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Interesterified fats in chocolate and bakery products: A concise review

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ABSTRACT

Interesterification is a reaction triggered by chemical catalysts or enzymes that leads to a random or targeted rearrangement of fatty acids esterified to the glycerol backbone molecule. As a result of and depending on the position change some physico-chemical properties of the fat, for instance solid fat content or crystallization behaviour, are significantly affected. These properties are in turn important with respect to the desire to control crystallization, flow properties, or functionality of the target products. This concise review summarizes recent research on the use of interesterified fats in chocolate technology, and in the production of baked foods. In both commodity categories, emphasis is placed on research work where enzymatically interesterified fats were used. With targeted interesterification physical product properties of chocolate such as the melting point can be modified, and it is also possible to generate ingredients (for example, shortenings) with a reduced trans fatty acid content.

1. Introduction

Fats and oils are essential in human nutrition, and an important component of many foods where they significantly contribute to product quality (O'Keefe & Sarnoski, 2017). As, in many cases, the desired properties (for instance, crystallization and melting behaviour) can not be reached by pure native fats or mixtures thereof, modification techniques such as fractionation, hardening or interesterification have been established (Kellens & Calliauw, 2013). Fractionation represents the most economic method as long as all of the fractions can be utilised. Hardening, on the other hand, is cost intensive because of the sophisticated technical equipment that is necessary, and the need for hydrogen. The third option is chemical or enzymatic interesterification, which started to replace hardening when the generation of trans fatty acids as a result of partial fat hardening was considered as critical. Another advantage is that the physico-chemical properties of cost-efficient base fats can be tailored to mimic the properties of more expensive fats.

The aim of this concise review is to briefly introduce into the basics of chemical and enzymatic interesterification, an to summarize the last ten years of research related to the application of enzymatically interesterified in chocolate technology and baked foods.

2. Principles and methods for fat interesterification

Physico-chemical properties of triacylglycerides (TAGs) basically depend on chain length and saturation degree of the fatty acids, and the position where they are esterified at the glycerol backbone molecule. Interesterification is a chemical reaction that induces a rearrangement of two particular fatty acids within a particular TAG, or the exchange of fatty acids between TAGs. Interesterification is therefore a two-step process that comprises of (a) an initial hydrolysis of and (b) a subsequent esterification at a glycerol moiety. In addition to triacylglycerols, other presumptive acyl donors are fatty acids such as palmitic or stearic, esterified fatty acids, or alcohols (Kim, Kim, Akoh, & Kim, 2014; Verstringe, De Clerq, Nguyen, & Dewittinck, 2013).

2.1. Chemical interesterification

Chemical catalysts such as alkali methoxides or ethoxides, or metals may be used for inducing stochastic between-TAG interesterification (Gibon, 2011), leading to triacylgylcerides in which the fatty acids are randomly distributed across the glycerol moiety. In most cases, this process is performed in batch mode and comprises the following reaction steps: (a) drying of the fat under vacuum and neutralisation with sodium hydroxide; (b) subsequent interesterification at, for example at 50–90 °C with sodium methoxide as catalyst; (c) its inactivation by adding citric acid; (d) the removal of the formed soaps and the catalyst with water; (e) the

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removal of residual water under vacuum; and (f) bleaching and desodoration to remove residual free fatty acids and methyl esters. The interesterification yield is then the amount of the desired TAGs, related to the amount of the initial substrate (Kellens & Calliauw, 2013).

2.2. Enzymatic interesterification

Another option is interesterifaction that is enzymatically triggered through the use of lipases (Adlercreutz, 2013). Here, 1,3-specific lipases are of considerable interest as they hydrolyse the ester bonds at position 1 and 3 of the glycerol moiety, whereas the fatty acids at position 2 (which are, in most cases, unsaturated) remain unaffected (O'Keefe & Sarnoski, 2017). Irrespective of the source of the enzyme (for instance, *Rhizomucor miehei*, *Thermomyces lanuginosus*, or *Candida antarctica*), its immobilisation in, for example, packed-bed enzyme reactors ensures higher process efficiency and simplifies the final purification of the interesterified oil. Prior to the reaction, it is mandatory to clarify the substrate to remove residual particles and enzyme inhibitors. Subsequent to the reaction, neutralisation and desodoration steps are applied to remove, for example, free fatty acids (Gibon, 2011; Won, Park, Choi, & Chang, 2012). Important factors that influence the activity of the lipases and, therefore, process efficiency are pH, temperature, the enzyme/substrate ratio, and residence time in the reactor; these should therefore be optimised (Kadivar, De Clercq, Van de Walle, & Dewettinck, 2014; Rodrigues & Fernandez-Lafuente, 2010; Stortz & Marangoni, 2011). For instance, a particular amount of moisture is necessary as reactant for hydrolysis. Excessive moisture, however, reduces the interesterification efficiency because water molecules may bind to the active size of the enzyme and therefore inhibit substrate binding (Adlercreutz, 2013; Kellens & Calliauw, 2013).

2.3. Comparison of process efficiency

The mostly addressed advantage of enzymatic interesterification is the specificity of the enzymes, which allows a better process control (Kellens & Calliauw, 2013; O'Keefe & Sarnoski, 2017). Additionally, the use of hazardous chemicals can be avoided, and the time scale of the reaction can be specifically adjusted so that partially interesterified fats are obtained. Chemical interesterification requires a higher energy input, and side reactions increase the effort for final clarification (Holm & Cowan, 2008). Disadvantages assigned to enzymatic interesterification are mainly enzyme costs, problems with enzyme purity, and the potential risk of cross-contamination in case of a continuous process.

3. Interesterified fats in chocolate manufacture

Liquid chocolate is a particulate system where milled cocoa particles and, depending on the type, sugar and milk solids, are suspended in cocoa butter (CB). The outstanding properties of cocoa butter (for instance, polymorphic crystallization, and a sharp melting point) result from the fact that mainly stearic acid (S; approx. 36% of fatty acids) or palmitic acid (P; approx. 25%) is esterified at position 1 or position 3 of glycerol, and oleic acid (O; approx. 33%) at position 2. The dominating TAGs are 15–16% POP, 23–26% SOS, and 35–38% POS (Jahurul et al., 2013).

Cocoa butter equivalents (CBE) are fats which may be used for an at least partial replacement of CB. The most important requirement is that they are comparable with respect to melting behaviour and polymorphism, fatty acid and TAG composition, and processing properties. The interest of chocolate producers in CBEs is, on the one hand, triggered by economical aspects (the price of cocoa butter almost doubled from 2006 to 2016 to approx. 2900 US$ per ton) and, on the other hand, by the request for new functionalities, as is the case in heat resistant chocolate for instance (Stortz & Marangoni, 2011). The current regulation in the European Union limits the application of CBEs to 5%; the admitted botanical sources (e.g., Shea or Mango kernel) are specified, and only refining and/or fractionation for modification is currently allowed according to directive 2000/36/EC of the European Parliament. Regulations in other countries differ: in the United States only cocoa butter is allowed, and Japan has no limitations concerning amount and composition of CBEs (Talbot, 2017). The production of CBEs by interesterification has, however, received considerable scientific interest in the past ten years.

3.1. Enzymatic interesterification of cocoa butter equivalents

Substrates that were used for interesterification in the production of CBEs all have oleic acid esterified at the central position of the glycerol backbone and comprise palm olein or its fractions, tea seed oil, olive oil and refined olive pomace oil, sunflower oil, or mango kernel oil (Table 1). For example, the interesterification of palm oil mid fractions using palmitic and stearic acid (Mohamed, 2012, 2013) or hardened soybean oil (Soekopitojo, Hariyadi, Muchtadi, & Andarwulan, 2009) as acyl donors resulted in CBEs with a TAG spectrum and a thermal behaviour comparable to that of cocoa butter. The purification of the reaction products to remove saturated TAGs, mono- and diacylglycerides, and free fatty acids is usually achieved through controlled crystallization and subsequent filtration. Many of the studies, however, do not specify the yield of the target product. One prominent exception is the work of Mohamed (2015) who, by using olive oil as substrate, palmitic and stearic acid as acyl donors, and an immobilised *R. miehei* lipase, reported a CBE yield of more than 90%. Recently, Kadivar, De Clercq, Danthine, and Dewettinck (2016a) used high oleic (HO) or high oleic high stearic (HOHS) sunflower oil as substrate and mixtures of free fatty acids as acyl donors, and obtained CBEs with 15.1% or 11.9% POP, 40.3% or 41.9% POS, and 19.2% or 24.2% SOS, respectively. They applied several methods for analysing the crystallization behaviour, and stated that the induction time of the first isothermal (20 °C) crystallization step decreased and more α crystals were formed when CBEs were added to CB. The subsequent polymorphic transition was however delayed by the presence of the CBE due to their higher concentration of low-melting TAGs (e.g. SOO, Fig. 1).

3.2. Application of interesterified fats in chocolate production

Important targets that foster CBE applications in chocolate production are the reduction of fat bloom reduction, and modification of the melting behaviour. After substituting 5, 10 or 20% CB with interesterified tea seed oil (fat content of chocolate, 35 g/100 g), Zarringhalami, Sahari, Barzegar, and Hamidi-Esfehani (2010) showed that the CBE significantly reduced fat bloom but also lowered the solid fat content (SFC; Fig. 2) and, consequently, chocolate hardness. In addition to the level of substitution of CB ($SFC_{20°C}$, 84.6%; $SFC_{35°C}$, 2.3%) by CBE ($SFC_{20°C}$, 71.0%; $SFC_{35°C}$, 4.0%), it was shown that pre-crystallization temperature is another factor that can be used for the optimisation of in chocolate with CB/CBE mixtures (Torbica, Pajin, & Omorjan, 2011; Torbica, Pajin, Omorjan, Lončarević, & Tomić, 2014): it affects susceptibility to fat bloom, but also gloss and colour. Another route to achieve increased melting points of chocolate is to use partly interesterified CB. Brüse, Wallecan, & Arruda (2012) demonstrated that enzymatic interesterification is capable of increasing the slip melting point from 26.0 °C to 42.5 °C, and that up to 6.6% replacement is possible without affecting appearance and mouthfeel. Kadivar, De Clercq, Mokbul, & Dewettinck (2016b) showed that, by incorporating