uses of palm oil in the form emulsion for various applications were studied. Palm oil is generally expressed different physical forms that can be obtained by mixing the various fractions altogether or with some other oil blends to achieve the required physical characteristics. Depending on the desired function, palm oil can be used as the dispersed medium or the dispersed phase. At present, the most important palm oil emulsions are w/o type, commonly used in the margarine [Cho96]. The dispersion stability of an emulsion is the important consideration for their use in any process. The emulsion must be stable, non coalescence and have well resistance for cream formation during the course of their employment in any process. The palm oil emulsion can be prepared by different emulsification process in order to avoid the crystallization, especially, droplet size and particularly structure of the TAGs present in the oil [Ahm96].

2.1.3 Preparation and stabilization of emulsions

According to the Chapter 2.1.2, emulsions are the systems of two immiscible liquids. When these liquids mix with each other with some mechanical means, they constitute an emulsion which can eventually separate again into two different liquid after some time. Generally emulsions can be produced by different systems like: high pressure systems, membrane systems, ultrasonic systems, rotor systems and disc like systems described briefly in somewhere [Urb06]. The high pressure system is still widely used for the manufacturing of emulsions. Numerous studies are available for the production of different type of emulsions with various manufacturing procedure in order to increase the efficiency of the process e.g. high pressure homogenizer [Dic88], membrane emulsification [Nak91], micro- channel emulsification [Kaw97], turbo-mixer [Lin01]. Micro-channel and membrane emulsification techniques are used for the production of double emulsions.

Emulsions are thermodynamically instable systems and tend to destabilize because of several factors. Their stability depends on different processes like creaming, coalescence and the flocculation. Coalescence is an irreversible process which tends to its final stage after the formation of larger droplets due to the fusion of smaller droplets during the emulsion process or thereafter. This can be reduced by the reduction of the interfacial tensions using surfactants. The molecular structure of the surfactant plays a dynamic role in the reduction of the interfacial tension which is time dependent. Surfactants can be used both in the oil or an aqueous phases depending on the requirements of the emulsion to be produced [Lin01, Lam05].

As mentioned above, stability is a very important factor and the parameter for the production and the application of an emulsion. Hence, it is noteworthy that the coalescence and sedimentation processes are the cause for the destabilization of w/o emulsions while instability in w/o/w occurs due to the creaming [Mar07].

Generally, emulsions can be stabilized with emulsifiers when used individually or may be by the mixture of different emulsifiers depending on the productions and the type of the emulsions. Furthermore, emulsifiers have more interaction with the continuous phase than the dispersed one. Hence the nonionic emulsifiers are widely used for stabilization of emulsions.

Numerous studies are available in the literature: Span series (sorbitan esters) with higher hydrophobic than hydrophilic character (low HLB) is widely used for w/o emulsion production [Mar07], mixture of span and tween series [Por04]. Moreover, Berg et al. [Ber04] studied the microstructure of w/o emulsion with other emulsifiers; Gasperlin et al. [Gas94] observed the structure of semisolid w/o emulsions stabilize by silicone emulsifier.

2.2 Drop formation

2.2.1 Theory of the drop formation

After the industrial revolution during the last century, diverse studies are done and presented in the literature in order to describe the procedure and the expressions for the prediction of drop formation from nozzles in liquid-liquid systems. Among the various studies, some are cited according to chronological order. By neglecting the kinetic and drag forces, Harkins and Brown [Har19] performed a fundamental study and observed the drop formation very slowly and developed an expression that predicted the so called “static drop volume”. When the drop formation occurred rapidly, both the kinetic and drag forces play significant role that were studied in details during the 50’s (e.g. Hay50, Sie56, Uey57, Nul58). Later on, Scheele and Meister [Sch68a, Sch68b] studied thoroughly the drop formation and predicted the drop volume and jetting velocity.

When a liquid is injected through a single nozzle into another immiscible liquid at very low flow rate, the drop formed at the tip of the nozzle called static drop volume, but at higher velocity, the series of the drops formed after necking and detaching from the nozzle [Rao66, Sch68a]. There are four major forces that involved in the drop formation mechanism. These forces are, namely: the buoyancy force due to the density difference between the two liquids, the inertial or kinetic force to separate the drop from the nozzle, the interfacial tension force and the drag force that are responsible to keep the drop on the nozzle tip. When these forces are at equilibrium then it can be expressed by the Equation 2.1:

$$F_B + F_I = F_S + F_D \qquad \text{(Eq. 2.1)}$$

These forces are:

The buoyancy force, $F_B = V_{FS} g \Delta\rho$ (Eq. 2.2)

The inertial force, $F_1 = \left(\frac{4}{3}\right)\rho' Q U_N$ (Eq. 2.3)

The interfacial force, $F_S = \pi\sigma D_N$ (Eq. 2.4)

The drag force, $F_D = 3\pi\mu U_F D_{FS}$ (Eq. 2.5)

Substituting the Equations 2.2 – 2.5 in the Equation 2.1 with the appropriate expressions for the forces, the resultant expression may be written for the volume V_{FS} of the drop formed at the nozzle tip at equilibrium state:

$$V_{FS} = \frac{\pi\sigma D_N}{g\Delta\rho} + \frac{3\pi\mu U_F D_{FS}}{g\Delta\rho} - \frac{4\rho' Q U_N}{3g\Delta\rho} \quad \text{(Eq. 2.6)}$$

The additional volume "V_{FN}" of the liquid that flows out the nozzle tip during the drop break up was calculated by the Equation 2.7:

$$V_{FN} = \left(\frac{Q^2 D_N{}^2 \rho' \sigma}{(g\Delta\rho)^2}\right)^{1/3} \quad \text{(Eq. 2.7)}$$

Thus the final drop volume "V_F" calculated by Scheeler and Meister [Sch68a] after introducing the correction factor "F" proposed by Harkin-Brown [Har19] is:

$$V_F = F(V_{FS} + V_{FN}) \quad \text{(Eq. 2.8a)}$$

Subsituting the approriate values of Equations 2.6 & 2.7 respectively, in the Equation 2.8a, is left with the result as described below in the Equation 2.8 in its modified versions:

$$V_F = F\left[\frac{\pi\sigma D_N}{g\Delta\rho} + \frac{3\pi\mu U_F D_{FS}}{g\Delta\rho} - \frac{4\rho' Q U_N}{3g\Delta\rho} + 4.5\left(\frac{Q^2 D_N{}^2 \rho' \sigma}{(g\Delta\rho)^2}\right)^{1/3}\right] \quad \text{(Eq. 2.8)}$$

The Equation 2.8 was derived when the velocity profile obtained is parabolic for the liquid through the nozzle and for the plane velocity profile, the term 4/3 in the Equation 2.3 should be considered as unity. The values used for the correction factor "F" for the liquid that remain partly at the tip of the nozzle after the detachment of the drop in the Equation 2.8 is described by the Figure 2.1. Then, later in the late 70's Horvath et al. [Hor78] derived an approximate expression for the estimation of the correction factor "F" values:

$$F = 0.6 + 0.4 \exp\left[-D_N\left(\frac{g\Delta\rho}{\pi\sigma D_N}\right)^{1/3}\right] \qquad \text{(Eq. 2.9)}$$

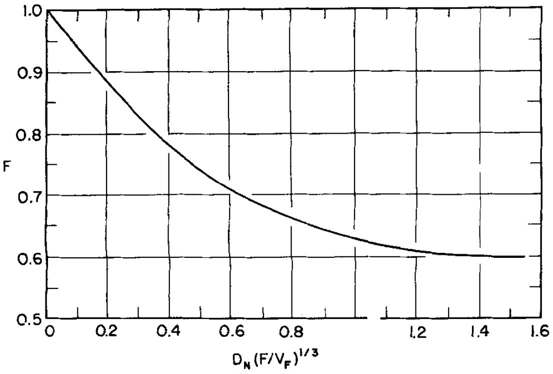

Figure 2.1 Harkin-Brown correction factor “F” for the use of Eq. 2.8 [Sch68a].

2.2.2 Drop formation from the emulsions

When a disperse phase is injected into another immiscible liquid at very low flow rate through an orifice or the capillary, two different drop formation mechanisms are observed. Qualitatively, these mechanisms may be classified as: firstly, almost static growth at the capillary tips, secondly, the necking and the detaching. It is obvious that the static approach as described here is insufficient to get through the insight of the dripping dynamics [Cra04]. With the evolution of time, the traditional approach of drop study were replaced with the comprehensive simulations of the dripping dynamics that involves the solution of the equations of mass and momentum conservation with certain boundary conditions applied. The use of one dimensional and two dimensional equations of motion and momentum [Egg94, Zha99], effect of the viscosity, flow rate and capillary diameters [Zha95, Zha97], drop generation in the flowing medium [Umb00, Ann03] are extensively studied. Later, Fang et al. [Fan04] described the production of spherical wax particles of uniform size in the coolant water at temperature lower than the freezing point of the wax.

It is worthwhile to consider the flow behavior of complex fluids like emulsions and the illustration of different forces acting on the drop formation in a diverse medium. Numerous distinct dimensionless parameters can be used in order to describe the relative importance of each of the forces involved in the droplet breakup. In the microfluidic droplet formation as described briefly in the very next Chapter 2.2.3, the capillary number is the most important to characterize the viscous stresses and the capillary pressure. The capillary number (*Ca*) for the droplet formation with relative to the continuous phase flow field is expressed by the Equation 2.10 and is consistent for the classic approach for the deformation and breakup of detached droplets in linear flow [Sto94].

The importance of the inertial and viscous forces is defined in terms of characteristic velocity of the flow and is described by the Reynolds number (*Re*), but, when the inertial force and the capillary pressure are more important than that of viscous stresses, Webber number (*We*) is frequently used to characterize the droplet breakup process. Generally, inertial force is least important in the microfluidics droplet breakup mechanism. Furthermore, the parameter which distinguishes the relative importance between the buoyancy and surface tension is given by Bond number (*Bo*) while Ohnesorge number (*Oh*) relates the viscous stresses and the surface deformation of the droplets. Typical values of these dimensionless numbers in microfluidics are: Ca varies 10^{-3} to 10^{1}; $Re << 1$; $Bo \approx 10^{-3}$, respectively [Chr07], the Oh value for the emulsions was observed by Chaleepa [Cha10] and figured out that $Oh < 1$ for low viscous emulsions and $Oh > 1$ for high viscosity. The general expressions for the dimensionless numbers are given by the Equations 2.10 - 2.14.

$$Ca = \frac{\mu G a}{\sigma} \qquad \text{(Eq. 2.10)}$$

$$Re = \frac{\rho D_H U}{\mu} \qquad \text{(Eq. 2.11)}$$

$$We = Re\,Ca \qquad \text{(Eq. 2.12)}$$

$$Bo = \frac{\Delta\rho g w^2}{\sigma} \qquad \text{(Eq. 2.13)}$$

$$Oh = \frac{\eta_o}{\sqrt{\rho\sigma L}} \qquad \text{(Eq. 2.14)}$$

In recent years, the precisely controlled droplet size and the polydispersity of the emulsion is demanded in various important applications. Few attempts were made to reduce the polydispersity of the emulsions. In these days droplet based applications are widely employed in microanalysis, protein crystallization, on-chip separation etc. [Tan08]. The uniform sized particles from emulsions gained many attentions for the transportation of the hydrophilic, hydrophobic drugs in the form of microspheres. The preparation of biodegradable micro-particles carriers like lactose, albumin, protein peptides and gelatin have received much more attentions for the controlled release of drug targeting [Men03, Wei08, Tro04].

2.2.3 Formation of smaller drops

Scheele and Meister [Sch68a, Sch68b] stated that "*Flow into the drop during the necking process can contribute significantly to the final drop volume and must be treated independently. Any empirical incorporation of this phenomenon into one of the force terms will cause errors in the dependence of drop volume on flow rate, nozzle diameter, and physical properties…* " Then after more than two decades, Skelland and Slaymaker [Ske90] studied the model proposed by the Scheele and Meister [Sch68a] for the liquid-liquid systems to observe the effects of the surface active agents on the drop size. They noted the drop sizes produced from the single nozzle in the nonjetting region and reported that the said model for predicting drop size give satisfactory agreement in the presence of the surface active agent.

On the other hand, after the development of the microfabrication techniques, the micro-structured devices were manufactured along-with the capillaries of very small dimensions. These capillaries were employed for the injection of emulsifying liquid into another immiscible liquid to obtain the smaller or narrower size distribution emulsions droplets [Chr07]. Furthermore, Serra and Chang [Ser08] reviewed the latest developments in the microfludic processes for the production of polymer particles. The most common methods used to obtain series of single smaller droplets are depicted in the Figure 2.2. Moreover, the use of capillary devices avoids the clogging or the blockage of the device whenever placed in the centre of the tools so that the droplets never meet the walls of the device.

The size of the droplet adversely affects the mass transfer processes. The smaller is the size of the droplet, the larger would be the surface area for mass transfer. So the mechanism of droplet formation from the microchannel has much importance for the better understanding of the mass transfer mechanism on micro level [Xu05].

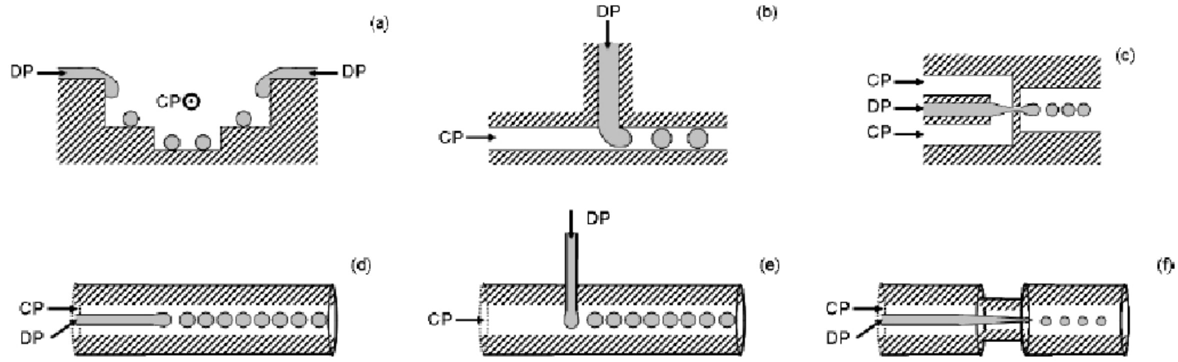

Figure 2.2 Different microfluidic devices for the emulsification of a liquid monomer. Microchannel-based devices: terrace-like device (a), T-junction device (b), FFD (c). Capillary-based devices: co-flow device (d), cross-flow device (e), FFD (f). CP and DP are respectively the continuous and to be dispersed phases [Ser08].

2.3 Solidification or crystallization

2.3.1 Fat crystallization

Edible oils and fats are largely described as the mixture of multi-components of triacylglycerols (TAGs) with a small amount of other components. TAG molecules are naturally composed of different crystalline forms or polymorphs, which exhibit significantly in different melting temperatures. Generally, the polymorphism or the crystalline arrangements in oils and TAGs exists in three basic forms: namely α (alpha) - the least stable with lowest melting temperature; β' (beta prime) form- intermediate stable; and β (beta) - the most stable and highest melting point. These polymorphisms are characterized into monotropic system [Him06]. The polymorphic arrangement leads to different morphologies of fat crystals. The α-form exist loosely packed platelets crystals while the most stable form β-form exhibits the densely needle crystals. The intermediate form, β'-form is to be found in the fine needle like crystals which makes it possible for the optimal rheological and texture properties. Therefore, it is suitable in the food industries, especially in margarine and shortening manufacturing. However, such a needle like crystal structure of fat leads to the high amount of liquid oil adhesion inside and between the crystals. Figure 2.3 describes the molecular properties of fat polymorphism [Him06, Sat99a, Sat99b].

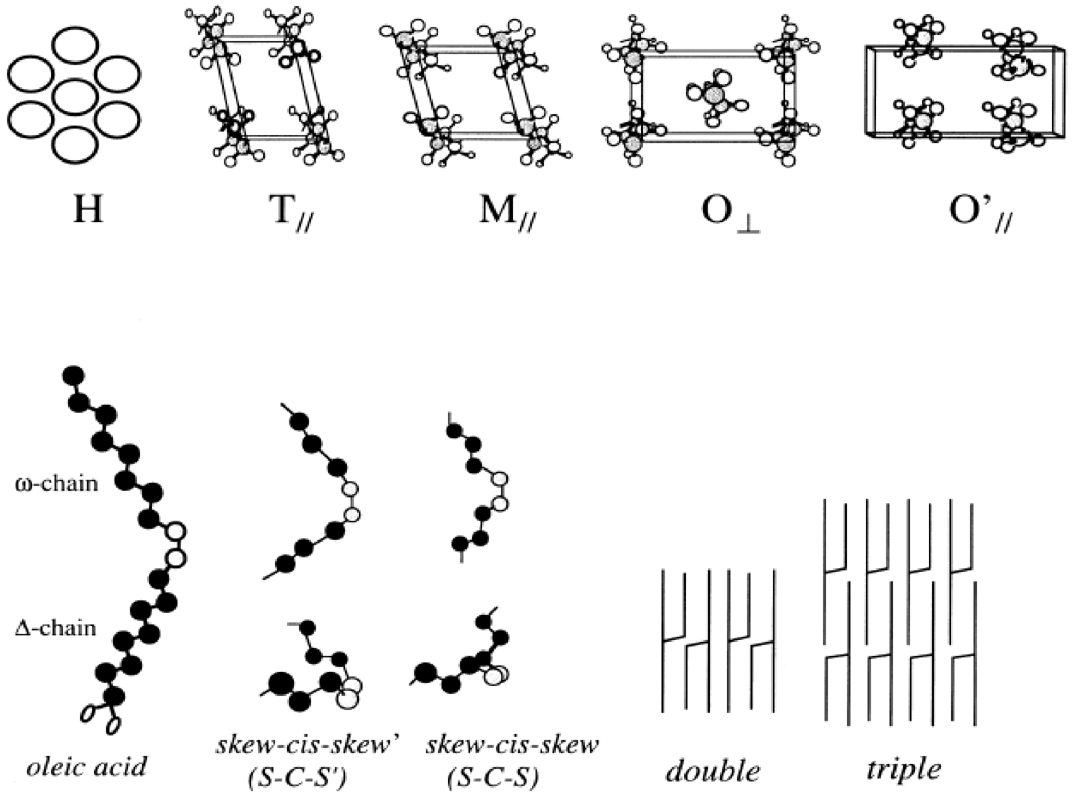

Figure 2.3 Molecular properties of fat polymorphisms [Sat99a, Sat99b].

Other important parameters that greatly affect the crystallization of the fats are the effect of the additives, influence of temperature on the physical properties of fat and fat based emulsions. Miskandar et al. [Mis02] observed the effect of emulsion temperature on the crystallization of palm based margarine in detail. Chen et al. [Che02] reported the isothermal crystallization kinetics of refined palm oil while the effect of additives on the crystallization of palm fraction in oil in water emulsion was examined by Awad and Sato [Awa01]. Generally, vegetable as well as animal oil crystallizes from the suspension in the form of spherulites with soft needles growth. The spherulites obtained from different oils solely or in combination with other oils or fats in shown in Figure 2.4, observed by various researchers.

The polymorphic forms of palm mid fraction (PMF) are highly influenced by the type and the amount of the additive used and the cooling temperature. The preferential formation of the "α" and/or the "β " forms of PMF are greatly affected by the said parameters. It was also observed that the other factors which alter the polymorphic forms of the fat crystals are:

supercooling and the rate of the nucleation. When the two forms have similar nucleation rate then the polymeric form having higher value of supercooling crystallizes more easily. This difference was observed in tripalmitin by Sato and Kuroda [Sat87].

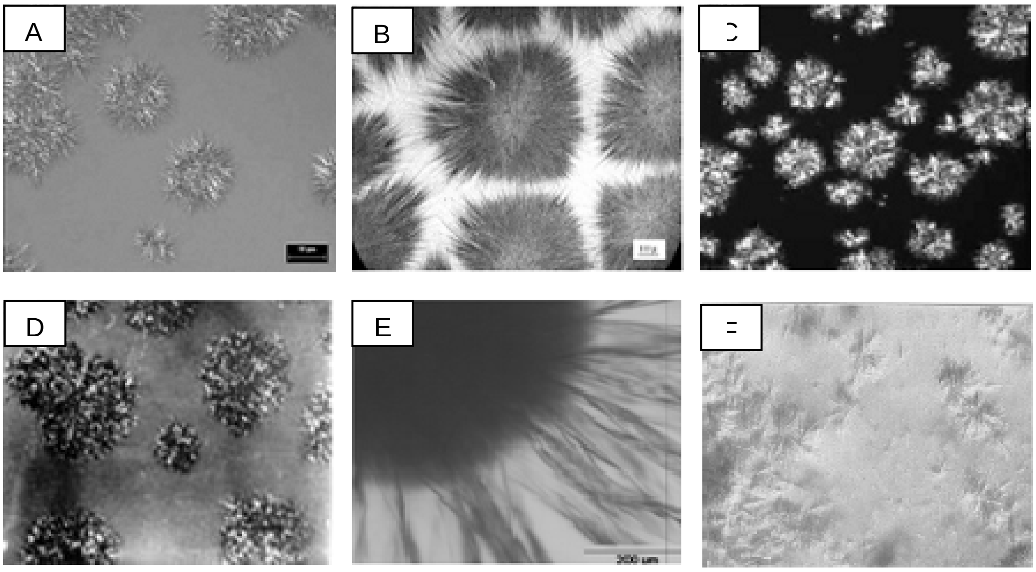

Figure 2.4 Crystal morphology of (A) palm oil [Che02], (B) fractionated palm kernel oil [Sch01], (C) milk fat [Wri02], (D) mixture of palm stearin/sesame oil [Tor00], (E) coconut oil with 15% Lauric acid [Cha10], (F) milk fat with single needle and agglomerate [Tie97].

Recently, the in-house work regarding the fat crystallization, crystal morphology and the effect of additives on the crystallization mechanism was reported by Chaleepa [Cha10]. A thoroughly studied regarding the fractional crystallization of coconut oil as a model substance was done and the effects of different additives on the polymorphic forms and the mechanism of crystallization was observed in detail. Earlier, Tiedtke et al. [Tie94] investigated the crystallization and separation of milk fats by solid layer crystallization. They investigated the diverse parameters in the process of solid layer crystallization in order to obtain quantity and quality based products. Moreover, higher melting fractions were acquired by the optimal post crystallization treatment of the said products.

2.3.2 Solidification/Crystallization of emulsion drops

Many materials are purified by the layer crystallization processes with higher melting points at ambient conditions. Therefore, it is the need of the hour to produce solidified materials which have the advantage of handling, storage and transportation especially the toxic compounds. Hence, Kallies et al. [Kal93] studied the direct solidification of particles during the drops formation from the melted material by layer crystallization. They noted that the solidification of single drops in colder atmosphere, nucleation starts from the surface which is directly in contact with the colder sites. Other parameters like, shape of the particles, surface roughness, stability was also observed. The complete solidification was occurred from outside to inside. Later, Inaba et al. [Ina96, Ina99] examined the drops solidification of different materials in the coolant and observed the similar behavior as described earlier in Chapter 2.1.1 in details.

Fat crystallization in the emulsion has many interests for both physical and food scientists because some emulsified fats in food crystallize at the ambient conditions [Sat99]. Emulsion crystallization has great potential not only for particle formation in the material science but is also important for the new purification processes. Davey et al. [Dav96] showed that the impure m-chloronitrobenzene crystallizes and purified in a single stage. Crystallization in the emulsions occurred when the conditions changed through cooling, chilling or supersaturation, so that the free energy of a solid phase is lower than the free energy of liquid [Har01]. In case of cooling, high degree of supercooling is required from microscopic to macroscopic size. It is to be believed that in the bulk of the melt, some impurities present in the bulk may be the starting point of the nucleation prior the supercooling to be reached which make the crystallization more rapidly. Skoda and Tempel [Sko63] noted when the dispersed droplets are very small then the number of droplets exceeds the number of impurities present in the bulk. Therefore, the fat droplets would be free of any impurity and hence crystallize through homogeneous mechanism. The Chapter 2.3.3 described the crystallization mechanisms in details.

Crystallization in emulsions is not as simple as it is described above. Crystallization in the emulsions droplets is influenced by diverse factors. These factors includes: the size of droplets, collisions between the droplets, impurity inside the droplets, the type of surfactants to be used in general and the effects of the oil-water interface in particular, are significant [Shi08]. As cited in the literature, oil-water interface plays a vital role in the crystallization process in the emulsion. Moreover, the surfactant at the oil-water interface in a bulk system prevail the interfacial freezing. In addition, it is figured out that the interfacial freezing act as a template for further crystallization. Hence, surfactant itself has great attention in the crystallization [Lei04, Slo05, Wil06, Slo07, Hen07].

Additives have been widely used in the modification of 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. In fat systems, these chemical interactions are not as much significant as in ionic and inorganic systems [Cha10].

As described in the above paragraphs, emulsion crystallization is greatly influenced by the impurities or additives. Both the nucleation and the crystal growth in the emulsion are affected by the additives present. Therefore, Kaneko et al. [Kan99] extensively elaborated the effect of sucrose ester in the crystallization kinetics of hexadecane while diacylglycerols influence to the oil phase was noted by Awad et al. [Awa01a]. Similarly, the additives in the emulsion and its consequential effects on the crystallization were thoroughly studied and illustrated by number of researchers; like, monoglycerides and triglycerides effects on semi-crystalline emulsion droplets stabilized with sodium caseinate [Dav00, Dav01], effect of additives on polymorphic forms of palm oil crystallization [Awa01], crystallization rapidness of palm kernel oil in oil-in-water emulsion by hydrophobic emulsifier additives [Awa02].
The crystallization behavior, polymorphic forms at various conditions, other parameters that highly influence the crystallization in the emulsion in the bulk as well as in the droplets forms have been studied broadly and summarized briefly in this section. The comprehensive detail of crystallization mechanisms within the emulsion is largely described in the Chapter 2.3.3.

2.3.3 Crystallization mechanism

There are common misunderstandings and misconceptions about the crystallization mechanism of emulsified fats. More often, it is wrongly assumed that fat crystallizes through a homogeneous mechanism. But the fact of the matter is that the homogeneous mechanism is only dominant when the size of the particle is reduced so that only single nuclei are present per droplet. Therefore, the overall mechanism may depend on the composition, purity of the fat as well as the structure of the emulsion. It is also noted that the kinetics of crystallization varied with the mechanism involved [Mul01, Klo00].

In the last decade and beyond, few attempts were made from different groups regarding the effect of polydispersity on the crystallization mechanism of emulsified fats. Perepezko et al. [Per02] studied the solidification of series of long-normal distribution size class of particles while Kashchiev et al. [Kas98] developed a theory which takes into account the effects of the polydispersity of emulsion crystallization kinetics and especially the effects of volume vs surface nucleation. They showed that the polydispersity enhanced the crystallization rate. Furthermore, Kloek et al. [Klo00] explained the mechanism of crystallization of different palm oil emulsions from their kinetic measurements of solid fat content (SFC). They found that the kinetics of pure palm oil droplets showed a heterogeneous nucleation mechanism, but the mechanism was most likely homogeneous by the addition or dilution of palm oil with sunflower oil. Whereas the fats have complex compositions, therefore, self-nucleating mechanism for the emulsion nucleation was proposed. They also suggest that the self-nucleating particles contain some high melting triglyceride fractions. Moreover, similar mechanism was observed in the crystallization kinetics of emulsion droplets by the addition or depletion of the fraction described elsewhere [Hin00].

On the other hand, a necessarily diverse mechanism was noted in the crystallization kinetics of emulsified hexadecane droplets. It was observed that mechanism is not well in agreement with the single exponential function as predicted by the standard nucleation theory, but somewhat slower as the crystallization occurred. They left with the conclusion that the changes in an emulsion may occur as the crystallization proceeds [Her99]. Meanwhile, Hindle et al. [Hin00] also found that the non-exponential nature of emulsion droplet crystallization in the hexadecane and cocoa butter emulsions. Contrary to the Herhold et al. [Her99], they argued that the result could be illustrated appropriately in terms of concurrent mechanisms of direct droplet nucleation.

It is noteworthy that in an emulsion, the fat first nucleates to α-form and then partially converts to β'-form which coexists with the α-form during the remaining entire course of the experiment while milk fat in bulk first crystallizes as β'-form and then the α-form [Hin00].

They also noted the α-form during the crystallization of emulsified cocoa butter. Meanwhile, Cambell et al. [Cam01] studied the difference in the crystallization kinetics and stability of palm oil versus lard emulsions and observed the β-form. More specifically, Lopez et al. [Lop00, Lop01] confirmed that emulsified TAGs crystallize through secondary nucleation mechanism and that of homogeneous nucleation is not logical as previously described by Walstra [Wal94]. They claimed that the α-form crystallization occurred in the bulk very straightaway that it could be considered as homogeneous and their properties are similar to that homogeneous crystallization, but their claim had no concrete evidence at slow cooling. The colloidal aspects of solid for crystals existed in the oil as isolated particles or in the form of an oil water interface still has least studied and have much more attraction.

2.4 Motivation and objectives

As described earlier in the Chapter 2.1.1 in detail that the PCMs are excellent candidates for transportation and storage of the thermally sensitive materials. Their application in food, chemical, and pharmaceutical industries is of great importance. Recently, in pharmaceutical industries, efforts are made in order to develop carrier systems which ensure the controlled and well defined drug release. Solid lipid nanoparticles are considered as alternatives for drug carriers [Jas09]. Earlier, numerous studies were conducted on albumin and lactose microspheres for drug delivery. They can be prepared of broader range of particle size and carry a variety of drugs [Zen95, Har03]. Trotta et al. [Tro04] reported the encapsulation of insulin into microspheres and argued the potential application for protein and peptide delivery. Similarly, Wei et al. [Wei08] studied the formation of uniform sized amphiphilic PELA microspheres by emulsion solvent extraction and premix membrane emulsification. They proposed that these microspheres might have great potential for protein drug carrier system.

It is worthwhile to note that all the observations described above were done using or combining one or more processes to obtain the microspheres in the working fluid. However, limited studies are available to acquire the desired results using direct contact of working fluid with other immiscible fluid at various physical properties e.g. (Ina96, Ina99, Nak04).

The formation of spherical particles of PCMs by means of single capillary or nozzle in direct contact cooling medium is rarely been studied and their solidification mechanism in the coolant was seldom observed. The solidification behavior of drops from PCMs is increasing the heat transfer resistance between the liquid PCM and the working fluid (thermal energy carrier). A direct contact type thermal energy storage system has got much attention in recent past and reported elsewhere [Fan04, Nak04]. However, limited research has done so far in connection to the direct contact solidification of PCM particles moving in the liquid coolant. Therefore, the concept to produce crystalline fine solid particles which encapsulate the biodegradable materials and drugs has drawn the great attention. To achieve this, there are certain factors that influence greatly and must be copped up with the idea of producing fine particles. These factors might be: temperature of the coolant (1); diameter of the nozzle or the droplet size (2) velocity of the injected stream (3); height of the cooling medium (4); addition of the additives in the coolant medium (5) etc.

The main motive and objective behind this work was to produce spherical particles of emulsions. The process of particles formation goes by emulsion drops coming out from single capillary that turned into solid form. To apply this idea and to achieve the desired objective, different parameters were studied thoroughly which are listed below:

a) Preparation and stabilization of water-in-oil (w/o) emulsions by means of different methods like a magnetic stirrer and a rotor stator system and their effects on the size and shape of the particles produced.

b) Effect of the surfactant concentration on the formation of uniform coarse emulsion.

c) Velocity/flow rate effects and the solidification/crystallization mechanism of the emulsion drop to be solidified at temperature below freezing point.

d) The effect of water content and the temperature of the emulsion on the size and shape of the particles.

e) The influence of the additives present in the coolant that affects not only on shape and morphology of the particles but also on their size.

f) The effect of capillary diameters on the size of particles.

- **g)** The crystallization behavior which occurred inside the particles during solidification. The mechanism of fat crystallization in emulsions and the crystal structure within the droplet. Pure palm oil droplets described with the heterogeneous nucleation mechanism, but can be altered by diluting or making impure to the homogeneous. In this case the fat must crystallize via a homogeneous.

The parameters mentioned above were investigated in details and the results obtained based on these observations are reported in Chapter 4. The findings of these examinations provided a better understanding about the formation and mechanism of the process. The estimations obtained are certainly a valuable addition in this field.

3. MATERIALS AND METHODS

This chapter contains a brief description on the strategy and protocol used for the preparation of emulsions by different mechanical methods and then the formation of drops from these emulsions. The solidification mechanism is also described briefly and the diverse factors are observed using different techniques.

3.1 Materials

Refined palm oil obtained from Fluka (Sigma-Aldrich Chemie GmbH, Germany) having m.p. 30-40^{o}C and composition linoleic acid 6-13%, myristic acid 0.5-6%, oleic acid 35-50%, palmitic acid 35-48% and stearic acid 3-7% was used as model substance for the preparation of emulsions. Sorbitan laurate i-e span 20 received from Merck (Merck Schuchardt OHG, Germany) was used as an emulsifier for the stabilization of the emulsions. Berliner Blau löslich (Riedel-de Haën AG, Germany) and Alizarin Red S (Fluka Chemie AG, Germany) were used as dyes for the microscope analysis of the emulsions and the particles produced from the emulsions. Polysorbate Tween 20 (Carl-Roth GmbH, Germany) was used in the coolant to reduce the interfacial tension. All the chemicals were used as obtained without further purification. Distilled water was used for all the scheme of experiments.

3.2 Experimental methods

The experimental section is differentiated into three different Sub-Chapters. These Chapters include the preparation methods of emulsions, formation of drops and the solidification of the drops in coolant. They are described briefly here:

3.2.1 Preparation of emulsions

The emulsions were prepared by two different means namely: magnetic stirrer and the ultra-turrax rotor stator. The preparation methods of emulsion were adopted as described by Porras et al. [Por04] for a magnetic stirrer; and for a rotor stator reported thoroughly by number of researchers [Men03, Cla05, Mar07, Urb06]. A brief description of the emulsion preparation by a magnetic stirrer and a rotor stator system is given.

Magnetic stirrer emulsification

Water-in-oil (w/o) emulsions batches were prepared using palm oil as a continuous phase, water as a dispersed phase, and span 20 as an emulsifier. The span 20 was used for the stability of the emulsions. The preparation method was adopted as described by Porras et al. [Por04] with some modifications. The emulsion was prepared at different temperatures. Palm oil, surfactant and the distilled water were heated from 45- 90^{o}C before they form emulsions. Both palm oil and span 20 were heated at a specified temperature and then mixed for “2” minutes at “700” rpm using a magnetic stirrer to achieve homogeneity. Water was poured drop-wise into the mixture of oil and surfactant. This allows the water to drain off along the stirrer and permits repeatable and homogeneous insertion of water into the surfactant-oil mixture phase. The mixture was then continuously stirred for 30 minutes. The total volume of the emulsion was kept 10 mL. The conditions were kept constant for the entire course of the experiment. The parameters which remained under consideration are the concentration of surfactant and the quantity of water present. The emulsions prepared were visually stable and there was no sedimentation or phase separation for 30 minutes. The emulsifier concentration was varied from 0.2 to 5.0% (by volume) to observe the minimum amount of surfactant required for the stability and water quantity was changed from 5 to 25 % by volume, too. The produced emulsion was then further analyzed by light microscope which is being illustrated in Chapter 3.3.

Rotor stator emulsification

Generally, rotor-stator systems consist of a rotor and an axially fixed stator around the rotor. The rotor stator systems can be operated for continuous and/or discontinues systems. Gear-rim dispersion geometry is used for the discontinuous systems in general. In gear-rim system, inertia and the shearing in the turbulent flow are the major forces which in result is the available energy for the effective drop break up. Here, the product throughput lies in the centre of the available range while the product stress are classified as medium to high depending on the number of revolution and the geometry of the dispenser [Sch04]. Figure 3.1 showed the gear-rim rotor stator geometry used for the emulsification process. The details of other influencing parameters on the emulsification process are described elsewhere [Sch04, Urb06].

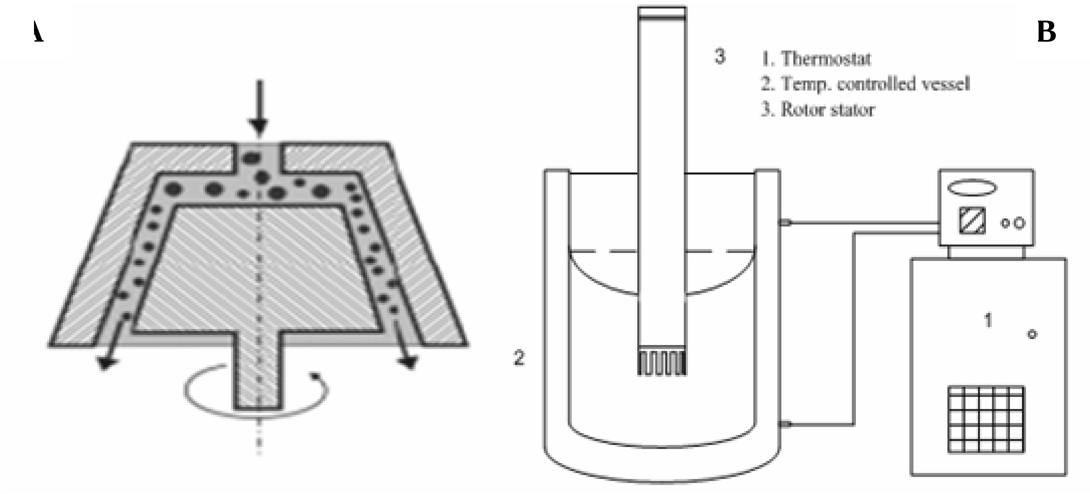

Figure 3.1 Schematic diagrams of (A) Geometry of rotor stator [Sch04, Urb06] and (B) emulsification system.

The emulsions were prepared by using palm oil with a concentration of 68% as the continuous phase, 30% distilled water as dispersed phase and 2% span 20 as an emulsifier. All the concentrations were measured volumetrically. Both palm oil and span 20 were heated to desired temperature separately before mixing. The surfactant was then dissolved in the oil at the same temperature. After that distilled water was added to the mixture of oil and surfactant also at the same temperature. The temperature was kept constant throughout the experiment. The mixture was then stirred continuously for 30 minutes with a rotor stator (T25 ULTRA-TURRAX®) by IKA® Werke GmbH & Co. KG, Germany, at four different tip speeds (8000, 9500, 13500 and 20500 rpm). The volume of the emulsion was 50 mL in a double jacketed temperature controlled vessel as shown in Figure 3.1 (B). No baffles were used in the vessel. The properties of the produced emulsions were determined by diverse measurements. The water droplets distributed in the emulsion were measured; more than 1000 droplets were analyzed to obtain a narrow size distribution. The details are presented in Chapter 3.3.1.

3.2.2 Preparation of emulsion drops

The prepared emulsions as described previously in the Chapter 3.2.1 were pumped using a syringe pump (Cole-Parmer, VERNON HILLS, USA) through a capillary situated at the bottom of the coolant vessel at different flow rates. The inner diameters of the capillaries were 0.5 mm and 1.0 mm. The total volume of the emulsion used for the preparation of emulsion drops from the capillary was 2-3 mL and the experiments were terminated between 18-20 minutes, so there was not much concern regarding the instability of the emulsion. The produced emulsion drops in the coolant turned into solid form in the coolant at low temperature. The solidification of the emulsion is being explained briefly in Chapter 3.2.3. The height of the coolant used in the jacketed vessel was 60 cm and it starts from the injection point of the drops till the collection point of the particles. The total volume of the coolant was 2000 mL. The schematic diagram of the experimental setup for the drop formation is described by Figure 3.2. The temperature of the coolant was kept at 8^oC and 10^oC for the emulsions produced by a magnetic stirrer and a rotor stator, respectively. Spherical drops of the emulsions were formed at the tip of a capillary and started ascending in the continuous coolant (water) system. The drops were almost spherical at the start of their upward acceleration. As the drops ascended in the coolant water, solidification started. These semi-solid spherical drops hereafter called particles were turned somewhat into an ellipsoid shape i-e circular from top view and disc like shape from side view as shown in the Chapter 4. The particles were collected at the top of the coolant for measurements.

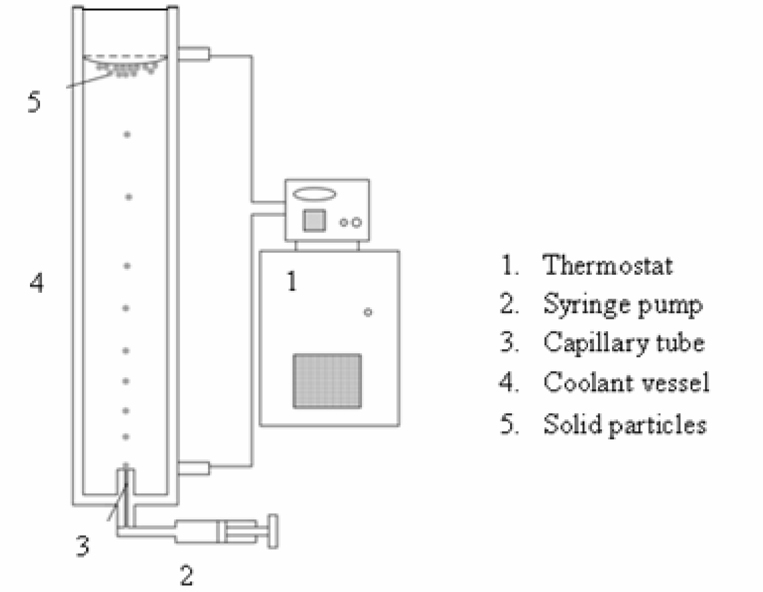

Figure 3.2 Schematic diagram of the experimental setup for the drop formation.

3.2.3 Solidification of drops

A brief description of the solidification of different materials in various coolant media are reported in the Chapters 2.1.1 and 2.3.2 and are studied by a number of research groups [Ina96, Ina99, Nak04, Iqb10, Iqb11]. They studied the direct contact heat and mass transfer between liquid drops and the continuous liquid coolant as well as solid particles and the liquid coolant. Emulsion drops produced by capillary as shown in Figure 3.2 starts ascending in stagnant coolant (water). Direct contact solidification of PCMs occurred in two steps in which direct heat transfer between the working material and coolant took place.

In the first step, liquid emulsion drops released from the capillary situated at the bottom of the temperature controlled coolant vessel exchanges the heat with the surrounding coolant. When the surface temperature of a liquid drop reaches to its solidification temperature, a thin solidified layer of the emulsion begins to envelop the emulsion drop. In this first cooling step, which is terminated by the start of solidification, the sensible heat of the drop is dissipated into the coolant by convective heat transfer inside as well as outside the liquid drop which now becomes a particle, a solidified emulsion particle.

In the second cooling step, which may initiated by the start of solidification of the particle surface, the latent heat of solidification released by freezing is transferred by conductive heat transfer through the solid enveloping layer forming on the particle and is transferred by convective heat transfer from the particle surface to the coolant. At this time, the sensible heat transfer rate from liquid PCMs contained in the core of drops is small compared to the latent heat of solidification transfer rate. Thus, the heat transfer in the liquid core is of little significance [Nak04]. After emulsion drops turned into solidified emulsion particles by exchanging the different heats with the coolant were collected at the top of the coolant. These particles were stored overnight at 4^{o}C in a refrigerator to note down the agglomeration of the particles.

The particles were then analyzed for further calculations. The solidified emulsion particles collected at the top of the coolant is shown in the Figure 3.3. Different hydrophilic dyes were used for the preparation of emulsions in order to observe the water droplets distribution and solidification mechanism within the solidified particles itself. The use of the different dyes is being intensively discussed in Chapter 3.3.3. The orientation or the distribution of water droplets within the solidified particle was observed in a way that the particle was cut down into thin slice like shape and observation were made under microscope.

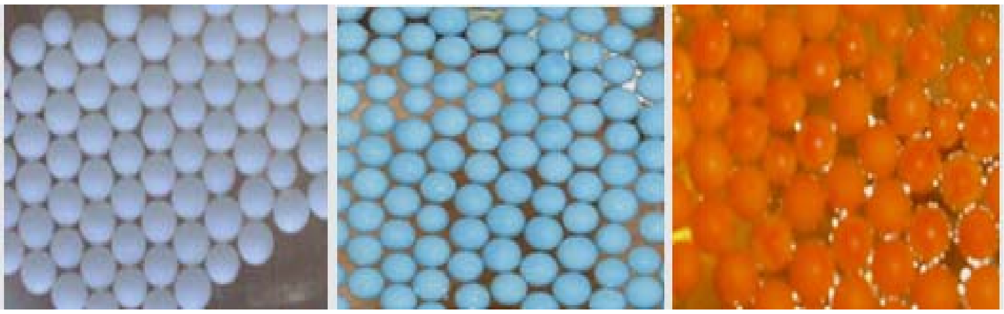

Figure 3.3 Photographs of the solidified emulsion particles with different colors.

3.3 Analysis

The properties of the emulsions produced by a magnetic stirrer and a rotor stator system was done with the help of a light microscope (x100, VHX-500F) supplied by Keyence, Neu-Isenburg, Germany attached with the microscope cell to maintain the temperature of the emulsions alike with that of emulsion preparation. Whereas the size and the shape of the solid emulsion particles was measured by light microscope (x16.5, BH2) provided by Olympus, Tokyo, Japan, also connected with the microscope cell to keep the temperature similar to that of temperature of coolant during solidification. Further details are given in Sub-Chapters of Chapter 3.3.

3.3.1 Properties of the emulsions

The produced emulsions were transferred to the microscope cell attached with the thermostat at the aforementioned temperature in order to investigate the droplet size distribution of the emulsions. The characterization of emulsions is difficult, especially, when they are concentrated, highly viscous, opaque and non-conductive. This is one of the drawbacks to characterize w/o emulsion. So in order to avoid this difficulty, the samples were diluted with the continuous phase. For each measurement, the emulsion sample was diluted five times with pre-heated palm oil (continuous phase) to make it transparent for better observations. All the experiments were carried out three times and the average values were taken. Diverse measurements were recorded for further calculations. Microscopy pictures were recorded with a *Keyence VHX500F* microscope and analyzed by AnalySIS software to measure the droplet size distribution and the mean diameter of the droplets distributed in the emulsion. Generally, in order to examine the emulsions and to describe the droplets size distribution within the emulsions, usually 300-400 droplets is analyzed. Nevertheless, in the emulsions characterization 1000-1200 droplets were analyzed. The average number (%) of droplets was then plotted against droplet size for narrow size distribution (see Chapter 4, Sub-Chapter 4.2.3). The schematic diagram of the measurement setup combined with the microscopic cell is shown in the Figure 3.4. On the other hand, viscosity and the interfacial tension of the emulsions were measured by standard operation procedures with the help of Rotational viscometer (VT550), Thermo Haake GmbH, Germany and Tensiometer (K10T), A. KRÜSS Optronic GmbH, Germany, respectively.

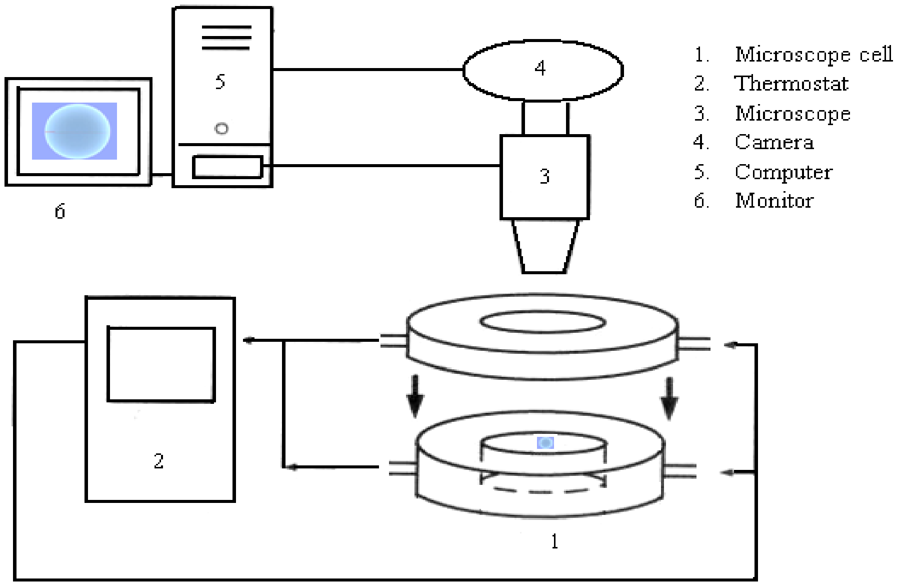

Figure 3.4 Schematic diagrams for the characterization of emulsion droplets and emulsion particles.

3.3.2 Microscopic analysis of emulsion particles

The emulsion drops turned to solidified emulsion particles in the coolant collected at the top of the coolant and were investigated under the microscope for their size and shape. The light microscope (x16.5, BH2) provided by Olympus, Tokyo, Japan was used for the measurement of the particle diameters. The diameters of 20 to 30 particles were measured and the average values were used for further calculations in each set of experiments, similar to the method adopted by Nakao et al. [Nak04] where they used 40-60 particles for their measurements and average values were calculated in case of solid particles. The solid particles were placed in the microscope cell at an aforementioned temperature of the coolant where the particles turned down to solid form. The observations were done accordingly as shown in the Figure 3.4 for the measurement of particles geometry.

Generally, when particles are not exactly spherical but somewhat ellipsoid in shape, then the particle diameter is described by an equivalent diameter. The equivalent diameter was calculated by the Equation 3.1 as described by Nakao et al. [Nak04].

$$d_P = (a^2 \cdot b)^{\frac{1}{3}} \qquad \text{(Eq. 3.1)}$$

In Equation 3.1, "a", "b" and "d_p" are the major, minor and equivalent diameters of the particles, respectively. The equivalent diameter gave the actual size of the non spherical particles. Therefore, the size of the particles has been described by an equivalent diameter as calculated from the equation so on and so far. Moreover, the interfacial tension of the coolant was reduced by adding 0.5% (by volume) surfactant (detergent) in the coolant. The addition of surfactant might affect the size of the drops obtained also influence the drops streams [Ske90]. The details about the shape, size, major and equivalent diameters of the particle are discussed in Chapter 4, Sub-Chapter 4.2.4 and 4.3.1.

On the other hand, the particles were cut down from the centre and thin slices were obtained. They were investigated under Keyence (x100, VHX-500F) light microscope for the observations of the location or the orientation of the water droplets inside the solidified emulsion particles. Prior to this, the particles were frozen by liquid nitrogen so that very thin slices can be obtained very easily. The orientation of the droplets then leads to the crystallization mechanism of the fat inside the particles below the freezing point. The main purpose was to observe the uniformity or evenly distribution of water droplets and then comparison with the distribution in the emulsion itself as well as within the particles.

3.3.3 Dye analysis of the emulsions and the drops

Berliner blau löslich and Alizarin Red S were dissolved in the distilled water for the preparation of emulsion and the microscopic analysis of the emulsion itself and the emulsion particles. The dye analysis was done to study the structure deep insight the solid particles produced out of the emulsion. The emulsions were prepared using both a magnetic stirrer and a rotor stator system for their analysis. Keyence (x100, VHX-500F) microscope was used to record the images of the emulsions and also employed in the characterization of the solid particles. Furthermore, the experiments were repeated using the same procedure in the presence of surfactant tween 20 in the coolant. As mentioned earlier in the previous Chapter 3.3.2 that the reduction in the interfacial tension resulted in the ultimate influence on the formation of single particles and the stream of the particles. The use of the detergent in the coolant exhibited the reduction in the size of the generated particles. Moreover, the effect of the emulsion temperature on the particle geometry was studied. The details are presented in the Chapter 4, Sub-Chapter 4.3.

4. RESULTS

This chapter contains the outcome of the different parameters studied in details for the preparations of emulsion and the formation of emulsion drops, their solidification behavior, surfactant concentration for the stabilization of emulsion, effect of the water quantity present in the emulsions, influence of flow rate, and size of the capillary used are described in Chapter 4.1. The effect of preparation methods, energy inputs on the size of the droplets and on the size and shape of the particles, and the solidification/crystallization mechanism within the solidified particles is illustrated briefly in Chapter 4.2. Furthermore, reduction in the size of the particles, effect of viscosity, influences of emulsions temperatures, and the use of the detergent in the coolant is presented in Chapter 4.3. Finally, the possibility and the range of errors is discussed and described thoroughly in Chapter 4.4.

4.1 Effect of different parameters

All the results presented and described in this chapter are obtained using a magnetic stirrer for the preparation of emulsions. The use of rotor stator equipment for the emulsion manufacturing and the comparison between the two processes are being disclosed in Chapter 4.2.

4.1.1 Surfactant concentrations

It is well-known that the average diameter of a drop resulting from an orifice, nozzle, or a capillary is strongly associated with the parameters of the injection nozzle exit. The injection velocity of the liquid through the nozzle determines the formation pattern of drops when other parameters such as the nozzle diameter and the physical properties of the emulsion and the temperature of the coolant are kept constant. The drops leave the capillary exit and start to ascend in the coolant where direct contact heat exchange occurs. The drops turn to the semi-solid form and then ultimately solidify during their upward movement in the coolant due to the density difference between the two materials. The solidified drops are referred as emulsion particles henceforth. Figure 4.1 (A) shows a photograph of particles floating on the coolant surface which were removed for further measurements. The top and the side view of the particle are also shown in Figure 4.1 (B, C). The diameters of the particles were measured by light microscopy (x16.5, BH2). The particles obtained were not exactly spherical but were somewhat elliptical in shape. Generally, when the particles are not spherical then the diameter of the particles is characterize as an equivalent diameter "d_p" as reported by Nakao et al. [Nak04] and is given by the Equation 3.1. The equivalent diameter predicts the actual size of non spherical particles. So from here onwards, the size of the particles is described by an equivalent diameter as calculated from the Equation 3.1.

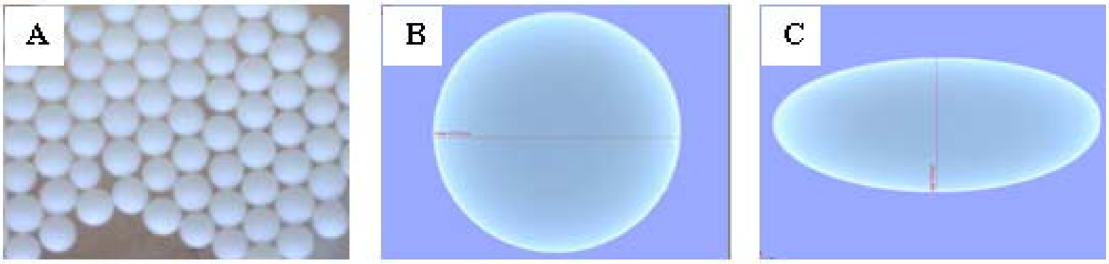

Figure 4.1 Photographs of the emulsion drops (A) (hence particles), microscope image of single particle (B) top view, (C) side view.

The equivalent diameter of particles at different surfactant concentration was measured at various flow rates. The effect of surfactant concentrations on the size of the particles is shown in Figure 4.2. The flow rate of injected emulsion stream was varied from 8 to 18 mL/h. The surfactant concentration was varied from 0.2 to 5% by volume. Figure 4.2 shows that the particles are up to 5 mm in size at 0.2% surfactant, even at low flow rates. The size was reduced to 3.5 mm when a surfactant concentration of 2% by volume was used, and there was no further decrease in size even when the surfactant concentration was increased to 5%. Moreover, there was no severe difference in size up to 1% of surfactant.

The effects of surfactant concentration and flow rates on the roundness of the produced solid particles were monitored. The roundness is the ratio of minor to major diameters of particles as described by the Equation 4.1. Figure 4.3 shows the roundness of the particles. The particles were roundest in shape at 12 mL/h. The roundness reached 0.83 – 0.85 even at low surfactant concentrations. At other flow rates, generally only a roundness of 0.78 – 0.80 was observed

$$\textit{Roundness of the particle} = \frac{minor\ diameter\ of\ the\ particle\ (b)}{major\ diameter\ of\ the\ particle\ (a)} \qquad \text{(Eq. 4.1)}$$

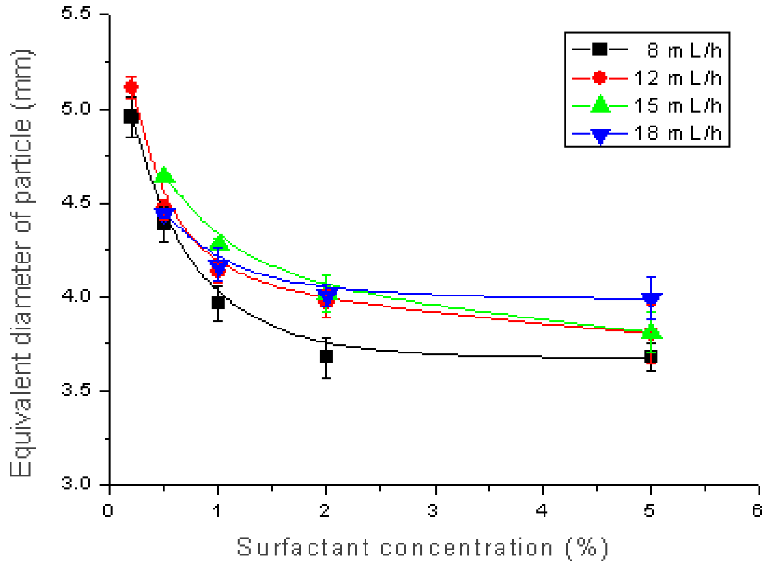

Figure 4.2 Effect of surfactant concentration on the equivalent diameter of the particles at different flow rates with a capillary size of 1.0 mm.

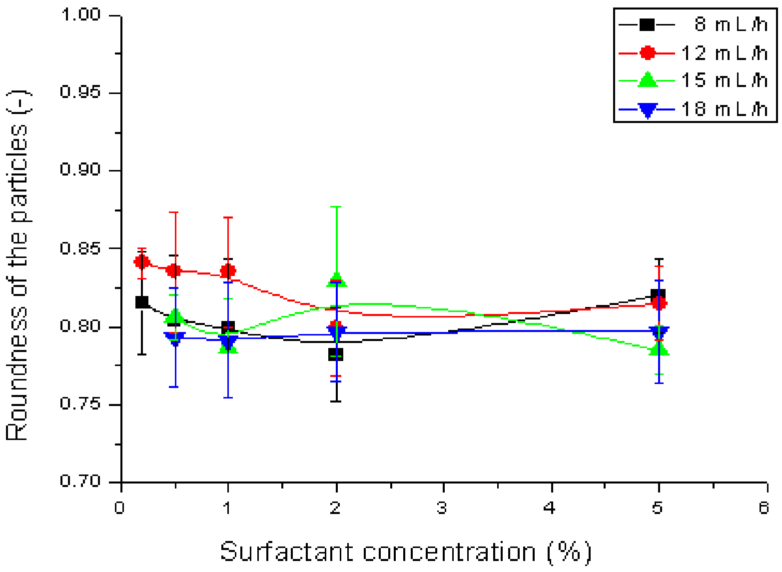

Figure 4.3 Effect of surfactant concentration on the roundness of the particles at different flow rates with a capillary size of 1.0 mm.

4.1.2 Water contents

In order to investigate the effect of water content on the formation and the roundness of emulsions particles with 12 mL/h and 2% surfactant concentration by volume at 60°C, the amount of water content was increased from 5% to 25% by volume. It was expected that with an increase in water content in the sample, the size of the particles will be higher, because more water droplets are available in the prepared emulsion. But from Figure 4.4, it is clear that the amount of water content present in the sample has no effect on the size of the particles. It is also evident from Figure 4.4 that the particle shapes e.g. roundness remains the same when the water amount was increased from 5 to 25% by volume. It has been observed that the increasing water content led to a decrease of the surface percentages of modes and a parallel increase of the percentages of intermediate droplets sizes. Moreover, liquid spans create less interaction between fatty acid chains present in the fats. So due to a short chain of span 20, smaller droplets of water formed with liquid spans [Mar07]. Moreover, the solidification behavior at lower water contents is similar to that of higher ones present in the sample of emulsions.

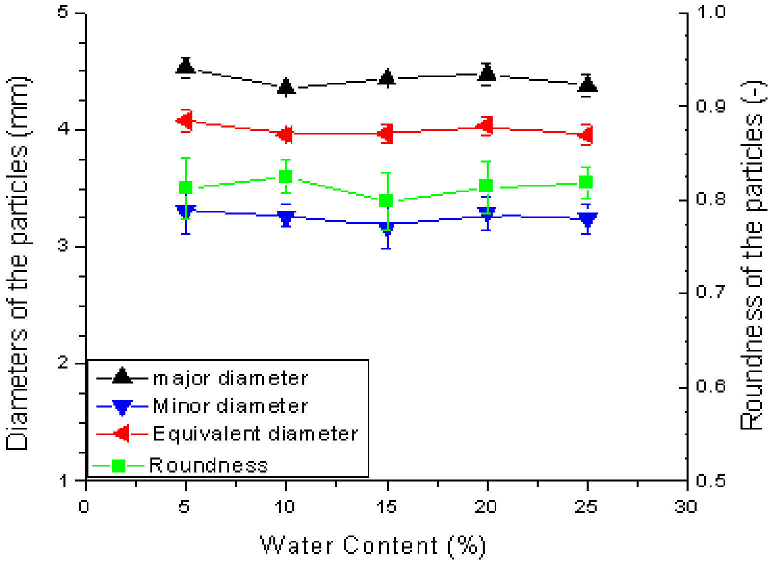

Figure 4.4 Plot of diameters and roundness versus water content at 12 mL/h and 2% (v/v) surfactant concentration at 60°C with the capillary size of 1.0 mm.

As the oil content of the emulsion increases at constant surfactant concentration, droplet size increases gradually. The occurrence of a minimum particle size at particular oil contents is not uncommon for emulsions containing nonionic surfactants, where the consideration of hydrophilic-lipophilic balance (HLB) value is important. These large particles were formed probably as a result of partial coalescence and the type of the palm oil used for the emulsion preparation.

4.1.3 Effect of flow rates

It is well known that the drop diameter is strongly associated with the drop formation pattern at the injection nozzle exit. The injection velocity of liquid through the nozzle determines the formation pattern of drops when other parameters are kept constant. When an emulsion is injected into another immiscible liquid via a capillary tube at low Reynolds numbers, two different drop formation mechanisms are observed: The drops are either formed directly at the needle tip (dripping) or they breakup from an extended filament due to Rayleigh instabilities (jetting) [Cra04]. Figure 4.5 describes the effect of flow rate on the formation of emulsion drops at the injection capillary tip. At low flow rates, single drops were formed at the capillary tip and were released at particular intervals. The drops then turn into solid particles in the coolant. At the intermediate and higher flow rates from 30 to 50 mL/h, jetting phenomena occurred and a group of drops with different sizes were generated.

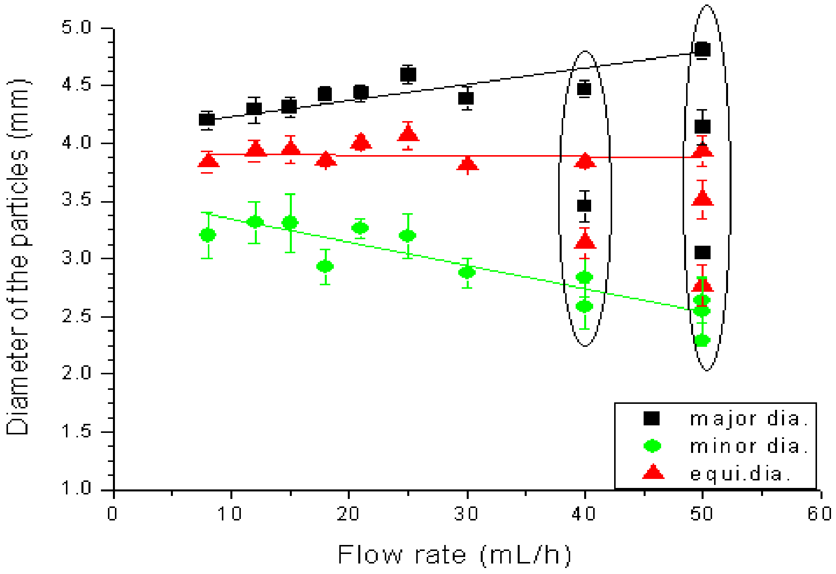

Figure 4.5 Effect of flow rates on the particle diameter at 15% (v/v) water and 2% (v/v) surfactant concentration at 60°C and 1.0 mm capillary size.

It is noted that, the transition point between the flow domains is of great importance because the dynamics of drop formation change significantly. Therefore, it is necessary to define the transition point when the initial rise in velocity of a drop is adequate low so that the drop will grow less than one drop diameter at the same time. At low flow rates of the emulsion, the drops from the capillary tip may be divided into two stages: static growth at the capillary and the necking and detaching.

4.1.4 Effect of the capillary size

As described earlier in Chapter 2.2.2, the drop formation is strongly influenced by the parameters governing it. These parameters include the effect of viscosity of the working fluid, flow rates etc. in general and the capillary diameters in particular. Therefore, the capillaries of different diameters (0.5 and 1.0 mm) were used to produce emulsion drops. The emulsions were prepared at various temperatures in order to reduce the viscosity of the emulsion because a viscous emulsion blocks the capillary of smaller sizes during the course of the experiments. Figure 4.6 shows the equivalent diameters and roundness of the particles generated at a flow rate of 12 mL/h with two different capillaries mentioned above.

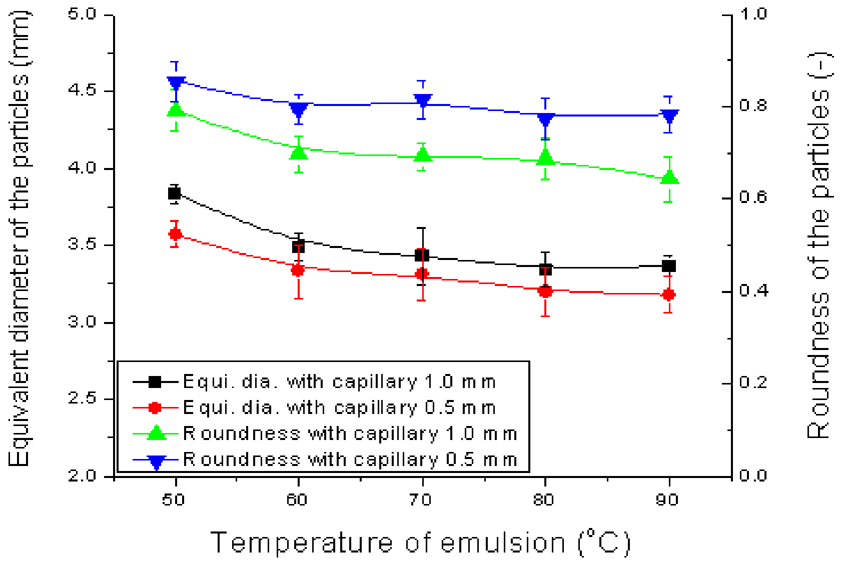

Figure 4.6 Plot of the equivalent diameter and the roundness of the particles generated by capillaries of 0.5 and 1.0 mm inner diameter versus temperature at 15% (v/v) water content and 2% (v/v) surfactant concentration.

It is noted that the average size of the smallest particles was 3.3 mm that obtained beyond 80°C with 1.0 mm and 3.2 mm at 90°C with 0.5 mm capillary pore. Surprisingly, there was not much difference in the equivalent diameters of the particles obtained with two capillaries. The particles are more rounds in shape at lower temperature with smaller capillary size. The roundness was 0.85 at 50°C which decreased to 0.78 at 90°C. This effect is being discussed in Chapter 5 in details.

4.2 Effect of preparation methods

The emulsions were produced by a magnetic stirrer and a rotor stator system by applying different energy inputs as described in the Chapter 3.2.1. The energy was transferred to the emulsions in the form of the rotational speeds of the stirrer and rotor. In this Chapter, the influence of the energy inputs applied to the emulsion by two different mechanical means for emulsions manufacturing and their effects on the droplets sizes, distributed in the emulsions is studied thoroughly. Moreover, the effects of the emulsion manufacturing processes on the size and the shape of the particles were monitored. The details of these parameters are extended to the following Sub-Chapters.

4.2.1 Results of the magnetic stirrer

The influence of the energy input through a magnetic stirrer on the emulsion properties is shown here. The energy input to the emulsion systems can be increased by increasing the rotation of the stirrer. With higher energy input it is possible to produce smaller droplets and emulsions with a smaller droplet size distribution [For01]. Figure 4.7 shows the water droplet distribution in the water-in-oil (w/o) emulsions produced by a magnetic stirrer at 700 rpm.

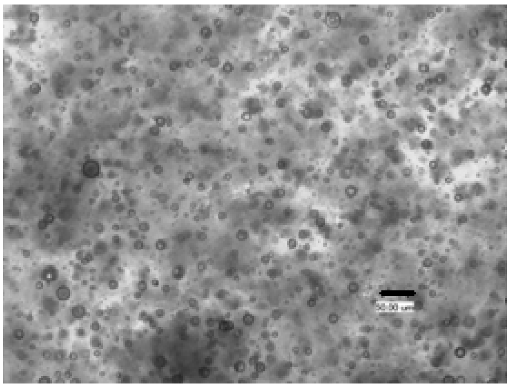

Figure 4.7 Light microscopic image of the emulsion prepared by magnetic stirrer at 700 rpm, 60°C and 30% water by volume. Scale bar: 50 µm.

4.2.2 Results of the rotor stator system

The influence of the energy input on the droplet size distribution in the emulsions produced by a rotor stator system (ultra-turrax) is shown here. The energy input is applied in the form of tip speed of the ultra-turrax. Smaller water droplets in the emulsion were produced by increase speed of the tip. The rotational speed of the rotor was varied from 8000 to 20500 rpm, 60°C and 30% water concentration by volume. The microscopic images of the produced emulsions are shown in the Figure 4.8.

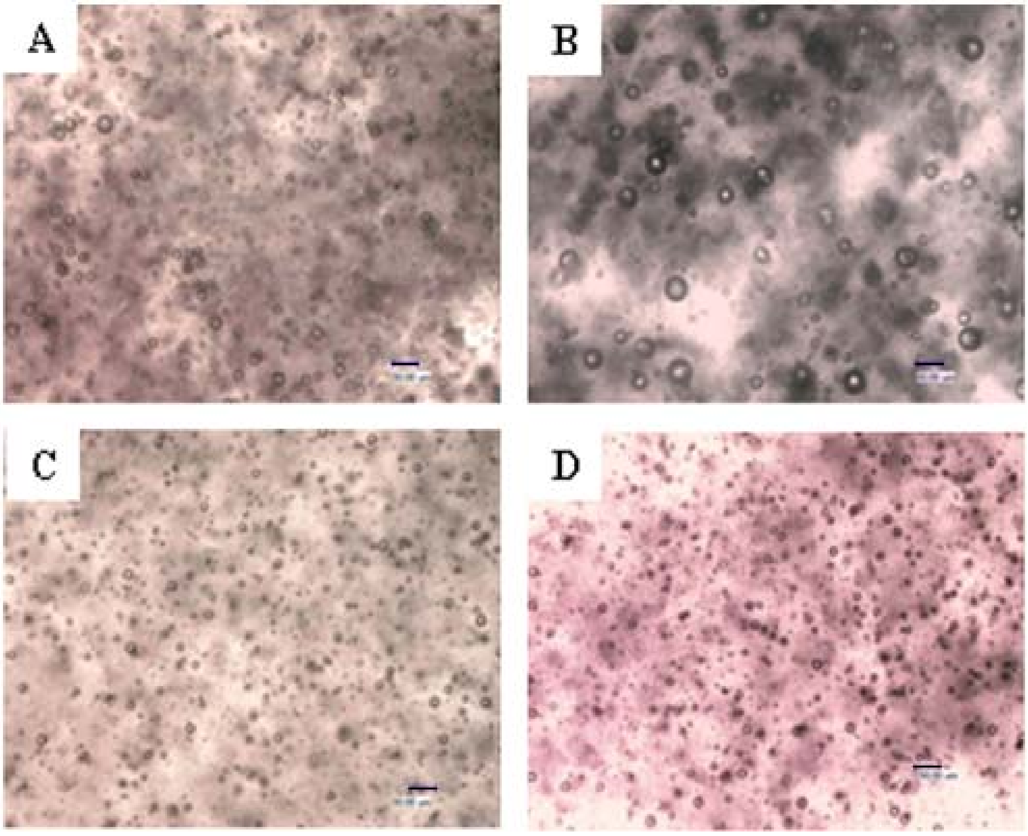

Figure 4.8 Light microscopic images of the emulsions produced by an ultra-turrax at (A) 8000, (B) 9500, (C) 13500, and (D) 20500 rpm. Scale bar: 50 µm.

The water droplets distributed in the emulsions produced both by a magnetic stirrer and the ultra-turrax were analyzed using the method as described in the Chapter 3.3.1. The droplets size obtained was plotted against the number based percentages. This was done to obtain a narrow distribution of droplet sizes as shown in the Chapter 4.2.3.

4.2.3 Effect of the energy input on the droplet size distribution

The distribution of droplet sizes in the emulsions is shown in Figure 4.9. From the Figure, it is clear that the droplets at 9500 rpm are uniform and sharply distributed around the mean or average value. As described earlier, the higher the energy input is the narrower will be the size distribution of the droplets. However, the reverse phenomenon was observed as the energy input in the form of tip speed was increased. It might be that the coalescence increased more than the droplet break-up as the speed was increased.

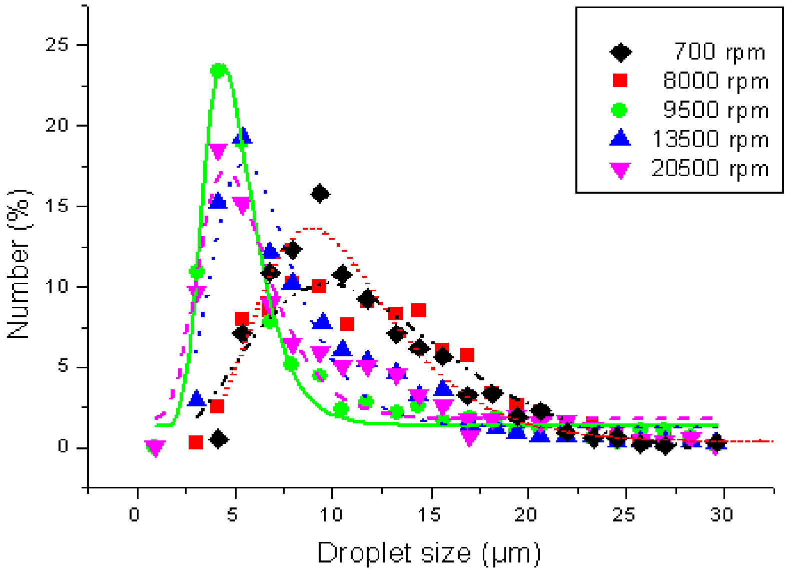

Figure 4.9 Size distributions of droplets of the produced emulsions.

Table 4.1 Influence of the energy input on the mean diameter of the droplets in the emulsions.

Energy input (rotational speed) [rpm]	Mean diameter (number based) [µm]
700	11.47
8000	12.32
9500	10.15
13500	9.23
20500	9.21

The relation between the energy inputs in the form of rotational speeds of a magnetic stirrer and a rotor stator for the production of emulsions and the mean droplet size by number based is given in the Table 4.1. The mean diameter of the droplets at 700 and 8000 rpm are relatively close to each other contrary to the other speeds. This difference could be due to the different manufacturing process of the emulsions.

4.2.4 Effect of the energy input on the particle size and shape

The properties of the emulsion were varied by changing the energy input for the emulsion preparation and its consequences on the drop formation from the capillary were observed. Figure 4.10 describes the particle major and equivalent diameters which were obtained from emulsions prepared at different energy inputs. Figure 4.10 shows that the equivalent diameter of the particles decreased from around 4.0 to 3.4 mm as the energy inputs in the form of rotational speed of the stirrer and the tip speed of the rotor for emulsion preparation increased from 700 to 20500 rpm, respectively. So it is evident that the smaller the water droplets in the parent emulsion, the smaller are the particles created by the process. The decrease in the major diameter also showed similar trends. The properties of the emulsion prepared solely affect the size of the particles produced from emulsion drops.

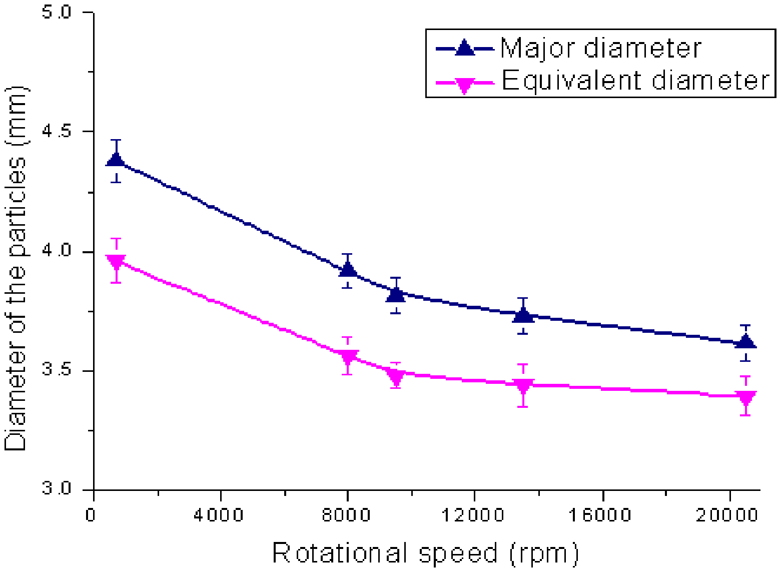

Figure 4.10 Relation between the size of the particles and the rotational speed.

Furthermore, the roundness of the particles is plotted as a function of the particle size in Figure 4.11 in order to investigate the effect of fine water droplets in the emulsion on the drop shape. In addition, the roundness was also plotted as a function of rotational speed of the stirrer and the tip of the rotor in Figure 4.12. From here the obvious influence on the shape of the solidified particles by the rotational speed can be seen.

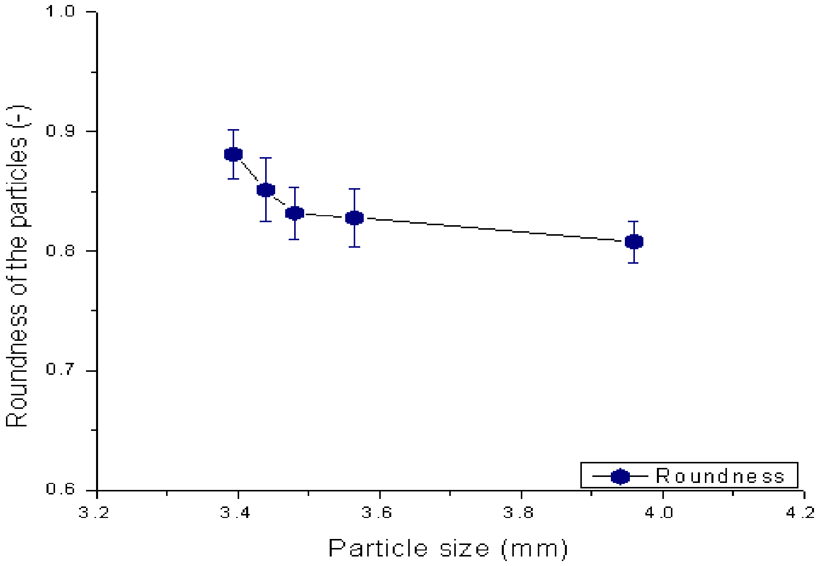

Figure 4.11 Relation between roundness and the size of the particles.

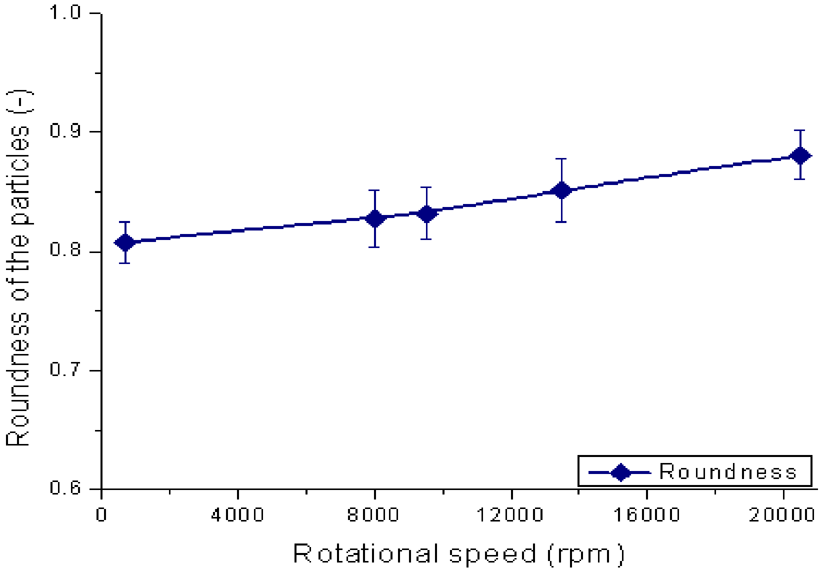

Figure 4.12 Plot of roundness of the particles versus rotational speed.

It was assumed that the fine water droplets in the emulsion might enhance the particles more in spherical rather than elliptical shape. The roundness of the particles increases up to 87-88% at a speed of 20500 rpm which was 78-80% at 700 rpm [Iqb10]. The higher the tip speed is, the smaller are the water droplets in the emulsion and hence the value of the roundness is higher.

4.2.5 Crystallization behavior of the particles

It is assumed when fats are emulsified, they will crystallize via a homogeneous mechanism. If the size of the particle is small, there is one or no nucleus per droplet and hence the dominant mechanism will be homogeneous nucleation. In order to observe the crystallization behavior, the particles were examined under a microscope. The cross-sectioned microscopic images of the particles are shown in the Figure 4.13. A thin layer of the particles was cut down from the centre of the particle. These images show the orientation or location of tiny water droplets inside the solidified emulsion particles. The water droplets were evenly distributed within the particles. Some fine and few coarse droplets in the particles appeared. Near these small droplets, the crystallization process occurred and the fat started to crystallize.

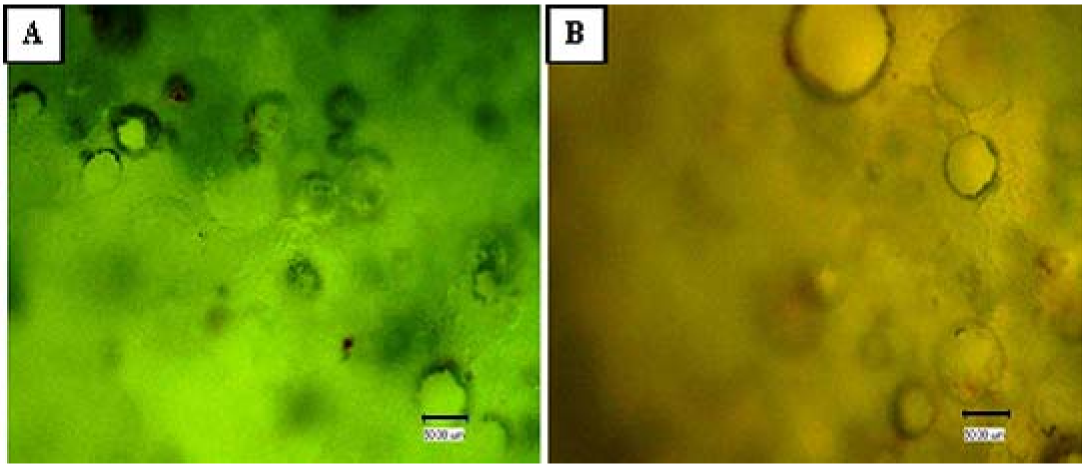

Figure 4.13 Cross-sectional images of particles using light microscope. Scale bar: 50 µm.

Kloek et al. [Klo00] described the crystallization mechanism of various palm oil emulsions from kinetic measurements of solid fat contents. It was reported that pure palm oil droplets showed a heterogeneous nucleation mechanism which altered to a homogeneous mechanism when palm oil was diluted with sunflower oil for 10%. They proposed a self-nucleating mechanism for emulsions because of the complex composition of the fat. Some fat molecules will have a higher molecular weight and/or be more saturated and hence have a higher melting point. Supercooling is needed to induce crystallization, but the bulk of the fat may not be undercooled sufficiently to crystallize. Therefore, the fraction may be and act as a nucleus and hence the mechanism would be homogeneous. Thus, Kloek et al. [Klo00] proposed self-nucleating particles consist of high melting triglyceride fraction. The drops of palm oil emulsion in the coolant behave as self-nucleating particles and hence crystallize. In Figure 4.13, pictures “A” and “B” are the cross-sectional images of particles with 30% water content by volume in the prepared emulsions by an ultra-turrax at 9500 rpm. They show the crystallization behavior within the solidified particles.

4.3 Size of the particles

The size of the particles plays a vital role not only in the chemical and process industries but also in the pharmaceutical and food industries in order to meet the desires of the market. The smaller particles are very effective in carrying the active pharmaceutical ingredients in the pharmaceutical fields. So the attempts were made to obtain the possible smaller particles in the present and current scenario for the production of the solidified particles. Therefore, different parameters namely: interfacial tension, influence of the temperature, and the effect of the viscosity of the working material were monitored. Therefore, the effect of above mentioned parameters were observed and are presented below in the Sub-Chapters of Chapter 4.3.

4.3.1 Reduction in the interfacial tension

The interfacial tension is one of the principal factors determining the size of the drops from the capillary or the orifice. It is the responsible force to keep the drop attached to the capillary pore until the interfacial force is higher than the shear force applied. Moreover, the drop grows at the capillary pore until the shear force is higher than the interfacial tension force. Therefore, hydrophilic detergent or an emulsifier (tween 20) was used in the coolant to reduce the interfacial tension between the coolant and the drops so that the two forces will attain equilibrium much earlier. The hydrophobic emulsifier (span 20) was used for the emulsion stability. Figures 4.14 and 4.15 illustrate the size and the shape of the particles obtained in the presence and absence of the detergent in the coolant.

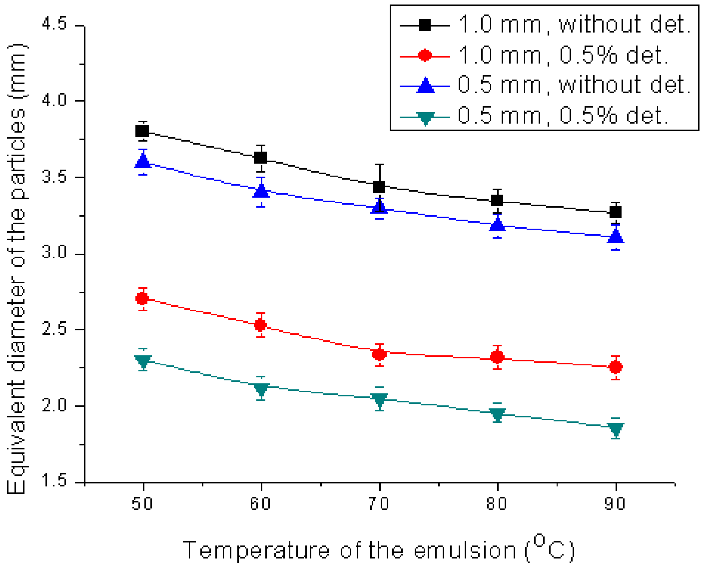

Figure 4.14 Comparison between the sizes of the particles in the presence and absence of detergent in the coolant obtained by 0.5 and 1.0 mm pore size of capillaries with 15% water by volume and at 9500 rpm.

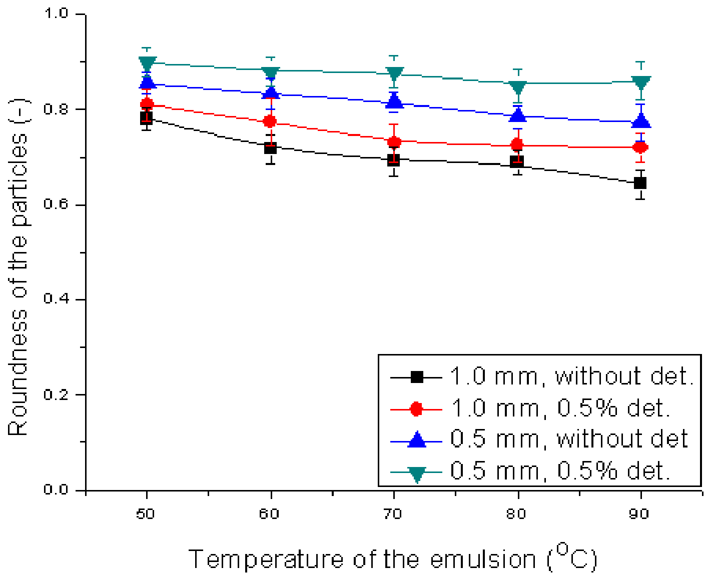

Figure 4.15 Comparison between the roundness of the particles in the presence and absence of a detergent in the coolant obtained by 0.5 and 1.0 mm pore size of capillaries with 15% water by volume and at 9500 rpm.

After drop detachment, an adequate amount of surfactant (detergent) present in the coolant adsorbs at the hemispherical interface before the critical pressure is reached to form the next drop. The adsorption of the surfactant is a kinetic process and is exhibited by the dynamic interfacial tension of the given surfactant [Gee07]. Hence, tween 20, a non-ionic surfactant was used in the coolant to provide a sufficient amount that adsorbs on the hemispherical interface to reduce the interfacial tension between the forming drops at the pore of the capillaries used.

4.3.2 Effect of the temperature

Temperature plays an important and vital role in the preparation and stabilization of emulsions especially water-in-oil emulsions. It influences significantly numerous variables such as the viscosity of each phase and the solubility of the non-ionic surfactants in either phase. Figure 4.16 shows the effect of temperature of the prepared emulsion on the equivalent diameter of the particles.

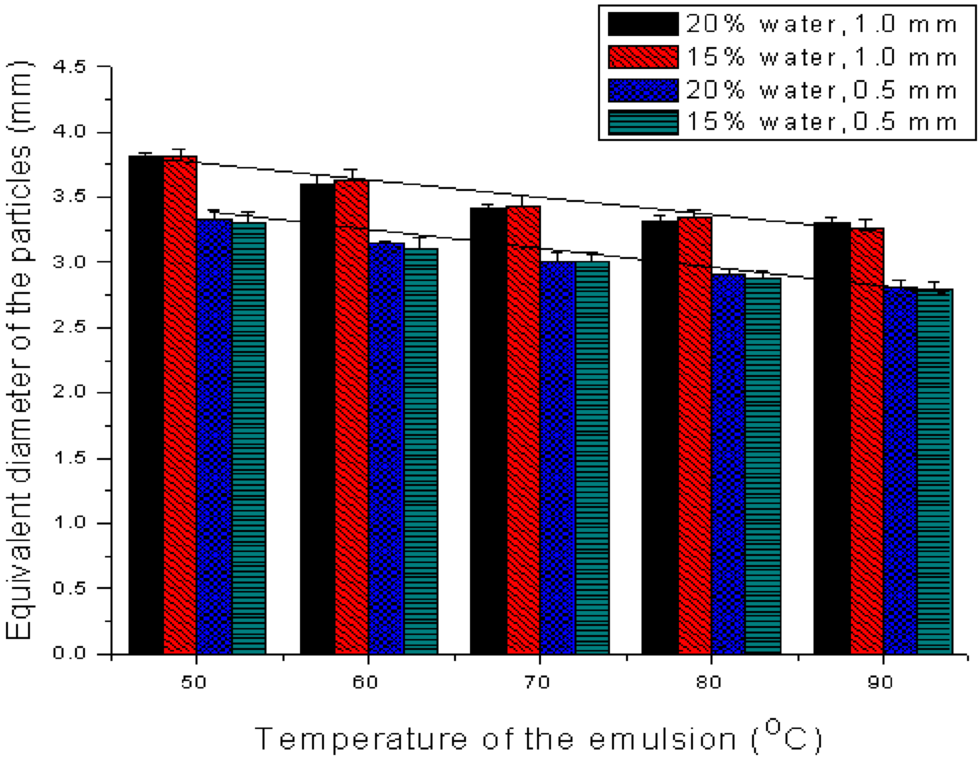

Figure 4.16 Influence of temperature on the size of the particles at 9500 rpm.

So, it is mandatory to observe the influence of temperature on the w/o emulsions stability. It is noted that at a higher temperature, the stability of the emulsions is slightly reduced in the first hour after preparation. With the time, the effect becomes significant as described by Ghannam [Gha05]. On the other hand, the viscosity of either phase reduces significantly with temperature. Therefore, the water droplets distributed in the emulsion gained much kinetic energy which ultimately raised the water droplet collision with each other. The collision between the water droplets then finally leads to the instability of the emulsions with time.

4.3.3 Effect of the viscosity

The effect of different rotational speeds of a rotor stator on the viscosity of the emulsions prepared was measured. The viscosity initially decreases with the increase of speed and then becomes almost constant with a further increase in the rotational speed. Figure 4.17 shows the effect of rotational speed on the viscosity of the emulsions produced.

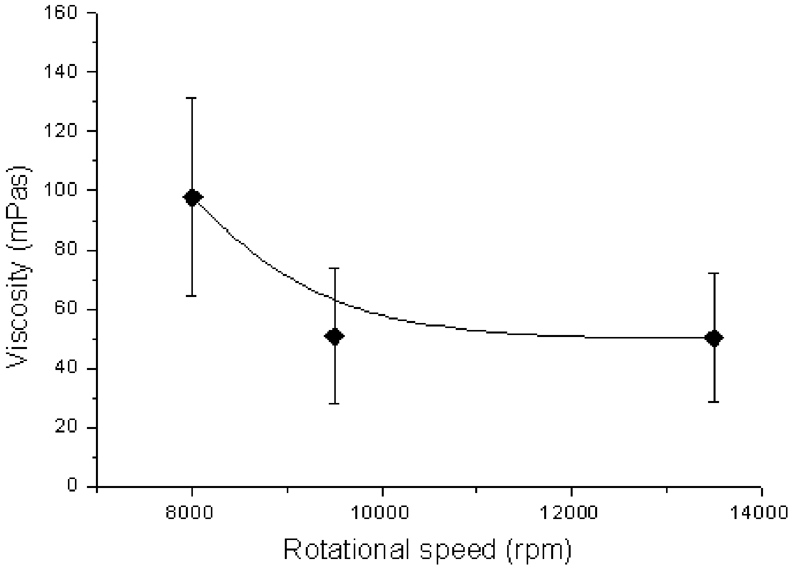

Figure 4.17 The viscosity versus rotational speed with 20% water by volume and at 60°C.

Figure 4.17 shows that the viscosity of the emulsions stays almost the same if the rpms are above 9500 and at 60°C and 20 % water by volume. Therefore, the flow behavior of the emulsions and drop formation from the capillary of two different pore sizes was done at various temperatures of the emulsions. The emulsions were prepared at 9500 rpm by a rotor stator system.

In order to describe the flow behavior, the dimensionless numbers; Reynolds numbers (*Re*) and Ohnesorge numbers (*Oh*) were plotted against the temperature of the emulsions. Figures 4.18 and 4.19 show the temperature effects on the dimensionless numbers at different water concentrations with a capillary of 0.5 and 1.0 mm pore size.

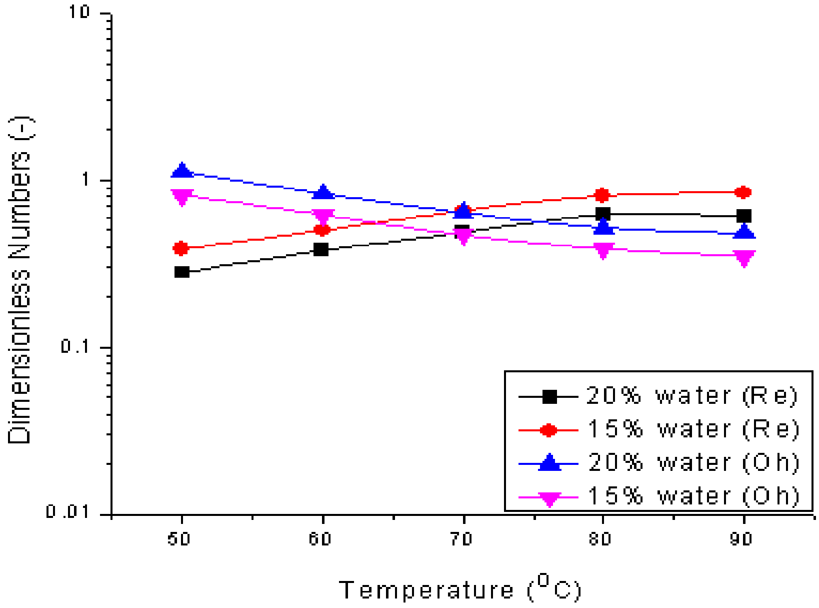

Figure 4.18 Flow behavior versus temperature of the emulsion at 0.5 mm capillary pore.

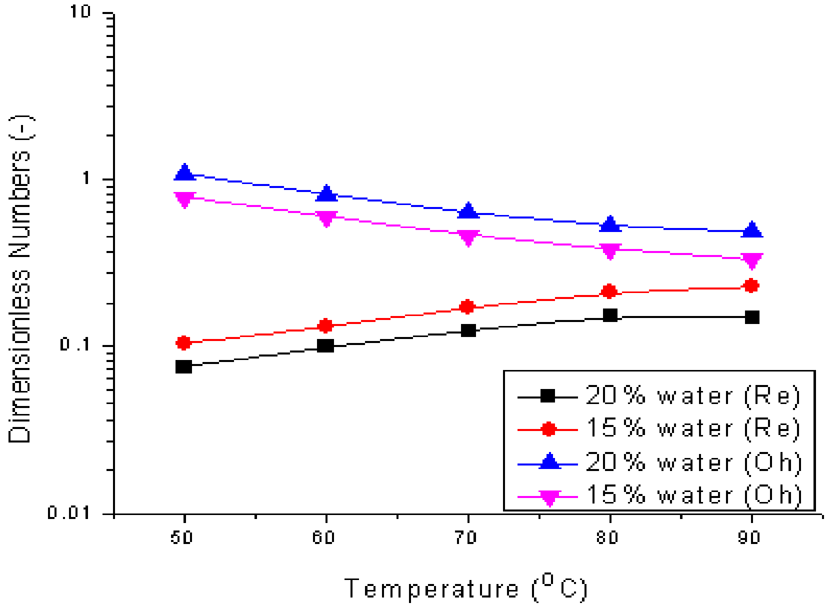

Figure 4.19 Flow behavior versus temperature of the emulsion at 1.0 mm capillary pore.

The data obtained from the dimensionless numbers are well in agreement with values estimated by Cramer et al. [Cra04] of the experiments for the generation of drops through a capillary in co-flowing streams. They estimated values of dimensionless numbers as: $0.01 \leq Re \leq 10$, $0.4 \leq Oh \leq 2.5$.

The flow behavior of complex fluids like emulsions are affected by number of different forces such as viscosity, surface tension, gravity, stress and their consequential effects are resulted in the formation of various drops, droplets size and size distributions. Dimensionless parameters are generally used to describe, predict and to relate the said effects on the surface formation or deformation of the drops at the desired conditions. Figure 4.20 shows the effect of velocity on the dimensionless numbers and reveal the effects of various factors.

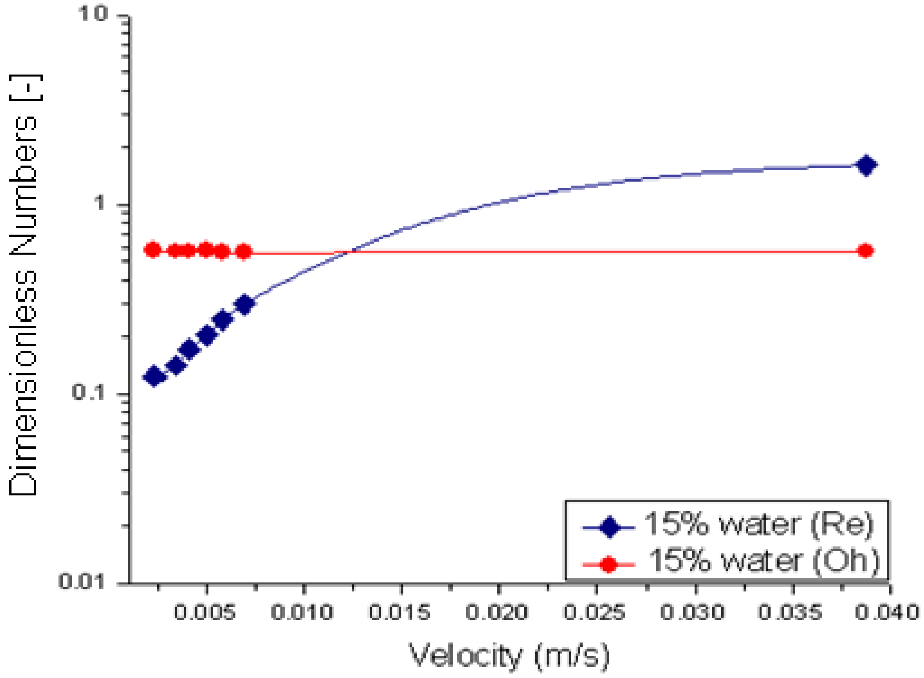

Figure 4.20 Relation between the flow rate and the dimensional parameters.

Chaleepa [Cha10] previously reported that with the water contents above 15%, the value of Ohnesorge number is below 1.0, which demonstrates that the water concentration above 15% in the emulsions has no significance effect on the viscosity and hence the viscosity effect has no influence on the flowing emulsions. Therefore, the emulsion above this water concentration is characterized as the low viscous fluid [Cha10].

4.4 Error analysis

An information and knowledge about anything is generally based on the results obtained from the experiments and their measurement particularly in physical sciences. Therefore, it is important to understand the method to deliberate the data obtained from the experiments and how to analyze in order to draw significant conclusions from it. Also, it is necessary to distinguish that all measurements of physical quantities are not accurate and have some uncertainties. Moreover, an investigation of the possible errors and their impact on the measured values is certainly essential because no measurement is error-free. Generally, an error or uncertainty in measurements have two fundamental components, namely: the numerical value estimated the quantity measured and the degree of uncertainty combine with the estimated values. In most of the cases, errors can be categorized into two appropriate classes:

- Systematic errors
- Random errors

Systematic errors comprise the errors arises from the measuring apparatus or instruments and shift the results in a systematic way to their mean or average values. Also, this may arise from the improper use of the equipment. Other sources of systematical errors are the external factors which may alter the experimental results. Also, the use of different equipments at different places may be affected by various systematic effects. Systematic errors in this work include the measurement uncertainty of the pipette, unusually variations of the thermostats, inaccuracies in the speed control of a magnetic stirrer and the rotor stator, inaccuracies in the metering of different samples, measurement uncertainty and the reading errors of the microscope measurement. Therefore, all experiments were done more than twice and in order to minimize the above mentioned uncertainties and reproducibility of the results. In each case, variation in the results shows similar trend and the mean values were used like, in case of equivalent diameter and the roundness of the particles produced.

Random errors included errors which fluctuate from one measurement to the other. They occurs randomly and in an irregular fashion like, the metrological changes occurred which is not possible to control and is inevitable. Also, these errors arise due to some other reasons namely, lack of sensitivity of the equipment, extraneous disturbances, imprecise definition and statistical processes. It is also noted that the random errors dislocate the measurements in an arbitrary direction while systematic errors are unidirectional. Some systematic errors can be eliminated to a large extent while random errors are unavoidable and must be lived with. Random errors in the experiments carried out here may occurred when measuring different materials with a pipette, transfer of the emulsion in the drop formation, use of syringe pump in different circumstance, removal and transportation of emulsion particles and off course human error in conducting the experiments.

5. DISCUSSION

In Chapter 5, the effects of different parameters on the preparation of emulsions and the generation of emulsion drops via a capillary of various pore sizes were observed and presented. The effect of the water concentration in the emulsions on the droplets size and hence on the particle size, the effect of surfactant concentrations, the influence of the temperature, viscosity and interfacial tensions and the crystallization mechanism within the particles were examined, too. This Chapter comprises the deliberations on the results demonstrated in Chapter 4 and the comparison with existing data. The available literature will be discussed for the observed factors. The reasons behind the effects of the parameters will be given and the use of the technique on broader canvas will be shown.

5.1 Effect of different parameters

Influences of surfactant concentrations on the stability of the emulsion produced by a magnetic stirrer, formation of emulsion particles via capillary, use of different water concentration in the emulsions and its consequential effects on the size and shape of the particle, and the effect of flow rates on the formation of continuous drop streams were shown in Chapter 4.1. The discussion and the correlation of the above mentioned parameters in accordance with the literature are presented here in Chapters 5.1.1 - 5.1.4 and 5.2.

5.1.1 Surfactant concentrations and energy input to the emulsion

In Chapters 4.2, the results for the effect of energy input to the water-in-oil emulsion prepared by a magnetic stirrer and a rotor stator system were presented. The surfactant concentration was varied from 0.2 to 5% by volume for the stability. It was observed that surfactant concentration of 2% by volume is sufficient for the stability of the emulsion. The observations are well in agreement with the results obtained e.g. by Porras et al. [Por04] in case of preparation of w/o emulsion with a magnetic stirrer by the use of a mixture of span and tween surfactants with an overall concentration of 5% by weight. Similarly, in the case of a rotor stator system, the use of a surfactant concentration for the production of stabilized w/o and w/o/w emulsions with span series are monitored elsewhere [Mar07]. They used the liquid spans (span 20, span 80) concentration 1% by weight and solid span 60 concentration was varied from 0.5 to 5% also by weight for the stability of emulsions. Therefore, it is noted that the use of a surfactant concentration in the current work is compatible and in accordance with the results reported in literature [Por04, Mar07]. Moreover, the mean diameter of the droplets distributed in the w/o emulsions were measured by the method described in the Chapter 3.3.1. The results are summarized in the Table 4.1 and show that as the energy input to the emulsion increases the droplets size decreases. But the difference in the droplet size between 700 and 8000 rpm is relatively small as compared to the energy input provided in the form of rotational speed. This might be due to the use of different processes for the production of the emulsions. However, in other cases, the droplet size decreases with the increase of energy input in the form of rotational speed of the rotor. Furthermore, the size distribution of the droplets around the mean value shows a narrow distribution at 9500 rpm (see Chapter 4.2.3) while at 13500 and 20500 rpm, the droplet size distributions are wider. The reason could be that the coalescence increased more than the droplet breakup when the speed was increased.

Droplet disruption and droplet coalescence in an emulsion are the two reverse physical processes. The droplets size of the emulsion produced by homogenizer mainly depends on the equilibrium of these processes. Emulsions are likely to be the complex systems in which droplets collide with each other in a regular and continuous fashion and repeatedly move around. During the homogenization process, droplet-droplet collisions are very high due to intensive mechanical agitation of the emulsion. Further, the resistance against the coalescence by an emulsifier mainly depends on the concentration, structure, and physicochemical properties of the emulsifier. Also, the capability of the span to produce w/o emulsions firmly depends on the chain-chain interaction between the interfaces of the surfactant and the oil used during the emulsion process [Mar07].

As mentioned above, the coalescence in the emulsion may occur due to the increase of the energy input during the emulsification process at higher speed. With the higher speed and much emulsification time (30 min.), fine emulsion can be obtained. According to Pal [Pal96], the fine emulsions are more monodisperse. Also, fine emulsions exhibited a greater tendency of fine droplets flocculation which ultimately leads to the coalescence of the emulsions. The tendency of flocculation could be due to the two mechanisms. Firstly, the Brownian motion becomes more important and results to increase droplet-droplet collision of fine droplets which leads to the flocculation and then eventually to the coalescence. Secondly, the droplets experience the van der Waals attraction force. Also, the decrease in droplet size induces an increase in the surface area. Further, the droplets become less stable and hence flocculate [Pal96]. Therefore, from Figure 4.9 and Table 4.1, it can be revealed that with an increase of rotational speed, fine emulsions were obtained which then further induce to the coarse emulsions due the phenomenon of flocculation and coalescence. Hence, the differences in the mean droplet diameters at higher speeds are negligible small compared with the lower ones.

5.1.2 Influence on the particle size and shape

The effects of surfactant concentration on the size and shape of particles produced by the emulsion drops at different flow rates were presented in Chapter 4.1.1. The results are shown in the Figures 4.1 - 4.3. As described earlier in the Chapter 5.1.1, the minimum surfactant concentration for the emulsion stability in case of w/o emulsion is reported as 2% by volume in accordance with the literature. Figure 4.2 showed the size of solidified particles in terms of equivalent diameters produced at various surfactant concentrations (0.2 to 5%) and at diverse flow rates (8 to 18 mL/h). Until a flow rate of 18 mL/h, single uniform size drops form at the tip of the capillary (1.0 mm) and leave the tip before the formation of the next drop. The effects of further increase in the flow rates when dripping to jetting phenomenon were observed will be discussed in a later stage.

It is observed that the particles equivalent diameter at a flow rate of 8 mL/h and a surfactant concentration of 0.2% by volume was 5.0 mm. The equivalent diameter of particles decreased to 3.5 mm at 2.0% at the same flow rate. At 12 mL/h and 2.0% surfactant concentrations, the particles of equivalent diameter 4.0 mm were obtained with a roundness of 83-85% (see Figure 4.3). The formation of pure hexadecane particles by 1.0 mm capillary in a coolant system was reported by Nakao et al. [Nak04]. They observed the formation pattern of the particles at three different flow rates and categorize into three different regions. At low flow rate (0.212 m/s), the particles were in a narrow size range 4.5-5.1 mm and were ellipsoid in shape rather than spherical, while at another flow rate (0.484 m/s) the particles were of 1.8 to 2.8 mm and at 1.03 m/s, the particles of two shapes were found one of which have diameters less than 3.5 mm and other more than 3.5 mm [Nak04]. Hence, the particles obtained in our system with the similar size of the capillary are in the range of 5.0 to 3.5 mm at different conditions. Therefore, the results obtained are well in agreement as reported by Nakao et al. [Nak04]. Likewise, the formation of wax particles in direct coolant water system was studied by Fang et al. [Fan04]. They achieved the spherical wax particles of good shape and desirable flowability in a water-cooling tower. The semi-refined and crystalline wax was used to produce wax particles at different temperatures of the coolant. They obtained wax particles of size 4-5 mm using the capillary or nozzle with a corresponding inner and outer diameter of the nozzle of 0.96 and 1.28 mm, respectively. Figure 5.1 shows the shape and the size of the emulsion particles obtained in this work exhibited the results well in agreement and are comparable with the results reported in the literature [Fan04]. Also, the results in both cases are likely to be obtained by a capillary of having a relative same size.

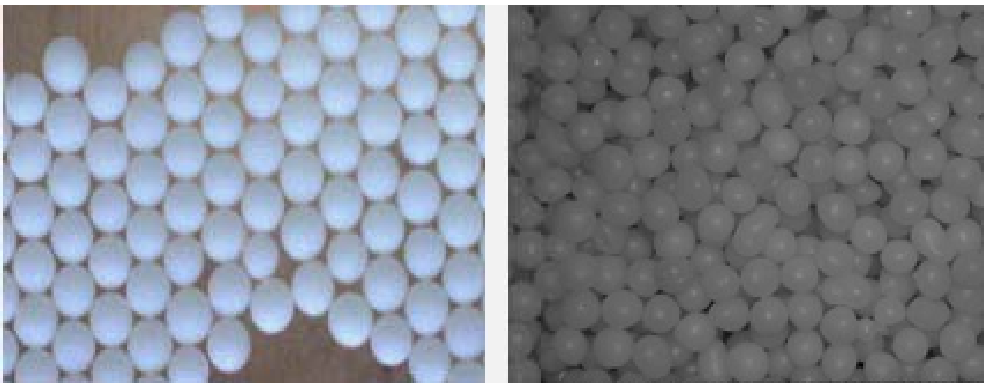

Figure 5.1 Comparison of the results of emulsion particles [Iqb10] (this work, left) and wax particles [Fan04] (right).

Furthermore, the effect of flow rate on the drop to particle formation is shown in the Chapter 4.1.3 (see Figure 4.5). It is noted from Figure 4.5 that at low flow rates, the equivalent diameter of the particles is small due to the formation of single drops at the capillary. When the flow rate was increased from intermediate to higher values (above 18 mL/h to 50 mL/h), the particles of different sizes were obtained. It was also observed that with increase in a flow rates, both the major and the minor diameters were affected. The major diameter increases while that of minor diameter goes on decreasing but the equivalent diameters remains the same with slight deviation from the mean value. The formation of particles of different sizes at higher flow rates might occur due to the change from dripping to jetting mechanism.

It is noteworthy that when a liquid is injected into another immiscible liquid at an appropriate low velocity (below the jetting mechanism, like in this case until 18 mL/h), drops form at the tip of the capillary and break off after attaining a certain size. When the velocity of the liquid through a capillary exceeds the critical velocity, known as jetting velocity, a jet of liquid from the tip of the capillary will be formed. The jet breaks up into drops of different sizes and also smaller drops may choke the capillary aperture and eventually an unstable stream of drops will be produced. Therefore, it is important that the operating velocity of the liquid through the capillary should be lower than the jetting velocity in order to obtain uniform sizes of the drops.

The effect of flow rate on the size of particles is shown in the Figure 4.5. Particles of two different sizes were obtained at a flow rate of 40 mL/h with a size range of 3-4 mm while at 50 mL/h particles of three different sizes were collected. The particles were categories into three different size ranges: 2.5-3.0, 3.3-3.8 and 3.9-4.4 mm, respectively. In both cases of different flow rates, the injection velocity of the emulsion through the capillary of inner diameter 1.0 mm was higher than the critical velocity and a dripping to jetting occurred. Hence, the jet of emulsion then breaks up into drops of diverse sizes and the resulting particles are of different shape and size. Likewise, Fang et al. [Fan04] observed the size of wax particles in the range of 3.48-3.63 mm at flow rates of 0.09-0.13 cm^3/s with a nozzle of inner diameter 0.96 mm in a jetting flow region. Also, Nakao et al. [Nak04] reported similar results when drops of hexadecane were solidified in a coolant (water and water- ethylene glycol solution) at flow rates of 0.212 -1.03 m/s. The results are slightly differing due to the physicochemical properties (viscosity, flow-ability, etc.) of the materials under observations.

5.1.3 Effect of water concentrations

In Chapter 4.1.2, the effect of water concentrations on the emulsion particles generated via a capillary were investigated. The water concentration was varied from 5 to 25% by volume in the emulsions which were used in the formation of emulsion drops. It was noted that as the water concentration was increased, no change in the size and the shape of the particles occurred. This exhibits that the water concentrations in the emulsions have no effect on the drop generation through a capillary using a prepared emulsion. The water concentrations in the emulsions have, however, an influence on the rheology of the emulsions. When the water concentration in the emulsion is low (5%), fine droplets are distributed in the emulsions which result in a viscosity higher compared to a higher concentrations of water. The smaller the droplet size is, the higher is the viscosity of the emulsion [Pal96]. As the water concentrations in the emulsions increases, the fine droplets come closer together and coalescence of the droplets occurs and this eventually reduces the viscosity of the emulsion. The volume fraction of the dispersed phase increases due to the increase of the water concentration in the w/o emulsion and hence, the system can be deliberated as a dense emulsion. The distance between the droplets in a dense emulsion is smaller and they are likely to come closer to each other and so experience the higher attractive force between them. Smoluchowski [Smo17] proposed a theory which explains the relation between the coalescences rate and the number of droplets to be coalesced resulting from a shearing effect. This theory is based on the assumption that all drops move along streamlines and every collision results in coalescence according to Equation 5.1:

$$C_s(V,V') = \frac{\gamma}{\pi}[(V)^{1/3} + (V')^{1/3}]^3 \, n(V)n(V') \qquad \text{(Eq. 5.1)}$$

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 amount of water dispersed in the emulsion. The volume (V) is related to the drop radius where the drop is considered as sphere in shape. The emulsion produced by a magnetic stirrer with all water concentrations were carried out at the same experimental conditions and thus the shear rate remains the same during the complete scheme of the experiment. Therefore, the coalescence rate of water droplets is directly related to the quantity of water and the sizes of the droplets. Hence, the viscosity of the emulsion decreases as the water concentrations in the emulsion increases at constant emulsifier concentration.

The reduction in viscosity of the emulsion at higher water concentration is due to droplet coalescence or flocculation. At a higher water concentration the palm oil emulsion is dense and above the maximum packing concentration, the viscosity becomes infinite high and the rheology is determined by the thin film of continuous phase between the droplets. Thus the rheological properties like the viscosity of the emulsion are according to the ratio of the surface tension and radius of the droplet [Pal96]. Therefore, it is expected that, with the increase in the drop radius, the surface tension, viscosity, stress and rheological properties decreases. Also, Anisa and Nour [Ani10] reported affects of the viscosity on the droplet diameter in water-in-oil emulsion and noted that with an increase of the water concentration in the dispersed phase, the rheology of the dispersed phase changes considerably due the interaction of the droplets. Therefore, coalescence at higher water contents would be faster and hence the decrease in the viscosity might broaden the droplet size distribution. Therefore, the water concentration in the emulsions discussed in terms of viscosity of the emulsion is not a unique factor which governs the drop formation by a capillary.

On the other hand, it is noteworthy that viscosities of the liquid used for the production of drops and the continuous phase have little influence on the volume of a drop breakup. It was found that drop necking and the drop breakup is greatly influenced by the viscous force especially in the growth, extension and breakup of the liquid stream and the generation of satellite drops [Kum70]. During the extension of thread, a longer time elapse is required for drop breakup. Whereas, the drop breakup is of weak dependence on the viscosity, but the volume of the drop breakup varies with the viscosity ratio of the two materials in an appropriate way. It shows a maximum value when the viscosity ratio approaches to “1” [Zha99a]. Furthermore, the effect of drop viscosity on the drop breakup was investigated by Cramer et al. [Cra04] in the water/k-Carrageenan system. The viscosity was varied by changing the concentration of k-Carrageenan in the system.

As the viscosity of the disperse phase increases, the corresponding viscous pressure in the thin thread of the disperse phase will be high which opposes the capillary pressure. Therefore, thread of the disperse phase is elongated and extended between the drop breakup and the capillary exit which leads to the generation of satellite drops. The stream of the same size of primary drops of disperse phase at different viscosities was observed at constant flow rate. The viscosity analogy between the observations reported by Cramer et al. [Cra04] and that of water concentration (viscosity change) in our system is shown in the Figure 5.2. Hence, it is revealed that the water concentration in the emulsion has no or negligible small effect on the drops generated by the produced emulsions.

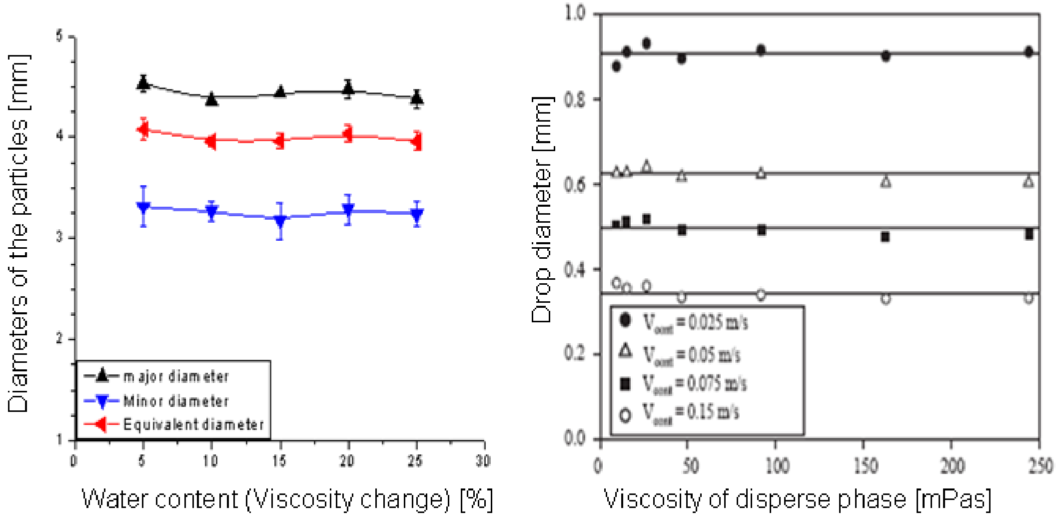

Figure 5.2 Analogous particle size versus water content (Left) at 12 mL/h using capillary of 1.0 mm inner diameter in this work and the viscosity effect on the drop size (right) [Cra04] using capillary of 0.1 mm inner diameter.

5.1.4 Effect of capillary size and the temperature of the emulsion

The effects of the capillary size used for the generation of emulsion drops at different temperatures were shown in the Chapter 4.1.4. The effects were observed on the size and shape of the particles. The size and shape of particles are referred in terms of equivalent diameter and roundness of the particles, respectively. As shown earlier in Figure 4.6, the smallest particles with 1.0 and 0.5 mm are 3.30 and 3.20 mm at 80 and 90^{o}C, respectively. The water concentrations in the emulsion have negligible small changes in the viscosity as described briefly in Chapter 5.1.3 despite the increased concentration to 25% by volume at 60^{o}C. This indicates that emulsion remains as w/o emulsions until the water concentration increased to 25% by volume. Besides this, Chaleepa [Cha10], noted that when the water concentration was above the 35% in the w/o emulsion, the type of the emulsion altered from w/o to o/w emulsion. Therefore, emulsions were prepared at constant water and surfactant concentrations as 15% and 2% by volume, respectively, but at different temperatures. Figure 4.6 show that the equivalent diameter of the particles decreases as the temperature of the emulsions increases. The variations in the equivalent diameters were observed in both sizes of the capillary till 80^{o}C while the reverse mechanism was observed at 90^{o}C. The opposite mechanism is due the phase inversions of the emulsion at higher temperature. Also, at lower temperature, the viscosity is high for the dense emulsions, but when the temperature increases, there will be no further change in the viscosity as reported by Anisa and Nour [Ani10]. In addition to the size of the particles, the particles are more rounds in shape when they were produced by the 0.5 mm capillary. Hence, it is noted that when the particles are small in size they would be more spherical and round in shape. So, in order to obtain smaller particles with the same system, tween 20 was used in the coolant to reduce the interfacial tension between the drop and the continuous coolant. This effect is discussed in Chapter 5.2.

5.2 Influence of energy input and interfacial tension

In Chapter 4.2, Sub Chapters 4.2.1 to 4.2.3 and 4.2.4, the emulsions manufactured by a magnetic stirrer and rotor stator system were characterize and the consequences on the drop size generated from these emulsions were reported. Figures 4.7 and 4.8 shows the images of emulsions produced by magnetic stirrer and rotor stator with 30% (v/v) water concentration at 60^{o}C. The water concentration was increased to 30% in both cases in order to characterize the emulsion matrix. Figures 4.10 - 4.12 exhibits the effects of rotational speed on the shape and the size of particles generated from the emulsion matrix. Figure 4.10 demonstrate the size of particles in terms of major and equivalent diameters. As the energy input increases in the form of rotational speed during the preparation of emulsions, the corresponding change in the size of drops occurred irrespective of the emulsion viscosity as described in Chapter 5.1.3. The size of particle was higher at lower energy input (stirring) which starts reducing when the higher energy was provided during emulsification up to some certain extent (9500 rpm) where droplets in the emulsions were fine and a narrow size distribution was observed. The reduction in the size could be due to the fine droplets existing in the emulsions. No further decrease in the size was observed at the conditions of interests nevertheless the emulsification was done at higher energy input (20500 rpm). This may illustrate that as the rotational speed increases, the fine poly disperse droplets in the emulsion arise and no further droplet breakup occurs. Also, droplets coalescence and flocculation occurred which eventually increases the droplet size rather than decreases it. This could be one of the reasons that the particle size remains constant regardless of the fact that an immense supply of energy during emulsification takes place.

Moreover, the shape of particles was presented in the Figures 4.11 and 4.12 as a function of the particle size and the rotational speeds. The particles were obtained from the emulsion as mentioned in the above paragraph. Likewise, the size of the particles, the shape was also affected by the energy input provided. However, particles are more spherical in shape with increasing the energy input contrary to the size which was the same at higher rotational speeds. From Figure 4.11, it is evident that the particles smaller in size exhibited more roundness compared with the bigger particles. This indicates that the emulsion rheology is not the only factor which determines or governs the size of the drops through the capillary produced by theses emulsions.

Furthermore, it is noted that the interfacial tension is one of the major factors which governs the size of the drop from the capillary or the orifice as described in the Chapter 4.3.1. Also, it is considerable as the dominant force that keeps the drops attached to the capillary tip before the interfacial and shear forces attain equilibrium. The drop at the capillary exit will leave earlier if the two forces approach to the equilibrium much faster. Therefore, the interfacial tension was reduced by the use of a detergent (tween 20) in the coolant medium. The employment of tween 20 in the coolant results on the size and shape of the particles obtained. The effects of the detergent on the size and shape of particles is shown in the Figures 4.14 and 4.15, respectively. From Figure 4.14, the equivalent diameter of particles observed at 50 and 90^{o}C without an emulsifier (0.5% by volume) in the coolant are 3.8 and 3.2 mm, respectively. The equivalent diameter of particles falls to 2.7 and 2.2 mm in the presence of tween 20 at the corresponding conditions. These measurements were obtained when the capillary size of 1.0 mm used. Likewise, the corresponding observations with capillary of 0.5 mm were 3.6 to 3.1 and 2.3 to 1.8 in the absence and presence of the detergent in the coolant at the specified temperature conditions of the emulsion.

On the other hand, the shape of the particles obtained at the conditions described in the above paragraph is shown in the Figure 4.15. It is recognized that the particle roundness reached to 89-90% in the presence of an emulsifier when a capillary size of 0.5 mm was used. This value lies in the range of 77-78% when there was no emulsifier in the coolant and capillary of 1.0 mm used. So, from these examinations, it can be revealed that the smallest particles give the highest roundness. It is monitored that the drop size decreases to 29-31% and 36-41% by the capillary of 1.0 and 0.5 mm inner diameter in the presence of detergent (0.5% by volume) in the coolant. Also, the roundness of the particles obtained was increased to 12-13% in the presence of an emulsifier. The percent decreases and increases indicate the reduction in size of the drop and the increment in the shape of particles when there was no emulsifier in the coolant with the same mentioned capillary sizes. The deviation or the decrease in the drop (particle) size in the presence of an emulsifier (detergent) is higher compared to the results reported [Ske90]. They noted that in the presence of a different surfactant in liquid-liquid system, the drops size predicted by Scheele and Meister [Sch68a, Sch68b]. The deviation observed was 12.9% and the difference in the results reported in this work could be due to the different liquid-liquid system for drop generations.

Further, the drop formation from the capillary is related with pressure difference exceeded the critical pressure, which determines the pore radius and the interfacial tension. The interfacial tension can be decreased by an emulsifier. The interfacial tension and the critical pressure can be related by the Equation 5.2 as described by Geerken et al. [Gee07]. Also, the drop size increases if the pressure difference increases at a constant emulsifier concentration. But, when the fast emulsifier is used, the drop diameter is nearly independent of the pressure difference.

$$p_{ctitical} = \frac{2\gamma}{r_{Nozzle}} \qquad \text{(Eq. 5.2)}$$

Hence, the dynamic interfacial tension is the dominant factor that governs the size of the drop from the pore of the capillary in our system, as the pressure difference is kept constant without altering the flow rate. Therefore, the drop diameter can be reduced by decreasing the interfacial tension using a fast absorbing emulsifier at constant flow rate.

5.3 Solidification/crystallization mechanism and behavior of the particles

The solidification/crystallization of emulsion drops in the coolant was presented in Chapter 4.2.5. Earlier, the crystallization mechanism and behavior of fats and fat emulsions was described extensively in Chapter 2.3. The crystallization mechanism occurring within the emulsion particles solidified in the coolant is shown in Figure 4.13. Prior to the crystallization occurring in the solidified particles, the particles solidify in a direct contact coolant below the freezing point of the emulsion. Therefore, it is important to illustrate the drop solidification mechanism.

In the solidification, the emulsion drops exchange heat with the coolant and this heat transfer results in two steps. At first, the emulsion drops releases heat to the liquid coolant surrounding the drop. When the surface of the drop attains a temperature below the solidification temperature, it starts solidify with a thin layer of the emulsion which envelops the emulsion drop. The sensible heat of the drop depleted into the coolant by convective heat transfer inside as well as outside of the emulsion drop. In the second step, the latent heat of solidification released by crystallizing the drop. Now heat transferred by conductive heat transfer through the solid layer of the emulsion which was developed during the first solidification step, and finally released to the coolant by convective heat transfer mechanism. In this case, the sensible heat transfer is negligible small compared to the latent heat of solidification and hence has little significance.

The crystallization and the structure inside the solid particle were examined by a light microscope and the cross-sectioned images of the solidify emulsion drops are shown in the Figure 4.13. As mentioned earlier in Chapter 4.2.5, the images were taken using a thin slice of the particle generated from the emulsion with 30% water, 2% emulsifier and the balance is the palm oil by volume. From the Figure 4.13, it can be seen that the water droplets which originally distributed in the emulsion are also evenly distributed in the particles. The two images show water droplets of different sizes, the fine and the coarse droplets which were also noted initially in the emulsion matrix. This also confirms the emulsion stability and the even distribution of droplets in the emulsion as well as in the particles. Despite the fact that the size distribution of droplets exhibits a narrow distribution in the emulsion prepared at 9500 rpm, but some coarse droplets exist in the emulsion as shown in the Figure 5.3. The detail images of the emulsion and the particle cross-sectioned are further annexed in the Appendix.

Generally, pure and mixture of TAGs grow as spherulites which are made of several crystalline ribbons that grow radially from a same central nucleus. The ribbons that result the spherulite are needle like shape in most of the cases. Irregular structures of spherulite are frequently observed due to deformation and the interface with the liquid may diffuse. Different morphologies of TAGs spherulites are due to difference of the driving force which causes changes to the mechanism of secondary nucleation of crystal layer. Higher driving forces may induce the surface rougher which eventually leads to the secondary nucleation in different layers simultaneously. The spherulitic growth of TAGs can be illustrated by the surface nucleation theory which is extensively applied to polymer crystallization. The progress or the advancement of the spherulite front may be controlled by the secondary nucleation at the frontal surfaces of the spherulites [Him06].

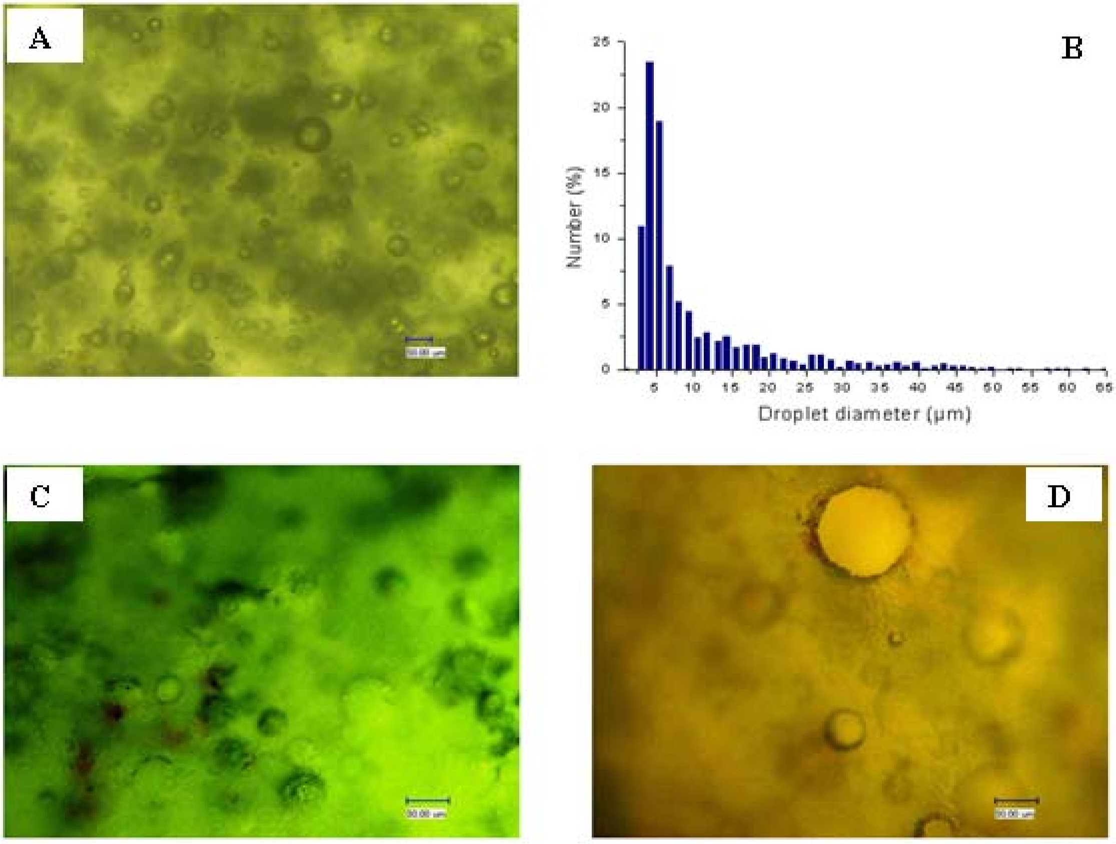

Figure 5.3 Droplets distribution at 9500 rpm: (A) light microscope image of emulsion, (B) size distribution, (C, D) light microscope images of thin layer of solidified particles generated from emulsion. Scale bar: 50 µm.

Figure 5.3 (B) shows that, there are some coarse particles in the emulsion lying in the range of 30 to 63 µm which are depicted in the Figure 5.3 (C, D). The droplets froze in the particles of size 50 µm and above are shown in “D” while the fine droplets less than 30 µm are exhibiting in “C” of the said Figure. It is also observed that the fine frozen droplets showing hairy like structure around the periphery which indicate the crystallization behavior of the fat which was emulsified and then solidify in the coolant below the freezing point. It means that the water droplets distributed carryout the crystallization of the emulsified fat surrounding it and grow in the form of fine needle like crystals.

As mentioned and illustrated earlier in Chapters 2.3.3 and 4.2.5, the mechanism of the crystallization of different palm oil emulsions shows the heterogeneous nucleation mechanism according to the kinetic measurements of solid fat contents, but the mechanism alters when the emulsion matrix was diluted with sunflower oil as described elsewhere [Klo00]. They proposed a self-nucleating mechanism for complex fat emulsion matrixes and noted that a supercooling is needed to induce the crystallization mechanism.

On the other hand, Chen et al. [Che02] observed during the isothermal crystallization kinetics of pure palm oil that at the end of the crystal growth, spherical crystals could be observed below the melting point of the oil similar as observed in the Figure 5.3 (C, D). They indicated that this might happen due the existence of the α-crystals inside the β'-crystals (the cocrystallization of α and β'-forms).

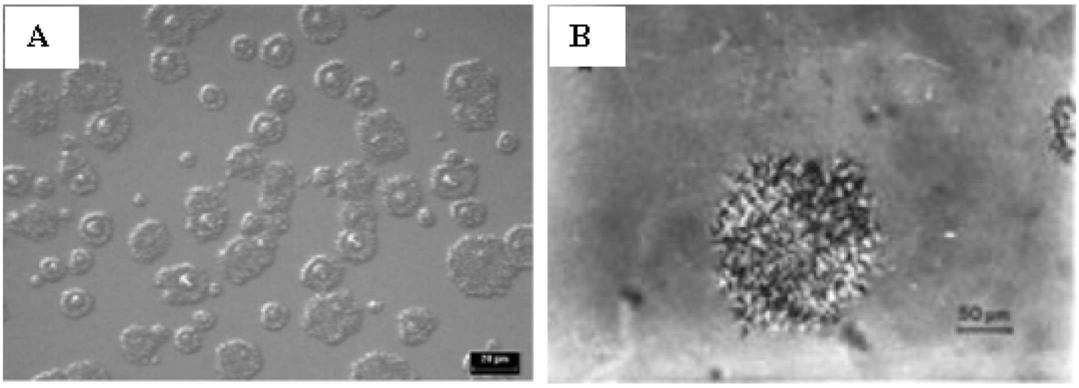

Figure 5.4 Isothermal crystallization: microscope images of (A) palm oil at 18°C [Che02], (B) 80% palm stearin/sesame oil solution at 35°C [Tor00].

Figure 5.4 shows the isothermal crystallization of palm oil at the end of the crystallization and the analogy of the crystal between the pure palm oil and the crystallization inside the particles of water-in-oil emulsion of palm oil can be drawn. Also, Toro-Vazquez et al. [Tor00] monitored the crystallization kinetics of palm stearin and sesame oil solution at different temperatures and crystallization time after the induction of crystallization. They observed that the higher melting temperature triglyceride in the palm stearin/sesame oil solution when once crystallizes under isothermal crystallization; it may boost the crystallization of other lower melting triglyceride. Furthermore, the crystallization process proceeded as of heterogeneous crystallization. It is assumed that the crystallization within the solid particles may follow the mechanism as described. Nevertheless, the crystallization mechanism within the emulsion particles is discussed briefly, but it is also noteworthy that the mechanism is still and certainly worth for further study and observations.

The process can be evaluated on the concept of generation of uniform emulsion particles has been achieved successfully. The process acquired by optimizing the parameters like emulsion stability, coalescence mechanism, drop to particle formation of emulsion and solidification of particles. It is also further accomplished with the size of particles being reduced using an appropriate emulsifier in the coolant. The crystallization mechanism within the particles was also observed, but need further investigation for the complete understanding. It also has advantages over the process described in the literature for the production of particles of diverse materials [Fan04, Nak04] in context of process parameters and the size of particles achieved. However, the crystallization behavior and mechanism is still an open point to be addressed.

6. CONCLUSIONS AND RECOMMENDATIONS

The preparation of water-in-palm oil emulsions which has been considered as one of the phase change materials (PCMs) by different methods and its effects on the stability and on the generation of emulsion drops which turned into the solidified form in a direct contact coolant were invested. Based on the observations from the experimental illustrations, following conclusions can be drawn:

1. The palm oil emulsions prepared by a magnetic stirrer and a rotor stator system were stabilized by the use of non-ionic surfactant (span 20). Different concentrations of the surfactant were used to stabilize the emulsion. The span 20 concentrations were varied from 0.2 to 5% by volume. It was noted that 2% (v/v) of span 20 concentration is the minimum concentration required for a sufficient stability of the emulsion.
2. The prepared emulsions were characterized and the mean size distribution of the droplets distributed in the emulsions was monitored. The water droplets distributed in the emulsion prepared by a magnetic stirrer at 700 rpm were of 11.47µm while in case of rotor stator system, the droplet sizes decreases with increasing energy input and narrow size distributions were observed at 9500 rpm. There was not much difference in size of droplets at 13500 and 20500 rpm due to the coalescence of fine droplets and the breakup of coarse droplets at higher energy inputs.
3. The size of the drop to particle generated by a capillary of 1.0 mm from the emulsions decreases from 4.0 to 3.4 mm at a flow rate of 12 mL/h when the energy input in the form of the rotational speed of the stirrer and rotor was increased from 700 to 20500 rpm. On the other hand, the size of the particles decreases to 3.2 mm by a capillary of 0.5 mm and an energy input applied to the emulsion was 9500 rpm. It was also observed that above 9500 rpm, the emulsion properties remained the same which indicates the smaller change in the particle size at two different capillary diameters.
4. The shape of the particles obtained is referred as the roundness of the particles and noted that the smaller particles are more round in shape. It was noted that the roundness increases to 87-88% at a particle size of 3.2 mm which was 77-78% at a particle size of 4.0 mm and above. Therefore, attempts were made to obtain the smaller particles in order to acquire the roundest particles. Hence, the interfacial tension between the generated drops and the coolant was reduced by the use of an emulsifier in the coolant.

5. An emulsifier (hydrophilic) was used in the coolant by an amount of 0.5% by volume in order to reduce the interfacial tension between the coolant and the generated drops from the capillary. The size of the particles obtained in the presence of an emulsifier was reduced by 29-31% and 36-41% of their original sizes by capillaries of inner diameters 1.0 and 0.5 mm. In other words, the size of the particles could be reduced from 3.8 to 2.7 mm and 2.3 to 1.8 mm in the presence of an emulsifier in the coolant.
6. Likewise, the particles obtained are more rounds in shape when an emulsifier was employed in the coolant. The roundness of the particles increased by a value of 12-13% of its value when there was no emulsifier in the coolant. The smallest particles achieved the roundness in the range of 89-90%.
7. At low flow velocities of the emulsion through the capillary (1.0 mm) single drops were formed at the capillary exit (dripping) which then leave the tip into the coolant. But, as the velocity increases above the critical dripping velocity, a jet stream formed which then disintegrated into drops of different sizes. In the jetting regions, particles were categorized into three different size ranges: 2.5-3.0, 3.3-3.38 and 3.9-4.4, respectively.
8. The water concentration in the emulsions was varied from 5-30% by volume in order to observe the viscosity effect of the drop formation. It is noteworthy that below the water concentration of 35%, the type of the emulsion remains w/o emulsion. It was found that when the water content in the emulsion matrix increases, the viscosity of the emulsion decreases by coarsening and polydispersity of the droplets. The Ohnesorge Number of the palm oil emulsion shows a value below “1” indicating that the water concentration or in other words the viscosity has no influence on the flow behavior of the emulsion through the capillary.
9. The drops then exchange the heat with surrounding coolant and turned into the solid form. The solidification occurred in two steps, first a thin solid layer of palm oil emulsion developed at the surface and envelops the drop, and then in the second step a complete solidification of the drop occurred. The sensible heat transfer was of negligible small compared with the latent heat of solidification during the solidification process and hence has little influence.
10. The palm oil emulsion particles were cross-sectioned at the centre to obtain a thin slice of the solid particle. Microscopy observation of thin slice of emulsion particle showed the fat crystallization within the particles. The orientation of water droplets within the

particles showed a similar location and a uniform distribution as it was observed in the emulsion. It was also found that fine frozen droplets showed hairy like structures around the periphery of the droplets indicating the palm oil crystallization which was emulsified and solidify below the freezing point. Therefore, it is presumed that the water droplets within the emulsion particles accomplish the emulsified fat crystallization and grow in the form of needle shape crystals on the periphery.

11. Moreover, the solid crystalline spherical particles have advantages over the other crystal shapes and solid formulations. The crystalline solid spherical particles have technological advantages which includes:
    a. good flowability due to uniform size and spherical shape which enables a homogeneous and an accurate filling of the active materials;
    b. high physical stability with minimal friction and generation of fine materials
    c. an excellent properties of coating due to spherical shape, smooth active surface, low surface to volume area and good ability to bear mechanical stresses. The particles can be coated with thin and thick coated materials at desired properties and conditions of interest.

In general, it can be concluded, that surfactant concentration can be minimized for the sufficient stability of the water-in-oil emulsions which then used for the generation of the emulsion particles. Furthermore, the process can be employed for the generation of fine particles with the use of other emulsion matrixes by optimizing the operating parameters like: varying the coolant temperature, the use of the capillary of smaller size, use of the additives in the emulsion matrix, reducing the interfacial tension between the coolant and the emulsion drops from the capillary, use of different coolant materials etc. Also, the current process is based on single capillary system for the particles generation which can be design and fabricated by the installation of multiple capillaries depending on the desired size of the product.

The concept of formation of emulsion particles, so-called crystalline emulsion particles have been acquired and prove successfully. The size of the particles was reduced to reasonably small particles by the use of an emulsifier in the coolant. The approach was established by the use of palm oil as a model substance and span 20 as an emulsion stabilizer. However, there are some open points to be addressed like: the use of food emulsifier to make it a more environmental friendly process for the stability of emulsion and to decrease the interfacial tension by some food grade emulsifier. Further studies are needed for the complete understanding of the crystallization mechanism. Also, more experiments should be executed with some complex materials like milk fat in order to prove and extend the concept on a broader canvas. Finally, the process would be the potentially alternative to carry out the hydrophilic-hydrophobic materials in a drug delivery system.

7. SUMMARY

Drops, particles or the granulations formation of various materials have been extensively studied and prepared in different process and chemical industries for their further applications and utilization. Drops are obtained by adopting a route of atomization, use of capillary or an orifice, etc. Fats have been employed diversely in the food, pharmaceutical, and cosmetic industries. Higher melting fats are considered as phase change materials (PCMs) which exhibit either a liquid or solid or semi-solid phase with the slight temperature change around the melting points. In food industries, drops are modified by enhancing their melting point and are used for the production of chocolate, cookies, margarines and shortenings. Generation of fine drops of emulsified fats have the advantage of their use in the dressing of food items as well as the alternative use of a drug carrier system for the hydrophilic-hydrophobic drugs. Therefore, emulsions drops by a capillary were generated and solidified in direct contact coolant in order to obtain the fine solid emulsion particles which are main objective of this work for their utilization in food and in the pharmaceutical industries.

The process of emulsion drops to particles generation has been developed by optimizing and modifying the parameters which have affects on the process. The parameters include: preparation and stabilization of w/o emulsion obtained by different mechanical means, viscosity of the emulsion in terms of water concentrations in the emulsion which affect the flow behavior, effect of the interfacial tension between emulsion drops and the coolant medium, reduction the size of the particles by the use of a detergent in the coolant, solidification mechanism of the drops in the coolant and the size and shape of the particles were monitored. Key parameters that govern the process are the stability of the emulsions and the use of an appropriate capillary size for the formation of particle size of the interest.

The process comprises mainly two parts namely: preparation of emulsions, and generation and solidification of emulsion drops. Palm oil was chosen as a fat model for the production of emulsions due to its properties, availability and the health prospective. Non-ionic emulsifier span 20 was used as an emulsion stabilizer while tween 20 was introduced as a detergent in the coolant to reduce the interfacial tension between the drops and the coolant. Emulsions were prepared by a magnetic stirrer and a rotor stator system with different energy inputs.

The emulsions were then pumped at various flow rates through a capillary of two different sizes and drops were generated. The drops were then solidified by exchanging heat with the surrounding coolant.

The viscosity of palm emulsion matrix was reduced by increasing the water concentration in the emulsion and was analyzed by dimensionless numbers. The Ohnesorge number value was below “1” at water concentration above 15% indicating the low viscous emulsion which has a negligible small effect on the emulsion flow behavior. Furthermore, the size of the particles was reduced by the use of a detergent in the coolant. The detergent reduces the interfacial tension between the drops and the coolant so that the shear force and the interfacial tension force attains equilibrium much earlier which results the decrease of drop size upto 42% of its original size when there was no detergent in the coolant.

The crystallization mechanism within the solid particles was observed and noted that needle like crystal grows at the periphery of the droplets which leads to the spherulitic growth of the emulsified fats. Different fat spherulites may be illustrated by a mechanism of nucleation of crystal layer which induces a rougher surface and thus eventually leads nucleation at different layers simultaneously.

The concept of generation of uniform emulsion particles and their solidification in a coolant has proven to be successful. Also, the particles of smaller sizes were obtained by reducing the interfacial tension between the working materials. However, there are still some points to be addressed and elaborated like e.g.: the use of food emulsifiers in the process, the crystallization mechanism within the particles, etc. More experiments are needed with some complex oil or fat systems to prove and extend the concept. Finally, the process likely to be a potential alternative in drug delivery systems and in food technologies.

8. NOTATIONS AND ABBREVIATIONS

Notations	***Units***	***Descriptions***
a	[mm]	Major diameter of particle
b	[mm]	Minor diameter of particle
Cs (V, V’)	[m/s]	Coalescence rate
D_{FS}	[cm]	Diameter of the attached drop at equilibrium
D_H	[cm]	Hydraulic diameter of the channel
dp	[mm]	Equivalent diameter of particle
F	[-]	Harkins-Brown correction factor
F_B	[dynes]	Buoyant force
F_D	[dynes]	Drag force
F_I	[dynes]	Inertial force
F_S	[dynes]	Interfacial tension force
g	[cm/sec^2]	Acceleration of gravity
G	[1/sec]	Predominant elongation or shear rate-of-strain
L	[cm]	Characteristics length
n(V)	[-]	Number of drop
Q	[cc/sec]	Volume flow rate of dispersed phase
U_N	[cm/sec]	Dispersed phase average velocity through the nozzle
D_N	[cm]	Nozzle inside diameter
U	[cm/sec]	Characteristic velocity
U_F	[cm/sec]	Velocity of the forming drop at the instant necking starts
V	[m^3]	Volume
V_F	[cc]	Drop volume after break off from the nozzle
V_{FN}	[cc]	Volumetric flow out of the nozzle during necking
V_{FS}	[cc]	Liquid volume attached to the nozzle when necking starts

Greek Symbols

a	[cm]	Characteristic size of the finger prior to enter the junction
α, β, β'	[-]	Polymeric forms of fat
μ	[g/cm.sec]	Continuous phase viscosity
w	[cm]	Characteristic width of the channel
ρ	[g/cc]	Density of continuous phase
ρ'	[g/cc]	Density of dispersed phase
σ	[g/sec^2]	Interfacial tension
η_o	[mPas]	Viscosity of the emulsion

Abbreviations

HLB	Hydrophilic-lipophilic-balance
PCM	Phase change material
PMF	Palm mid fraction
TAG	Triglyceride
SFC	Solid fat content

Dimensionless Numbers

Bo	$\frac{\Delta\rho g w^2}{\sigma}$	Bond Number
Ca	$\frac{\mu G a}{\sigma}$	Capillary Number
Oh	$\frac{\eta_o}{\sqrt{\rho\sigma L}}$	Ohnesorge Number
Re	$\frac{\rho D_H U}{\mu}$	Reynolds Number
We	$Re\ Ca$	Webber Number

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10. APPENDIX

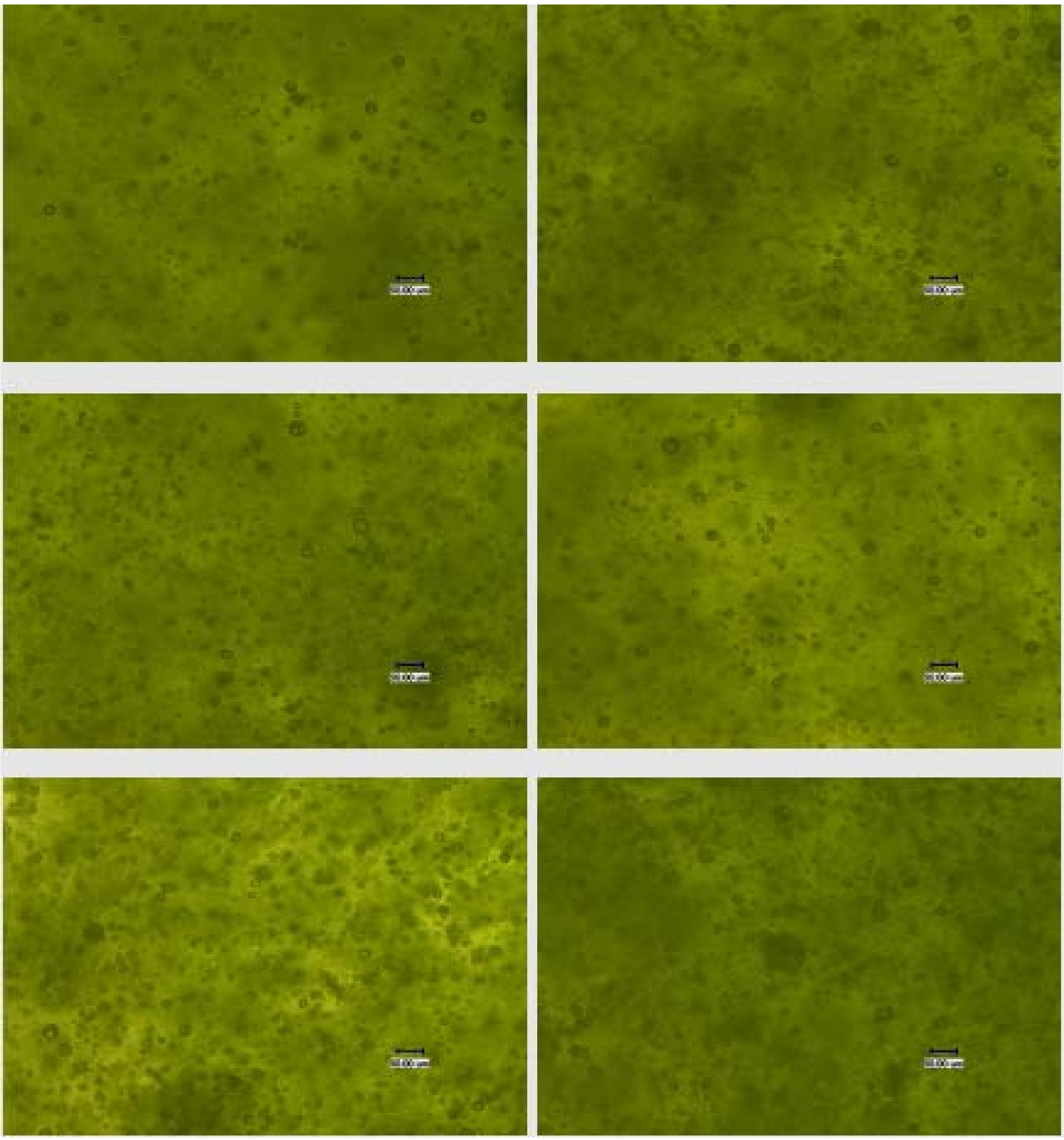

Figure 10.1 Light microscopic image of the emulsion prepared by a magnetic stirrer at 700 rpm at 60°C and 30% water by volume. Scale bar: 50 µm.

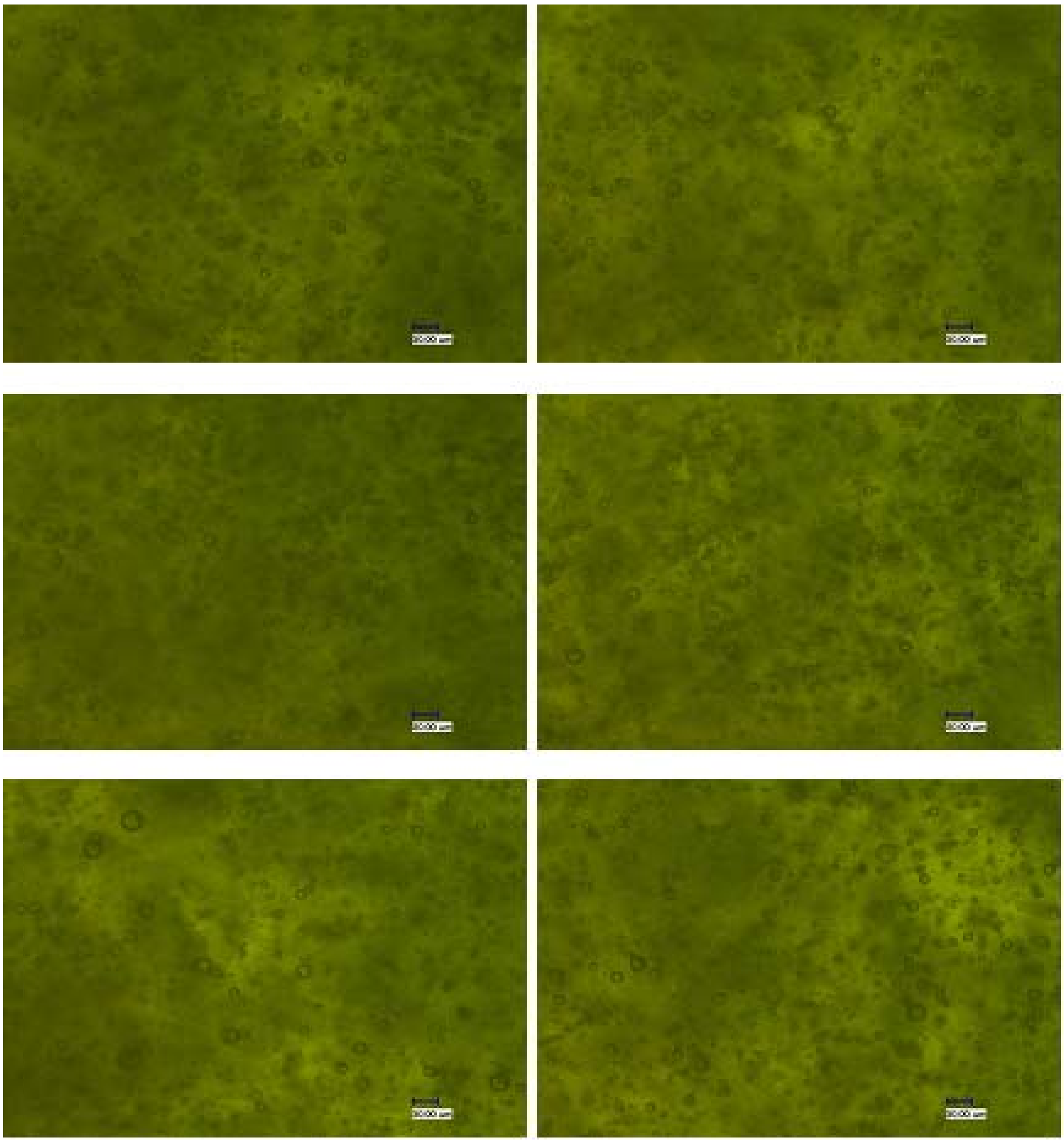

Figure 10.2 Light microscopic image of the emulsion prepared by an ultra-turrax at 8000 rpm at 60°C and 30% water by volume. Scale bar: 50 µm.

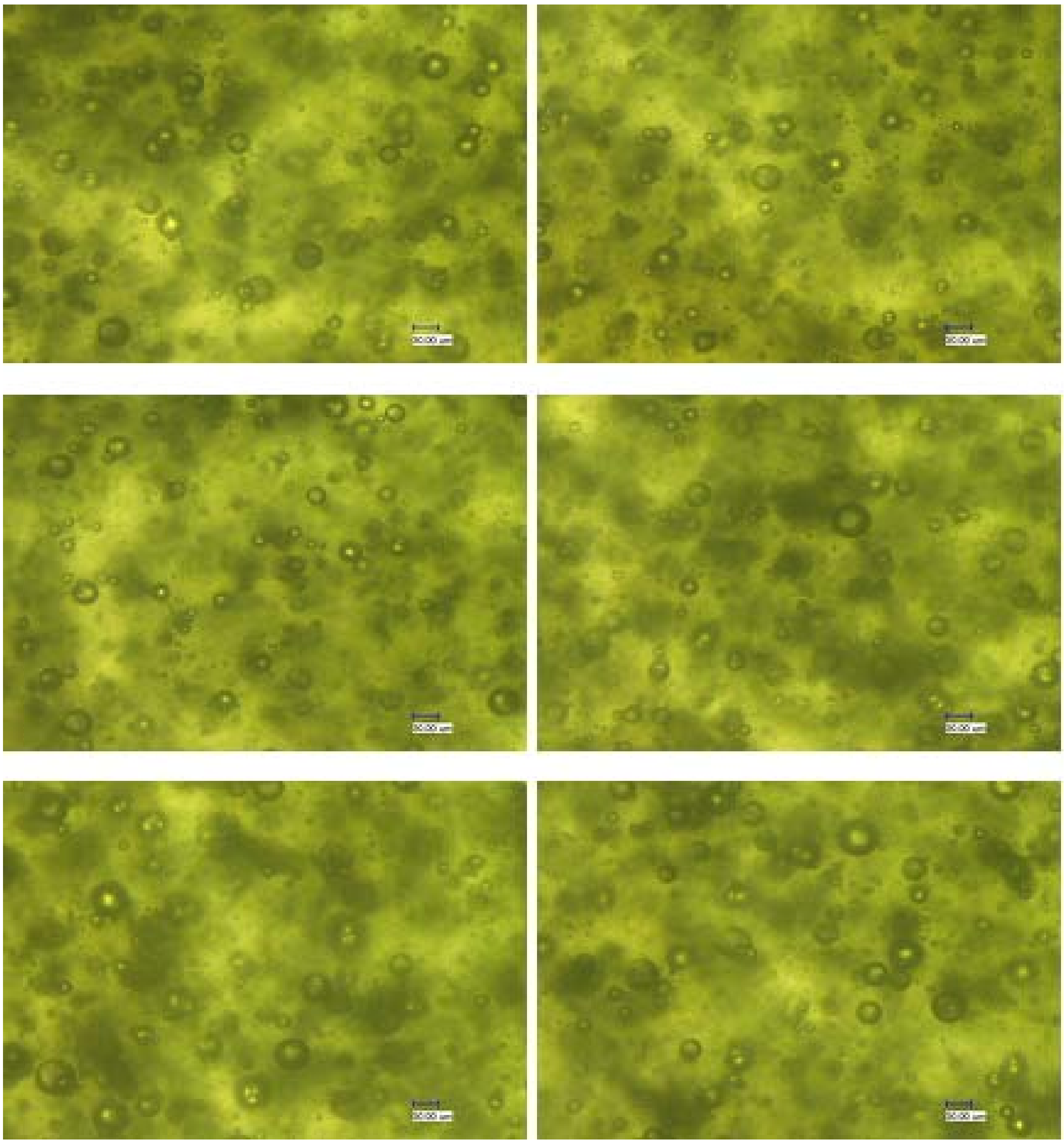

Figure 10.3 Light microscopic image of the emulsion prepared by an ultra-turrax at 9500 rpm at 60°C and 30% water by volume. Scale bar: 50 µm.

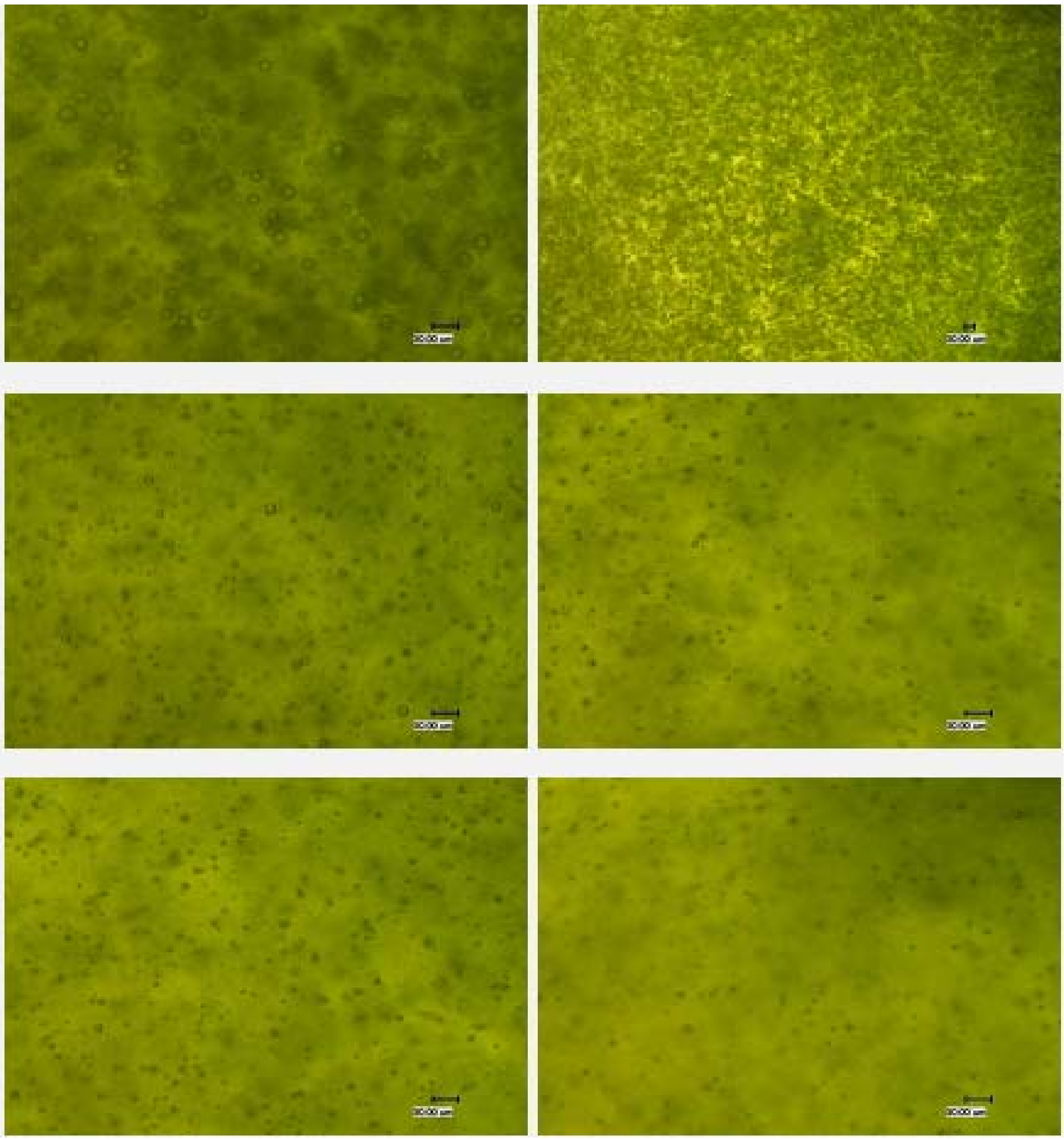

Figure 10.4 Light microscopic image of the emulsion prepared by an ultra-turrax at 13500 rpm at 60°C and 30% water by volume. Scale bar: 50 µm.

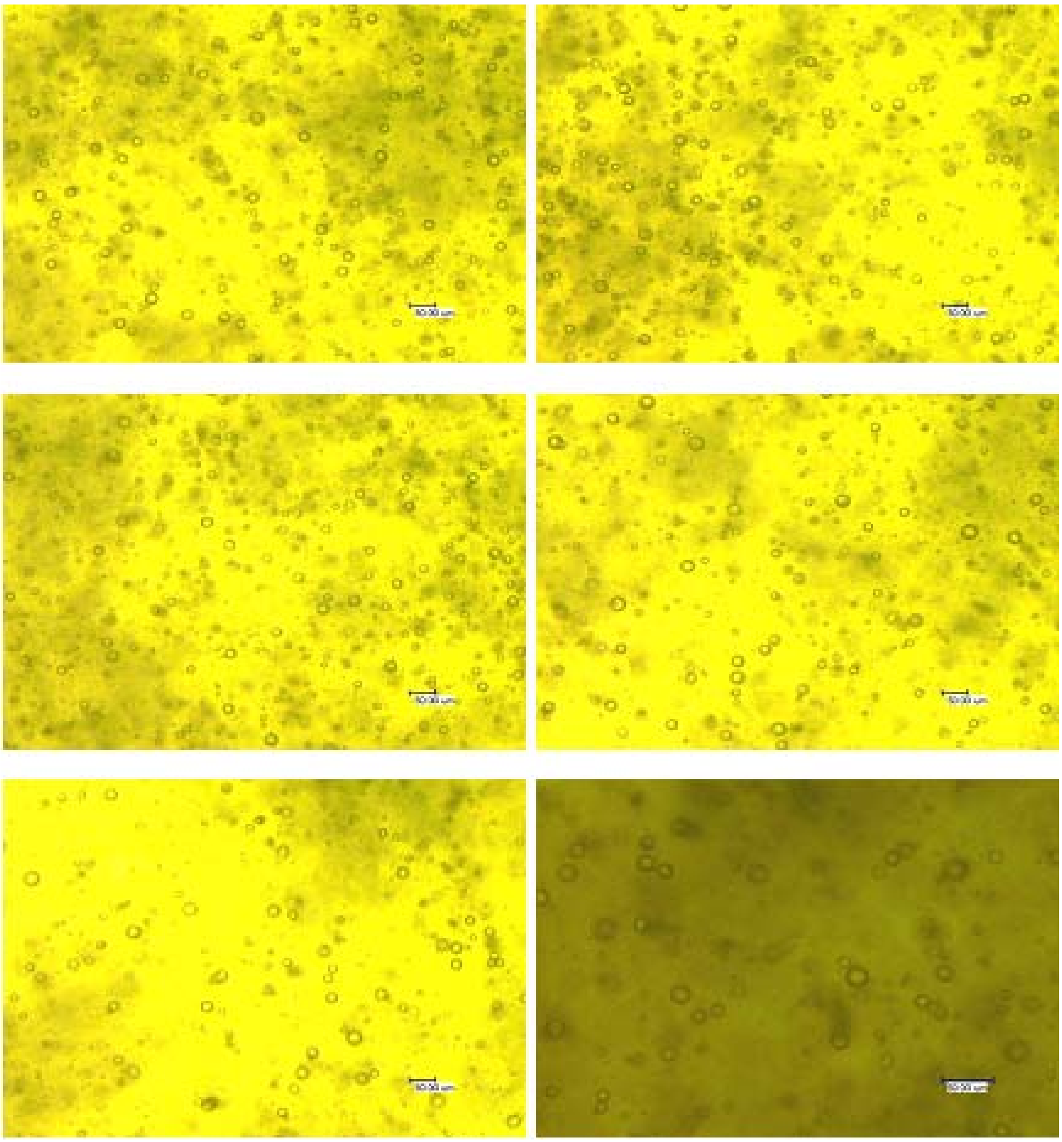

Figure 10.5 Light microscopic image of the emulsion prepared by an ultra-turrax at 13500 rpm at 60^{o}C and 30% water by volume. Scale bar: 50 µm.

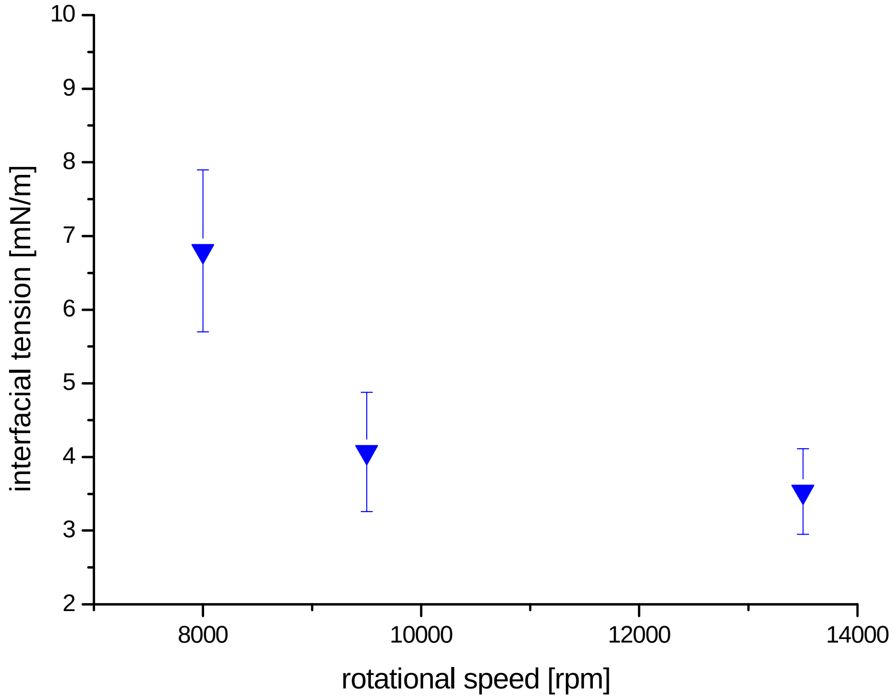

Figure 10.6 Relation of interfacial tension between the water and the emulsion prepared at different speeds of an ultra-turrax at 60°C and 30% water by volume.

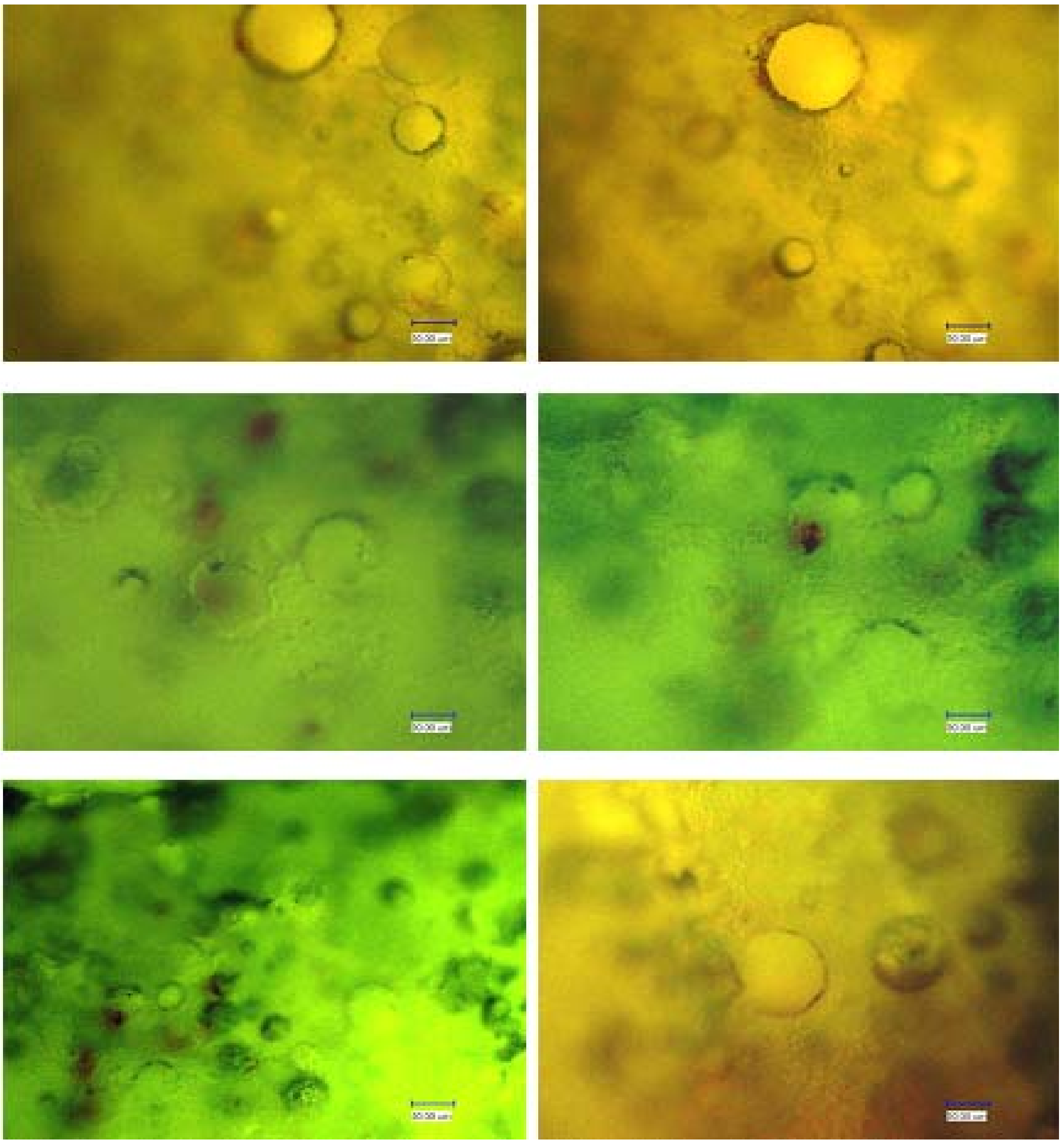

Figure 10.7 Cross-sectional images of thin slice of solid particle using light microscope. Scale bar: 50μm.

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4. List of Publications

a) Journals

[1] **Iqbal, J., Ulrich, J.,** (2011) Crystalline phase change particles: *Chemical Engineering Science (Submitted).*

[2] **Iqbal, J., Petersen, S., Ulrich, J.,** (2011) Emulsion solidification: Influence of the droplet size in the water-in-oil emulsion on the generated particle size: *Chemical Engineering and Technology 34 (4), 530.*

[3] **Iqbal, J., Ulrich, J.,** (2010) Spherical particle generation by phase change materials: Near monosize particles from emulsions: *Chemical Engineering and Technology 33 (6), 1011.*

[4] **Iqbal, J., Kim, H., Yang, J. S., Baek K., Yang, J. W.,** (2007) Removal of arsenic from groundwater by micellar-enhanced ultrafiltration (MEUF), *Chemosphere 66 (5) 970.*

[5] **Kim, H., Baek, K., Lee, J., Iqbal, J., Yang, J. W.,** (2006) Comparison of separation methods of heavy metal from surfactant micellar solutions for the recovery of surfactant, *Desalination 191 (1-3) 186.*

b) Conferences

[1] **Iqbal, J., Petersen, S., Ulrich, J.,** (2010) Emulsion solidification: Influence of the droplet size in the water-in-oil emulsion on the generated particle size: *17th International Workshop on Industrial Crystallization (BIWIC)*, September 8 -10, Halle (Saale), Germany.

[2] **Iqbal, J., Kim, H., Baek, K., Yang, J. W.,** (2005) Effect of clay and other anions in the removal of chromate from groundwater using MEUF, *KIChE Spring Meeting,* April 22 - 23, Yeosu, Korea.

[3] **Kim, H., Baek, K., Lee, J., Iqbal, J., Yang, J. W.,** (2005) A study on the effect of different carbon sources on the activity of alginate-immobilized anaerobic sludge, *KIChE Spring Meeting,* April 22 - 23, Yeosu, Korea.

[4] **Kim, H., Baek, K., Lee, J., Iqbal, J., Yang, J. W.,** (2005) Comparison of separation methods of heavy metal from surfactant micellar solutions for the recovery of surfactant, *2^{nd} KAIST-UCSB Student Symposium*, September 5 - 6, Daejeon, Korea.

[5] **Iqbal, J., Kim, H., Yang, J. W.,** (2005) Removal characteristics of arsenic with various cationic surfactants using micellar-enhanced ultrafiltration, *KSEE Fall Meeting,* November 3 - 5, Seosan, Korea.

[6] **Iqbal, J., Kim, H., Baek, K., Yang, J. W.,** (2005) Effect of clay and other anions in the removal of chromate from groundwater using MEUF, *The 18th symposium on Chemical Engineering Daejon/Chungnam (Korea) - Kyushu (Japan),* December 2- 4, Cheonan, Korea.

AFFIRMATION

I hereby affirm that I wrote this dissertation without any inappropriate help by any third party and without using any other means than indicated whatsoever.

This dissertation has not been presented to any other examination board either in the present or a similar form, neither in Germany nor anywhere else according to the best of my knowledge.

This dissertation has been written at Martin-Luther-University Halle-Wittenberg under the supervision of Prof. Dr.-Ing. Dr. h.c. Joachim Ulrich. There have been no prior attempts to be made to earn a PhD degree at any university.

Halle (Saale) 20.07.2011

Javed Iqbal