UNIVERSIDADE FEDERAL DA PARAÍBA

CENTRO DE TECNOLOGIA

PROGRAMA DE PÓS-GRADUAÇÃO EM CIÊNCIA E TECNOLOGIA DE ALIMENTOS

FABRINE FELIPE HILÁRIO

ÉSTERES DE AÇÚCAR: SÍNTESE, PROPRIEDADES E APLICABILIDADE NA INDÚSTRIA DE ALIMENTOS

JOÃO PESSOA – PB

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Dissertação apresentada ao Programa de Pós-Graduação em Ciência e Tecnologia de Alimentos, Centro de Tecnologia, Universidade Federal da Paraíba em cumprimento aos requisitos para obtenção do título de Mestre em Ciência e Tecnologia de Alimentos.

Orientadora: Profª. Marta Maria da Conceição

JOÃO PESSOA - PB

2020

Catalogação na publicação
Seção de Catalogação e Classificação

H641é Hilário, Fabrine Felipe.
Ésteres de açúcar : síntese, propriedades e aplicabilidade na indústria de alimentos / Fabrine Felipe Hilário. - João Pessoa, 2020.
58 f. : il.

Orientação: Marta Maria da Conceição.
Dissertação (Mestrado) - UFPB/CT.

1. Tecnologia de alimentos. 2. Esterificação. 3. Glicolipídios. 4. Lipases. 5. Surfactante biodegradável. 6. Aditivo alimentar. I. Conceição, Marta Maria da. II. Título.

UFPB/BC CDU 664(043)

Elaborado por Larissa Silva Oliveira de Mesquita - CRB-15/746

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Dissertação:_____em_____/_____/2020

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Dedico este trabalho aos meus pais, Maria de Fátima Felipe e Félix Hilário, por todo amor, apoio e incentivo para alcançar os meus sonhos.

AGRADECIMENTOS

Agradeço, em primeiro lugar, a Deus, por ter me dado saúde e força para superar todas as dificuldades e por tornar possível este momento.

Agradeço a todos os professores do Programa de Pós-Graduação em Ciência em Tecnologia de Alimentos, por todo esforço dedicado a todos os alunos e por todo conhecimento a mim transmitido. Agradeço especialmente à minha orientadora, Profa. Dra. Marta Maria da Conceição, por toda paciência e tempo que se dedicou a me ajudar durante o processo de realização deste trabalho.

Ao Laboratório de Combustíveis e Materiais (LACOM) por todo suporte oferecido. Em especial aos meus colegas de laboratório, Frankin Xavier, Georges Cavalcanti, Aleir Silva, Elizeu Cordeiro e João Lopes, por todo o apoio e incentivo oferecido.

Agradeço à minha banca examinadora, Profa. Dra. Rita de Cássia Ramos do Egypto Queiroga e Profa. Dra. Jailane de Souza Aquino, pela disponibilidade em contribuir para o enriquecimento deste trabalho.

A minha mãe, Maria de Fátima Felipe, minha heroína que sempre me deu amor, apoio e incentivo nas horas difíceis, de desânimo e cansaço. Ao meu pai, Félix Hilário, que apesar de todas as dificuldades me deu suporte e me fortaleceu durante todos esses anos.

Ao meu irmão, Félix Hilário Neto, por toda a paciência e companheirismo durante esses anos morando longe de nossos pais.

Sou grata pela amizade de Thaisa Cidarta, Jéssica Ferreira, Polyana Ferreira, Mychelle Andrade, Cristina Fernandes, Cibelly Maria e Joellington Marinho, que construí durante o mestrado e que pretendo levar por toda a minha vida.

A Coordenação de Aperfeiçoamento de Pessoal de Nível Superior - CAPES pela bolsa concedida.

A todos que contribuíram para a realização deste trabalho, seja de forma direta ou indireta, fica registrado aqui o meu muito obrigada!

“A ciência e a vida cotidiana não podem e não devem ser separadas.”

Rosalind Franklin.

RESUMO

Os ésteres de açúcar são surfactantes não iônicos produzidos a partir de matérias-primas renováveis, como carboidrato e ácido graxo. Sua síntese pode ocorrer pela via química ou pela via enzimática. Devido suas propriedades físico-químicas, os ésteres de açúcar podem formar e estabilizar emulsões do tipo óleo em água, como pão, sorvete e molho, e emulsões de água em óleo, como chocolate e margarina. Além disso, são capazes de atuarem como substituto não calórico de gordura e na fabricação de sistemas de distribuição coloidal de qualidade alimentar. Na indústria alimentícia o interesse na sua produção e utilização também se deve por serem biodegradáveis, não-tóxicos, inodoros e insípidos, além de apresentar propriedades biológicas vantajosas aos alimentos. Ademais, os ésteres de açúcar apresentam propriedades semelhantes, e por vezes melhores, em comparação aos surfactantes derivados da petroquímica. Assim, levando em consideração o crescimento no interesse dos ésteres de açúcar como uma alternativa de surfactante mais seguro e ecológico, a presente revisão teve por objetivo abordar a síntese química e enzimática, suas vantagens, desvantagens e principais avanços, bem como as propriedades e aplicações dos ésteres de açúcar na indústria de alimentos. Para tal, foi desenvolvido uma revisão narrativa no qual foi empregado a análise da literatura exposta sob a forma de artigos científicos publicados, preferencialmente nos últimos 10 anos, em periódicos nacionais e internacionais obtidos em bases de dados como Science Direct, National Center for Biotechnology Information, Scientific Electronic Library Online, Google Acadêmico e Portal de Periódicos Capes. Também, foram averiguadas as patentes desenvolvidas com a finalidade de produzir e aplicar os ésteres de açúcar em produtos alimentícios específicos, bem como foi realizado um levantamento das diretrizes governamentais estabelecidas pela Agência Nacional de Vigilância Sanitária, European Food Safety Authority, Codex Alimentarius, Food and Drug Administration e World Health Organization. Desta forma, foram desenvolvidos tópicos explorando aspectos importantes dos ésteres de açúcar, como a sua síntese química, com e sem solvente e a síntese enzimática com o uso da enzima lipase em meios reacionais contendo solvente orgânico ou solventes verdes, como os líquidos iônicos, carbono supercrítico e solventes eutéticos profundos, assim como a síntese enzimática associada ao uso de peneiras moleculares. Adicionalmente, foram abordadas as propriedades físico-químicas, como a ampla faixa de valores de balanço hidrofílico-lipofílico e capacidade de formar e estabilizar emulsões, espumas e micelas, e as propriedades biológicas, antimicrobiana e antitumoral, apresentadas pelos ésteres de açúcar. Por fim, foi investigado as funções dos ésteres de açúcar na indústria de alimentos visando a produção de pães, chocolates, sorvetes, molhos, maionese e suas aplicações como substituto de gordura e em sistemas de distribuição coloidal (microemulsões e nanoemulsões). Em decorrência da sua natureza e de suas propriedades físico-químicas e biológicas, os ésteres de açúcar se apresentam como uma alternativa atraente, para uso industrial, em comparação aos surfactantes convencionais derivados de matérias-primas à base de petróleo. Ademais, os ésteres de açúcar sintetizados a partir da esterificação enzimática em meios reacionais contendo solventes verdes acarretam na obtenção de produtos alimentícios benéficos à saúde humana e sustentáveis ambientalmente.

PALAVRAS-CHAVE: Aditivo Alimentar; Esterificação; Glicolipídio; Lipase; Surfactante Biodegradável.

ABSTRACT

Sugar esters are non-ionic surfactants produced from renewable raw materials, such as carbohydrate and fatty acid. Its synthesis can occur by chemical or enzymatic pathway. Due to their physico-chemical properties, sugar esters can form and stabilize oil-in-water emulsions, such as bread, ice cream and sauce, and water-in-oil emulsions, such as chocolate and margarine. In addition, they are able to act as a non-caloric fat substitute and in the manufacture of food-grade colloidal distribution systems. In the food industry, the interest in their production and use is also due to the fact that they are biodegradable, non-toxic, odorless and tasteless, in addition to presenting advantageous biological properties to food. Furthermore, sugar esters have similar, and sometimes better, properties compared to surfactants derived from petrochemicals. Thus, taking into account the growth in the interest of sugar esters as a safer and more ecological surfactant alternative, the present review aimed to address chemical and enzymatic synthesis, its advantages, disadvantages and main advances, as well as the properties and applications of sugar esters in the food industry. To this end, a narrative review was developed in which the analysis of the literature exposed in the form of published scientific articles was used, preferably in the last 10 years, in national and international journals obtained from databases such as Science Direct, National Center for Biotechnology Information , Scientific Electronic Library Online, Google Scholar and Capes Journal Portal. Also, the patents developed for the purpose of producing and applying sugar esters in specific food products were investigated, as well as a survey of government guidelines established by the National Health Surveillance Agency, European Food Safety Authority, Codex Alimentarius, Food and Drug Administration and World Health Organization. Thus, topics were developed exploring important aspects of sugar esters, such as their chemical synthesis, with and without solvent, and enzymatic synthesis with the use of the enzyme lipase in reaction media containing organic solvent or green solvents, such as ionic liquids, carbon supercritical and deep eutectic solvents, as well as enzymatic synthesis associated with the use of molecular sieves. In addition, the physical and chemical properties were addressed, such as the wide range of hydrophilic-lipophilic balance values and the ability to form and stabilize emulsions, foams and micelles, and the biological, antimicrobial and anti-tumor properties, presented by the sugar esters. Finally, the role of sugar esters in the food industry was investigated in order to produce breads, chocolates, ice cream, sauces, mayonnaise and their applications as a fat substitute and in colloidal distribution systems (microemulsions and nanoemulsions). Due to their nature and their physical-chemical and biological properties, sugar esters are an attractive alternative for industrial use, compared to conventional surfactants derived from petroleum-based raw materials. In addition, sugar esters synthesized from enzymatic esterification in reaction media containing green solvents result in food products that are beneficial to human health and environmentally sustainable.

KEYWORDS: Esterification; Food Additive; Glycolipid; Lipase; Biodegradable Durfactant.

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LISTA DE ABREVIATURAS E SIGLAS

2M2B	2-Methyl-2-Butanol
Å	Ångström
A/O	Água em Óleo
Al	Aluminum
ANVISA	Agência Nacional de Vigilância Sanitária
Asp	Aspartic Acid
Aw	Water Activity
BHL	Balanço Hidrofílico-Lipofílico
CALB	Lipase B de *Candida antarctica*
CMC	Critical Micellar Concentration
DMF	Dimethylformamide
DMSO	Dimethylsulfoxide
EI	Emulsification Index
His	Histidine
LIs	Líquidos Iônicos
MICs	Minimum Inhibitory Concentrations
O	Oxygen
O/A	Óleo em Água
SC-CO_2	Dióxido de Carbono Supercrítico
SDS	Sodium Dodecyl Sulfate
SEPs	Solventes Eutéticos Profundos
Ser	Serine
Si	Silicon

SUMÁRIO

1 INTRODUÇÃO

Os ésteres de açúcar (EAs) são surfactantes não-iônicos que possuem a capacidade de promover a mistura de componentes imiscíveis, como óleo e água, pela redução da tensão superficial na interface das fases imiscíveis (PÉREZ et al., 2017; REN; LAMSAL, 2017). Esta propriedade se deve a natureza anfifílica da molécula, uma vez que, os EAs são tipicamente obtidos pela formação da ligação éster entre açúcares e ácidos graxos que são responsáveis pela fração hidrofílica e pela fração hidrofóbica da molécula, respectivamente (AN et al., 2019; ZHENG et al., 2015).

Ésteres de açúcar são comumente empregados na indústria de alimentos, de cosméticos, farmacêutica e de limpeza, por consequência de suas propriedades como emulsificante, espumante, estabilizante e na formação de micelas (CASAS-GODOY et al., 2016; KOUMBA IBINGA et al., 2019; PÖHNLEIN et al., 2014). Suas propriedades físico-químicas e biológicas (antimicrobiana e antitumoral) são dependentes do açúcar presente na fração hidrofílica, do comprimento da cadeia de carbonos da fração hidrofóbica e do grau de esterificação da molécula (NETA et al., 2015). Porém, apenas os ésteres de sacarose são autorizados para atuarem como aditivo alimentar em bebidas e alimentos específicos (CODEX ALIMENTARIUS, 2020).

Por possuírem uma ampla faixa de valores do balanço hidrofílico-lipofílico (BHL), no intervalo de 1 a 16, os ésteres de sacarose podem ser utilizados na indústria de alimentos para aplicações específicas. Assim, os ésteres de sacarose que apresentam altos valores de BHL (>8) são emulsificantes apropriados para formar e estabilizar emulsões de óleo em água (O/A), como pão, molho e sorvete, em contrapartida os que possuem baixo BHL (<7) são bons emulsificantes de emulsões de água em óleo (A/O), como chocolate (HAYES et al., 2019; PÉREZ et al., 2017). Ademais, os ésteres de açúcar que possuem alto grau de esterificação, como os poliésteres de sacarose (BHL≤3) podem ser utilizados como substituto não calórico de gordura na produção comercial de *snacks* e *cookies* (JANDACEK, 2012; ZHENG et al., 2015). Outra aplicação importante dos ésteres de sacarose se deve a formação de microemulsões e nanoemulsões que atuam como sistemas de entrega e excipiente de bioativos lipofílicos em alimentos e bebidas (NETA et al., 2015; ZHANG et al., 2020).

A produção dos ésteres de açúcar pode ser realizada mediante a utilização de métodos químicos ou enzimáticos. O método químico com e sem solvente requer mais energia e possui baixa seletividade quando comparado com o método enzimático. Além disso, a síntese por via

química possui a desvantagem da utilização de elevadas temperaturas que em combinação com o catalisador alcalino, promovem a descoloração do produto, a degradação dos carboidratos e a formação de subprodutos tóxicos (CASAS-GODOY et al., 2016; GUMEL et al., 2011; VAN KEMPEN et al., 2013). Já as conversões enzimáticas promovem condições amenas de reação, baixa toxicidade e elevada pureza dos produtos de interesse. Também apresentam alta especificidade e regioseletividade e fornecem produtos com estrutura e funcionalidades controladas. Como consequência, a síntese por via enzimática, catalisada pela enzima lipase, é frequentemente utilizada para a produção dos ésteres de açúcar (AN et al., 2019; GUMEL et al., 2011; ZHENG et al., 2015).

As lipases (EC 3.1.1.3) são hidrolases que catalisam tipicamente a hidrólise de lipídios em meio aquoso, contudo, na presença de um teor de água moderado, o equilíbrio da reação muda para a síntese da ligação éster (BANIK et al., 2017; BRITO CUNHA et al., 2019; GUMEL et al., 2011). As lipases são produzidas por muitas espécies de plantas, animais, insetos e microrganismos. No entanto, do ponto de vista industrial, as lipases microbianas ganham atenção superior devido à sua seletividade, estabilidade, especificidade de substrato e produção em larga escala (BHARATHI; RAJALAKSHMI et al., 2019). As lipases microbianas podem ser produzidas por fungos filamentosos, bactérias e leveduras, onde a Lipase B de *Candida antarctica* (CALB) destaca-se como a lipase mais utilizada em reações orgânicas e está disponível comercialmente nas formas livre e imobilizada (HAYES et al., 2019).

Uma condição limitante presente na síntese dos EAs pelo método enzimático, é a baixa solubilidade apresentada pelos açúcares na maioria dos solventes orgânicos, no qual as lipases apresentam sua atividade de catálise na reação de esterificação (PÖHNLEIN et al., 2014; TARAHOMJOO; ALEMZADEH, 2003). Entre as propostas desenvolvidas com o objetivo de aumentar a solubilidade dos açúcares destacam-se os meios de reação mais seguros, ou seja, solventes não tóxicos e compatíveis com aplicações alimentícias, como os sistemas de líquidos iônicos (LIs), o dióxido de carbono supercrítico (SC-CO_2) e os solventes eutéticos profundos (SEPs) (GUMEL et al., 2011; HAYES et al., 2019; REN; LAMSAL, 2017). Além de superar a pouca miscibilidade dos açúcares nos meios reacionais, a concentração de água deve ser cuidadosamente removida e controlada durante a reação de esterificação enzimática, a fim de evitar a hidrólise da ligação éster e aumentar a taxa de conversão do produto final de interesse (FORESTI et al., 2007; HAYES et al., 2019). A remoção da água pode ser alcançada por diferentes métodos, como o uso de peneiras moleculares, tubos abertos e pervaporação (GUMEL et al., 2011; ŠABEDER et al., 2006; TARAHOMJOO; ALEMZADEH, 2003).

Na indústria alimentícia o interesse na produção desses surfactantes se deve em grande parte por serem biodegradáveis, inodoros, insípidos, não tóxicos e produzidos a partir de recursos renováveis, como açúcares e ácidos graxos (CHANG; SHAW, 2009; NETA et al., 2015; VAN KEMPEN et al., 2013). Os surfactantes à base de açúcar, como os ésteres de açúcar, possuem potencial para substituir os surfactantes derivados de combustíveis fósseis, que possuem baixa biodegradabilidade e alta toxicidade, devido às suas propriedades ideais de surfactantes, biodegradabilidade e biocompatibilidade (AN et al., 2019; REN; LAMSAL, 2017). Consequentemente, os ésteres de açúcar fazem parte da tendência comercial de desenvolver produtos que contém surfactantes mais ecológicos e com propriedades semelhantes ou melhores aos obtidos por surfactantes derivados da petroquímica (ENAYATI et al., 2018; GAUDIN et al., 2019; NETA et al., 2015). Desta forma, considerando o crescimento no interesse e no consumo dos ésteres de açúcar, por ser uma alternativa mais segura à saúde e ao meio ambiente, esta revisão bibliográfica narrativa tem como objetivo explanar sobre a abordagem clássica e os recentes avanços na síntese dos ésteres de açúcar pelo método químico e enzimático, além de analisar suas propriedades físico-químicas e biológicas e explorar suas principais aplicações na indústria de alimentos.

2 METODOLOGIA

O presente trabalho trata-se de uma revisão narrativa. Segundo Murphy (2012), uma revisão narrativa apresenta um somatório (não sistemático) e uma análise da literatura disponível sobre um tópico de interesse específico. Assim, metodologia empregada para a realização do artigo de revisão foi baseada na análise da literatura, pertinente ao tema, com base em artigos científicos publicados em periódicos nacionais e internacionais, de patentes concedidas e diretrizes governamentais estabelecidas pela Agência Nacional de Vigilância Sanitária (ANVISA), da European Food Safety Authority (EFSA), do Codex Alimentarius, do Food and Drug Administration (FDA) e da World Health Organization (WHO).

Os artigos indexados nesta revisão, por sua vez, foram obtidos por meio das bases de dados de periódicos da Science Direct, da National Center for Biotechnology Information (NCBI), Scientific Electronic Library Online (Scielo), Google Acadêmico e Portal de Periódicos Capes, que permitem o acesso à artigos publicados em periódicos de elevado fator de impacto. A busca foi realizada mediante a utilização de palavras-chave como ésteres de açúcar, esterificação química, esterificação enzimática, lipases, peneiras moleculares, propriedades e indústria de alimentos. Desta forma, foram incluídas principalmente as produções científicas que abordavam os ésteres de açúcar como tema principal de suas respectivas pesquisas, sendo preferencialmente publicadas nos últimos 10 anos, ou seja, de 2010 a 2020.

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4 RESULTADO

O resultado obtido mediante o desenvolvimento deste trabalho proporcionou a elaboração do artigo de revisão descriminado abaixo:

4.1 ARTIGO 1: SUGAR ESTERS: SYNTHESIS, PROPERTIES AND APPLICABILITY IN THE FOOD INDUSTRY

Sugar esters: synthesis, properties and applicability in the food industry

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ABSTRACT

Background: Sugar esters are nonionic surfactants produced from renewable raw materials, such as carbohydrate and fatty acid. Their synthesis can occur by the chemical route, using alkaline catalysts in the presence or absence of an organic solvent, or by the enzymatic route, preferentially catalyzed by the enzyme lipase in a reaction medium containing green solvents. Due to their wide range of hydrophilic-lipophilic balance values and their emulsifying, stabilizing, foaming and micelle-forming properties, sugar esters can be applied in the production of different foods, such as bread, chocolate, ice cream, sauce and light mayonnaise. In addition, they can be used as a noncaloric fat substitute and in the manufacture of food-grade colloidal distribution systems. In the food industry, the interest in their use is also due to the fact that they are biodegradable, nontoxic, odorless and tasteless, in addition to presenting advantageous biological properties to food.

Scope and approach: The present review aims to addresses chemical and enzymatic synthesis, its advantages, disadvantages and main advances, as well as the properties and applications of sugar esters in the food industry.

Key findings and conclusion: Due to its amphiphilic nature and their physicalchemical and biological properties, sugar esters present themselves as a more attractive alternative than conventional surfactants derived from raw materials petrochemical. In addition, sugar esters synthesized from enzymatic esterification in reaction media containing green solvents result in food products beneficial to human health and environmental sustainability.

Keywords: Chemical esterification; Enzymatic esterification; Food additive; Glycolipid; Lipase; Biodegradable surfactant

1. Introduction

Sugar esters (EAs) are nonionic surfactants obtained by forming the ester bond between sugars and fatty acids that are responsible for the hydrophilic fraction and the hydrophobic fraction of the molecule, respectively (An et al., 2019; Zheng et al., 2015). Due to the high emulsifying, foaming, stabilizing, micellar and detergent effect, EAs are extensively used in the food, cosmetics, pharmaceutical and cleaning industries (Casas-Godoy et al., 2016; Pöhnlein et al., 2014).

In the food industry, the interest in the production of these surfactants is largely due to them being biodegradable, odorless, tasteless and nontoxic; in addition, they have biological properties (antimicrobial and antitumor), which make them an interesting alternative to conventional surfactants (Hayes et al., 2019; Van Kempen et al., 2013). Because they have a wide range of hydrophilic-lipophilic balance (BHL) values – in the range 1 to 16 – sugar esters form and stabilize oil-in-water emulsions (BHL > 8), such as bread, sauce and ice cream, and emulsions of water in oil (BHL < 7), such as chocolate. Sucrose polyesters (BHL ≤ 3) can act as a noncaloric fat substitute, as they are not hydrolyzed by gastric enzymes (Hayes et al., 2019; Jandacek, 2012). In addition, the ability to form micelles allows the application of sugar esters in delivery systems and excipients of lipophilic bioactives in foods (Zhang et al., 2020).

Sugar esters can be produced by chemical or enzymatic methods. Chemical synthesis can occur in solvent or solvent-free systems and has some disadvantages, such as low selectivity and the use of high temperatures that in combination with the alkaline catalyst promote product discoloration and the formation of toxic by-products (Casas-Godoy et al., 2016; Gumel et al., 2011; Van Kempen et al., 2013). On the other hand, enzymatic synthesis, preferentially catalyzed by the enzyme lipase in organic or green solvents, has high specificity and regioselectivity, makes use of moderate temperatures and provides products with controlled structure and functionality (An et al., 2019; Gumel et al., 2011; Zheng et al. , 2015). However, enzymatic synthesis must overcome the low solubility presented by sugars in most organic solvents, in which lipases present their catalysis activity in the esterification reaction (Neta et al., 2015; Pöhnlein et al., 2014). In addition, water must be carefully removed and controlled during the enzymatic esterification reaction, in order to increase the conversion rate of the final product of interest (Hayes et al., 2019).

The surfactants on the market are produced mainly by petroleum-based raw materials. In contrast, sugar-based surfactants, such as sugar esters, are made up of renewable, inexpensive, affordable and environmentally harmless raw materials. Thus, sugar esters are part

of the commercial trend of producing products that contain more ecological surfactants and have properties similar to, or better than, those obtained by surfactants derived from petrochemicals (Enayati et al., 2018; Gaudin et al., 2019; Neta et al., 2015). Taking into account the growth in interest in surfactants with lower environmental and health riches, especially when considered for use in the food industry, this article aims to explain the classic approach and recent advances in the synthesis of sugar esters using chemical and enzymatic methods, in addition to analyzing its physicalchemical and biological properties and exploring its main applications in the food industry.

2. Sugar esters

Sugar esters are surfactants derived from renewable raw materials such as carbohydrates and fatty acids, which have the ability to promote the mixture of immiscible components, such as oil and water, by reducing the surface tension at the interface of immiscible phases (An et al., 2019; Nguyen et al., 2019). The first report on sugar esters occurred in 1880 in a description of the synthesis of sucrose octaacetate (Hass, 1968). However, the main advances in the synthesis of sugar esters occurred in the 1950s' (Osipow et al., 1956). In 1959, the Hass-Snell process was developed, and it was subsequently improved and marketed by Dai-Nippon Sugar Manufacturing Co., Ltd., in Japan, aiming at the synthesis of sucrose esters to act as food additives (Hass et al., 1959; Hayes et al., 2019).

In recent years, carbohydrate-based surfactants have been recognized by consumers as a healthier, safer and more environmentally sustainable alternative when compared to surfactants derived from petrochemical products (Enayati et al., 2018). As a result of their biological and physicalchemical properties, there is a growing interest in the production of these molecules, especially sucrose esters, in which the global demand for the market was valued at more than US$76 million in 2019 and should reach US$106 million by 2025, presenting a compound annual growth rate (CAGR) of 5.7%, with the food segment responsible for dominating the market with applications in bakery, confectionery, cereals, dairy products, meat products, soups and sauces (Hayes et al., 2019; Markets and Markets, 2020).

In the European Union (EU), sucrose esters are authorized to be used as a food additive with a maximum allowed level ranging from 120 mg/kg to 20,000 mg/kg in 37 food categories (European Food Safety Authority, 2018). In the United States of America (USA), sucrose esters act as an emulsifier, stabilizer and foaming and vitrification agent in specific foods for human consumption, with a maximum level ranging between 200 mg/kg and 20,000 mg/kg (Codex

Alimentarius, 2019). In Brazil, the National Health Surveillance Agency (ANVISA) authorizes the use of sucrose esters as a food additive to exercise the function of stabilizer and emulsifier in foods and beverages, with a maximum allowed limit of between 0.10 and 1.0 g/100g or g/mL (ANVISA, 2020). Table 1 summarizes the guidelines for the use of sucrose esters as a food additive in foods and beverages, with the maximum limits allowed in Brazil, the United States of America and the European Union.

Table 1 – Sucrose esters as a food additive in foods and beverages.

Food category	Maximum limit (mg/kg)		
	Brazil	USA	EU
Candies, confectionery and chocolates	500	5.000	5.000
Non-alcoholic drinks with flavors	100	200	5.000
Bubble gum	500	12.000	10.000
Edible ice cream	500	5.000	5.000
Sauces	1.000	2.000	10.000
Oils, fats, vegetable creams and margarines	1.000	5.000	10.000
Desserts and dessert powders	500	5.000	5.000
Soups and broths	200	2.000	2.000
Nutritional/Food* Supplements	500	20.000	QS

QS (*Quantum Satis*) - Sucrose esters can be added individually or in combination.
* According to the codex alimentarius, it includes vitamin and mineral supplements in unit dosage forms, such as capsules, tablets, powders, solutions, etc., where the national jurisdictions of the United States regulate these products as foods.
* According to EFSA, they refer to food supplements as defined in Directive 2002/46 / EC of the European Parliament and of the Council, excluding food supplements for babies and young children. Source: ANVISA, 2020; Codex Alimentarius, 2020; EFSA, 2018.

According to Ordinance No. 540 of the Brazilian legislation of 1997, a food additive is any ingredient that, when intentionally added to food, without the purpose of nourishing, has the objective of modifying its physical, chemical, biological or sensory characteristics during the manufacture, processing, preparation, treatment, packaging, conditioning, storage, transport or handling of a food. The approval of a food additive in Brazil, as well as the exclusion or extension of its use, takes into account the references of the Codex Alimentarius of the European Union and, in a complementary way, the Food and Drug Administration (FDA, USA) (Brazil, 1997).

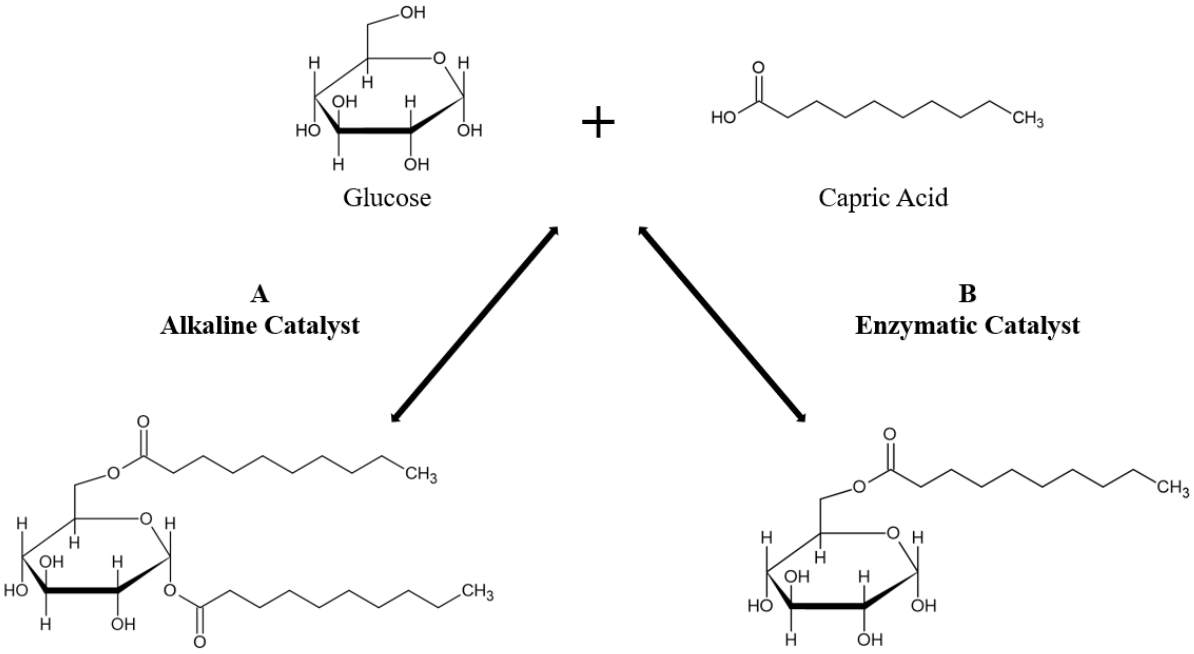
The Food and Drug Administration (2019) has determined that sucrose esters can be used safely in current good manufacturing practices as long as they meet certain prescribed conditions. For example, sucrose esters can only be prepared using solvents generally recognized as food safe or regulated, such as methyl ethyl ketone and ethyl acetate. In addition, the acid value of sucrose esters cannot exceed 6, the ignition residue content (sulfated ash) must be below 2% and the used dose of sucrose esters must not exceed the amount reasonably necessary to achieve the desired effect. The Panel on Food Additives and Nutrient Sources Added to Food (ANS) examined the safety and determined that sucrose esters do not cause toxicological problems, provided that oral exposure is within the acceptable daily intake (IDA) of 40 mg/kg weight body/per day (EFSA, 2010). The Joint FAO/WHO Committee of Specialists in Food Additives (JECFA), in turn, has determined the IDA of up to 30 mg/kg body weight/per day (WHO, 1997).

3. Synthesis of sugar esters

The synthesis of sugar esters occurs from the esterification reaction between a sugar (CH2O) n, as an acyl acceptor, and one or more fatty acid (RCO2H), an acyl donor (Gumel et al., 2011). The acyl acceptors most commonly used are monosaccharides (glucose, fructose, xylose and ribose), disaccharides (sucrose, lactose and trehalose), trisaccharides (maltotriose) and sugar alcohols (sorbitol and xylitol). The acyl donors most used for obtaining sugar esters are capric (C10: 0), lauric (C12: 0), myristic (C14: 0), palmitic (C16: 0), stearic (18: 0), oleic (C18: 1), behenic (C22: 0) and erucic (C22: 1) acid (Pérez et al., 2017; Van Den Broek & Boeriu, 2013).

The esterification reaction can occur either by the chemical method, using alkaline catalysts, or by the enzymatic method, in which an enzyme catalyst is used, preferably the lipase enzyme, for the reaction catalysis, as illustrated in Figure 1 (Gumel et al., 2011).

Figure 1 – Synthesis of sugar esters by the chemical (A) and enzymatic (B) method.



Source: Author (2020).

Chemical method synthesis is the main way of obtaining sugar esters present on the market, due to their low cost and high operational speed when compared to the enzymatic method (Hayes et al., 2019; Pérez et al., 2017). However, chemical synthesis is not satisfactory from an ecological and health point of view, as it makes use of high temperatures, which, in combination with the alkaline catalyst, promote product discoloration, carbohydrate degradation and the formation of toxic by-products. (Gumel et al., 2011). Chemical reactions also have low selectivity, thus providing a heterogeneous mixture of products with different degrees of esterification and different acylation positions, such as diesters and triesters that can affect the quality of the surfactant. Thus, the chemical synthesis process becomes suitable only for the production of sugar esters with a high degree of esterification (Van Den Broek & Boeriu, 2013; Van Kempen et al., 2013).

In contrast, enzymatic synthesis offers a high degree of specificity and regioselectivity, in addition to making use of moderate temperatures between 40 °C and 60 °C, which avoids the degradation of substrates and products during the reaction. In addition, enzymatic methods can achieve high yields with greater production of monoesters, and formation of diesters to a lesser extent, in addition to being advantageous from an environmental point of view, as enzymes act in milder reaction conditions than chemical processes, as well as being easily biodegradable and generally not having toxic effects when they reach the environment after use (Gumel et al., 2011; Jegannathan & Nielsen, 2013; Van Den Broek & Boeriu, 2013).

However, the enzymes can present some disadvantages when they are implanted in the medium of production on a large scale; some of the limitations are related to the use of soluble enzymes, which result in a high cost production, with low operational stability and difficulties in recovering the enzymes (Filho et al., 2019). The choice of the solvent is important to dictate the stability of the enzyme during the synthesis of the esters. Moreover, it is extremely important to balance the water activity (Aw) of the reaction medium to increase the conversion rate of the final product (Gumel et al., 2011; Hayes et al., 2019).

4. Synthesis by the chemical method

4.1 Chemical synthesis with solventes

The first studies on the synthesis of sugar esters were described in the 1950s. Sucrose esters were obtained using the solvent dimethylformamide (DMF) to solubilize sucrose and the acyl donor present in the medium. This process was subsequently improved and marketed by the Japanese company Dai-Nippon Sugar Manufacturing Co., Ltd. in the late 1960s, with the objective of producing sucrose esters as a food additive (Hayes et al., 2019; Osipow et al., 1956; Zheng et al., 2015).

In industry, the synthesis of sugar esters is carried out through the esterification or transesterification of sugar with fatty acids in a reaction medium containing an organic solvent, such as dimethylformamide (DMF) or dimethylsulfoxide (DMSO), and a neutral or alkaline catalyst at a temperature generally greater than 100 ºC, under reduced pressure (Gumel et al., 2011; Hayes et al., 2019). Table 2 shows the synthesis of sugar esters with different degrees of esterification obtained by chemical reactions in the presence of organic solvents, with their respective substrates, catalysts and reaction conditions.

Table 2 – Sugar esters produced by chemical synthesis in the presence of solvent.

Solvent	Substrates		Catalyst	Reaction Condition	Degree of Esterification (Yield %)	Reference
	Acyl Acceptor	Acyl Donor				
DMF	Sucrose	Methyl Stearate	K_2CO_3	3 h, 90-95°C, 80-100 mm	Monoesters (36%) Diesters (58%)	Osipow et al. (1956)

Butanol	Sucrose	Methyl Palmitate	Lithium Oleate	30 min, 170-180°C, 133-400 Pa	Monoesters (1,45%) Diesters (3,8%) Triesters and Polyesters (94,5%)	Liu et al. (1999)
DMSO	Sucrose	Octanoate, Laurato, Myristate and Ethyl Palmitate	K_2CO_3	Ultrasound (40 kHz), 2 h, 70 ºC, 11kPa	Monoesters (92-95%)	Huang et al. (2010)
DMSO	Raffinose	Methyl Laurate	K_2CO_3	Ultrasound (40 kHz) 2 h, 65 °C, 10 kPa	Monoesters (±80%)	Lu et al. (2013)

DMF (dimethylformamide); DMSO (dimethylsulfoxide); K_2CO_3 (Potassium Carbonate).

Sugar esters obtained by high temperature processes are often contaminated with toxic by-products and form a heterogeneous mixture of sugar esters with different degrees of esterification and different acylation positions (Gumel et al., 2011). In order to solve the reactive acylation problem of the reagents, the ultrasonic intensification technique has been implemented in chemical esterification (Hayes et al., 2019). According to Hang et al. (2017), the low ultrasonic frequency works by increasing the yield of sucrose monoesters, while the high ultrasonic frequency works by increasing the yield of sucrose diesters.

4.2 Chemical synthesis without solvents

Chemical solvent-free processes for obtaining sugar esters were also developed in order to avoid the use of toxic solvents. Feuge et al. (1970) developed a synthesis process that used melted sucrose (at 180 ºC) and fatty acids in the presence of lithium, potassium and sodium soaps, which acted by solubilizing and catalyzing the esterification reaction at a temperature between 170 ºC and 187 ºC. The process was subsequently licensed to the Japanese company Mitsubishi-Kasei Food Corporation (Zheng et al., 2015).

However, chemical synthesis without solvents does not eliminate problems of multiple substitution, color degradation and the presence of residues in the final products, such as the potassium soaps used, which need to be frequently removed by molecular distillation,

ultrafiltration, reverse osmosis or recrystallization (Gutiérrez et al., 2018; Hayes et al., 2019; Van Den Broek & Boeriu, 2013; Zheng et al., 2015). Table 3 shows the synthesis of sugar esters by the chemical route in solvent-free reaction systems.

Table 3 – Sugar esters produced by chemical synthesis in solvent-free systems.

Substrates		Catalyst	Reaction Condition	Degree of Esterification (Yield %)	Reference
Acyl Acceptor	Acyl Donor				
Sucrose	Methyl Oleate	Potassium Oleate	8 h, 145-150°C, 8 mm Hg	Polyesters (90%)	Rizzi & Taylor (1978)
Sorbitol	Lauric, Miristic, Palmitic and Stearic Acid	NaOH	5 h, 220 °C	Monoesters (1%) Diesters (4%) Triesters (85%)	Smidrkal et al. (2004)
Sucrose	Methyl Palmitate	KOH, Mg Stearate	4 h, 125-135°C	Monoesters (41%) Diesters (33%)	Fitremann et al. (2007)
Mannitol	Oleic Acid	SO3H-Carbon	12 h, 180°C	Monoesters (84%)	Reddy et al. (2015)

NaOH (Sodium Hydroxide); KOH (Potassium Hydroxide); Mg (Magnesium).

Sucrose esters were obtained in a chemical process using sucrose reagents, palm oil methyl ester, an alkaline catalyst (K_2CO_3) and sucrose esters to stabilize the medium, at temperatures ranging from 120 to 140 ºC, for up to 4 hours. At the end of the reaction, monoesters (15%), diesters (25%), triesters and other sucrose esters were obtained with higher degrees of esterification (60%) (Claverie et al., 2004). Recently the chemical production of sucrose esters without solvent has been studied using emulsifiers (sucrose esters, potassium palmitate and glycerol monostearate) in the range of 5 to 15 % to improve the compatibility of the reagents, with potassium carbonate as a catalyst. Higher productivity of sucrose esters and greater selectivity in the production of monoesters were obtained with the emulsifier potassium palmitate as a contact agent, at a concentration of 5%, with an optimal temperature of 120 ºC, during 26 hours of reaction (Gutiérrez et al., 2018).

5. Synthesis by the enzymatic method

5.1 Lipases in enzymatic synthesis

Lipases, triacylglycerol ester hydrolases (EC 3.1.1.3), are enzymes belonging to the hydrolases class that typically act by catalyzing the hydrolysis of triglycerides, releasing glycerol, diacylglycerols, monoacylglycerols and free fatty acids. However, in conditions of low water activity in the reaction medium, lipases are able to catalyze synthesis reactions, such as esterification and interesterification, where fatty acids, carbohydrates, alcohols, acids and esters act as lipase substrates (Brito e Cunha et al., 2019; Khan et al., 2017).

Lipases can be found in cells of animals, plants and different microorganisms, such as bacteria, fungi and yeasts. However, lipases of microbial origin are the most widely used in the industrial environment, as they allow large-scale production and the vast majority are not harmful to health. Lipases, with industrial application, of bacterial origin are produced by the genera *Pseudomonas* and *Staphylococcus*, however the latter genus is not indicated for use in food, due to the possible production of toxins. Among the filamentous fungi, the genera *Rhizopus*, *Rhizomucor* and some *Aspergillus* species stand out as producers of industrial lipases. A large number of lipases are also produced by yeasts, the most important being the species *Candida antarctica*, which are widely used in biotechnological processes because they have high thermal stability and good enantioselectivity with their substrates; that is, they react exclusively or faster with a determined isomer of the substrate (Almeida et al., 2020; Bharathi & Rajalakshmi, 2019; Gumel et al., 2011).

The enzymatic reactions catalyzed by the lipases occur at the active site of the enzyme, which comprises the catalytic triad formed by the amino acids serine, histidine and aspartic acid (Ser-His-Asp) (Khan et al., 2017). As a result of its extensive substrate specificity, commercial accessibility, nondependence on a cofactor and ability to work in high concentrations of substrate, both in aqueous solutions and in organic and green solvents, lipases are widely used in biotransformation processes (Rodrigues et al., 2019). The high versatility shown by lipase enzymes, therefore, allows their application in a variety of industrial segments, such as detergents, pharmaceuticals, leather, textiles, cosmetics, the paper industry, biodiesel production and in the food industry – in the latter, aiming at the synthesis of aromas, the accelerated maturation of cheeses, the improvement of the texture of breads, preparation of structured oils and fats and the production of nonionic surfactants, such as sugar esters, monoglycerides and lysolecithin (Bharathi & Rajalakshmi, 2019; Lai et al., 2018).

However, the use of soluble lipases in the industrial context has some obstacles, such as high acquisition costs, low operational stability and difficulties in recovery and reuse. In contrast to these limitations, immobilized enzymes have great potential for industrial application, since they have greater stability in a wide range of operational conditions and allow easy recovery and reuse of enzymes, thereby significantly reducing the cost of processes involving the use of lipase (Chapman et al., 2018; Filho et al., 2019).

Enzymatic immobilization consists of confining the enzyme in a solid support that is insoluble in aqueous medium and in organic solvents. Immobilization methods can be classified into physical and chemical methods, according to the modes of interaction between the enzyme and the support. In the physical method, the interactions between the lipase and the support occur through weaker bonds, such as hydrogen bonds and van der Waals forces, which makes these interactions reversible and affect the catalytic activity of enzymes less. In the chemical method, in turn, the interaction between the enzyme lipase and the support is stronger and occurs through covalent bonds, which makes the interaction irreversible and the enzyme more stable for extreme processes, both in terms of pH and temperature (Filho et al., 2019; Liu et al., 2018; Zhao et al., 2015)

The application of lipases in the food industry, in order to synthesize surfactants, such as sugar esters, also needs to overcome the low miscibility of acyl receptor substrates in organic media, in which enzymes traditionally exhibit their esterification activity. In order to solve this problem, different methods have been proposed (Gumel et al., 2011; Neta et al., 2015). One of the proposals to increase the solubility of sugars is the addition of dimethyl sulfoxide (DMSO) in the reaction system; however, this reagent can interfere with the activity and stability of the enzyme (Castillo et al., 2003). Another approach already taken is related to the use of organic solvents, such as pyridine and dimethylformamide (DMF), in which the reaction substrates and lipase are soluble, however the toxicity of these solvents is not compatible with their application in the food industry (Gumel et al., 2011; Pöhnlein et al., 2014).

5.2 Enzymatic synthesis in organic solvents

A solvent considered suitable for the synthesis of sugar esters, catalyzed by lipase, must be able to dissolve sufficient amounts of both substrates, sugar and fatty acid (Gumel et al., 2011). However, the solubility of the substrates in organic solvents is considerably different, which hinders the progress of the esterification reaction, as it is difficult to obtain a high concentration of both substrates within a single phase. In addition, the lipase enzyme cannot

have its activity and stability affected by the organic solvent used (Van Den Broek & Boeriu, 2013; Zheng et al., 2015). Table 4 shows the synthesis of sugar esters in the presence of organic solvents, using sugars with different degrees of polymerization and fatty acids as substrates for the enzyme lipase.

Table 4 – Sugar esters produced by enzymatic synthesis in organic solvents.

Solvent	Substrates		Lipase	Reaction Condition	Degree of Esterification (Yield %)	Reference
	Acyl Acceptor	Acyl Donor				
Hexane	Oligofructose	Lauric Acid	CALB	96 h, 60 ºC, MS (3Å)	Monoesters e Diesters (>80%)	Casas-Godoy et al., 2016
DMSO 2M2B	Glucose	Palmitic Acid	CALB	48 h, 55 ºC, 96 rpm, MS (3Å)	Monoesters (97,17%)	Ren & Lamsal (2017)
Hexane	Lactose	Lauric Acid	CALB	12 d, 50 ºC, MS (4Å)	Monoesters (93%)	Enayati et al. (2018)
DMSO t-Butanol	Oligomaltose	Capric, Lauric, Myristic and Palmitic Acid	CALA	72 h, 60 ºC, 400 rpm, MS (4Å)	Monoesters (22%)	Nguyen et al. (2019)

DMSO (Dimethylsulfoxide); 2M2B (2-Methyl-2-Butanol); CALB (*Candida antarctica* Lipase B); CALA (*Candida antarctica* Lipase A); MS (Molecular Sieve).

The influence of organic solvents on the synthesis of sugar esters has been studied extensively and interpreted in several ways. Parameters such as the partition coefficient, solvent dielectric constant, polarity and electron acceptance index and Hildebrand's solubility parameter have been used to explain the effect of different organic solvents on the reaction rate of enzymatic esterification. Among the parameters mentioned, the partition coefficient is the one that best correlates the lipase activity with the reaction medium used (Gumel et al., 2011). The partition coefficient, also called "log P," measures the hydrophobic/hydrophilic property of an organic solvent that can influence enzymatic catalysis. Solvents with a high log P value are hydrophobic and those with a low log P value are hydrophilic (Pérez et al., 2017).

Greater activities of the lipase enzyme are found in organic solvents with values of log P > 3 (n-hexane and n-heptane), that is, in nonpolar solvents; however, sugars are poorly soluble

in these solvents. In contrast, solvents with lower log P values may partially cosolubilize substrates, but often inactivate lipase, due to their ability to remove water particles essential for the enzyme's biocatalytic activity (Hayes et al., 2019; Wang et al., 2016). According to Li et al. (2015), due to its partial interaction with water bound to the immobilized lipase, the methyl ethyl ketone (MEK) solvent (log P = 0.29) can help to fold the enzyme into a conformation that favors the conversion of monoesters to diesters, while in the solvent 2-methyl-2-butanol (log P = 0.35) the conformation is less favorable for conversion. Thus, this study demonstrates that solvents of different polarities can influence the formation of enzymes and determine the degree of esterification of sugar esters.

The ionization capacity and polarity of a reaction medium with organic solvents can be favorably modified by mixing two or more solvents with different polarities (Gumel et al., 2011). A double solvent system containing dimethyl sulfoxide (DMSO) and acetone (1:10 v/v) was used for the synthesis of xylose ester esterified with capronic acid (C6), after 24 hours of reaction, with the ideal conditions of 16% from lipase (w/v), a molar ratio of xylose to caprylic acid of 1:4 (v/v) and temperature of 60 °C, a conversion rate of 64% was obtained (Abdulmalek et al., 2016).

The use of organic solvents in enzymatic synthesis on an industrial scale provides some advantages, such as the reversibility of the thermodynamic balance of hydrolysis reactions, suppression of water-dependent side reactions and substrate specificity (Neta et al., 2015). However, only a few solvents, such as acetone, acetonitrile, pyridine, 2-methyl-2-butanol (2M2B), dimethylformamide (DMF) and dimethyl sulfoxide (DMSO), can significantly solubilize sugar on a large scale, although the toxicity and the environmental safety of these solvents make them of concern for use in the food industry (Hayes et al., 2019).

5.3 Enzymatic synthesis in green solventes

Due to the environmental and health risks related to organic solvents, different reaction media classified as green solvents have been studied, such as ionic liquids (ILs), supercritical carbon dioxide (SC-CO2) and deep eutectic solvents (DESs) (Gumel et al., 2011; Hayes et al., 2019; Ren & Lamsal, 2017).

Ionic liquids represent liquids composed entirely of ions, formed by anions and organic cations (Van Den Broek & Boeriu, 2013). They have been attracting attention as a promising alternative to organic solvents due to their high chemical and thermal stability, nonvolatility and ability to dissolve a variety of materials, such as polar, nonpolar, organic, inorganic and

polymeric compounds (Mai et al., 2014). The hydrophilic/hydrophobic polarity can be regulated by changing the combination of anions and cations present in ionic liquids (Van Den Broek & Boeriu, 2013). It has been reported that ILs are capable of dissolving a greater amount of monosaccharide, disaccharide, oligosaccharide and polysaccharide than organic solvents (Koumba Ibinga et al., 2019). For example, the solubility of sugars such as glucose, sucrose and lactose can exceed 100 g/L in ionic liquid (Gumel et al., 2011).

It is reported that enzymes have greater reactivity, selectivity and stability when present in a reaction medium containing ionic liquids (Zheng et al., 2015). Productivity is also improved by using mixtures of two ionic liquids of different polarities compared to pure ILs (Pérez et al., 2017). According to a study by Mai et al. (2014), *Candida antarctica* lipase B, a lipase used for the esterification of glucose with lauric acid (C12), retained 86% of its initial activity when using the [BMIm] [TfO mixture] (more polar)/[BMIm] [Tf2N] (less polar) (1: 1 v/v), when compared to the use of pure IL [BMIm] [TfO], in which an initial activity of 36% was obtained. In the optimized reaction conditions (66.86 °C, molar lauric acid/glucose ratio of 7.63 and enzymatic load of 73.33 g/L), an experimental conversion yield of 96.4% was obtained and the enzymes and the ionic liquids used could be recycled and reused effectively for up to 10 cycles.

Reactions with ionic liquids can also be carried out in the presence or absence of enzymes, since ILs can act both as a reaction solvent and as a catalyst (Koumba Ibinga et al., 2019). Lin et al. (2016) described the synthesis of glucose esters esterified with lauric acid (C12), at 40 °C, for 10 hours, with tetrabutylammonium acetate [Bu4N] [AC] and without the presence of enzymes. These results indicate the viability of ionic liquids as new solvents for the synthesis of sugar esters. However, due to the high price of ionic liquids, their use for biocatalytic reactions on an industrial scale has been minimal, but it is expected that the costs related to the production of ILs will decrease as new applications are developed for their use (Hayes et al., 2019).

In addition to ILs, supercritical fluids can also be used as a reaction medium for the enzymatic esterification of sugar esters. Supercritical fluids, such as supercritical carbon dioxide (SC-CO2), exist in the form of vapor and liquid in equilibrium above their temperature and critical pressure (Van Den Broek & Boeriu, 2013). SC-CO2 has advantages over organic solvents due to its nontoxicity, nonflammability and low cost (Pérez et al., 2017). However, SC-CO2 has the disadvantage of reacting with the primary amino groups present on the surface of the enzyme to form complexes of carbamate (NH2COOH), which results in the reduction of enzymatic activity (Van Den Broek & Boeriu, 2013).

The enzymatic synthesis of different sugar esters was performed and showed a 65% yield in 2-methyl-2-butanol and 67% in supercritical carbon dioxide at 10 MPa after 24 h of the reaction performance. In addition, the yield increased to 74% when molecular sieves were added to the reaction mixture with SC-CO2 (Habulin et al., 2008). The synthesis of esters catalyzed by lipase was also carried out in a mixed two-phase system of ionic liquids and supercritical carbon dioxide. The glucose conversion was up to 95.5% under optimized conditions. The enzymatic activity in the biphasic system was 18.19 μmol/g/min, much higher when compared to the use of pure LI. In addition to improving the reaction rate and yield, the combination of SC-CO2 and ILs also makes product separation and recycling of enzymes and ionic liquids easier (Chang et al., 2018).

Deep eutectic solvents (DESs) have also received attention in enzyme catalysis reactions in recent years (Hayes et al., 2019). DESs consist of a mixture of quaternary ammonium salt with a hydrogen donor, which, after being heated, is left in a liquid state at room temperature. Deep eutectic solvents have a low melting point, high thermal stability and solubility for various substances. In addition, they are classified as ecologically correct, biodegradable, nontoxic, nonflammable and nonvolatile (Hayes et al., 2019; Kim et al., 2016; Liu et al., 2015;).

Recent work shows that it is possible to synthesize sugar esters with deep eutectic solvents (Andler et al., 2017; Siebenhaller et al., 2016). Pöhnlein et al. (2015) synthesized glucose esters using lipase B from *Candida antarctica* in several deep eutectic solvents. DESs were prepared by mixing ammonium salts and hydrogen bonding donors under constant stirring at 100 °C until a clear liquid was formed. The substrates were initially dissolved in 3.5 ml of DES. The reaction was initiated by adding 100 mg of lipases to the reaction medium and incubating for 3 days at 70 °C. The DESs formed by choline and urea chloride (CC: U) and choline and glucose chloride (CC: Glc) provided a successful synthesis of glucose esters. Additionally, it was observed that the DES consisting of choline chloride and glucose acted simultaneously as a solvent and substrate for the reaction.

However, one of the most frequent problems encountered when using DESs as solvents is the high viscosity of the medium. Thus, thermophysical properties of deep eutectic solvents, such as density, viscosity, polarity and conductivity, are important areas of study to verify the feasibility of using DESs in the intended applications, in addition to allowing adaptations in the preparation of solvents (Craveiro et al., 2016; Koumba Ibinga et al., 2019).

5.4 Enzymatic synthesis in association with the use of molecular sieves

Another obstacle present in enzymatic esterification is the need to keep water activity (Aw) low in the reaction media, especially in the final stages of the reaction, in order to achieve high conversions (Hayes et al., 2019). However, this problem is especially critical, as water is also a product of the esterification reaction, in which, in addition to influencing the activity and selectivity of the lipase enzyme, its accumulation forces the balance of the reaction towards hydrolysis (Gumel et al., 2011). Furthermore, it has been reported that the optimal water activity for the reaction depends on the enzyme source, the enzyme immobilization support and the solvent used in the reaction (Neta et al., 2015).

Thus, during the esterification between sugar and fatty acid, the water generated must be removed from the reaction mixture in order to avoid hydrolysis and to displace the reaction for the synthesis of sugar esters, with a consequent increase in the yield of sugar products in interest. To this end, different water removal methods have been developed, such as the use of molecular sieves, open tubes, pervaporation, microwave irradiation, azeotropic distillation, dry gas bubbling, saturated saline and two-phase solvent systems (Gumel et al., 2011; Hayes et al., 2019; Neta et al., 2015). Among the methods of removing water from the reaction medium, used in the synthesis of sugar esters, molecular sieves are extensively used (An et al., 2019; Casas-Godoy et al., 2016; Enayati et al., 2018; Ren & Lamsal, 2017; Zhang et al., 2014). Molecular sieves, also called “synthetic zeolites,” belong to a group of microporous crystalline materials traditionally formed by aluminosilicate (Moliner et al., 2015).

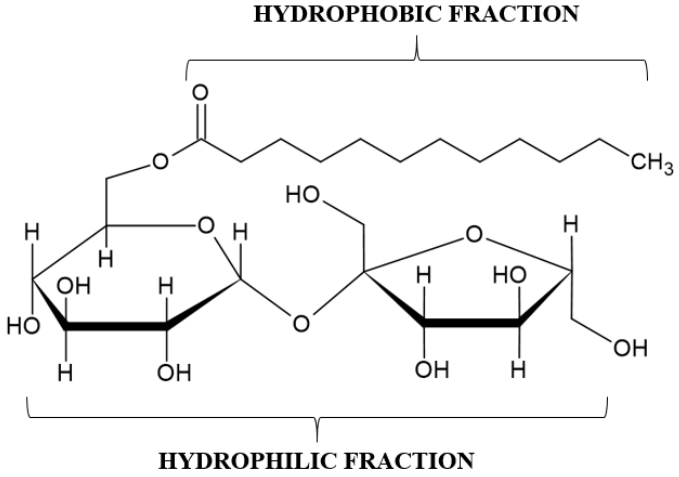
The structure of the molecular sieves is built from connections of the tetrahedra TO4, where T denotes Si (silicon) and Al (aluminum). Thus, in hydrothermal conditions, the Si and Al tetrahedra (primary building blocks) are connected to a corner sharing network (secondary building blocks), by means of oxygen atom (O) bridges, forming rings and prisms of varying sizes that combine to generate structures with a regular distribution of well-defined cavities and pores and of molecular dimensions. According to the pore dimensions, molecular sieves can be classified into small pores (< 4 Å), medium pores (4–6 Å), large pores (6–8 Å) and super-large pores (> 8 Å) (Luna & Schuchardt, 2001). The pore dimensions and topology that define the crystalline structure are important characteristics of molecular sieves, as the size, shape and dimensions of the pores and cavities, present in the structure, determine their application as adsorbents and catalysts in specific chemical processes (Bacakova et al., 2018; Moliner et al., 2015).

The adsorption properties of molecular sieves are determined by the ability of molecules to penetrate empty sieve cavities, which is limited by the dimensions and size of pores (Bacakova et al., 2018). The application as a catalyst is also related to the porous character of molecular sieves, since their microporous nature allows the access of reagents to active sites to be controlled, as well as the reactivity by selectivity of the form of reagents, intermediate transition states and products (Moliner et al., 2015). In the synthesis of sugar esters, the use of molecular sieves is aimed at controlling and removing the water generated during the esterification of sugar with fatty acids, increasing the reaction yield. However, studies have also observed that the use of isolated molecular sieves, that is, without the presence of enzymes, has a catalytic action in esterification reactions, mainly forming products with multiple fatty acid substitutions. Thus, molecular sieves can have a dual function, as a catalyst and water adsorbent, in an esterification reaction, thereby favoring the formation of sugar esters (Enayati et al., 2019; ter Haar et al., 2010).

6. Physical and chemical properties of sugar esters

Sugar esters have the ability to promote the mixing of immiscible components, such as oil and water, by reducing surface and interfacial tension. This property is due to the amphiphilic nature of sugar esters; in other words, these molecules present in the same structure a polar fraction (hydrophilic), soluble in water, and an apolar fraction (hydrophobic), insoluble in water, in which the polar part is composed of sugar and the nonpolar part is formed by fatty acid, as illustrated in Figure 2 (Zheng et al., 2015).

Figure 2 – Structure of the sucrose ester esterified with lauric acid.



Source: Author (2020).

Sugar esters can be presented as a solid, waxy or liquid material, depending on their composition (Szuts & Szabó-Révész, 2012). In addition, the nature and degree of polymerization of sugar, the length of the carbon chain, the degree of saturation and the amount of fatty acids, together with the different degrees of esterification and the vast possibilities of connections between the hydrophilic group and the hydrophobic group present in the molecule, also act by contributing to the unique physicochemical properties of sugar esters. As a result, these molecules can exhibit different active surface properties, including varying values of BHL (hydrophilic-lipophilic balance), emulsification properties, foam formation and stabilization capacity and micelle formation (Hayes et al., 2019; Zheng et al., 2015).

6.1 Hydrophilic-lipophilic balance

The hydrophilic-lipophilic balance (BHL) is based on the premise that in an oil and water system there is an optimal balance between the hydrophilic and hydrophobic portions of a surfactant molecule, leading to maximum emulsification efficiency and emulsion stability. Thus, BHL corresponds to the balance of strength and size of the hydrophilic and lipophilic portions present in a surfactant (Chen, 2015; Zheng et al., 2015). The BHL of nonionic surfactants is obtained using the Griffin method, in which it is calculated by multiplying by 20 the ratio of the molecular mass of the hydrophilic portion of the molecule by the entire molecular mass of the surfactant, thus promoting a BHL scale in which the values range from 0 to 20 (Rosen & Kunjappu, 2012; Zheng et al., 2015).

BHL values give an indication of the relative affinity of a surfactant molecule with the oily and aqueous phases of a medium (Chen, 2015). Therefore, surfactants that have a BHL in the range of 8 to 16 are more hydrophilic molecules, and thus more suitable for use in oil-in-water (O/W) emulsions, as well as monoesters applied in the manufacture of ice cream and cake dough. In contrast, surfactants with BHL values in the range of 3 to 6 are qualified as hydrophobic, consequently they are commonly used in water-in-oil (W/O) emulsions, as well as the diesters and triesters applied in the production of chocolates. Surfactant molecules that have a BHL between 7 and 9 have their hydrophilic and hydrophobic portions balanced, consequently they show no preference between emulsion forms, being used in the manufacture of chewing gum. Surfactants with a BHL around 3, such as sucrose polyesters, are not amphiphilic, and are therefore used in fat replacement (Hayes et al., 2019).

Sugar esters have a wide range of hydrophilic-lipophilic balance values. The different BHL values can be obtained by varying the size of the carbon chain of fatty acids and by the

degree of esterification in the molecules of sugar esters. Thus, the longer the fatty acid chain and the greater the degree of esterification of the sugar esters, the lower the BHL value; on the other hand, the smaller the fatty acid carbon chain used in the synthesis and the lower the degree of esterification, the higher the BHL value of the corresponding sugar ester (Nelen & Cooper, 2007; Zheng et al., 2015).

6.2 Emulsification

Because of the ability to reduce the surface tension of water, the emulsification process is the most important function of sugar esters (Pérez et al., 2017; Zheng et al., 2015). Sucrose esters, widely used in the food industry, offer an advantage over most other commercial emulsifiers, as they can exhibit hydrophilic-lipophilic balance values in the range of 1 to 16 (Nelen & Cooper, 2007).

According to Zhang et al. (2014), the carbon chain length of the hydrophobic portion of sugar esters is the most important factor that influences the surface properties, while the degree of esterification and the hydrophilic portion show less effect. Thus, esters that have a longer carbon chain have a better emulsification capacity than those that have a shorter one. Among the esters synthesized with fructose, sucrose and lactose esterified with oleic acid (C18), the lactose esters are the best to act as emulsifiers, as they have demonstrated the ability to reduce the surface tension from 52.0 to 38.0 mN m-1 in coconut milk, with an emulsification index (EI) of 54.1% (Neta et al., 2012).

Glucose esters esterified with palmitic acid (C16), in turn, had a better ability to reduce surface tension than sodium dodecyl sulfate (SDS), a commercial surfactant already established in the food industry. In addition, it has been observed that glucose esters esterified with capric (C10), lauric (C12), myristic (C14) and palmitic (C16) acids, at a concentration of 0.5% (w/w), have a better capacity to stabilize emulsions when purchased with traditional surfactants, such as SDS and sucrose esters, presenting values of emulsion stability index equal to 824.8, 1117.3, 1470.4 and 1659.3, respectively (An et al., 2019).

6.3 Foaming

Food products consisting of foams are thermodynamically unstable. The decrease in surface tension, promoted by sugar esters, is also relevant for the preparation of these foods,

due to the decrease in surface tension facilitating the increase of the water and air interface area, resulting in a greater foaming capacity (Pérez et al., 2017; Zheng et al., 2015).

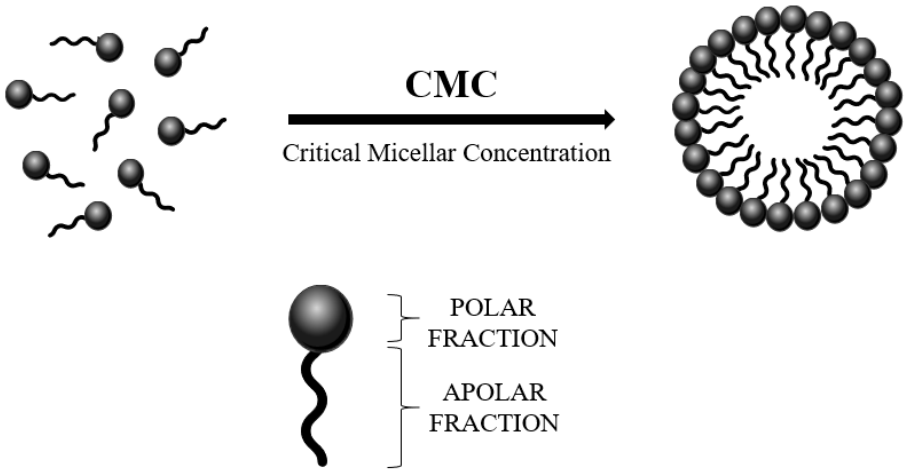
Surfactants that have a high BHL value are the most efficient in the formation and stabilization of foams; consequently sucrose esters, which may have a high BHL value (11–16), are able to reduce surface and interfacial tensions and produce stable foams (Nelen & Cooper, 2007). According to Van Kempem et al. (2014), despite the similarity in surface tension between oligofructose esters and sucrose esters, with the same fatty acid, oligofructose esters showed greater foam stability. Additionally, it was found that oligofructose esters esterified with intermediate fatty acids (C10–C16) provided the greatest stability of the foams, in comparison to the oligofructose esters esterified with short fatty acids (C4–C8).

The foamability of nine sugar esters, formed by sucrose, maltose, lactose, caprylic acid (C8), capric acid (C10) and lauric acid (C12), was measured at 25 °C. It was found that the foaming capacity varied with the concentration of the sugar monoesters, with the length of the fatty acid carbon chain and with the polar group of the molecule. Thus, the foaming power increased as the concentration of the sugar esters increased from 0.1 to 0.5 g/L. In general, sugar monoesters esterified with lauric acid (C12) showed better foaming power than monoesters esterified with caprylic (C8) and capric acid (C10), indicating that the formation of foams increases with the increase of the acidic carbon chain fat esterified to sugar. Finally, the polar groups maltose (glucose + glucose) and lactose (glucose + galactose), formed from two pyranosides, showed a better ability to form foam than sucrose, formed by a pyranoside (glucose) and a furanoside (fructose) (Zhang et al., 2014).

6.4 Micelle formation

When present in aqueous solutions, the amphiphilic nature of sugar esters also allows the formation of thermodynamically stable molecular aggregates, called “micelles”. Micelles start to form during a special concentration, called “critical micellar concentration” (CMC), which depends directly on the molecular structure of the surfactant and on experimental conditions (Figure 3). By the time they reach the CMC, any additional surfactants that are added to the system are employed to form new micelles or promote the growth of preexisting aggregates (Könnecker et al., 2011).

Figure 3 – Micelle formation after critical micellar concentration (CMC).



Source: Author (2020).

Sugar esters have a critical micellar concentration of 0.05–0.20 g/L (Hayes et al., 2019). Studies show that the CMC of sugar esters decreases as the carbon chain of fatty acids increases (Rosen & Kunjappu, 2012). The temperature also affects the formation of micelles and the activity of the surface, since the increase in temperature decreases the CMC and increases the size of the micelles (Molina-Bolívar & Ruiz, 2008).

Studying sucrose esters esterified with capric acid (C10) and lauric acid (C12), Krawczyk (2018) proved that the micelles of the studied surfactants are not spherical; in addition, it was observed that the temperature and type of surfactant impact their properties of aggregation to form micelles, since the tendency of the studied molecules to form micelles decreases as the temperature and the length of the carbon chain of the esterified fatty acids decrease. In addition, the degree of hydration together with the strength of hydrogen bonds between water and the polar fraction of surfactants influence the impact of temperature on the process of micellization of sugar esters.

7. Biological properties of sugar esters

7.1 Antimicrobial property

The antimicrobial property is the most prominent biological property exerted by sugar esters (Zheng et al., 2015). The esters' antimicrobial mechanism involves their interaction with the cell membrane of microorganisms, causing autolysis. It is believed that the lithic action on cell membranes occurs due to the stimulation of autolytic enzymes. Furthermore, the

antimicrobial activity of sugar esters depends directly on the sugar used, on the fatty acid chain esterified to sugar and on the degree of esterification (Pérez et al., 2017).

According to Wagh et al. (2012), lactose and sucrose esters are effective against Gram-positive bacteria, in which lactose esters stand out for exhibiting minimal bactericidal concentrations against *Listeria monocytogenes* isolates (5 to 9.5 mM) and *Mycobacterium* isolates (0.2 to 2 mM). Lactose esters esterified with lauric acid (C12) also exhibited the ability to inhibit the growth of *L. monocytogenes* present in yogurt, milk and cottage cheese (Chen et al., 2014). Additionally, lactose esters esterified with unsaturated fatty acids also showed the ability to exhibit antimicrobial activity against eight pathogenic species (*Escherichia coli*, *Listeria monocytogenes*, *Salmonella enteritidis*, *Enterococcus faecalis*, *Pseudomonas aeruginosa*, *Staphylococcus aureus* (Lucarini et al., 2016).

The antimicrobial activity of sugar esters was tested against pathogenic bacteria, including *Bacillus cereus*, *Staphylococcus aureus*, *Escherichia coli* and *Salmonella typhimurium*, and against the deteriorating bacterium *Bacillus subtilis*. The sucrose esters esterified with capric acid (C10) showed stronger antibacterial action against the five bacteria tested, especially against Gram-positive bacteria. The minimum inhibitory concentrations (MICs) against Gram-positive and Gram-negative bacteria were 2.5 and 10 mM, respectively. These results show the ability of sucrose esters to act as a multifunctional food additive in food industries (Zhao et al., 2015).

The effects of sugar esters on the formation of biofilms by foodborne pathogenic bacteria have also been investigated. According to Furukawa et al. (2010), sugar esters esterified with long carbon chain fatty acids (C14–16) significantly inhibited the formation of biofilms by *Staphylococcus aureus* and *Escherichia coli*, at a concentration of 0.001% (w/w). It was found that the activities of the esters correlated positively with the increase in the length of the carbon chain of fatty acids. Thus, it is recognized that sugar esters have great potential as an inhibitor of the biofilm formation of foodborne pathogens (Zhang et al., 2015).

Antifungal properties were also detected against several species of fungi of the genera *Aspergillus*, *Penicillium*, *Cladosporium* and *Alternaria*, before which it was found that sucrose esters less esterified with fatty acids were more active in reducing the growth of fungi (Zheng et al., 2015). The antifungal activity of different sugar esters was tested against four strains of fungi that spoil food (*Penicilium oxalicum*, *Aspergillus tubingensis*, *Mucor circinelloides* and *Rhizopus nigricans*). Fructose esters obtained greater antifungal activity, mainly against *Penicilium oxalicum* and *Aspergillus tubingensis*, affecting not only the size but also the thickness and the pigment production of the fungal colonies (Zhao et al., 2014).

These studies demonstrate the attractive properties of sugar esters in preventing food contamination; however, the complex matrix of foods tends to decrease the antimicrobial properties exhibited by esters, due to their multiple interactions with starch, proteins, sugars, oils and fats, which are the main components of food products (Nelen & Cooper, 2007; Pérez et al., 2017).

7.2 Antitumor property

Sugar esters are also promising candidates to act as antitumor agents. Maltose esters esterified with capric acid (C10) and palmitic acid (16), by lipases from *Thermomyces lanuginosus* and *Candida antarctica*, showed inhibitory effects under two tumor cell lines, Hep-G2 and HeLa. The maltose ester esterified with palmitic acid showed a greater antitumor effect on tumor cells (Ferrer et al., 2005).

Sucrose esters esterified with oleic acid (C18) and lauric acid (C12) have also been shown to inhibit the growth and proliferation of Ehrlich carcinoma ascitic tumor cells. The antitumor activity of the aforementioned esters increased by increasing their concentrations, reducing the viability of tumor cells to < 50% with the addition of sucrose esters at 1.2 g/L (Ye et al., 2016). Sugar esters with longer-chain fatty acids are shown to be more effective in antitumor activity than short-chain ones, with monoesters being more efficient than sugar esters with a high degree of esterification (Nishikawa et al., 1976).

8. Applications in the food industry

The food industry is the industrial sector that most uses sugar esters, which are used, preferably, in their solid form (Hayes et al., 2019). The food industry has great interest in sugar esters, because in addition to their physicalchemical properties that improve the production of some food products, they can be safely consumed by humans in quantities of up to 125 mg/kg body weight/per day (Neta et al., 2015). However, only sucrose esters are widely applied in the food industry, acting as an emulsifier, stabilizer, humectant and dispersant (Zheng et al., 2015).

Due to the wide range of hydrophilic-lipophilic balance values, sugar esters are widely used in food products formed by oil-in-water (O/W) and water-in-oil (W/O) emulsions (Koumba Ibinga et al., 2019; Pérez et al., 2017). Among their applications in food processing in oil-in-water emulsions (BHL > 8), they can be used in the manufacture of yogurt, mayonnaise, sauces, cereal bars, breads, coffee and confectionery foods. In contrast, in water-

in-oil emulsions (BHL < 7) they are used in products such as margarine and chocolate. In addition to acting as an emulsifier, sugar esters can play additional roles in food, both by improving the texture, aeration and crystallization of sugar, and by preventing protein browning and fat proliferation (Hayes et al., 2019). In the following subsections, the functions of sugar esters are specified in the manufacture of breads, chocolates, ice cream, sauces and mayonnaise, as well as their applications as a fat substitute and in colloidal distribution systems.

8.1 Bakery

In the bakery industry, surfactants such as sugar esters are used to stabilize aerated systems, control the agglomeration of fat globules, assist in mixing and emulsifying ingredients, improve consistency and interact with flour components to improve palatability (Rajendran et al., 2009). Due to their chemical structure, sucrose esters interact with gluten and starch. The interaction with gluten allows a more flexible gluten network to be obtained that better resists the mechanical forces applied during the kneading of the dough and guarantees a maximum gas retention that improves the texture. The interaction with starch inhibits its retrogradation (Nelen & Cooper, 2007).

The effect of sucrose esters on white bread formulated with sugarcane dietary fiber was examined. The expansion and stickiness of the dough, the volume, firmness and elasticity of the bread, as well as the sensory evaluation, decreased as each dietary fiber increased. However, the properties of the bread improved with the addition of sucrose esters. Breads formulated with dietary fiber substituted in 10 g/100 g of wheat flour were classified as favorable by consumers when sucrose esters were added to 1.5 g/100 g of wheat flour (Sangnark & Noomhorm, 2004). Gómez et al. (2004) reported that sucrose esters increased bread dough stability, although the extent of this effect depended directly on the surfactant concentration (0.3% – 0.7% (w/w, wheat flour). Besides that, it was observed that sucrose esters (0.3%) had a high effect on the loosening of breadcrumbs during prolonged tasting times.

8.2 Chocolates

Sugar esters with a low BHL value are used in the manufacture of chocolates. They work by decreasing and controlling viscosity, reducing friction between the components, inhibiting the formation of sugar crystals and preventing the formation of the proliferation of fat present in chocolate (Nelen & Cooper, 2007). Evidence also shows that the use of sucrose

polyesters can improve the quality and shelf life of products containing cocoa butter such as chocolates, since they work by stabilizing the βV crystals present in cocoa butter. Crystals in the βV form are more desirable, as they provide the desired gloss and a better texture quality for chocolates (Oh & Swanson, 2006). In addition, sucrose polyesters can also replace conventional cocoa butter, providing low-fat chocolates that have texture and mouthfeel properties similar to conventional chocolates (Suber & Miller, 1996).

8.3 Ice creams

Ice cream is an aerated emulsion that requires emulsifiers in its formulation to improve its organoleptic properties. Emulsifiers work by reducing the freezing time and improving the quality of the dough beat, thus producing an ice cream with a fine and rigid texture that melts slowly and evenly (Nelen & Cooper, 2007; Zheng et al., 2015). For this purpose, sugar esters with BHL equal to or greater than 11 are used (Hayes et al., 2019; Nelen & Cooper, 2007). According to Buck et al. (2006), sucrose esters added to standard ice cream mixes decrease surface tensions as BHL and ester concentrations increase. In addition, sucrose esters at a concentration of 0.25% tend to prevent the agglutination of the fat particles.

8.4 Sauces and mayonnaise

In the manufacture of sauces, sucrose esters with a high BHL value (15) are used, which act by interacting more strongly with the proteins in the medium, protecting them against denaturation and the Maillard reaction, which leads to the formation of more stable emulsions in the texture and color (Nelen & Cooper, 2007; Neta et al., 2015). Due to thermodynamic instability, oil-in-water (O/W) emulsion systems, such as sauces, are easily destabilized after thawing. Thus, the instability of freezing and thawing of emulsions (O/W) stabilized with 1% by weight of three types of sucrose esters was investigated. Emulsions stabilized with sucrose esters esterified with stearic acid (C18) and palmitic acid (C16) showed high stability, whereas emulsions stabilized with sucrose esters esterified with lauric acid (C12) were less stable in freezing and thawing (Ariyaprakai & Tananuwong, 2015). Sucrose esters with a high BHL value can also be used in the manufacture of low-fat mayonnaise (40–55 % oil). They are used for the purpose of optimizing viscosity, decreasing the size of oil particles and increasing stability, since the lower the fat content, the less stable the emulsion is (Nelen & Cooper, 2007; Neta et al., 2015).

8.5 Fat replacement

Sucrose polyesters, also called “olestra,” are used in the food industry in the commercially produce food products such as snacks, biscuits and fries for frying potatoes (Zheng et al., 2015). The olestra is formed by a sucrose molecule with six to eight of its hydroxyls esterified with long-chain fatty acids. Its physical properties can be modified by changing the composition of its esterified fatty acids. Thus, when sucrose is esterified with polyunsaturated fatty acids, the molecule behaves similarly to a liquid oil. However, when sucrose is esterified with saturated fatty acids, the olestra molecule is preserved in a solid state (Rogers, 2011).

Olestra acts as a noncaloric fat substitute, as it is not hydrolyzed by the gastric lipases present in the small intestine, consequently it is not absorbed from the small intestine into the blood and body tissues (Jandacek, 2012; Neta et al., 2015). However, the use of olestra in food is directly associated with symptoms in the gastrointestinal tract of consumers, such as soft stools and colic, in addition to affecting the absorption and storage of lipophilic compounds, such as fat-soluble vitamins A, D, E and K, which causes a reduction in the bioavailability of these compounds. Thus, the FDA (Food and Drug Administration) determined that foods containing olestra, in their formulation, must contain additional levels of fat-soluble vitamins, in order to compensate for the interference in the absorption of vitamins in the gastrointestinal tract (Jandacek et al., 2010; Zheng et al., 2015).

8.6 Microemulsions and nanoemulsions

Sugar esters can also be applied in the manufacture of food-grade colloidal distribution systems, specifically microemulsions and nanoemulsions, which can incorporate lipophilic ingredients in aqueous foods or drinks that need to remain transparent, such as fortified water, soft drinks and sauce (Neta et al., 2015; Zheng et al., 2015). In addition to being used as a delivery system for hydrophobic bioactive substances, nanoemulsions can be used as an excipient system, in which, when coingested with natural foods, such as fruits and vegetables, they increase the bioavailability of hydrophobic bioactive (Zhang et al., 2020).

Stable microemulsions and nanoemulsions have already been obtained using sucrose esters esterified with palmitic acid (C16) together with lemon oil as an oily phase. Nanoemulsions ($r < 100$ nm) were formed at low surfactant-oil ratios and depending on homogenization conditions, whereas microemulsions ($r < 10$ nm) were formed at higher

surfactant-oil ratios (Rao & McClements, 2011). Sucrose esters esterified with lauric acid (C12) exhibited good emulsification properties in the nano delivery system of banana flavor and aroma in food and beverages, without the use of organic solvents. The use of sucrose esters at a concentration of 5.0% (w/w) formed micelles with a particle size of between 1.3 nm and 2.1 nm (Edris & Malone, 2011). The controlled release of coffee aroma was also achieved with nanoemulsions of sucrose esters esterified with palmitic acid (C16) in order to enrich the aroma in instant coffee (Lee et al., 2017).

9. Conclusions

The growing interest in sugar esters is due to their physicalchemical and biological properties, which, in combination with their biodegradable, nontoxic and environmentally sustainable profile, present themselves as a more attractive alternative than conventional surfactants derived from raw materials petrochemical. In addition, its nature allows the selection of the sugar and fatty acid used in the synthesis, as well as the degree of esterification of the molecule, which leaves room for a process of obtaining sugar esters that may have their properties improved for specific applications in the food industry.

In the process of synthesis of sugar esters, enzymatic esterification, using lipase enzymes, receives greater attention in scientific research because it is a safer and ecological alternative to the detriment of chemical synthesis, as they promote reactions in mild conditions, with low toxicity and high purity of the products of interest. Combined with enzymatic synthesis, green solvents are also possibilities that present fewer environmental and health risks. However, it is necessary to carry out further studies with the combined use of green solvents and the enzyme lipase to obtain optimized processes that make it possible to adequately solubilize the substrates without impairing the enzymatic activity. Thus, sugar esters together with enzymatic esterification and green solvents form a triad with the potential to obtain food products beneficial to human health and environmental sustainability.

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5 CONCLUSÕES

Os ésteres de açúcar são surfactantes que possuem aplicações vantajosas na indústria de alimentos em comparação aos surfactantes derivados da petroquímica, por serem biodegradáveis, inodoros, insípidos e não tóxicos à saúde e ao meio ambiente. Ademais, os ésteres de açúcar possuem propriedades de superfície, como a capacidade de formar e estabilizar emulsões, espumas e micelas, que em conjunto com suas propriedades antimicrobiana e antifúngica, os tornam uma alternativa interessante em detrimento aos surfactantes convencionais, pois mostram a capacidade dos ésteres de açúcar em atuarem como aditivo alimentar multifuncional nas indústrias de alimentos.

A ampla gama de valores de balanço hidrofílico-lipofílico, controlada pela seleção do açúcar e dos ácidos graxos utilizados na síntese, bem como pelo grau de esterificação apresentada pela molécula de surfactante, deixa espaço para o design e a síntese dos ésteres de açúcar com aplicações específicas para a indústria de alimentos. Consequentemente, espera-se que no futuro a oferta de ésteres de açúcar formados por sacarose se expanda para novas moléculas formadas por açúcares diferentes, que por vezes mostraram ser mais vantajosos em suas propriedades quando comparado com os ésteres de sacarose já produzidos e utilizados na indústria. Apesar dos ésteres de açúcar serem conhecidos há anos e muito trabalho científico tenha sido realizado com foco em suas propriedades físico-químicas e biológicas, muitas indagações acerca de sua natureza e das múltiplas estruturas possíveis de serem obtidas também estão abertas para futuras pesquisas.

Junto a premissa que os surfactantes formados por materiais renováveis, como o açúcar e o ácido graxo, vêm ganhando interesse científico e no mercado por serem uma alternativa mais segura para a saúde e ambientalmente sustentável, o uso de catalisadores biológicos, chamados de enzimas, fornece uma alternativa mais segura e ecológica para o processo de síntese dos ésteres de açúcar, em detrimento à síntese química. Em decorrência de sua alta especificidade e regioseletividade as enzimas fornecem ésteres de açúcar mais específicos, com estrutura e funcionalidades controladas. A imobilização das lipases também se mostra uma alternativa benéfica para sua aplicação em processos de esterificação enzimática em larga escala, no qual as indústrias demandam, pois, a imobilização melhora a estabilidade térmica e química do biocatalisador e possibilita uma fácil recuperação e reutilização das enzimas, reduzindo significativamente os custos operacionais.

A água gerada na reação de esterificação enzimática, na qual pode interferir na formação da ligação éster e promover a reação de hidrólise, pode ser controlada pelo uso de peneiras moleculares que além de atuar como agente dessecante atua como catalisador da reação, favorecendo a formação do produto de interesse. Já a fraca miscibilidade dos substratos doadores e aceitadores de acila em solventes orgânicos continua sendo o principal desafio na síntese dos ésteres de açúcar. No entanto, as abordagens com os solventes verdes , tais como os líquidos iônicos (LIs), dióxido de carbono supercrítico (SC-CO_2) e os solventes eutéticos profundos (SEPs), mostram que são promissores para a formação dos ésteres de açúcar, uma vez que são mais seguros, ou seja, não apresentem riscos ambientais e de saúde ao mesmo tempo que conseguem solubilizar os substratos mantendo a estabilidade e a atividade enzimática. Assim, os ésteres de açúcar junto com a esterificação enzimática e os solventes verdes formam uma tríade com potencial para obter produtos alimentícios não nocivos à saúde humana e sustentáveis ambientalmente.