Journal of Oil Palm Research Vol. 23 December 2011 p. 1141-1145

IMPROVED SUSTAINABLE FRACTIONATION OF PALM OIL USING POLYGLYCEROL FATTY ACID ESTERS

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ABSTRACT

A series of GRAS polyglycerol esters (PGE) has been produced and investigated for improving the dry fractionation of palm oil. Results show that the hydrophobic PGE can reduce the fractionation time and hence the energy consumed during fractionation. This will help to increase throughput for the process and the overall carbon footprint as a result of reducing energy use in the process. The fractionated oleins also exhibited better cloud points of between 7°C and 8°C, and an average iodine value of 57 Wijs. Crystal size was observed to be homogeneous, with the majority of the crystal sizes being in the range of 100 to 300 microns. It was also observed that this crystal size posed no filtration difficulty, as evidenced by the 76% to 78% olein yield obtained during pressing with a squeezing pressure of 5 bars. The stearins obtained were medium hard with iodine values between 33 and 35 Wijs, and slip melting points between 52°C and 53°C.

Keywords: polyglycerol fatty acid ester, GRAS, dry fractionation, palm oil.

Date received: 18 August 2010; **Sent for revision:** 23 August 2010; **Received in final form:** 11 October 2010; **Accepted:** 25 July 2011.

INTRODUCTION

Dry fractionation of palm oil is widely carried out by Malaysian refineries since the establishment of the downstream processing sector in the 1970s. More than 70% of palm oil produced in Malaysia in 2009 was fractionated into oleins and stearins for liquid and solid applications, respectively. To establish the Malaysian oil palm industry on a more sustainable basis, MPOB and the Malaysian oil palm industry have embarked on a series of actions aimed at sustainable production of palm oil and palm oil products. Sustainability of the fractionation process can be achieved in many ways. One of the ways by which sustainability of the fractionation process can be improved is through the use of additives to enhance the crystallisation process.

Traditionally, there are three different fractionation processes which have been used in the industry. These are dry fractionation, solvent fractionation and detergent (wet) fractionation (Faur, 1997). Dry fractionation is the simplest and cheapest process and no auxiliary agents such as solvents or detergents are introduced during processing. However, dry fractionation is considered to be less efficient than the other two solvent or detergent fractionation processes (Timms, 2005). Over the years this less efficient dry fractionation has been compensated for by improved filtration technology – with membrane filters, rotary drum filters and Florentine filters. The latter two have been phased out by the industry due to the more efficient high pressure membrane presses. Recently, separation efficiency has been further increased by the application of high pressures of up to 5 MPa or more (Willner and Weber, 1994).

Alternatively, separation efficiency can also be improved by influencing the crystal morphology. Influencing the crystal morphology can be effected through the use of additives. Polysaccharide esters of fatty acids, comb polymers and bovine brain have been reported to influence the crystallisation of oils and fats, and to improve separation efficiency (Smith, 2001).

Polyglycerol fatty acid esters (PGE), synthesised with polyglycerol and fatty acids, are bio-gradable surfactants widely used as functional additives in

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food, cosmetics, toiletries and the pharmaceutical industries (Nash and Babayan, 1963; Babayan *et al.*, 1964; Nash and Knight, 1967; Matsushita and Shinoyama, 1986). Hydrophobic PGE have been used as crystallisation controllers and crystal structure modifiers, causing the retardation of crystal growth and modifying polymorphic transformations. In previous work, it has been reported that hydrophobic polyglycerol stearic acid ester accelerated the nucleation of palm mid fraction (Sakamoto *et al.*, 2004), and that hydrophobic polyglycerol mixed fatty acid ester retarded the crystal growth of n-hexadecane (Sakamoto *et al.*, 2005) and palm olein (Kuriyama *et al.*, 2001). In a separate study using PGE mentioned above, it was found that there was no significant difference in performance between the addition of 0.1 and 0.5 wt. % of PGE (POMREQ 2010).

Figure 1 shows the basic structural formula of PGE. The advantage of PGE is that their hydrophobicity and hydrophilicity can be easily modified by changing: (a) the degree of polymerisation of the glycerol groups, (b) the degree of esterification with fatty acid moieties, and (c) the chemical structures of the fatty acid moieties. The PGE are all derived from vegetable materials, forming a series of GRAS-compliant additives. PGE can therefore be used as food emulsifiers, offering several functional properties such as acid resistance, salt resistance, thermal stability and savouriness (Ushikusa *et al.*, 1990; Katsuragi, 1999; Garti and Yano, 2001).

In our study, four kinds of PGE were used as additives for the enhancement of the fractionation process. These were polyglycerol palmitic acid ester, polyglycerol stearic acid ester, polyglycerol oleic acid ester and polyglycerol mixed fatty acid ester. The effect of these PGE on the dry fractionation process of palm oil was the subject of this study.

MATERIALS AND METHODS

Materials

Commercial-grade refined, bleached and deodorised (RBO) palm oil was purchased from Cargill Palm Products Sdn Bhd (Port Klang, Selangor, Malaysia).

PGE were synthesised from polyglycerol produced by Sakamoto Yakuhin Kogyo Co. Ltd (Osaka, Japan) and commercially available fatty acids, namely, palmitic acid (98% pure, Miyoshi Yushi Co., Ltd), stearic acid (98% pure, Miyoshi Yushi Co., Ltd) and oleic acid (75% pure, Miyoshi Yushi Co., Ltd.). The polyglycerol and fatty acids were mixed and reacted with 0.04% sodium hydroxide for 10 hr at 240°C-250°C under nitrogen flow at atmospheric pressure. The reactions were stopped when the acid values of the products became less than 5.0. The four kinds of PGE synthesised are shown in *Table 1*.

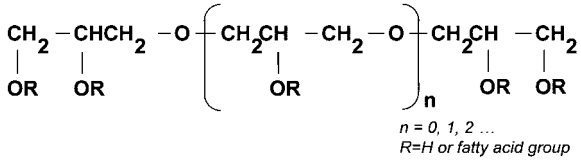

Figure 1. Structual formula of polyglycerol fatty acid ester.

Dry Fractionation

PGE were added to RBD palm oil at a concentration of 0.5 wt. % (wt-wt%). The oil containing PGE was then melted at 80°C to homogenise it and to destroy all crystal memory. The melted oil was then charged into a 3-litre water-jacketed crystalliser, agitated at a stirring rate of 100 rpm. The oil was then cooled down to 24°C over a period of 60 min, and then held at 24°C for 120 min to complete the fractionation process.

After 120 min, the slurry was separated into olein and stearin fractions by membrane filtration at a squeezing pressure of 0.5 MPa. The membrane filtration press used was supplied by Yabuta Kikai Co., Ltd (Osaka, Japan).

Analytical Methods

Iodine value of the oils was determined according to the AOCS method Cd 1b-87 (1997), while cloud point was determined by the AOCS method Cc 6-25 (1997). Slip melting point was determined by AOCS method Cc 3-25 (1997).

Crystal morphology was observed using an Olympus BX-51 microscope fitted with an Olympus DP-20 camera. Measurement of particle sizes of the

TABLE 1. LIST OF SYNTHESISED POLYGLYCEROL FATTY ACID ESTERS (PGE)

PGE	HLB[a]	Melting point (°C)[b]
PGE-P (polyglycerol palmitic acid ester)	1.9	48.4
PGE-S (polyglycerol stearic acid ester)	1.8	57.6
PGE-O (polyglycerol oleic acid ester)	1.7	<-20
PGE-Mix (polyglycerol mixed-fatty acid ester)	1.6	42.8

Note: [a] HLB values were calculated in accordance with Griffin's equation (Griffin, 1988).
[b] Melting points were measured by DSC (Sakamoto *et al.*, 2004).

RBD palm oil crystals in the crystallising slurry was carried out using the Olympus microscope with micro glass slides as containers for the slurry at the end of the fractionation process.

RESULTS AND DISCUSSION

Iodine Values of Olein and Stearin

Figure 2 shows the iodine values of the olein and stearin fractions. After fractionation of the RBD palm oil (IV 51.7 Wijs) without additives, oleins (IV 51.7 Wijs) and stearins (IV 36.8 Wijs) were obtained. The IV of the olein fractions with added PGE were about 57 Wijs. There were no observable significant differences between the iodine values of oleins with and without PGE.

In the case of the stearin fractions, there was a difference in the iodine values between the stearins without additives and those with PGE. The iodine values of stearins with PGE were all lower than the iodine values of stearins without additives. Specifically, the iodine values of stearins decreased to 35.3 Wijs with the addition of PGE-P, to 34.6 Wijs with the addition of PGE-S, to 35.3 Wijs with the addition of PGE-O and to 33.5 Wijs with the addition of PGE-Mix. It appears that adding PGE can affect the crystallisation and filtration of crystallised RBD palm oil, resulting in less entrained olein in the stearin. This was evidenced by the lower iodine values of the stearins obtained with the addition of PGE.

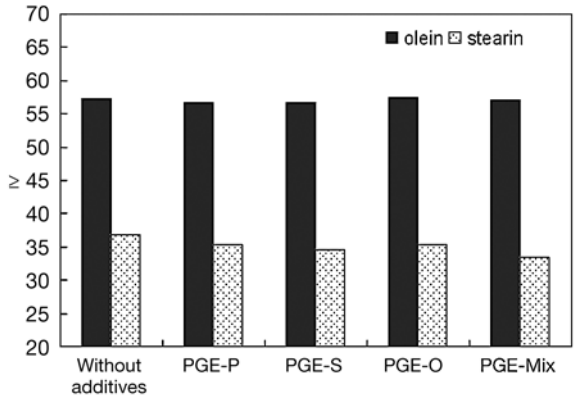

Figure 2. Iodine values (IV) of olein and stearin fractions without additives and with PGE-P (0.5 wt.%), PGE-S (0.5 wt.%), PGE-O (0.5 wt.%) and PGE-Mix (0.5 wt.%).

Yields of Olein

Figure 3 shows the yields of the olein fractions with the addition of PGE. The yield of olein without additives was 76.5 wt. %. There was no significant difference between the yields of olein obtained without additives and those with the addition of PGE-P, PGE-S, and PGE-O. The addition of PGE-Mix remarkably increased the yield of olein from 76.5 wt. % to 79.0 wt. %. These results indicate that the addition of PGE-Mix appeared to improve the efficiency of filtration of the oil, resulting in higher separation efficiency of the olein and the stearin fractions, possibly because of lower olein entrainment by the stearin due to the homogenity of the crystal morphology of the stearins.

Cloud Points of Olein

Cloud point is related to the unsaturation level of the olein fraction. The more unsaturated the olein fraction, the lower will be the cloud point. *Figure 4* shows the cloud points of the olein fractions obtained without additives and those obtained with PGE. Cloud points of oleins with the addition of PGE-P and PGE-S were about 1°C higher than that of olein obtained without additives. Cloud point of olein with PGE-O did not differ from that without additives. On the other hand, cloud point of olein with the addition of PGE-Mix decreased slightly from 7.4°C to 7.0°C. This means that there were slightly higher unsaturation and lower

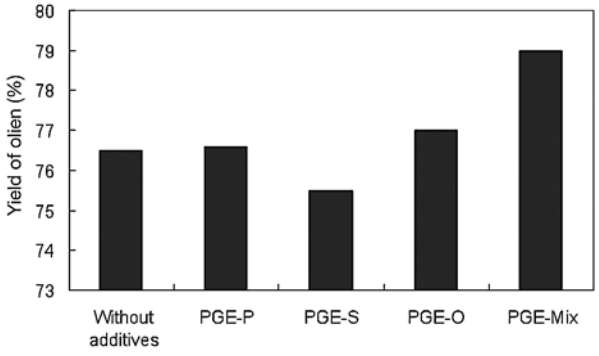

Figure 3. Yields of olein fractions without additives and with PGE-P (0.5 wt.%), PGE-S (0.5 wt.%), PGE-O (0.5 wt.%), PGE-Mix (0.5 wt.%).

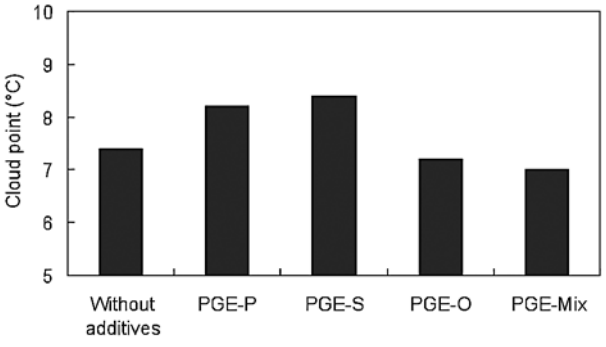

Figure 4. Cloud points of olein fractions without additives and with PGE-P (0.5 wt.%), PGE-S (0.5 wt.%), PGE-O (0.5 wt.%), PGE-Mix (0.5 wt.%).

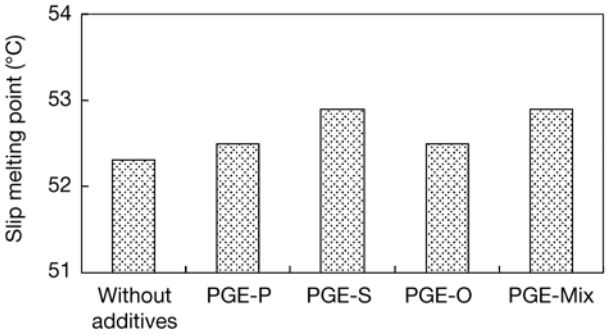

Figure 5. Slip melting points of stearin fractions without additives and with PGE-P (0.5 wt.%), PGE-S (0.5 wt.%), PGE-O (0.5 wt.%), PGE-Mix (0.5 wt.%).

saturation fatty acid chains in the olein fraction after the addition of PGE-Mix.

Slip Melting Points of Stearin

Figure 5 shows the slip melting points of stearin fractions obtained without additives and with PGE. Slip melting point of stearin obtained with addition PGE-P and PGE-O were both at 52.5°C. This was no different from slip melting point of the stearins obtained without additives, *i.e.* 52.3°C. On the other hand, slip melting point of stearin obtained with the addition of PGE-S and PGE-Mix were both at 52.9°C which was slightly higher than slip melting point without additives. These results indicate that the residual olein content of the stearin fraction with the addition of PGE-Mix was lower than that of stearin obtained without additives. This is in sync with the observation of lower iodine values of the stearins obtained with added PGE.

Crystal Morphological

Figure 6 shows the optical micrographs of RBD palm oil crystals without additives and those with PGE, crystallised at 24°C for 2 hr as outlined earlier. RBD palm oil without additives formed both granular and small, fine crystals. These crystals were observed to agglomerate to form non-uniform crystals (*Figure 6A*). On the other hand, crystals of RBD palm oil with PGE exhibited different morphologies and sizes, compared to those without additives. Smaller and more uniform crystals were observed (*Figures 6B*, *6C*, *6D* and *6E*). The average size of the crystal particles was about 380 um without additives (*Figure 6A*), about 180 um with PGE-P (*Figure 6B*), about 120 um with PGE-S (*Figure 6C*), about 280 um with PGE-O (*Figure 6D*), and about 290 um with PGE-Mix (*Figure 6E*).

In general, during the crystallisation process, the stearin crystals would grow. The growing crystals would then agglomerate, trapping olein within the particles (Timms, 1991). In the case of crystallisation with the addition of PGE-Mix, the smaller and more uniform crystal size might have contributed to a reduction in aggregation to form granular crystals, thereby reducing the entrapment of olein in the stearin as supported by the micrographs shown.

CONCLUSION

The effects of using four types of polyglycerol fatty acid esters as additives in the dry fractionation of RBD palm oil were examined on a bench-scale pilot plant. Results show that adding PGE-Mix remarkably affected the crystallisation process of palm oil. This was reflected in the improved

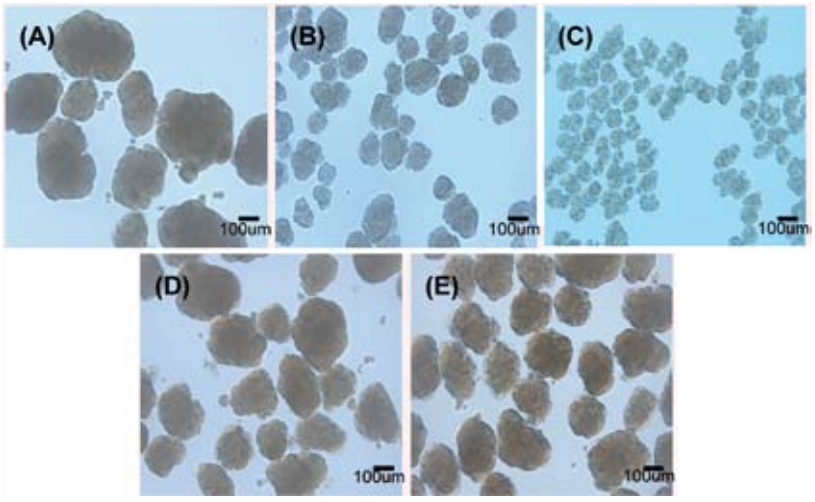

Figure 6. Microscopic images of crystallisation of refined, bleached and deodorised (RBD) palm oil and with the addition of PGE at 24°C for 2 hr. (A) RBD palm oil, (B) with 0.5 wt.% of PGE-P, (C) with 0.5 wt.% of PGE-S, (D) with 0.5 wt.% of PGE-O, (E) with 0.5 wt.% of PGE-Mix.

efficiency of filtration of the RBD palm oil slurry due to the morphological changes, which had resulted in the formation of more uniform crystals. This in turn would have reduced the amount of trapped olein in the stearin crystal. The results also imply that the addition of PGE-Mix may reduce the time for the crystallisation and filtration processes. It may also reduce the pressure of filtration which could lead to better cloud points of the oleins. The use of polyglycerol fatty acid esters in the dry fractionation of RBD palm oil will be the simplest and the least expensive technique for improved sustainability through the reduction of energy use and processing cost. However, all these still need to be applied and optimised at the plant scale.

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