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A laboratory investigation of the anhydrous milkfat fractionation using a membrane technique

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Abstract

Anhydrous milkfat (AMF) exhibits a broad melting point range (−40 to 60 °C) which can be separated into fractions of different and narrow melting point ranges using membrane technology. In this study, five different hydrophobic polymeric membranes (three composite membranes in the nanofiltration (NF) category, i.e. MWCO (300–400 Da) and (700–1000 Da), and two membranes in the ultrafiltration (UF) category, i.e. polysulfone MWCO 10 kDa and PVDF MWCO 30 kDa, were evaluated for AMF fractionation in a stirred and heated cell, in a batch mode filtration. The effect of different operating conditions of pressures (200, 300, and 400 psi at constant temperature 55 °C), fractionating temperatures (40, 30, 23, 20, 17, 13.5, and 10 °C at the optimum pressure (300 psi)), and stirring speeds (50–600 rpm) were investigated. The fractionation was confirmed by thermal profile analysis and solid fat contents (SFC) for both, the permeate fat and the rejected fat using differential scanning calorimetry (DSC). The qualities of milkfat fractions have been assessed using ATR-FTIR spectrophotometer. For an in depth investigation, Raman microscopy and scanning electron microscopy images and spectrum were recorded. The results indicate that at the optimum operating conditions of pressure (300 psi) and moderate stirring speeds (100 rpm), and at constant fractionation temperatures (30, 23, 20, 17, and 13.5 °C) carried out separately, using the UF membrane (30 kDa), AMF can be successfully fractionated. All fractions have the same quality of the intact fat. A mathematical model based on the experimental data have been derived to predict milkfat permeate ($g\,min^{-1}$) at different operating temperatures (°C).

Keywords: Membrane processes; AMF; UF; NF; SFAs; USFAs; Triglyceride (TGs); Hydrophobic; Hydrophilic; Milkfat fractionation; Dead-end UF; Fouling; DSC; ATR-MIR spectroscopy

1. Introduction

Anhydrous milkfat (AMF) has a broad melting point range (−40 to 60 °C) that in some cases interfere with its compatibility as food ingredient. For instantce, AMF is incompatible with cocoa butter (CB) triglycerides (TGs) as it causes eutectics effect (decrease melting point). While, high melting point fraction (HMF) is fully compatible with CB TGs and could be added to confectionery fats as the bloom inhibitor without decreasing the melting point or the hardness [1]. On the other hand, low melting point fractions can be used in nutritional foods and soft spreads or blended during conventional agitating to make butter of improved spreadability.

AMF composes mainly of 99.8% milkfat and 0.2% water. The milkfat portion composes mainly of 98.8% (TGs), and the residue is traces of di, mono glycerides, and sterol along with the carotene colour and fat-soluble vitamins [1–3]. The TG is a neutral fat composes of three fatty acids (FAs) joint together on the glycerole backbone [2,3]. There are at least 400 different chemical compositions of FAs in milkfat, such as long chain, short chain, saturated and unsaturated FAs [1]. In fact, the most abundant fatty acids in milkfat are C16:0 and C18:1 that contribute to the hydrophobic tendency of AMF. The physical properties of AMF are generally expressed in terms of crystallization and melting behaviour of milkfat [1,4]. These properties affect the AMFs compatibility as food ingredients for food manufacture.

The conventional methods for AMF fractionation are [1]: (1) Crystallization from melted milkfat, which considered the oldest and the most common applied method [5–8]. But, very slow process, and produce less pure frac-

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tions, in a limited temperatures range. (2) Crystallization from milkfat dissolved in solvent, used mainly for laboratory researches because of the direct contact with the solvent, which might contaminate the milkfat, and change flavour [1,8]. (3) Supercritical fluid extraction [1,7,9] which is highly efficient but very expensive. (4) Short path distillation [1,10], which has so far been investigated only on an experimental basis.

According to those methods, the produced milkfat fractions that have been defined according to the melting points (mps) range as follows [1]:

(i) very high melting point range mp > 45 °C;
(ii) high melting point range (mp 35–45 °C);
(iii) middle melting point range (mp 25–35 °C);
(iv) low melting point range (mp 10–20 °C);
(v) very low melting point range (mp < 10° C).

The fractions can be distinguished by fatty acids, TGs composition, mp, and solid fat index. However, the separation of milkfat TGs by molecular size were not possible by melt crystallization due to the average MW of the various fractions were ranging from 714.8 to 769.7 Da compared to 727.5 Da for the intact milkfat [11]. The separation by MW is achievable by supercritical gas extraction applications producing high purity end products. Similar to dry crystallization and supercritical gas extraction, membrane technology can also be employed to produce the fractions. As during cooling to temperatures lower than the melting points range, nuclei of the high melting point TGs form and grow into crystals of 0.1–2 μm in length [4]. At a specific temperature under the effect of pressure, fat crystals or even the nuclei can be separated from the melted fat according to their MW or particle sizes by an appropriate membrane. At the same time the melted fat is allowed to permeate through the membrane. Thus, the key factor in membrane technology is to choose the optimum membranes that can fractionate the different TGs molecules and give the highest possible flux. The temperatures of these fractions are therefore very important parameters in such operations.

The main objective of this study is to fractionate AMF into different and narrow melting point range fractions using appropriate flat sheet membranes incorporated in a stirred heated cell. Five different membranes in the nanofiltration (NF) and ultrafiltration (UF) categories have been evaluated. The effects of the operating pressures, temperatures, and stirring speeds have been studied to determine the useful operating conditions.

2. Mechanism of milkfat fractionation by membrane technology

It has been reported [12] that the mechanism of fat fractionation by membrane technology is based on three main aspects: (1) the melted fats (nonpolar media) are not an absolute homogeneous phases, as at microscopic level, several organized structures could be observed, such as polar lipids, impurities, and water inclusions; a micelle organization could remain just above the melting point of a nonpolar melted fat. The solid state is a mixture of several polymorphic forms, leading to other "micellar structures" due to aggregate ions in a given range of temperatures; the interactions between the TGs and the membrane layer, as in front of a hydrophobic membrane layer, only TGs of hydrophobic tendency will pass through the membrane, and vice versa.

According to that a filtration process can be achieved as aggregates could remain in the retentate, while free TGs cross easily the barrier. Those aggregates are assumed to contain mainly the high melting point TGs. As a result, at a given temperature the retentate is enriched in aggregates with a HMP fraction and vice versa for the permeate (Fig. 1).

3. Experimental investigations and methods

3.1. Membrane apparatus

The dead-end filtration experiments were conducted in a magnetic stirred cell (STERLITECHTM HP4750, US) in a batch operation mode. The cell was placed on a magnetic stirrer and the magnetic spin bar fitted into the cell provided the agitation. A membrane sheet can be fitted to the cell. The membrane active area is 14.6 cm^2. The pressure was employed via high-pressure regulator of nitrogen cylinder (Fig. 2). Heating and cooling were applied via water bath. Permeate was collected in a beaker placed on an electric balance (Sartorius CP 4202 S, Germany) and it was connected to a computer. The permeate flow data were directly recorded in excel in g min^{-1} for further analysis.

3.2. Materials and preparations

The AMF used in this study was obtained from Fonterra Ltd and was frozen under −18 °C in a laboratory freezer. Five different membranes were evaluated (SR2 and SR3, Koch Membrane Systems, USA) (MWCO 300–400 Da), 7450 HydraCoRe, Hydranautics USA (MWCO 700–100 Da), K-131 (MWCO 10 kDa), and M-100 (MWCO 30 kDa) (Koch Membrane Systems, USA) (Table 1). Each membrane was cut into 5 cm diameter by a single-edged razor blade using the stainless steel porous disk as a template. The membrane was washed with warm solution of 0.5 wt% NaOH, rinsed with ultra pure water and gently dried with towel tissue to remove any excess water drops just before being installed in the cell. For adequate drying in place, warm air was employed via normal hair dryer. For membrane cleaning 0.5 wt% NaOH solution was used.

3.3. Operating conditions

Three pressures (200, 300, and 400 psi) and a range of fractionation temperatures (40, 30, 23, 20, 17, 13.5, and 10 °C)