Chinese Journal of Chemical Engineering xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Chinese Journal of Chemical Engineering

journal homepage: www.elsevier.com/locate/CJChE

Materials and Product Engineering

Formation of crystalline particles from phase change emulsion: Influence of different parameters

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ARTICLE INFO

Article history:
Received 21 September 2015
Received in revised form 28 November 2015
Accepted 30 November 2015
Available online xxxx

Keywords:
Emulsion
Particle formation
Size
Phase change
Interfacial tension

ABSTRACT

Solidification or crystallization of phase change emulsion in the form of fine emulsion drops in a direct contact coolant at temperatures below their freezing point was studied. This work is mainly focused on the size and shape of the generated particles from phase change emulsified fats. Size of the particles is the major or key factor being considered during their formation, however, other factors that govern the particle size and shape were also observed. The operating parameters of the process were optimized in order to obtain particles of smaller size ranges in the window of current operating conditions. The crystallization of complex emulsion matrices is very difficult to control in the bulk at desired requirement. Hence, the emulsion drop to particle formation has advantage in comparison with the bulk solidification or crystallization. The main objective of this work is to achieve spherical emulsion particles in a direct contact cooling system. Parameters like: stability, characterization, viscosity, and the effect of different energy inputs were examined. Moreover, the effects of the capillary size, interfacial tension, temperature of the emulsion on the particle size were also monitored.

1. Introduction

The materials used for the storage of thermal energy for a short span of temperature are called phase change materials (PCMs). 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 liquid to solid with the slight gradient of temperature. The phase change materials (PCMs) have great importance in industry keeping in view their storage and transportation. 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 [1,2]. Although, phase change materials have been extensively studied for a number of applications during the past few decades, their application in the form of solid spherical particles below the freezing point has received great attention in recent years [1–3]. Despite the fact that PCMs have a wide range of potential applications in different fields, their use in the form of emulsion solid particles is limited, especially, in the area of pharmaceutical industries. Therefore, the use of emulsion of phase change materials in the form of solid particles is of great importance. Emulsion solidification is one of the techniques among others for PCM systems. Generally, a variety of PCMs may be employed for the preparation of solid particles, however, oils, fats and their commonly derivates available in the market are observed to melt at ambient temperatures. Hence, their use as PCMs is of great interest. They possess the properties that make them suitable for the preparation of phase change materials (PCMs) in the temperature range of 0–110 °C. Below 0 °C, water, water–salts and water–organics eutectics exhibit high latent heats and above 110 °C, fatty acids are not suitable for thermal application due to the thermal degradation. Hence, palm oil with melting temperature range 35–40 °C was selected as PCM despite the fact that it is widely used in the food industry. The solidification behavior and drop formation pattern were obtained from palm oil emulsion which was used as model substance in our previous studies [4,5].

Emulsions comprise the systems in which droplets of one liquid dispersed in another immiscible liquid. They are generally classified into two types, namely, w/o and o/w emulsions. In the first type of emulsions, water droplets dispersed in the oil phase, and in the second type oil droplets distributed in the water medium. Food emulsions lie in the first type while water in the crude oil in the petroleum industry belongs to the second category [6]. The emulsions can also be further classified into more complex forms like: w/o/w or o/w/o emulsions. These complex emulsions are referred as double emulsions. Emulsions are not stable systems, so it is accepted that emulsifiers or surfactants are used to stabilize the emulsion matrix [7]. Moreover, emulsifiers have more affinity to the continuous phase than to the dispersed one; thus Span, a nonionic emulsifiers with higher hydrophobic than hydrophilic character is adequate to form w/o emulsion of palm oil, a phase

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http://dx.doi.org/10.1016/j.cjche.2015.12.026
1004-9541/

Please cite this article as: J. Iqbal, *et al.*, Formation of crystalline particles from phase change emulsion: Influence of different parameters, *Chin. J. Chem. Eng.* (2016), http://dx.doi.org/10.1016/j.cjche.2015.12.026

change material. Generally emulsions can be produced by different systems like: high pressure systems, membrane systems, ultrasonic systems, rotor systems and disc like systems as described briefly [8]. Different parameters like: thermal and physical properties, preparation method, surfactant type, mass ratio, and microstructure that influence the emulsion properties of PCMs have been extensively studied [1,4,5,9–12].

The mechanism of drop formation from a capillary tube, nozzle or orifice into another immiscible liquid has received great attention for over a century. Different variables that governed the drop formation mechanism are density of dispersed and continuous phases, interfacial tension, nozzle design including shape and size, and viscosities of both phases [13]. 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, and 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 [14], therefore, the effect of the viscosity, flow rate and capillary diameters [15,16], drop generation in the flowing medium [17,18], uniform wax particles in coolant below the freezing point [19] have been studied extensively. The solidification behavior of drops produced from phase change materials (PCMs) has got great importance. Therefore, the different parameters which influence the process were studied. The purpose of this study was to monitor the different factors like: the emulsion characteristic *i.e.*, preparation methods and energy inputs, viscosity of the emulsions, effect of capillary size, interfacial tension and the temperature of the emulsion were observed. In addition, the crystallization mechanism that happened within the solid particles during solidification was also examined.

2. Experimental

2.1. Chemicals

Refined palm oil obtained from Fluka (Sigma-Aldrich Chemie GmbH, Germany) having m.p. 30–40 °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 emulsion. 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.

2.2. Experimental method

The emulsions were prepared by using palm oil as a continuous phase at different concentrations, distilled water as dispersed phase and Span 20 as an emulsifier. Both palm oil and Span 20 were heated at different temperatures 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 at the same temperature. The water compositions in the emulsion matrices were varied from 5%–30% by volume. The type of emulsion remains the same until 30% of water concentration in the emulsion. The mixture was then stirred continuously for 30 min with a magnetic stirrer at 700 $r \cdot min^{-1}$ and the other matrices of emulsions were prepared with an ultra turrax T25 (IKA® Labortechnik) at four different tip speeds (8000, 9500, 13,500 and 20,500 $r \cdot min^{-1}$). The temperature was kept constant throughout the experiment. The emulsion was stable up to 30 min as reported previously [4,5]. The properties of the emulsions produced by a magnetic stirrer and a rotor stator system were obtained with the help of a light microscope (×100, VHX-500F) supplied by Keyence, Neu-Isenburg, Germany attached to the microscope cell to maintain the temperature of the emulsions alike with that of emulsion preparation. Whereas the size and the shape of the solidified emulsion particles were measured by a light microscope (×16.5, BH2) provided by Olympus, Tokyo, Japan, also connected to the microscope cell to keep the temperature similar to that of temperature of coolant during solidification. The viscosity of the emulsions was measured by standard operating procedures with the help of a Rotational Viscometer (VT550), Thermo Haake GmbH, Germany. The schematic diagram of the experimental setup is described by Fig. 1. In this figure, photographs of the actual experimental setup and magnified image of the solid particles obtained have also been included.

The prepared emulsions were pumped using a syringe pump (Cole-Parmer, VERNON HILLS, USA) through a capillary of various sizes situated at the bottom of the coolant vessel. The purpose of the emulsion feeding by capillary of two different sizes was to generate uniform drops of various sizes. The inner diameters of the capillaries used were of 0.5 mm and 1.0 mm, respectively. 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 and 20 min, so there was not much concern regarding the instability of the emulsion. The produced emulsion drops in the coolant (water) turned into solid form in the coolant at low temperature. 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 temperature of the coolant was kept at 10 °C. Spherical drops of the emulsions were formed at the tip of the 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 [4]. The particles were collected at the top of the coolant for further measurements. Tween 20 was used in the coolant to reduce the interfacial tension between the coolant and the emulsion drops.

3. Results and Discussion

The experiments were carried out in order to observe the influence of different parameters on the rheology of emulsions and their effects on the size and the shape of the particles produced from these emulsions. These parameters include: emulsifier concentration, energy input, viscosity, size of the capillary used for the drop formation, temperature of the emulsions, and the effect of the interfacial tension between the working materials and the coolant. The drops of the emulsion are then called particles after solidification in the coolant. The size of the particles, obtained, was measured by a light microscope. When the 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 Eq. (1) as described elsewhere [3].

$$d_p = \left(a^2 \cdot b\right)^{\frac{1}{3}} \tag{1}$$

where, d_p is the equivalent diameter of single particle and "a" and "b" are the major and minor diameters of the individual particle measured by Eq. (1), the equivalent diameter of single particle was then calculated. In these experiments, 20–30 particles were measured and then the average value was used similar to the method described in the literature [3] where they used 40–60 particles for the measurements of their sizes and then mean value was calculated in case of solid particles.

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