Real-time Monitoring of the Crystallisation of Palm Oil and its Products by Focused Beam Reflectance Measurement (FBRM)

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INTRODUCTION

The importance of dry fractionation as one of the most widely practiced modification processes for palm oil and its products cannot be denied. For decades, the versatility of palm oil has been expanded and enhanced using this technique which is fully reversible, inexpensive and environmental-friendly. Palm oil not only can be fractionated using a single step, but can also undergo a multi-step fractionation process to produce a variety of sub-products bearing improved physical and chemical characteristics that differ greatly from the mother oil. This procedure generates an abundance of raw material which finds usage in food applications such as cooking and salad oils, margarines, spreads, confectionery fats, ice cream, emulsifiers and *vanaspati*, among others (Deffense, 2008).

The first step in the fractionation process of palm oil and its products is the crystallisation stage. Crystallisation in the context of oils and fats involves controlled cooling of the oil or fat melt to below its melting point to initiate the crystallisation of the highest melting triacylglycerol component (Hartel, 2013). Numerous research studies over the last four decades have shown that proper control of operating parameters, such as temperature, agitation and cooling rate during the crystallisation stage, are crucial in determining the characteristics of palm oil crystals (Miskandar *et al.*, 2004; Kellens, 2007; De Graef *et al*., 2009; Vuillequez *et al.*, 2010). The quality of crystals produced eventually affects the performance of the subsequent filtration stage, and this will have a profound influence on final product quality (Deffense, 2009). It has been reported that crystals which are uniform in shape, morphology and composition allow optimal separation of these crystals from the liquid fraction (Calliauw *et al.*, 2007a). Therefore, an understanding of the characteristics and behaviour of crystals during the crystallisation stage of the fractionation of palm products is imperative in order to efficiently optimise processing conditions for producing the correct amount, size and shape of crystals for enhanced filtration and product quality.

Several important key aspects in the characterisation of crystals during crystallisation include crystal population (numbers), crystal size distribution (CSD) as well as detection of the different events which occur during the progression of crystallisation. Most crystal characterisation studies on oils and fats in the past have been performed using common optical and laser measurement techniques such as

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image analysis, particle size analysers and laser particle counters (Van Putte and Bakker, 1987; Chawla and de Man, 1990; Fitzgerald *et al.*, 2001; Tarabukina *et al.*, 2009; Kuriyama *et al*., 2011). However, these conventional methods have drawbacks which often require extracting samples from the system under study, followed by a dilution step of the samples (where needed), and the apparent delay in analysing the samples. This more often results in changes in the sampled material and eventually does not provide an accurate representation of the material under actual processing conditions. A large factor contributing to this is the limited number for instruments capable of providing continuous, real-time *in situ* monitoring of the crystallisation process.

The Focused Beam Reflectance Measurement (FBRM) is a non-destructive technique which has gained increasing popularity in the last decade as a useful tool for the in-process measurement and characterisation of particles in real-time within particulate suspension systems and processes such as granulation, flocculation, dissolution and crystallisation (Fang *et al.*, 2011). Its operation lies in the principle of laser backscattering involving the use of rotating optics which scan through a suspension and measure the number and size of particles within a specified focal point. There are several advantages in using *in situ* devices such as FBRM: the measurements are performed immediately within the solution, and sample preparation and transportation steps are eliminated, thus reducing the number of errors which may arise from sampling procedures (Heinrich and Ulrich, 2012).

The utilisation of FBRM for real-time characterisation of particles has been well-documented in pharmaceutical and fine chemicals (Kougoulos *et al.*, 2005; Abu Bakar *et al.*, 2010; Saleemi *et al.*, 2012), biotechnology (McDonald *et al.*, 2001; Pearson *et al.*, 2003; Whelan *et al.*, 2012) and food industries (Haddad Amamou *et al.*, 2010; Arellano *et al.*, 2012; Ndoye *et al*., 2013). Useful information such as crystal size distribution, polymorphic forms and changes in crystallisation mechanisms can be conveniently acquired through the use of FBRM which further assists in controlling final product quality and designing of downstream processes (Nagy *et al.*, 2013). In spite of the extensive use of this technique in various particulate processes within different industries, only a few studies have reported its application within oils and fats systems in general, and these have mainly focused on the crystallisation of palm oil-based products. This paper highlights the principles of the FBRM technique and reviews existing and current developments on the *in situ* monitoring of crystallisation in palm oil-based products using this method.

WHAT IS THE FOCUSED BEAM REFLECTANCE MEASUREMENT (FBRM) TECHNIQUE?

The FBRM set-up consists of a cylindrical probe in which a scanning laser beam is passed through a sapphire window at the end of the probe and a set of optical components rotating at high speed causes this beam to move in a circular path (*Figure 1a*). As the beam passes through the suspension system in study within the specified measurement zone, it can cross through the surface of a particle in its pathway. When this happens, the light from the laser beam will be reflected back into the probe. The duration that the laser beam takes to cross through a particle (Δt) is then multiplied by the velocity of the scanning beam (v_b) resulting in a chord length (s), which is defined as the distance of the path of the laser beam crossing the particle (Ruf *et al.*, 2000) (*Figure 1b*).

The chord length depends on the orientation and geometry of the particle at the time of measurement. At any one time, thousands of chord lengths are measured and these are sorted according to differently sized channels. The FBRM technique measures particles within a size range of between 0.8 µm and 1000 µm, and these measurements can be grouped into 38 intervals or 90 intervals, depending on the model used. All measured chord lengths in their respective intervals are collated to produce a real-time chord length distribution (CLD) depicted as a histogram (*Figure 1c*). The count-based distributions, which can either be weighted or unweighted, are used to analyse changes occurring within the process. The former is more susceptible to changes in coarse particles while the latter is sensitive to small changes in finer particles, thus allowing one to monitor events such as nucleation, crystal growth or agglomeration during the crystallisation process.

The number of counts and chord lengths reported are largely influenced by the solids concentration and the particle diameter and shape, respectively (Barrett and Glennon, 1999). However, CLD cannot only be used as a definitive representation of the actual particle

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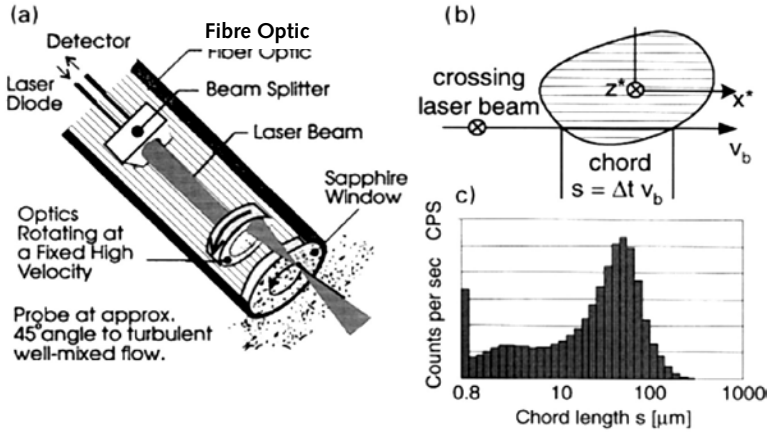


Source: Ruf *et al.* (2000).

Figure 1. FBRM principle. (a) FBRM probe, (b) chord length measurement, and (c) histogram of the chord length counts.

size. It only gives an indication of the actual crystal size distribution (CSD). To transform CLD to CSD, a relationship must be developed to correlate the two based upon some assumption of the particle geometry (the simplest assumes a spherical geometry). A straight-forward method for quantifying real-time CSD is by coupling FBRM with an online image analyser such as an in-process video or microscope which provides *in situ* images of particle size and structure. Nevertheless, this does not limit the use of FBRM for other qualitative monitoring purposes, such as providing indications of particle population, detection of multiple events during a process, and as a means to assess the dynamic changes in particle size distribution during the crystallisation process. This would allow prediction of the trends in final product size and quality.

RECENT STUDIES ON THE APPLICATION OF FBRM IN THE CRYSTALLISATION OF PALM PRODUCTS

In recent years, a few research studies have been published on the behaviour and characteristics of particles in real-time during the crystallisation of palm oil products. One of the first reports on the utilisation of FBRM in palm oil crystallisation was published by Simon *et al.* in 2009. Their study compared an external bulk video monitoring (BVM) approach with FBRM for the detection of apparent nucleation in palm oil from the melt. They found that BVM detected a cloud formation much earlier compared with FBRM. This cloud, which could be visually observed by the naked eye, is a direct result of the generation of a large number of nuclei with sizes well below the detection limit of FBRM. A comparison between slow (0.67°C/min) and fast (2°C/min) cooling rates during palm oil crystallisation revealed that the time it took for the BVM approach to detect the onset of nucleation compared with FBRM at the higher cooling rate was three times faster than when the slower cooling rate was used. Their study identified a drawback in FBRM in that it is only capable of detecting nucleation when the initial crystals that formed had reached a certain size within the size range detectable by the laser optics of the instrument. Hence, determination of the actual time needed for nucleation to occur would be more accurate through visual observation of any changes in clouding within the crystalliser.

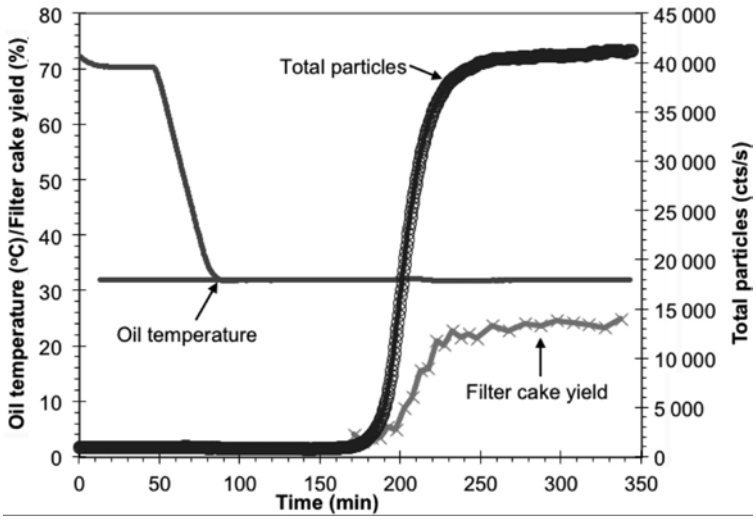
A couple of years later, Hishamuddin *et al.* (2011a) published a second study on the application of FBRM in monitoring the crystallisation of palm oil at different isothermal temperatures ranging between 24°C and 32°C. They successfully demonstrated the capability and usefulness of the FBRM technique in tracking the evolution of crystal size and behaviour, as well as in detecting crystallisation and melting mechanisms in palm oil. Their study showed that final mean sizes of palm oil crystals expressed as mean chord length (MCL) increased from 240 µm at 24°C to 380 µm at 26°C, but started decreasing from 370 µm to 315 µm as holding temperatures increased from 28°C to 30°C, respectively. This was plausibly due to the occurrence of secondary nucleation at temperatures above 26°C, when they observed a simultaneous increase in total particle counts and a decrease in MCL

as detected by FBRM. They also found that at 32°C, final MCL was much shorter at 220 µm while crystal population numbers were lower compared with those recorded between 24°C and 30°C. This was presumably due to a lower degree of supercooling and fewer number of triacylglcyerols which are able to crystallise at 32°C.

In their study, Hishamuddin *et al.* also discovered that the profiles of filter cake yields obtained after filtration of the crystal slurry correlated well with the total number of particles within the system at all the temperatures studied. An example is given in *Figure 2* for palm oil crystallised at 32°C. Primary and secondary nucleation, crystal growth, agglomeration and deagglomeration of the crystals were further characterised for the palm oil system based on the responses in total particle counts, MCL and CLD measurements. The melting behaviour of palm oil upon subjecting it to an initial isothermal crystallisation step was also deciphered. Based on the results obtained from FBRM, it was proposed that the entire melting process of palm oil consisted of several mechanisms: (i) straight melting of crystals, (ii) deagglomeration of crystals caused by the melting of bridges that link the crystals together, (iii) secondary nucleation from agitation effects, and (iv) crystal ripening. The results from FBRM also indicate that the melting process of palm oil was largely completed by 46°C although a small degree of cloudiness was observed throughout the bulk of the oil. These findings have generated new insights into the changes in the mechanisms and behaviour of particles during the melting of pre-crystallised palm oil, which contribute significantly to the current knowledge on the melting characteristics of palm oil.

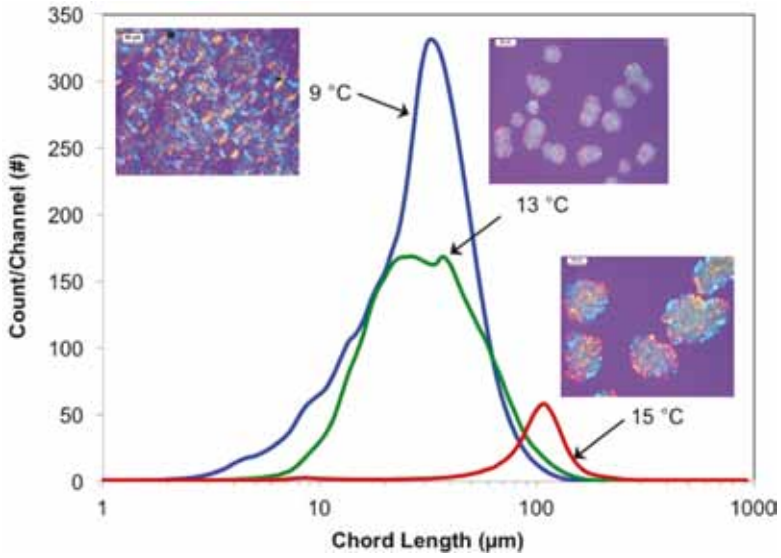
In situ monitoring of crystal characteristics during the crystallisation of palm-based products using FBRM was further extended to palm olein in the work by Hishamuddin *et al.* (2011b). Previous studies have reported that palm olein crystallisation is frequently complicated by long nucleation induction times, sluggish crystal growth rates and irregular crystal sizes (Siew and Ng, 1996; Calliauw *et al.*, 2007a). The irregularity in crystal sizes produced during palm olein crystallisation greatly affects the filtration stage; only when crystals are uniform in shape, morphology and composition can the efficient separation of crystals from the liquid fraction be achieved (Calliauw *et al.*, 2007b). Hishamuddin *et al.* (2011b) investigated the in-process changes in particle size and the evolution of palm olein crystallisation at different isothermal temperatures between 9°C and 15°C using FBRM and optical microscopy. They found the crystal population to be noticeably smaller while crystal sizes were significantly larger at higher temperatures, confirming results from earlier studies on the effects of temperature on the crystal size distribution in palm-based systems using conventional particle sizing methods. *Figure 3* shows CLD of palm olein crystals at 9°C, 13°C and 15°C and their respective microscopic images. The mode crystal size more than trebled from approximately 32 µm obtained at the lower temperature of 9°C compared with 108 µm at 15°C. This could be due to a lower degree of supercooling at higher temperatures which only allows a limited number of triacylglycerol species of the higher melting type to crystallise under these conditions.

Their study also discovered the occurrence of a significant agglomeration event at 9°C which was signaled by a sudden large drop in the total crystal population and a simultaneous increase in the mean crystal size as measured by FBRM. This phenomenon however was



Source: Hishamuddin *et al.* (2011a).

Figure 2. Total particle counts profile and filter cake yield of palm oil crystals at 32°C.



Source: Hishamuddin *et al.* (2011b).

Figure 3. Final CLD of palm olein crystals at various isothermal temperatures and their microscopic images.

not detected at the higher temperatures studied, and may be attributed to a higher supercooling at 9°C which caused a substantial surge in the total number of crystals, and subsequently allowed increased contact between crystals to establish a crystal network. Crystallisation was also found to occur in a two-step manner at temperatures below 15°C as depicted by the total particle numbers which increased twice in a successive manner, indicating primary and secondary nucleation events. By complementing the FBRM results with optical microscopy and visual observation of the sample, Hishamuddin *et al.* were able to observe the formation of a near gel-like structure of the slurry which was only present below 13°C. This confirmed earlier studies on palm olein crystallisation which showed a vitreous phase would form when the oil was subjected to a large supercooling as reported by Deffense (1998; 2009).

Particle sizing studies comparing the differences in CLD between palm oil and blends of palm oil, palm stearin, palm olein and soyabean oil have also been carried out using FBRM (Zaliha *et al.*, 2013). At 30°C, CLD of a blend containing palm oil, palm stearin and palm olein in a ratio of 50: 30: 20 showed a normal distribution, and crystals were found to be smaller at 51 µm compared with an average crystal size of 65 µm for a blend of palm oil, palm stearin and soyabean oil in the same ratio. CLD of palm oil showed a bimodal distribution with mode crystal sizes at 21 µm and 61 µm compared with both blends. Crystal population was observed to be higher in the blend containing palm olein compared with that of palm oil (control) and the blend containing soyabean oil. This study shows that the induction time for nucleation increased in the blends over that of palm oil as the control. This was possibly due to the higher amount of trisaturated triacylglycerols present within the blends, for which this TAG group has been shown to play an important role in nucleation (Sulaiman *et al.*, 1997).

Studies on the effect of an additive on palm oil crystallisation have also been performed using FBRM. Saw *et al.* (2014) reported that when a polyglycerol ester, PGEmix-8, was added into palm oil during crystallisation at 24°C in dosages ranging from 0.1% to 0.7% w/w, the total number of crystals increased while the average crystal size of the slurry decreased. When the highest dosage of 0.7% of PGEmix-8 was used, a much broader crystal size distribution accompanied by a significant shift in the crystal size distribution were observed, with peak chord lengths decreasing from 96 µm (palm oil without additive) to 34 µm. The olein yields obtained after filtration of the slurry increased between 3% and 6% when PGEmix-8 was added into palm oil over that of palm oil without the additive. This was mainly due to the homogenous crystal sizes generally produced with the addition of PGEmix-8, which allowed easier filtration of the slurry and further reduced the olein entrainment. Based on this study using FBRM, PGEmix-8 was identified to be a suitable nucleation-enhancing and crystal growth-retarding additive in the fractionation of palm oil.

CONCLUSION

FBRM presents a valuable technique for the in-process monitoring of changes in crystal population, size and behaviour, thus enabling us to gain insight into what truly occurs within the crystalliser when an oil or fat system undergoes crystallisation. Its application allows us to deepen our understanding on how process conditions affect crystal characteristics, and further enables proper control and optimisation of the crystallisation stage in

the fractionation of palm products so as to ensure better filtration of the crystals produced so that the desired quality characteristics of the final product are achieved. The emergence of a limited number of studies on the real-time monitoring of the crystallisation behaviour of palm oil-based products using FBRM within the last decade as highlighted in this article has shown that this technique is still relatively 'new' within the oils and fats field and certainly leaves more avenues to be explored.

In combination with imaging techniques such as the conventional optical microscope, or the more sophisticated in-process particle video microscopy, FBRM proves to be a powerful tool for tracking particle size behaviour and deciphering the many crystallisation and melting mechanisms of palm-based products as and when they occur. The application of this technique in industrial fractionation plants would assist manufacturers to better optimise crystallisation conditions towards attaining the preferred characteristics of crystals, and consequently improve the separation efficiency in the filtration stage, thereby minimising product losses through a reduction in entrainment. Proper control of the crystallisation stage would potentially help in saving valuable time and costs associated with failed batches within industrial crystallisers, and allow manufacturers to continuously achieve consistent product quality.

ACKNOWLEDGEMENT

The author thanks the Director-General of MPOB for permission to publish this article.

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