INSTITUTO SUPERIOR DE ENGENHARIA DE LISBOA

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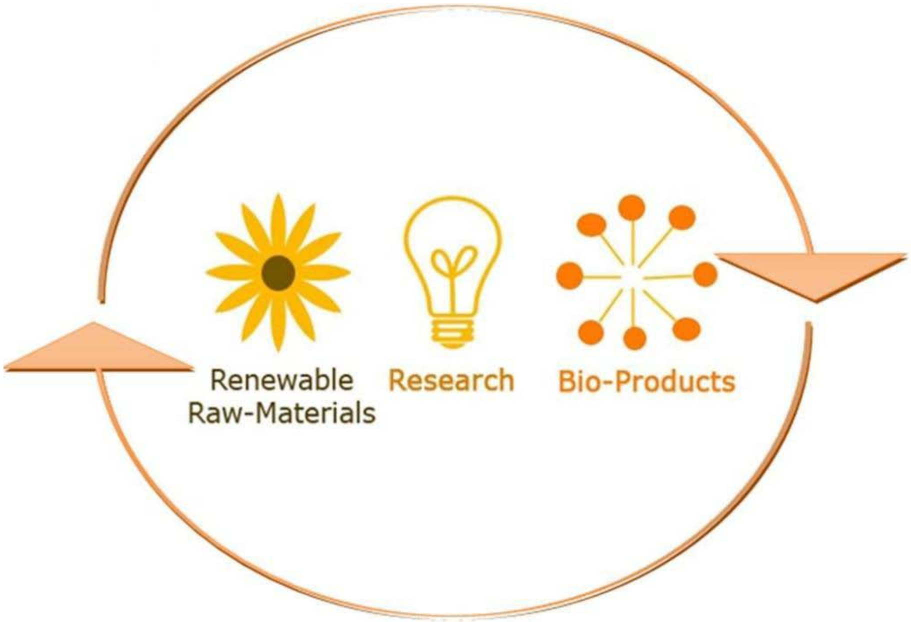

Production of Surfactants from Bio-Materials

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(Licenciado)

Trabalho Final de Mestrado para obtenção do grau de Mestre
em Engenharia Química

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Acknowledgements

> "From error to error one discovers the entire truth."
> **Sigmund Freud**
> *Austrian psychologist (1856 - 1939)*

As all pathways through science shows, all development comes in a sequence of experience and error and sometimes great discoveries rise from chance and accident. "Step by step, even the smallest creature can change the course of the world." (J.R.R.Tolkien, *Fellowship of the Ring*)

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List of Abbreviations and Symbols

A	Specific surface area
A_3	Frequency Factor
BDE	Bond Dissociation Energy
COSY	Correlation Spectroscopy
CPB	Companhia Petroquímica do Barreiro
d	Average diameter of particules
DABCO	1,4-diazabicyclo[2.2.2]octane
DAI	Sociedade de Desenvolvimento Agro-Industrial, S.A.
DE	Degree of Esterification
DEAD	Diethyl Azodicarboxylate
DMA	N,N - Dimethylaniline
DMA	Dynamic Mechanical Analysis
DMAP	N,N - Dimethylaminopyridine
DMF	Dimethyl formamide
DMP	Dimethyl pyrolidone
DMSO	Dimethyl sulphoxide
DSC	Differential Scanning Calorimetry
E_a	Activation Energy
EGDE	Ethylene glycol dimethyl ether
EO	Ethylene Oxide
EU	European Union
FAE	Fatty Acid Ester
FAME	Fatty Acid Methyl Esters
FCUL	Faculdade de Ciências da Universidade de Lisboa
FTIR	Fourier Transform Infrared Spectroscopy
GFAE	Glucose Fatty Acid Esters
HLB	Hydrophilic Lipophilic Balance
HMBC	Heteronuclear Multiple Bond Correlation
HPLC	High Pressure Liquid Chromatography
HSQC	Heteronuclear Single Quantum Correlation
ICTPOL	Instituto de Ciência e Tecnologia de Polímeros

INETI	Instituto Nacional de Engenharia, Tecnologia e Inovação
IP	Integrated Project
ISEL	Instituto Superior de Engenharia de Lisboa
IST	Instituto Superior Técnico
k	Kinetic constant for the transesterification
K_c	Equilibrium constant for the transesterification
MEKP	Methyl Ethyl Ketone Peroxide
MMA	Methyl methacrylate
mmHg	Millimiters of mercury (Unit of pressure)
NMR	Nuclear Magnetic Resonance
P&G	Procter & Gamble Company
PEG	Polyethylene Glycol
pH	Cologarithm of the activity of dissolved hydrogen ions
PMMA	Poly(methyl methacrylate)
PO	Propylene Oxide
PPG	Polypropylene Glycol
ppm	part per million
PTC	Phase transfer catalysis
rpm	rotation per minute
RSN	Relative Solubility Number
SFAE	Sugar Fatty Acid Esters
SME	Small and Medium Enterprises
T	Absolute Temperature
T_g	Glass-transition temperature
TLC	Thin Layer Chromatography
TMMA	Transesterified Methyl Methacrylate
TPP	Triphenylphosphine
UNL	Universidade Nova de Lisboa
γ	Interfacial tension

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Abstract

This Dissertation work was performed in the context of a European project, BIOPRODUCTION, and aimed to study the development of the production process of two types of functional biomaterials: sugar fatty acid esters (SFAE) and functionalized methacrylates.

Synthesis at laboratorial scale of SFAE was carried out using as raw-materials different saccharides, namely sucrose, glucose and sugar cane molasses (polysaccharides mixture), and fatty acid methyl esters (FAME) from vegetable oils, such as rapeseed and coconut. This synthesis includes two steps: acetylation of sugars with acetic anhydride, and transesterification of acetylated sugar with FAME, using lanthanide triflates as catalyst.

Different stoichiometries were tested, as well as different processes in order to avoid sugar degradation. Emulsification preliminary tests were performed, as well the empirical calculation of respective HLB. The product characterization by FTIR an NMR was also performed, as well as the iterative optimization of the synthesis process.

The modification of methyl methacrylate (MMA), at a laboratorial scale, was carried out by their transesterification with conventional polyols, in order to produce larger molecular weight methacrylates. The product was crosslinked with different curing systems for subsequent application in rubber coatings.

Finally, additional characterization studies will be necessary for both products, namely surface tension for biosurfactantes and mechanical properties for modified MMA polymers.

Key words: biomaterials, biosurfactants, SFAE, modified MMA

Resumo

Este trabalho foi desenvolvido no âmbito de um projecto europeu, BIOPRODUCTION, tendo em vista o desenvolvimento de dois tipos de biomaterias funcionais: ésteres de açúcares com ácidos gordos (SFAE) e metacrilatos funcionais.

A síntese laboratorial do biosurfactante SFAE foi efectuada utilizando como matérias-primas diferentes sacáridos, nomeadamente sacarose, glucose e melaço de cana-de-açúcar (mistura de polissacáridos), e ésteres metílicos de ácidos gordos (FAME) de óleos vegetais, tais como colza e coco. Esta síntese é constituída por dois passos: acilação dos açúcares com anidrido acético, e transesterificação do açúcar acilado com FAME, utilizando triflatos de lantanídeos como catalisador.

Diferentes estequiometrias foram testadas, bem como diferentes processos de modo a evitar a degradação dos açúcares. Foram efectuados testes preliminares de emulsão e calculou-se, empiricamente, o respectivo HLB. Procedeu-se à caracterização do produto através de FTIR e RMN e também à optimização iterativa do processo de síntese.

A modificação, à escala laboratorial, de metacrilatos de metilo (MMA) realizou-se recorrendo à sua transesterificação com polióis convencionais. Efectuaram-se testes de reticulação do produto com diferentes catalisadores e iniciadores para posterior aplicação em revestimentos de borracha.

Por fim, para ambos os produtos serão necessários estudos adicionais de caracterização, nomeadamente tensão superficial para os biosurfactantes e propriedades mecânicas para polímeros modificados com MMA.

Palavras-chave: biomaterias, biosurfactante, SFAE, MMA modificado

I – Introduction

1 – Scope

The work presented in this dissertation was performed under a trainee program offered by *Instituto de Ciências e Tecnologia de Polímeros* (ICTPOL) within the context of a European Project, named *Sustainable, Microbial and Biocatalytic Production of Advanced Functional Materials* (BIOPRODUCTION).

This project comprises seven SME's (Small and Medium Enterprises), four large companies, six research centers and six university departments, and also integrates scientific activities and complementary skills from fourteen EU-countries, being partly supported by the European Commission.

The aim of the integrated project is the development of novel sustainable biological processes of functional biopolymers and biosurfactants, made from renewable sources. With this purpose, the scientific and technical objectives, summarized in Figure 1, include the development of:

- Novel biocatalysts – exploration of microorganisms and/or enzymes in order to obtain low-cost production;
- Metabolic pathway engineering of multiple reactions;
- Innovative downstream processing operation for the recovery of bioproducts;
- Digital bioproduction and bioprocessing – application of advanced modeling, monitoring and control methods to bioprocesses.

The synthesis of sugar fatty acid esters (SFAE) is a small part of ICTPOL work task, embraced by the Research & Technological Development (RTD) Activity of Advanced Functional Biomaterials (WP5). ICTPOL contribution on this project includes the collaboration of IST, UNL and INETI. Moreover, ICTPOL collaboration with CPB includes the scale-up of novel polymers to an industrial scale.

It is also important to mention the cooperation of other partners in the work performed by ICTPOL, as they kindly provide samples, share knowledge and characterize and test products.

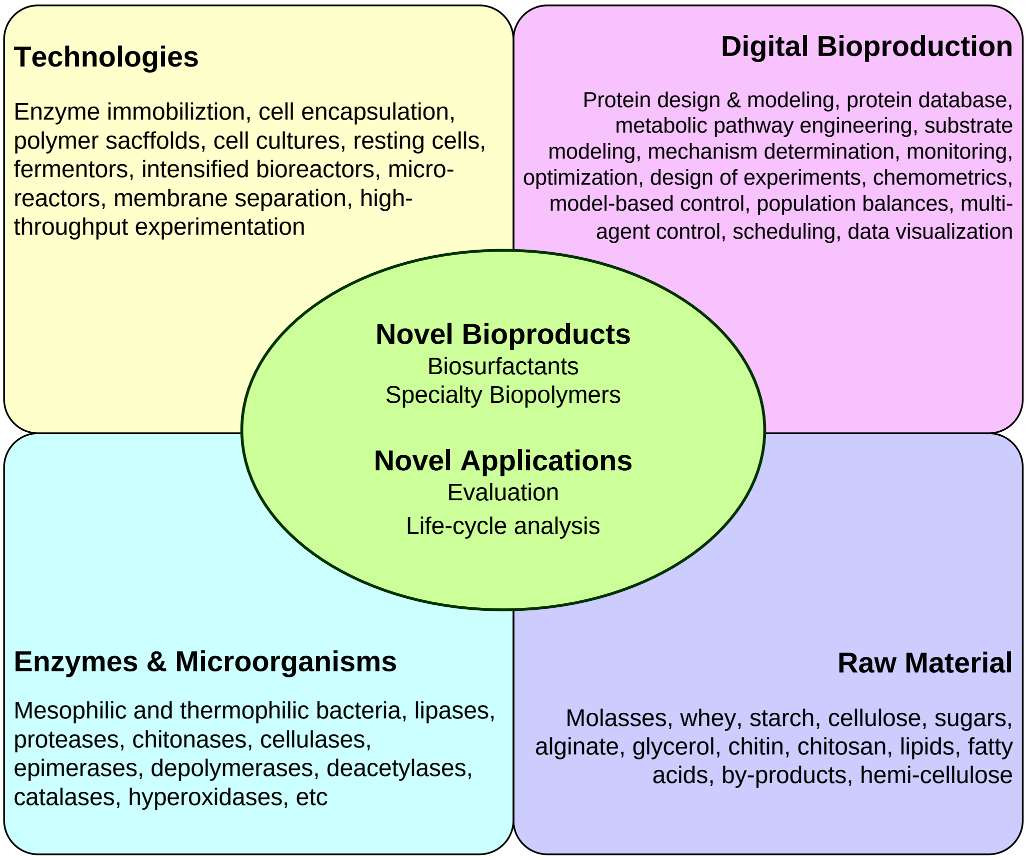

Figure 1 – The Bioproduction Concept.

2 – Objectives

The present dissertation aimed to study the production process of two types of functional biomaterials: biosurfactants (SFAE) and functionalized acrylates oligomers.

The specific objectives for the SFAE were:

a) Synthesis of SFAE using renewable raw-materials;
b) Test different saccharides (sucrose, glucose, sugar cane molasses)
c) Test different stoichiometry;
d) Design and optimization of the process at a laboratorial pilot scale.

Regarding functionalized acrylates production, the ultimate goal was to perform the transesterification of methyl methacrylate (MMA) with conventional polyols. For this, different stoichiometries were tested as well as different laboratory synthesis processes.

3 – Organization of the Dissertation Document

This dissertation is organized in four parts. The first part presents a brief scope and aim of this Master's dissertation within the BIOPRODUCTION project.

Chapter II presents the description of the work performed in the synthesis of SFAE.

Chapter III compiles the preliminary study of functionalized acrylates.

Although, chapter II and chapter III deal with different type of products, I both cases the essential key aspect is that the transesterification has to be performed at rather low temperature, in the case of SFAE to avoid thermal degradation of the sugar molecule, and in the case of acrylic oligomers to avoid the premature reaction of the double bound.

Finally, conclusions and future trends are presented at Chapter IV.

II – Synthesis of Sugar Fatty Acid Esters

1 – Introduction

1.1 – Sugar Fatty Acid Esters

Sugar Fatty Acid Esters – SFAE (Figure 2) are non-ionic surface active materials (surfactants) obtained from renewable resources and are an alternative of petrochemical-based surfactants. Sucrose esters are defined in Directive 98/86/EC as the mono-, di- and tri-esters of sucrose with fatty acids occurring in food fats and oils (Commission 1998).

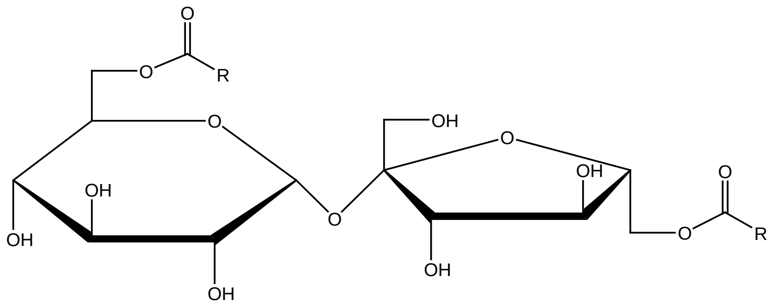

Figure 2 – Molecular structure of a SFAE, in particular a di-ester.

These surfactants are biodegradable, non-toxic and non-allergenic (Devulapalle, Gómez de Segura et al. 2004; Becerra, Toro et al. 2008), and their properties may be adjusted by controlling the degree of esterification and the nature of fatty acid and sugar (Devulapalle, Gómez de Segura et al. 2004).

SFAE can be applied in several areas, such as pharmaceuticals, cosmetic, health care, food and detergent industries (Devulapalle, Gómez de Segura et al. 2004; Sabeder, Habulin et al. 2006; Csóka, Marton et al. 2007; Becerra, Toro et al. 2008). They can be used as emulsifiers and foaming agents in various products, such as, bread, ice-cream, cakes, sauces, margarine, fat substitutes and dairy-based drinks (Husband, Sarney et al. 1998; Scotter, Castle et al. 2006), they are also used as solubilizing agents, lubricants, penetrating enhancers

Sucrose esters have been found in plants, such as wild tomato and wild potato species. Thus, they have been associated to aphid resistance and presenting antifungal properties (Chortyk, Pomonis et al. 1996).

1.1.1 – Synthesis of SFAE

SFAE are synthesized by esterification using carbohydrates and fatty acids as raw materials. In this reaction, the challenge is to attach a carbohydrate molecule to a fat and oil derivative (Hill and Rhode 1999), due to their different natures and non-miscibility, as carbohydrates are hydrophilic and fats are hydrophobic.

The carbohydrates tested in this work were sucrose and glucose, which are amongst the cheapest and more abundant carbohydrates.

Sucrose (Figure 3) is a non-reducing disaccharide and its components, D-glucose and D-fructose, are glycosidically linked through their anomeric carbon atoms (Lichtenthaler and Peters 2004; Queneau, Fitremann et al. 2004). Thus, constitutes a β-D-fructofuranosyl α- D-glucopyranoside (Lichtenthaler and Peters 2004). Sucrose is the most abundant pure organic molecule produced at the industrial scale, over 125 Mt per year (Lichtenthaler and Peters 2004; Queneau, Fitremann et al. 2004).

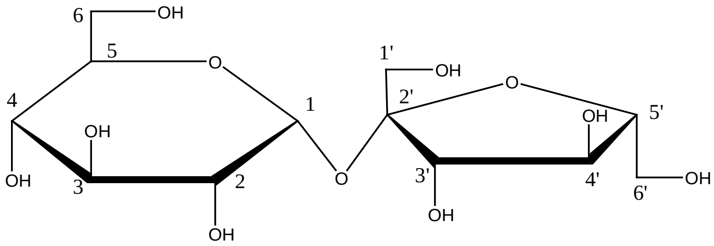

Figure 3 - Common structural representation of sucrose.

D-glucose is an aldohexose and the most abundant monosaccharide. This compound presents different properties, according to its molecular structure. Thus, these different properties due to the mutarotation of this monosaccharide, which reaches an equilibrium between the open chain structure (Figure 4, B) with the two cyclic structures (Figure 4, A and C) (Solomons 2002).

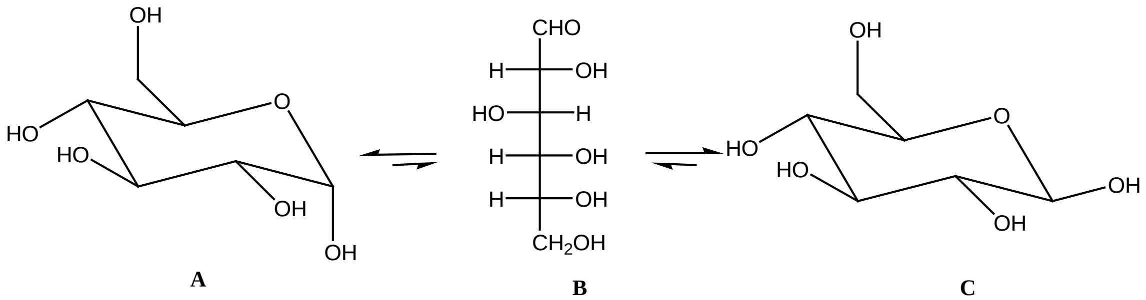

Figure 4 – Mutarotation of D-glucose: A) α-D-glucose; B) Fischer projection D-glucose; C) β-D-glucose.

These two cyclic structures, designated hemiacetals, are the result of an intramolecular reaction between the hydroxyl group in the carbon five (C5) with aldehyde group (C1). Moreover, the hemiacetal carbon atom is called the anomeric carbon, and the two cyclic structures are diastereomers, only differing in the C1 configuration (Solomons 2002).

The hydrophobic reactants tested in this work were fatty acid methyl esters (FAME), also known as biodiesel, from rapeseed oil or coconut oil. FAME, as such natural oils, are low cost raw materials and easily available with standard quality.

The FAME production process is well known, consisting on the transesterification of triglycerides with methanol, using, for example, sodium methoxide as catalyst, (Figure 5). In this synthesis, the final product is a mixture of fatty acid methyl esters, because the triglycerides used come from vegetable oils, which are mixtures of different triglycerides, and in the production of FAME is also produced glycerol.

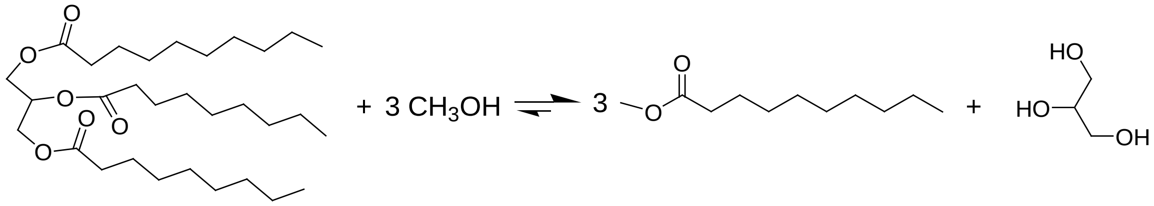

Figure 5 - FAME Production: transesterification reaction.

The composition of coconut oil and rapeseed oil are presented (Table 1), showing the distribution of fatty acid components, namely, caprylic, capric, lauric, myristic, palmitic, stearic, oleic, linoleic, linolenic and euricic (Nelson 2003).

Table 1 - Compositions of coconut oil and rapeseed oil.

Vegetable Oil	***Distribution of Acid Components*** *(%)*								
	C8	C10	C12	C14	C16	C18	C18:1	C18:2	C18:3
Coconut	8	7	46	15	9	2	6	1	-
Rapeseed	-	-	-	-	3.5	0.9	64.1	22.3	8.2

The literature search has reported different catalysts used in the synthesis of SFAE, both acid and alkaline catalysis. In this work, the catalysts used which showed more success were with the rare earth triflates, which are a special Lewis acid catalyst.

Recently, rare earth triflates, Ln(OTf)$_3$, were found to be stable in water and work efficiently as Lewis acid catalyst (Kobayashi and Hachiya 1995). Moreover, these catalysts could be almost completely recovered after the reaction and reused without loss of activity (Kobayashi and Manabe 2000; Fortuna, Musumarra et al. 2006).

Lanthanide trifluoromethanesulfonates (triflates) act as stronger Lewis acids because of the electrowithdrawing capacity of the trifluoromethanesulfonates anion (Fortuna, Musumarra et al. 2006) and to have strong affinity to carbonyl oxygens (Kobayashi and Hachiya 1994). These catalysts are soluble in water and also in many organic solvents and exhibit low toxicity (Fortuna, Musumarra et al. 2006).

1.1.1.1 – Reactions

The reaction of an alcohol with a carboxylic acid is called esterification. In this reaction esters can be produced with formation of water. A typical example is demonstrated in Figure 6.

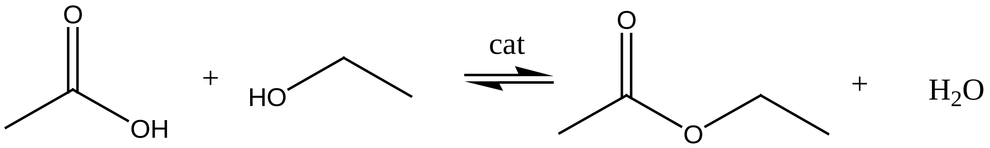

Figure 6 - Example of an esterification reaction: Formation of ethyl acetate.

However, this reaction is reversible, reaching a kinetic equilibrium. To extend the equilibrium for the formation of more ester it is usual to distillate water as soon as it is formed. Thus, reduced pressure can be applied to remove the water more easily from the system.

The transesterification is an equilibrium reaction (Figure 7) where the ester alkyl group, R$_1$, is exchanged with other alkyl group, R$_2$, from an alcohol. The equilibrium can be extended for the formation of more products proceeding with the distillation of the volatile by-product.

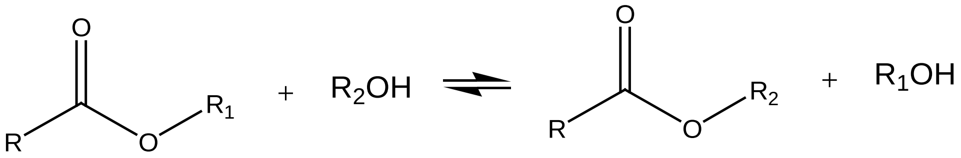

Figure 7 - General transesterification reaction.

1.1.1.2 – Selectivity

Sucrose molecule comprises eight hydroxyl groups (three primary and five secondary) and because of that many products can be obtained from a simple reaction, resulting from different degrees of substitution and different positions of the substituents (Lichtenthaler and Peters 2004; Queneau, Fitremann et al. 2004). Moreover, chemical reactions of unprotected sucrose at a single hydroxyl group are difficult to obtain (Lichtenthaler and Peters 2004).

The reactivity of primary and secondary hydroxyl is different so that the three primary ones are preferentially alkylated, acylated, oxidized an displaced by halogen in the follow order: 6-OH ≈ 6’-OH >> 1’-OH (Lichtenthaler and Peters 2004).

Secondary hydroxyls are more reactive for smaller electrophilic reagents due to electronic and conformational factors (Queneau, Chambert et al. 2008). Thus, the 2-OH is the most reactive, being the most electropositive and readily deprotonated (Lichtenthaler and Peters 2004), and 1’-OH and 3’-OH have also a singular behavior (Queneau, Chambert et al. 2008).

Regioselectivity can be achieved depending on the nature of the electrophilic reagent, on the catalyst used and on the solvent (sucrose is soluble in water, DMF and DMSO, and has a very low solubility in other solvents) (Lichtenthaler and Peters 2004; Queneau, Chambert et al. 2008).

In addition, the relative reactivity of hydroxyl groups only favours the kinetics of the first substitution, and further substitutions are slower (Lichtenthaler and Peters 2004; Queneau, Fitremann et al. 2004; Queneau, Chambert et al. 2008).

1.1.1.3 – Literature Review

Sucrose esters may be synthesized by various methods and techniques. In fact, the patent literature shows a considerable growth in this field.

Initial reports of SFAE synthesis by transesterification involved the use of some rather toxic solvents, such as DMF and DMP, at 90-95 ºC, for 9 to 12 hours, under 80-100 mmHg pressure and potassium carbonate as catalyst. The reported yield was 85 % for the sucrose monoester and 15 % for the diester, after purification (Osipow, Snell et al. 1956).

This process is known as the Hass-Snell process, developed in 1959 and due the use of toxic solvents is not approved for the use of SFAE in food technology as it yielded odorous products which contain toxic solvent residues (Osipow, Snell et al. 1956).

A classic chemical route to synthesize SFAE is under the so-called Mitsunobu conditions (Mitsunobu 1967; Molinier, Kouwer et al. 2006; Molinier, Kouwer et al. 2007). Mitsunobu reaction involves the condensation of an acidic pronucleophile (carboxylic acid) and an alcohol, promoted by triphenylphosphine (TPP) and diethyl azodicarboxylate (DEAD) (Laven and Stawinski 2009).

Molinier *et al* have reported several studies on the synthesis of sucrose monoesters via the Mitsunobu reaction. These studies reported the obtention of two sucrose monoesters isomers in the positions 6 and 6’, approximately 85 % and 15 %, respectively, after HPLC (Molinier, Kouwer et al. 2006) and also the obtention of sucrose diesters isomers in the positions 1’,6’, 1’,6 and 6,6’ (Molinier, Kouwer et al. 2007). This synthesis occurs at room temperature and DMF is using as solvent (Molinier, Kouwer et al. 2006; Molinier, Kouwer et al. 2007).

A study was performed using a catalytic amount of DMAP together with NaOH. This reaction was again faster and led to very good yields even in dilute solutions, although the tendency of polysubstitution upon increasing the sucrose concentration rises nearly as without DMAP. The yields were slightly improved with the decreasing of the reaction temperature (Thévenet, Wernicke et al. 1999).

Another synthesis of sucrose monoester was performed with heterogeneous catalysis in an environmentally friendly process, at low temperature using HMS-TBD (triazabicyclo[4.4.0]dec-5-ene – TBD – anchored in a functionalized silica). This catalyst leads to a selective esterification of sucrose with methyl dodecanoate, under nitrogen, at 110 ºC and DMSO as solvent. The selectivity is higher than 60 % in monoester, with more than 90 % yield, in an equimolar proportion. Using a four times excess of sucrose the selectivity in monoester increase to 90 %, with a similar yield (Kharchafi, Jerome et al. 2005).

SFAE was synthesized using sucrose octaacetate and FAME of vegetable oil by an ester-ester interchange reaction with a sodium metal catalyst, on a solvent-free process. High yields on SFAE were obtained with the reaction taking place during 2 hours, at 105 ºC and by applying a vacuum to reduced pressure of 5 mmHg (Akoh and Swanson 1990).

SFAE can be produced, in laboratory, via enzymatic synthesis in an organic media. These reactions are conducted under mild conditions, which minimize side reactions, especially lipases. Furthermore, enzymatic synthesis can also be performed in non-toxic solvents (Sabeder, Habulin et al. 2006).

The most interesting lipases are immobilized from *Candida antarctica* and *Rhizomucor miehei* (Sabeder, Habulin et al. 2006).

The yields achieved via enzymatic synthesis are low, yet. A study of production of sucrose ester monolaurate, using *Candida antarctica* and *Rhizomucor miehei*, and different solvents, such as 2-methyl-2-butanol, acetone and methyl ethyl ketone, have reported yields lower than 21 %, for both enzymes and using a temperature range of 50-70 ºC, which is the temperature that immobilized lipases are generally more active (Walsh, Bombyk et al. 2009).

During the esterification of sugar and fatty acid, water is generated and has to be removed from the mixture in order to increase the yield. This can be executed by several methods, such as evacuation in vacuum, using open tubes or even using molecular sieves (Sabeder, Habulin et al. 2006).

Recently, supercritical carbon dioxide has been investigated as a medium for enzymatic reactions. This medium accelerates the reaction rate, reduces mass transfer resistance and enable an easily separation of products and reactants. However, sugars have low solubility in pure supercritical carbon dioxide. Therefore, organic solvents expanded by supercritical carbon dioxide could become an alternative reaction media (Tai and Brunner 2009).

There have been reported several advantages of carbon dioxide expanded liquids (Tai and Brunner 2009):

- Abilities to alter the physical-chemical properties, such as viscosity and dielectric constant, of the solvent;
- Comparable or better product selectivity than in neat organic solvents or supercritical carbon dioxide;
- Milder process pressure compared to supercritical carbon dioxide;
- Increased reaction rates and turnover frequencies;
- Substantial replacement of organic solvents with dense-phase carbon dioxide.

Although, this is purely wishful thinking, and no yield reports are available so far.

1.1.2 – Market Overview

Surfactants are an important class of chemical products not only because their large variety of applications in household, industry and agriculture, but also bearing in mind the market volumes. In 2002, the worldwide production of surfactants amounted to 17-19 Mt. Thus, the expected future growth rates are 3-4 % per year globally, and 1.5-2 % in the EU (Font: BIOPRODUCTION document - SFAE Position Paper, 2006).

Despite of environmental impact, the majority of surfactants in the market are derived from petroleum. Thus, the industry is looking for new ways of producing surfactants from renewable raw materials. Biosurfactants produced by microorganisms and/or derived from renewable raw materials are under growing relevance.

However, current regulations do not give competitive advantage for biosurfactants versus petrochemical-based surfactants. Additional policies and measures could increase their market share above 40 % by 2010 (Font: BIOPRODUCTION document - SFAE Position Paper, 2006).

1.2 - Surface Active Materials

Surfactants are surface-active materials in which the chemical structure consists of a non-polar hydrophobic (or lyophobic) portion and a hydrophilic (or lyophilic) portion, example given, Figure 8 (Shaw 1992; Myers 1999; Tadros 2005). In SFAE's, the saccharides provides the hydrophilicity and fatty acid chain the hydrophobicity.

As surfactants possess lyophobic and lyophilic characteristics they are amphipathic molecules (Tadros 2005), which means that they have some affinity for two immiscible phases (Figure 9) (Myers 1999).

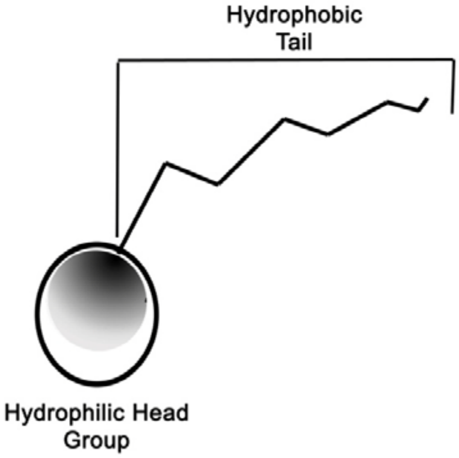

Figure 8 – Typical surface active material structure, showing hydrophilic and hydrophobic portions.

This kind of molecules has the ability to be adsorbed at interphases. The driving force for surfactant adsorption is the lowering of the free energy of the phase border (Shaw 1992; Myers 1999; Tadros 2005).

Adsorption of surfactant molecules at the interphase lowers the interfacial tension, so that the higher the surfactant adsorption the larger the reduction in interfacial tension. The degree of surfactant adsorption at the interface depends on surfactant structure and the nature of the two phases (Shaw 1992; Tadros 2005).

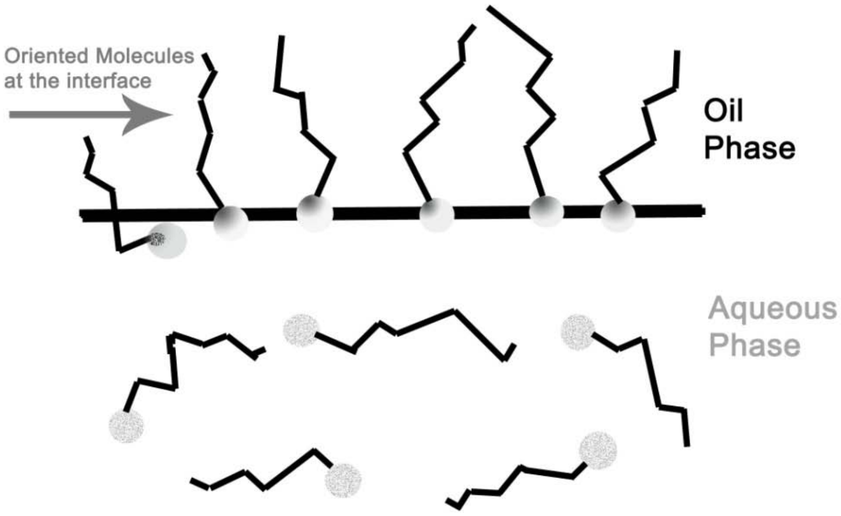

Figure 9 – The preferential orientation of high HLB surfactant molecules.

The interfacial tension, γ, that is, the interface free energy per unit area, which is the amount of work necessary to expand the interface, gives in mN.m^{-1} (Holmberg, Jönsson et al. 2002; Tadros 2005).

Surfactants also have the ability to aggregate in solution, forming micelles. The driving force for micellization is the reduction of contact between hydrocarbon chain and water, thus reducing the free energy of the system (Tadros 2005).

In the micelle, the hydrophobic groups are directed towards the interior of the aggregate and the hydrophilic head group is directed toward the solvent (Figure 10). Micelles are in a dynamic equilibrium and the rate of exchange between a surfactant molecule and the micelle depends on the structure of the surfactant molecule (Myers 1999; Holmberg, Jönsson et al. 2002; Tadros 2005).

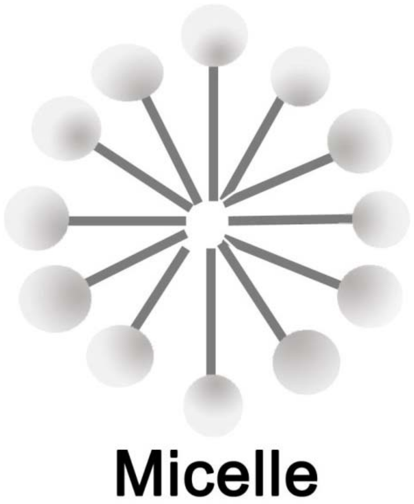

Figure 10 - Orientation of hydrophobic chains and hydrophilic heads.

1.2.1 – Classification of Surface Active Materials

Surfactants may be classified in several ways, depending on their application, physical characteristics, and chemical structure.

According to the application, surfactants may be classified as emulsifiers, foaming agents, wetting agents, and dispersants, and may also be classified according to some physical characteristics, such as the solubility in water or oil, or even its stability in severe environments. This classification does not specify the chemical nature of the surfactant, which calls for a classification according the chemical structure of the surfactant (Myers 1999; Holmberg, Jönsson et al. 2002).

A simple classification based on the nature of the hydrophilic group classify surfactants in four main classes: anionic, cationic, non-ionic, and zwitterionic (Tadros 2005).

1.2.1.1 – Anionic Surfactants

Anionic surfactants are used in industrial applications because they present relatively low cost manufacture, being the most widely used class of surfactants (Tadros 2005), constituting 70-75 % of worldwide surfactant consumption (Myers 2006).

In this class of surfactants the hydrophobic group it is a linear alkyl group, and the most commonly hydrophilic groups are carboxylates, sulphates, sulphonates and phosphates. A general formula could be (Tadros 2005):

Carboxylates	$C_nH_{2n+1}COO^-X$
Sulphates	$C_nH_{2n+1}OSO_3^-X$
Sulphonates	$C_nH_{2n+1}SO_3^-X$
Phosphates	$C_nH_{2n+1}OPO(OH)O^-X$

with “n” between 8 or 16 atoms and X as a counter ion, usually sodium.

Carboxylates, commercially known as soaps, are low cost and have low toxicity and ready biodegradability. Generally, commercial soaps have in the structures a mixture of fatty acids obtained from natural oils, such as coconut oil and palm oil (Tadros 2005). In the presence of hard water, containing bivalent ions such as Ca^{2+} and Mg^{2+}, soaps precipitate. This could be avoided with the modification of the carboxylates by introducing hydrophilic chains, which result in modified carboxylates, such as ethoxy carboxylates and ester carboxylates (Tadros 2005).

Sulphates are the largest and most important of these synthetic surfactants. In the past, those were produced by reaction of an alcohol and sulphuric acid, resulting esters of sulphuric acid. More recently, the sulphating methods consist in using mixtures of chlorosulphonic or sulphur dioxide with air, instead of sulphuric acid. To improve the solubility, sulphates are chemically modified by the reaction with ethylene oxide. Because of their chemical instability (hydrolyzing to the alcohol), they are now replaced by sulphonates, which are chemically more stable (Tadros 2005).

Sulphonates have the sulphur atom directly attached to a carbon atom of the alkyl group, providing the stability against hydrolysis. The most common of these surfactants are alkyl aryl sulphonates, for example, sodium alkyl benzene sulphonate. It is usual to achieve chemical modifications with the reaction of ethylene oxide, improving their solubility by the increase of HLB (Tadros 2005).

Phosphates, such as alkyl phosphates and alkyl ether phosphates, are produced by treating the fatty alcohol or alcohol ethoxylates with a phosphorylating agent, typically phosphorous pentoxide, P_4O_{10}, obtaining a mixture of mono- and di-esters of phosphoric acid. These surfactants are used in the metalworking industry due to their anticorrosive properties (Tadros 2005).

1.2.1.2 – Cationic Surfactants

Cationic surfactants are usually water soluble, specifically with only one long alkyl group, generally compatible with most inorganic ions and hard water, but they are incompatible with metasilicates, highly condensed phosphates and protein-like materials (Tadros 2005).

These surfactants are chemically stable, can tolerate electrolytes and stable to pH variations, both acid and alkaline, but are insoluble in hydrocarbon oils. They are incompatible with almost anionic surfactants, although, they are compatible with non-ionic compounds (Tadros 2005).

The most important classes of cationic surfactant are amine salts, quaternary ammonium compounds and amine oxides (Myers 2006). An example of a quaternary ammonium compound is dodecyl trimethyl ammonium chloride, $C_{12}H_{25}(CH_3)_3NCl$. It is common to modify chemically these cationics by reaction with ethylene oxide to further improve their water solubility (Tadros 2005).

Cationic surfactants have a tendency to adsorb when at negatively charged surfaces, and because of that, they are used as anticorrosive agents for steel, as flotation collectors for mineral ores, as dispersants for inorganic pigments, as bactericides and several other applications (Tadros 2005; Myers 2006).

1.2.1.3 – Non-ionic Surfactants

There are two important classes of non-ionic surfactants, those based on ethylene oxide, referred to as ethoxylated surfactants, and those with multi-hydroxyl groups (Tadros 2005).

The viscosity of a non-ionic surfactant solution increases gradually with an increase in its concentration, but at a critical concentration the viscosity increases rapidly and a gel-like structure appears due to the formation of a liquid crystalline structure, usually detected as the “cloud point” (Tadros 2005).

Several classes can be distinguished for ethoxylated surfactants (Tadros 2005):

- Alcohol ethoxylates;
- Alkyl phenol ethoxylates;
- Fatty acid ethoxylates;
- Mono-alkanolamide ethoxylates;
- Sorbitan ester ethoxylates;
- Fatty amine ethoxylates;
- Ethylene oxide - propylene oxide copolymers (very high HLB).

Glycol esters, glycerol and polyglycerol esters, glucosides and polyglucosides and even sucrose esters are examples of non-ionic surfactants with multi-hydroxyl functionality (Tadros 2005).

Alcohol ethoxylates; are generally produced by the ethoxylation of a fatty alcohol chain. A typical example is dodecyl hexaoxyethylene glycol mono-ether, having the chemical formula $C_{12}H_{25}O(CH_2CH_2O)_6OH$, sometimes abbreviated as $C_{12}E_6$. The solubility of alcohol ethoxylates depends both on the alkyl chain length and on the number of ethylene oxide units in the molecule (Tadros 2005).

Alkyl phenol ethoxylates are prepared by the reaction of ethylene oxide with the appropriate alkyl phenol. The most common alkyl phenol ethoxylates are those based on nonyl phenol. These surfactants are cheap to produce, but have a potential toxicity and are of difficult biodegradability. Thus, the by-product of degradation is nonyl phenol, which has a considerable toxicity. Nevertheless, it is still used, outside European Union, because of their advantageous properties, such as solubility in aqueous and non-aqueous media, good emulsification and dispersion properties (Tadros 2005).

Fatty acid ethoxylates are produced by the reaction of ethylene oxide with a fatty acid and presents the following general formula $RCOO\text{-}(CH_2CH_2O)_nH$. These surfactants are generally soluble in water, but needs enough ethylene oxide units and the alkyl chain length of the acid not too long. They are compatible with aqueous ions. Although, these surfactants suffers hydrolysis in highly alkaline solutions (Tadros 2005).

Sorbitan esters are produced by reacting sorbitol with a fatty acid at a high temperature (> 200 ºC). First sorbitol dehydrates to 1,4-sorbitan and then esterification occurs, producing a mixture of mono-, di- and tri-esters, with a low HLB number. This surfactant is referred as *Spans*, an *Atlas* commercial trade name (later on used by *ICI*). Sorbitan esters are unsoluble in water, but are soluble in most organic solvents, and have been used in cosmetic and pharmaceutical applications (Tadros 2005).

There is a surfactant family derivative from sorbitan ester, which is produced by the reaction of ethylene oxide on a hydroxyl group remaining on the Sorbitan ester. This surfactant family is commercially known as *Tweens*, presenting solubility in water and high HLB number. As an alternative, the sorbitol can be first ethoxylated and then esterified. However, this product presents different properties then *Tweens* (Tadros 2005).

Natural fats and oils, such as castor oil, have been ethoxylated, producing solubilizers for pharmaceutical applications (Tadros 2005).

Amine ethoxylates are produced by the reaction of ethylene oxide with a primary or secondary fatty amine. When it has low ethylene oxide content and if the pH is acid, these surfactants acquire a cationic character. Furthermore, they are not soluble in water, but are soluble in acid solutions. Thus, at high pH theses surfactants become soluble in water. At neutral pH and high ethylene oxide content they act very similarly to non-ionics (Tadros 2005).

Ethylene oxide – propylene oxide copolymers (EO/PO), also known as polymeric surfactants, are commercialized under various trade names, such as *Pluronics* (*Wyandotte*) and *Synperonic PE* (*ICI*). There are two types: those prepared reacting polyoxypropylene glycol (difunctional) with ethylene oxide or mixed EO/PO, giving the following structure $(EO)_n(PO)_m(EO)_n$; and those prepared reacting polyethylene glycol (difunctional) with PO or mixed EO/PO, giving the following structure $(PO)_n(EO)_m(PO)_n$ (Tadros 2005).

Many surfactants derived from mono- or polysaccharides have been synthesized by reacting with the hydroxyl groups, namely esterification of sucrose with fatty acids, giving SFAE. In this reaction, the challenge is to graft the hydrophobic group to the hydrophilic structure. Another sugar surfactant it is alkyl polyglucosides, which is produced by the reaction of a fatty alcohol with glucose. These classes of surfactants are environmental friendly, because they are sensitive to biodegradation and the main raw materials are provided from renewable resources (Tadros 2005).

1.2.1.4 – Zwitterionic Surfactants

Zwitterionic surfactants containing, or have the potential to form, both cationic and anionic surfactants under specific conditions, and for that, presents an amphoteric character (Myers 2006).

The principal classes of these surfactants are (Myers 2006):

- Imidazoline derivatives;
- Betaines and Sulfobetaines;
- Phosphatides.

These surfactants are very dependent on the pH of the solution, in which they are dissolved. In fact, in acid pH the molecule acquires a positive charge and act as a cationic surfactant, whereas in alkaline pH the molecule become negatively charged and act as an anionic surfactant. There is a specific pH value that both ionic groups show equal ionization, this is the isoelectric point of the molecule (Tadros 2005).

These surfactants are usually soluble in water, reaching a minimum of solubility at the isoelectric point; exhibit a great compatibility with other surfactants, forming mixed micelles; they are chemically stable in all pH range (Tadros 2005).

Their properties, such as wetting, detergency, foaming, and others, are affected by changes in pH, in which way, that at the isoelectric point the properties of zwitterionic surfactant are similar to those of non-ionics. Below and above the isoelectric point the properties shift towards those of cationic and anionic surfactants, respectively (Tadros 2005).

Zwitterionic surfactants exhibit excellent dermatological properties. In fact, they are frequently used in cosmetics - shampoos and other personal care products (Tadros 2005).

1.2.2 – Surfactant in the Environment

1.2.2.1 – Biodegradability

The use of surfactants is currently growing, raising up the problems of surfactant disposal as a very important aspect. The ecosystem has the ability to absorb and degrade waste products, but human population generates more waste products than the ecosystem can degrade.

Surfactants have a major impact on groundwater. Even though it may be technologically possible to remove all residual surfactants from effluent steams, the economic costs are totally unacceptable. To solve this problem biosurfactants can be a major choice, instead of classical surfactants, allowing the nature to take its course by natural biodegradation mechanisms. If biodegradation doesn’t occur, the surfactant is stable and persists for rather long time in the environment (Holmberg, Jönsson et al. 2002; Tadros 2005).

Biodegradation can be defined as the elimination or destruction of chemicals through the biological activity of living organisms in nature (Holmberg, Jönsson et al. 2002; Tadros 2005; Myers 2006). Concerning surfactants, biodegradation can be divided into two categories:

1. Primary degradation – the elimination of any surface-active properties by the modification of the chemical structure;
2. Ultimate degradation – the material is completely removed from the environment as byproducts (carbon dioxide, water, inorganic salts, or other materials) as a result of the biological activity.

The rate of biodegradation of the surfactants depends on several variables, which are: surfactant concentration, pH and temperature. The surfactant structure has the biggest influence on the rate of biodegradation (Tadros 2005).

1.2.2.2 – Rules for Biodegradation

After extensive research it was proposed that the nature of the hydrophobic group determined its relative susceptibility to biological action, whereas the nature and mode of attachment of the hydrophilic group has minor significance (Holmberg, Jönsson et al. 2002; Myers 2006).

With this purpose, the following general rules for biodegradation were developed (Holmberg, Jönsson et al. 2002; Myers 2006):

1. The chemical structure of the hydrophobic group is the primary factor to control biodegradability (high degrees of substitution, especially at the alkyl terminus, inhibit biodegradation);
2. The nature of the hydrophilic group has a minor effect on biodegradability;
3. The greater the distance between the hydrophilic group and the terminus of the hydrophobe, the greater the rate of primary degradation.

1.2.3 – Technological Future

Surfactants have been used at least for 2300 years. The alkali metal soaps were used as article trade by the Phoenicians as early as 600 B.C., and were also used by the Romans. The first synthetic surfactant was developed in Germany during World War I, and since then surfactant consumption has increased continuously (Myers 2006). Thus, actually, surfactants constitute a consolidated class of industrial chemicals at expansion.

Some classes of surfactants have a large potential for growth. An example is non-ionic surfactants, which possess characteristics, such as good performance at lower temperatures, low foaming, and relative stability at high temperatures and under severe chemical conditions, that are advantageous for many technological applications (Myers 2006).

Soaps are a particular case because of their special characteristics, and their consumption levels are expected to maintain due to population growth (Myers 2006).

The large diversity of lyophobic and lyophilic groups and the development of new raw-materials sources provides an exceptionally list of choices to select a surface active material for a specific need. However, there will always be the need for new and improved surfactants, conferring a potential for research and development (Myers 2006).

Next, some ideas to surfactant use and possible growth potential are presented (Myers 2006):

- Multifunctional surfactants (for example, detergent and fabric softener in one structure);
- More ecologically acceptable chemical structures;
- New surfactants based on renewable raw-materials;
- Highly biocompatible surfactants;
- Materials that allow energy savings on their manufacture or functionality at lower temperatures.

1.3 – Surfactants in Emulsion Formation and Stabilization

Emulsions are a class of disperse systems consisting of two immiscible liquids, in other words, one liquid phase very well dispersed in another liquid phase which is immiscible with the first. Moreover, to disperse these two immiscible phases one needs a third component, the emulsifier (Tadros 2005).

There are three classes which may be distinguished: oil-in-water (O/W), water-in-oil (W/O) and oil-in-oil (O/O). Thus, emulsions may be classified according to the nature of the emulsifier or the structure of the system (Tadros 2005). This classification is presented in Table 2.

Table 2 - Classification of emulsion types.

Nature of emulsifier	Structure of the system
Simple molecules and ions	Nature of internal and external phases
Non-ionic surfactants	O/W, W/O
Ionic surfactants	Micellar emulsions
Surfactants mixtures	Microemulsions
Non-ionic polymers	Macroemulsions
Polyelectrolytes	Bilayer droplets
Mixed polymers and surfactants	Double and multiple emulsions
Liquid crystalline phases	Mixed emulsions

Emulsions are used in several applications in industry, such as (Goodwin 2004; Tadros 2005):

- Food emulsion – mayonnaise, salad creams, deserts;
- Personal care and cosmetics – hand creams, lotions, hair sprays, sunscreens;
- Agrochemicals – self-emulsifiable oils which produce emulsions on dilution with water, emulsion concentrates and crop oil sprays;
- Pharmaceuticals – anaesthetics of O/W emulsions, liquid emulsions, double and multiple emulsions;
- Paints – emulsions of alkyd resins, latex emulsions;
- Dry cleaning formulations – water droplets emulsified in the dry cleaning oil;
- Bitumen emulsions – stable in the containers but when applied to the road chippings they coalesce to form a film of bitumen;
- Emulsions in the oil industry – to remove water droplets contained in the crude oil;
- Oil stick dispersions – emulsification of oils spilled from tankers;
- Emulsification of unwanted oil – pollution control.

1.3.1 – Thermodynamics of Emulsion Formation and Breakdown

Throughout the emulsification process the interface has a large expansion due to the free energy variation. This change in free energy comprises two terms: a surface energy term and an entropy of dispersion term (Goodwin 2004; Tadros 2005). Thus, both terms are positive. From the second law of thermodynamics:

$$AG = \Delta A\gamma_{12} - T\Delta S \qquad \text{(Eq. 1)}$$

where γ_{12} refers to the interfacial tension of liquid 1 versus liquid 2.

In most cases, $\Delta A\gamma_{12} >> T\Delta S$, which means that emulsion formation is non-spontaneous and the system is thermodynamically unstable. Moreover, emulsions will breakdown if there are no other stabilization mechanism. In the presence of a surfactant (stabilizer) an energy barrier is created between the droplets and the system becomes kinetically stable (Tadros 2005).

1.3.2 – Mechanism of Emulsification

Emulsification is a dynamic process which needs oil, water, surfactant and energy. Since γ is positive, the energy required to expand the interface is large and positive. Moreover, the entropy of dispersion, $T\Delta S$, cannot compensate the energy term (Goodwin 2004; Tadros 2005; Myers 2006).

Given that the emulsion formation is non-spontaneous, to produce the droplets, energy is necessary. The formation of large droplets for macro-emulsions is easy in contrast with the formation of small droplets (nano-emulsions), which are difficult to produce and requires a large amount of surfactant and/or energy (Goodwin 2004; Tadros 2005).

Several processes may occur during emulsification, such as break up of droplets, adsorption of surfactants, droplet collision which lead to coalescence and droplet collision with no coalescence (Goodwin 2004; Tadros 2005). These processes are evincing in Figure 11.

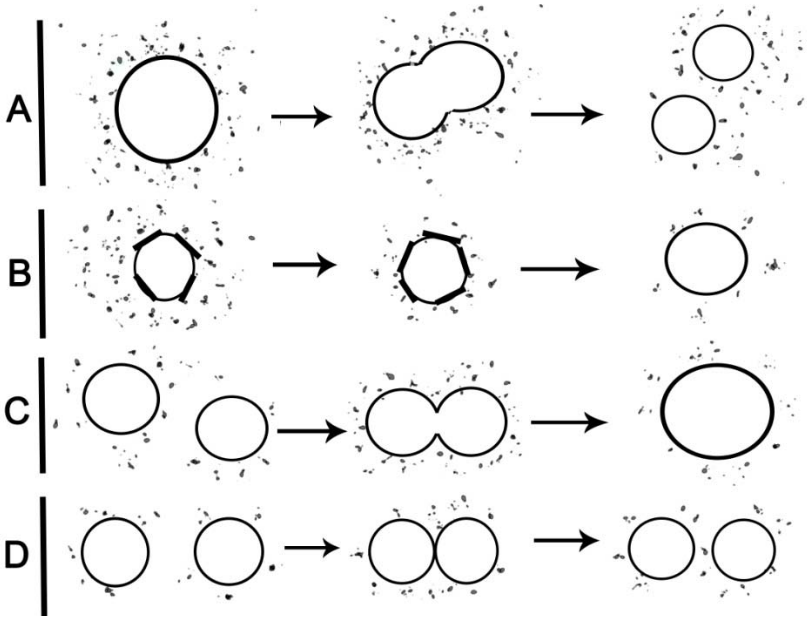

Figure 11 – Schematic of the various processes occurring during the emulsion formation: a) break up of droplet; b) adsorption of surfactants; c) droplets collision which lead to coalescence; d) droplets collision with no coalescence. Drops are represented by thin lines and the surfactants by heavy lines and dots.

To describe emulsion formation two main factors are to be considered: hydrodynamics and interfacial science. To estimate emulsion formation it is usual to measure the droplet size distribution, for example, with laser diffraction techniques, a useful average diameter, d:

$$d_{nm} = \left(\frac{S_m}{S_n} \right)^{1/(n-m)} \qquad \text{(Eq. 2)}$$

An alternative description of emulsion quality uses the specific surface area, A:

$$A = \pi s^2 = \frac{6\phi}{d_{32}} \qquad \text{(Eq. 3)}$$

1.3.3 – Surfactants in Emulsification

Surfactants play a major role in the formation of emulsions, lowering the interfacial tension and causing a reduction in the droplet size. Surfactants prevent coalescence of recently formed drops (Tadros 2005).

The amount of surfactant necessary to produce the smallest drop size will depend on its activity, a, in the bulk, which determines the reduction in interfacial tension, as given by the Gibbs adsorption equation (Goodwin 2004; Tadros 2005):

$$-d\gamma = RT\Gamma d\ln(a) \qquad \text{(Eq. 4)}$$

where R is the gas constant, T is the absolute temperature and Γ is the surface excess (number of moles adsorbed per unit area of the interface).

Surfactants also play major roles in deformation and break-up of droplets, allowing the existence of interfacial tension gradients, which is crucial for the formation of stable droplets (Goodwin 2004; Tadros 2005; Myers 2006).

In the absence of surfactants the interface is not capable of endure a tangential stress. Thus, the liquid motion is continuous. The presence of surfactants during emulsification has two consequences (Goodwin 2004; Tadros 2005):

1. Affect the equilibrium shape of the drop;
2. Formation of γ gradients, which slow down the motion of the liquid inside the drop and reducing the amount of energy needed to deform and break-up the drop.

Emulsifiers prevent coalescence during emulsification due to the formation of γ gradients, which is formed when the liquid flow out from the thin layer between two drops (pushed together), inducing a γ gradient (Tadros 2005).

1.3.4 – Hydrophilic-Lipophilic Balance

The hydrophilic-lipophilic balance (HLB) is a concept first introduced by Griffin in 1949 (Griffin 1949; Guo, Rong et al. 2006), which is a semi-empirical scale based on the relative percentage of hydrophilic to Lipophilic groups in the surfactant molecules (Griffin 1949; Goodwin 2004; Tadros 2005). Thus, the HLB's range varies between 0 to 20, meaning that the minimum value is the most lipophilic and the maximum value is the most hydrophilic (Tadros 2005; Myers 2006).

Furthermore, HLB is one of the most widely used indicators of a surfactant suitability for a given application (Tadros 2005; Guo, Rong et al. 2006). Table 3 summarizes HLB rages and their application.

Table 3 – Surfactant HLB and their applications (Tadros 2005).

Application	HLB range
W/O emulsifier	3 – 6
Wetting agent	7 – 9
O/W emulsifier	8 – 18
Detergent	13 – 15
Solubilizer	15 – 18

Actually, there are a large number of works to relate HLB value with various characteristics of a surfactant, which allow the development of reproducible techniques to determine HLB value experimentally or computationally (Guo, Rong et al. 2006).

There are several equations that allow calculating the HLB value of surfactant mixtures. The average HLB number is given by:

$$HLB = x_1 HLB_1 + x_2 HLB_2 \qquad \text{(Eq. 5)}$$

where x_1 and x_2 are the weight fractions of the two surfactants HLB_1 and HLB_2 (Goodwin 2004; Tadros 2005).

Griffin developed simple equations to determine the HLB value of relatively simple non-ionic surfactants (Tadros 2005). For example, Eq. 6 is used to determine the HLB value of polyhydroxy fatty acid ester, where S is the saponification number of the ester and A is the acid number.

$$HLB = 20\left(1 - \frac{S}{A}\right) \qquad \text{(Eq. 6)}$$

Davies devised a method for calculating the HLB number from surfactants chemical formulae, using empirically determined group numbers (Tadros 2005). For Davies, the HLB value is an additive and constitutive indicator and the group numbers are assigned to various structural elements (Guo, Rong et al. 2006). Thus, the HLB value is given by:

$$HLB = 7 + \sum\left(hydrophilic\,group\,numbers\right) - \sum\left(lipophilic\,group\,numbers\right) \qquad \text{(Eq. 7)}$$

Table 4 - Hydrophilic group numbers for Davies method.

Groups	Davies
SO_4Na^+	38.7
COOK	21.1
COONa	19.1
SO_3Na	11
N (tertiary amine)	9.4
Ester (free)	2.4
COOH	2.1
OH (free)	1.9
O (Ether)	1.3
CH_2CH_2O	0.33
OH (sorbitan ring)	0.5
Ester (sorbitan ring)	6.8

Table 5 - Lipophilic group numbers for Davies method.

Groups	Davies
CH	0.475
CH_2	0.475
CH_3	0.475
CF_2	0.87
CF_3	0.87
Phenyl	1.662
CH_2-CH_2-CH_2-O	0.15
$CH(CH_3)$-CH_2-O	0.15
CH_2-$CH(CH_3)$-O	0.15

1.3.5 – Relative Solubility number

The relative solubility number (RSN) has been used in surfactant industry to assist formulation, quality control and product selection. Thus, RSN is useful in the selection of stabilizers and demulsifiers (Wu, Xu et al. 2004).

RSN value is empirically defined as the volume in milliliters of distilled water necessary to produce persistent turbidity in a benzene/dioxane solvent system consisting of 1 gram of surfactant sample and 30 milliliters of solvent, determined by titration (Wu, Xu et al. 2004).

However, the standard RSN method uses a toxic solvent system. So it has been developed a new procedure for determination of RSN using less-toxic solvents, such as toluene and ethylene glycol dimethyl ether (EGDE) (Wu, Xu et al. 2004).

This method is a practical alternative to the HLB method of estimation hydrophilic-lipophilic balance of surfactants. In fact, it was found that RSN values determined at certain molar concentration, within the same surfactant family, showed a good linear relationship with classic HLB values. Wu *et al* established an empirical relationship between RSN and HLB, given by:

$$HLB = A \times RSN + B \qquad \text{(Eq. 8)}$$

where A and B are empirical constants varying with surfactant family, depending on characteristics of the hydrophilic and lipophilic groups (Wu, Xu et al. 2004).

HLB can be determined by experimentation and calculated from simple equations. However, the experimental determination of the HLB value is complicated and subjective; the applicability of these equations is limited and in many industrial applications it is difficult to obtain sufficient structural information to allow the calculation. Furthermore, the RSN procedure may be applied in day-to-day industrial operations with low time consumption. Therefore, the RSN measurement is often the chosen method in both industry and research (Wu, Xu et al. 2004).

Like HLB, higher RSN numbers indicate a more water-soluble surfactant and lower numbers indicate a more oil-soluble surfactant. Moreover, surfactants with RSN < 13 are generally insoluble in water, surfactants with RSN value between 13 and 17 are dispersible in water at low concentrations and form gels at high concentrations, and surfactants with RSN > 17 are usually soluble in water (Wu, Xu et al. 2004).

2 – Experimental

2.1 – Synthesis of SFAE

2.1.1 – Raw Materials

The following raw materials were used in the production of the SFAE:

i. Sucrose

A commercial sample of sucrose, derived from sugar cane, was kindly offered by DAI, which come from the lot number 07082/18:16.

Some important properties of this pure sucrose are:

- Molecular weight = 342.3 $g.mol^{-1}$
- Volumetric mass = 1.587 $g.cm^{-3}$
- Melting point = 186 ºC

ii. Glucose

The sample of D-glucose used in this work was kindly shared by Rui Galhano, and was purchased from VWR, with the product number 1.04074.1000 (VWR catalog). This sample has a grade of 99 % and a molecular weight of 180.16 $g.mol^{-1}$.

iii. Molasses

The sample of molasses (sugar cane) used in this work was kindly offered by DAI. Typically, sugar cane molasses has the following composition (weight):

- Sucrose: 47.1 %
- Glucose: 9.0 %
- Fructose: 12.8 %
- Moisture: 19.5 %
- Ash: 11.6 %

iv. Acetic Anhydride

The used acetic anhydride was from *Panreac*, ACS grade (99 % purity), from lot number 0000034127.

Some important properties of acetic anhydride are:

- Molecular weight = 102.09 g.mol^{-1}
- Volumetric mass = 1.08 g.cm^{-3}
- Melting point = 139.8 ºC

v. FAME

Two different samples of FAME were used, one obtained from rapeseed oil and the other from coconut oil, which typical acid compositions are presented on Table 1.

Both FAME samples were produced inside of the research group using the methanolysis method and sodium methoxide as catalyst (*vide* Appendix I). These samples were purified by washing with water and an aqueous acid solution (0.01 M), and then centrifuged. The water content of these samples was analyzed by Karl Fisher method, which reveals a maximum content of residual moisture of 400 ppm.

vi. Lauric Acid

The sample of lauric acid was gently offered by *Companhia Industrial de Resinas Sintéticas, CIRES, S.A.*, with 99 % purity.

vii. Sodium Acetate

Used as catalyst in the first step, sodium acetate was produced inside the research group reacting sodium hydroxide with acetic acid in excess. The purification was carried out in the rotary evaporator applying reduced pressure to remove water and acetic acid, obtaining a white powder as final product.

viii. Lanthanide Triflates

Three lanthanide triflates were tested, scandium, praseodymium and gadolinium, as showed in the following table.

Table 6 - Lanthanide triflates tested and their properties (Font: Merck).

Lanthanide	***Product Number***	***Assay** (%)*	***MW** (g.mol^{-1})*
Sc	418218	99	492.16
Pr	425702	98	588.11
Gd	425176	98	604.46

ix. Titanium (IV) Isopropoxide

From *Merck*, this catalyst has 98 % purity, 284.25 g.mol^{-1} molecular weight, and a specific weight of 0.96 g.cm^{-3}.

x. DABCO

This catalyst was kindly offered by CPB, in the crystalline form, over 99 % purity.

xi. Imidazole

This catalyst was kindly offered by CPB, over 99 % purity.

2.1.2 – Experimental Apparatus

An experimental set-up was designed for the synthesis of SFAE as shown in Figure 12.

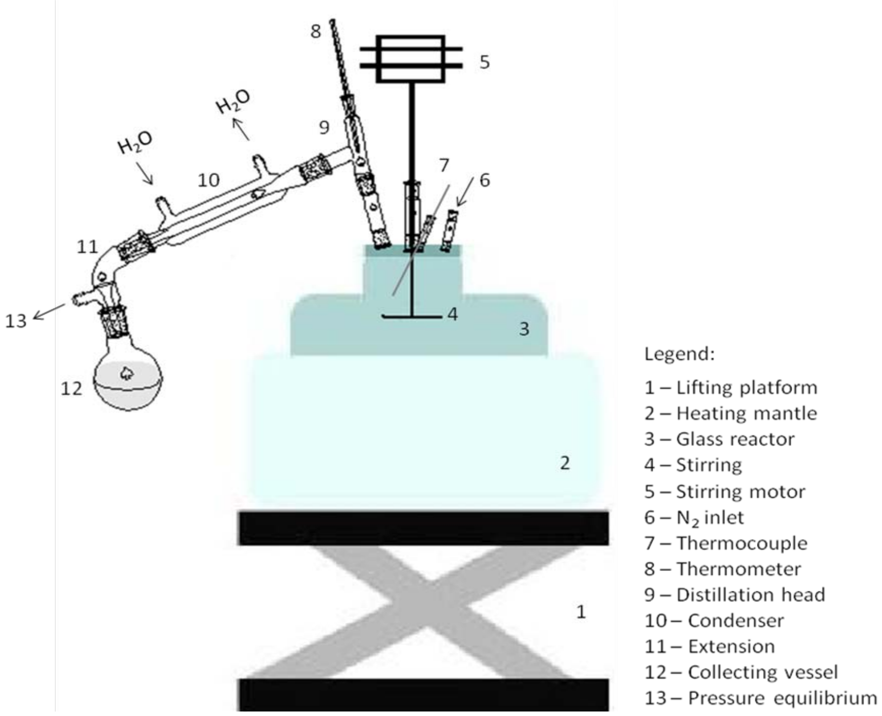

Figure 12 - Experimental apparatus for the synthesis of SFAE.

In the first step, the acetylation step, there is no need to use the distillation arm connected to the reactor, therefore the distillation arm was only linked to the reactor after the acetylation step, keeping on the rest of the experimental set-up.

2.1.3 – Reaction Design Plan

The synthesis of SFAE was achieved in two steps: acetylation of sucrose with acetic anhydride; and transesterification of acetylated sucrose with FAME.

In the first step, the amount of acetic anhydride used correspond to the total acetylation of all hydroxyl groups, that sucrose becomes octa-acetylated and glucose becomes penta-acetylated, with an excess of 20 % of acetic anhydride. Sodium acetate was used in a catalytic amount of 0.01 (mole fraction).

This reaction occurs at atmospheric pressure, under inert atmosphere with an inlet of N_2 to minimize the inlet of moisture, temperature below 75 ºC and strong stirring (300 rpm for solid sugars and 500 rpm for molasses).

Before the entrance of sucrose or glucose in the reactor, they have to be micromized in order to reduce the particle’s size and so increase the superficial area accessible to react. Molasses has to be slowly added to the reactor, once this acetylation reaction is exothermal and occur in a liquid phase, which promote a close contact between the molasses with acetic anhydride and strongly rises the reaction temperature, and also due to the hydrolysis of the excess of acetic anhydride.

The reaction time depends on the amount of sugar in the reactor and their particle size. For example, a batch with 30 g of powdered sucrose, the first step is prolonged for 8 hours. The reaction progress was controlled by TLC, using 0.5 mm silica gel plates 60 F254 (*Merck*) and $CH_3COCH_3/CH_3COOC_2H_5/H_2O/CH_3COOH$ (15:30:2:1) as developing system. The TLC revelation was carried out with an alcoholic solution of sulfuric acid (10 %, in volume) and applying heat. When the TLC revealed the disappearance of sucrose or D-glucose bands the reaction was considered complete.

In the second step, a distillation arm is connected to the reactor, as described in the Figure 12, and then FAME is added to the mixture that has resulted from the first step. Two different stoichiometric proportions were tested, 4:1 and 1.1:1 of FAME and sucrose or glucose, and both revealed promising results.

For this step the temperature inside the reactor is to be kept below 80 ºC and when the temperature reaches the value of 65 ºC the catalyst for transesterification is added and reduced pressure is applied to the system. The N_2 tip inlet is immersed into the mixture in order to remove volatile by-products, with the stirring as stronger as possible, typically 500 rpm.

Different catalysts were tried, but only with lanthanide triflates the results revealed a significant better performance. The lanthanide triflates tested were scandium triflate, praseodymium triflate and gadolinium triflate, and 0.5 % (molar) was enough to catalyze these reactions.

Since the reaction begins a condensate appears in the top of the distillation arm, being collected in a vessel at the end of distillation arm (Figure 12). At this point, the thermometer at the top of the distillation arm displays 36 ºC.

The terminus of this reaction is reached when the condensation of the volatile by-product stops, even with the increase of N_2 flow and increase of temperature to 90 ºC. For the biggest batch, using 200 g of sugar, 600 g of acetic anhydride and 250 g of FAME, approximately, in a 2 L reactor, this reaction runs for 5 hours.

2.2 – Characterization of SFAE

To carry out FTIR and NMR experiments the product was purified in the rotary evaporator in order to remove the acetic anhydride in excess, as well as formed acetic acid and residual moisture.

2.2.1 – FTIR

Fourier transform infrared spectroscopy (FTIR) was used to characterize the SFAE and the raw-materials by the identification of the main molecular structural groups. FTIR (ATR mode) was performed in Nexus equipment from *Thermo-Nicolet* using a Smart MIRacle ^{TM} ATR (Attenuated Total Reflection) accessory, from Pike Technologies, with a ZnSe single reflection ATR heated plate. The experiment was conducted with a resolution of 4 cm^{-1}, 128 scans, and measured in the range of 4000-600 cm^{-1}.

2.2.2 NMR

All proton (^{1}H) and carbon (^{13}C) spectra traces were performed with a *Brucker* 400 MHz instrument. COSY and HSQC experiments were done according to the *Brucker* operations manual and techniques (Derome 1990; Nakanishi 1990).

The spectra of the substituted glucose were acquired from a solution in DMSO-d_6 (20 mg of product dissolved in 1 mL of solvent) prepared in a 5 mm tube, using a frequency of 400 MHz for ^{1}H and 100 MHz for ^{13}C. The probe was used at room temperature, and the spectras were acquired using 16, 30, 90 and 5000 scans (^{1}H, COSY, HSQC and ^{13}C, respectively) of a sequence with a 9.8 and 10.0 µs excitation pulse (^{1}H, COSY and HSQC, and ^{13}C, respectively), a delay of 1.00 s, 1.50 s and 2.00 s (respectively ^{1}H, COSY and HSQC, and ^{13}C), and 0.16 s, 0.31 s, 1.85 s and 3.98 s acquisition time (respectively, HSQC, COSY, ^{13}C, and ^{1}H) (100 µs broadband proton decoupling).

2.2.3 – Emulsification: Preliminary Tests

The emulsification tests were carried out in glass tubes using distilled water and vegetable oil. Thus, two kinds of emulsification were made, W/O and O/W, using 9 mL of vegetable oil with 1 mL of water and 9 mL of water with 1 mL of vegetable oil, respectively. After the introduction of the two phases, a couple of SFAE drops were added into the tubes which was then strong shacked. Lastly, it was measured the time that emulsions stay stable.

This procedure is summarized in the following figure:

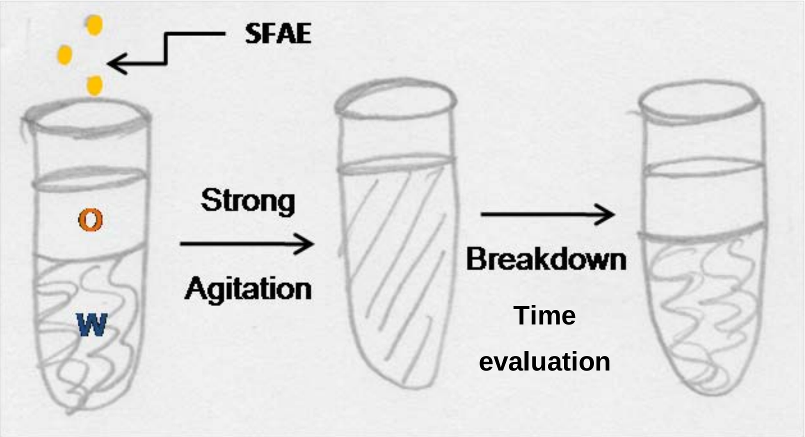

Figure 13 – Schematic of emulsification test, pointing the formation and the breakdown steps.

2.3 – Optimization of the Production Process

The production process was continuously improved in order to satisfy the technical specifications recommended from BIOPRODUCTION project for SFAE, such as:

- Critical Micellar Concentration lower than 100ppm;
- Able to reduce the surface tension of water below 35 mN/m;
- Cost target: < 1.3€/kg as 100% active;
- Ability to precisely control the number of C16-18 or C12-14 alkyl chains grafted per sucrose molecule, target is 2-3 alkyl chains per head group;
- Not producing dark colored products as those would negatively impact the finished-product color.

Some adjustments in the molar ratio of sucrose and FAME in the reactant mixture were performed considering the required specifications, particularly in the number of alkyl chains grafted per head group. The use of different sugars, such as sucrose, glucose and molasses, envisages the diversification of SFAE applications and the cost reduction, especially with the molasses, which are the less expensive of all.

Other adjustments were developed for in order to reduce the production time, such as, N_2 flow, stirring, reduce pressure and effective rate of volatile products removal.

As showed in Figure 7, the transesterification is an equilibrium reaction which can be extended to the formation of more products by removing the volatile by-product. This can be demonstrated by the following kinetic equation:

$$\frac{d[(R_2COOR)]}{dt} = k.[R_1COOR].[R_2OH] \qquad \text{(Eq. 9)}$$

where k is the kinetic constant for the transesterification; $[R_1COOR]$ and $[R_2OH]$ are the concentration of the antecedent ester and volatile by-product, respectively.

Moreover, $[R_1COOR]$ and $[R_2OH]$ are not independent due to equilibrium, as represented by the following equation:

$$K_c = \frac{[R_2COOR].[R_1OH]}{[R_1COOR].[R_2OH]} \quad \text{(Eq. 10)}$$

where K_c is the equilibrium constant. Therefore, the equilibrium can only be extended to the formation of more products, SFAE, with the continuously removal of the formed volatile by-product, particularly for low concentrations of $[R_1COOR]$ and $[R_2OH]$, where the reverse reaction tends to dominate.

3 – Results and Discussion

3.1 – Characterization of Raw-Materials

The raw-materials (sucrose, glucose, molasses, acetic anhydride, FAME and lauric acid) were only characterized by FTIR. For the interpretation of the FTIR spectra a data base for frequencies was used (Coates 2000).

3.1.1 – Sucrose

A sample of sucrose was analyzed by FTIR and the obtained infrared spectrum is presented in the Appendix II (Figure 26), where the narrow band at 3560 cm^{-1} corresponds to the stretching frequencies of O-H and the broad band at 3384 cm^{-1} and 3329 cm^{-1} corresponds to normal “polymeric” stretching frequencies of O-H. At 2941 cm^{-1} and 2912 cm^{-1}, were identified C-H stretching bands of methylene, respectively asymmetric and symmetric bands. Methylene C-H bending band was identified at 1429 cm^{-1}. The band at 1344 cm^{-1} and 1322 cm^{-1} can be associated with O-H bending in-plane, primary and secondary alcohol, respectively. C-O stretching bands from alkyl substituted ether, secondary alcohol, cyclic ether and primary alcohol were identified at 1126 cm^{-1}, 1115 cm^{-1}, 1066 cm^{-1} and 1051 cm^{-1}, respectively. The band at 989 cm^{-1} was identified as related to cyclic structure vibrations.

3.1.2 – Glucose

The FTIR spectrum of glucose is presented in the Appendix II (Figure 27), where the broad band at 3359 cm^{-1} corresponds to O-H stretching of normal “polymeric” frequencies. C-H stretching bands of methylene were indentified at 2943 cm^{-1} and 2912 cm^{-1}, respectively asymmetric and symmetric bands. Methylene C-H bending band was identified at 1430 cm^{-1}. The bands at 1340cm^{-1} and 1223 cm^{-1}, were identified as O-H bending in-plane of primary and secondary alcohols, respectively. C-O stretching bands from alkyl substituted ether, secondary alcohol, cyclic ether and primary alcohol were identified at 1146 cm^{-1}, 1111 cm^{-1}, 1049 cm^{-1} and 1022 cm^{-1}, respectively. The band at 995 cm^{-1} was identified as related to cyclic structure vibrations.

3.1.3 – Molasses

A sample of sugar cane molasses was analyzed by FTIR and the obtained infrared spectrum is presented in the Appendix II (Figure 28), where the broad band at 3315 cm^{-1} corresponds to stretching frequencies of O-H (primary and secondary) and some moist. C-H stretching bands were indentified at 2943 cm^{-1} and 2897 cm^{-1}, respectively asymmetric and symmetric bands. At 1403 cm^{-1} and 1338 cm^{-1} were identified C-H bending frequencies, methyl and methylene, respectively. C-O stretching bands from cyclic ether and primary alcohol, and alkyl substituted ether and secondary alcohol, were identified at 1111 cm^{-1} and 1045 cm^{-1}, respectively. The band at 991 cm^{-1} was identified as related to cyclic structure vibrations. The broad band in the region lower than 900 cm^{-1} can be associated with inorganic compounds that characteristic of the ash.

3.1.4 – Acetic Anhydride

The FTIR spectrum of acetic anhydride is presented in the Appendix II (Figure 29), where the bands at 1822 cm^{-1} and 1751 cm^{-1} corresponds to a open-chain acid anhydride. At 1429 cm^{-}1 and 1367 cm^{-1}, were identified as asymmetric and symmetric C-H methyl bending, respectively. The band at 1113 cm^{-1} was associated to C-O stretching.

3.1.5 – FAME

A sample of FAME from rapeseed oil was analyzed by FTIR and the obtained infrared spectrum is presented in the Appendix II (Figure 30). In this spectrum, the following bands where indentified: C-H stretching at 2928 cm^{-1} and 2859 cm^{-1}, asymmetric and symmetric vibrations, respectively; an ester band at 1747 cm^{-1}; C-H bending vibrations at 1462 cm^{-1}, 1438 cm^{-1} and 1366 cm^{-1} characteristics of asymmetric methyl, asymmetric methylene and symmetric methyl, respectively; and $(CH_2)_n$ rocking vibrations at 723 cm^{-1}. Were also identified bands associated with C=C bonds, namely C-H stretching at 3010 cm^{-1} and C-H bending out-of-plane at 1010 cm^{-1}.

3.1.6 – Lauric Acid

The FTIR spectrum of lauric acid is presented in the Appendix II (Figure 31), where the bands at 2953 cm^{-1}, 2914 cm^{-1}, 2870 cm^{-1} and 2848 cm^{-1}, were identified as C-H stretching of methyl asymmetric, methylene asymmetric, methyl symmetric and methylene symmetric, respectively. At 1697 cm^{-1}, was identified a carboxylic acid band. Methyl and methylene C-H bending vibrations were identified at 1470 cm^{-1} and 1429 cm^{-1}, respectively. C-O stretching and O-H out-of-plane frequencies were identified at 1302 cm^{-1} and 935 cm^{-1}, respectively. Were also identified a band associated with $(CH_2)_n$ rocking vibrations at 721 cm^{-1}.

3.2 – Characterization of SFAE

For the SFAE characterization some techniques where used, namely:

- FTIR
- NMR
- Calculation of the HLB number
- Preliminary test of emulsification

The results obtained from BIOPRODUCTION project partners are also mentioned in this point.

3.2.1 – FTIR

The presented FTIR spectra of the SFAE result from the different raw-materials tested in this work.

Figure 14 shows the FTIR spectrum of the SFAE obtained from sucrose and rapeseed FAME (1:4), where the band at 3008 cm^{-1} corresponds to the stretching frequencies of C-H in the carbon atoms with double bonds. C-H stretching bands were indentified at 2924 cm^{-1} and 2854 cm^{-1}, respectively, asymmetric and symmetric. An ester band was identified at 1741 cm^{-1}. At 1462 cm^{-1}, 1435 cm^{-1} and 1367 cm^{-1}, were identified C-H bending bands, methyl and methylene asymmetric and methyl symmetric, respectively. C-O stretching and cyclic ether stretching bands were identified at 1224 cm^{-1} and 1171 cm^{-1}, respectively. The band at 1020 cm^{-1} was associated with the vibrations of the cyclic structure. At 895 cm^{-1} and 723 cm^{-1}, were identified C-H bending out-of-plane band and $(CH_2)_n$ rocking vibrations, respectively.

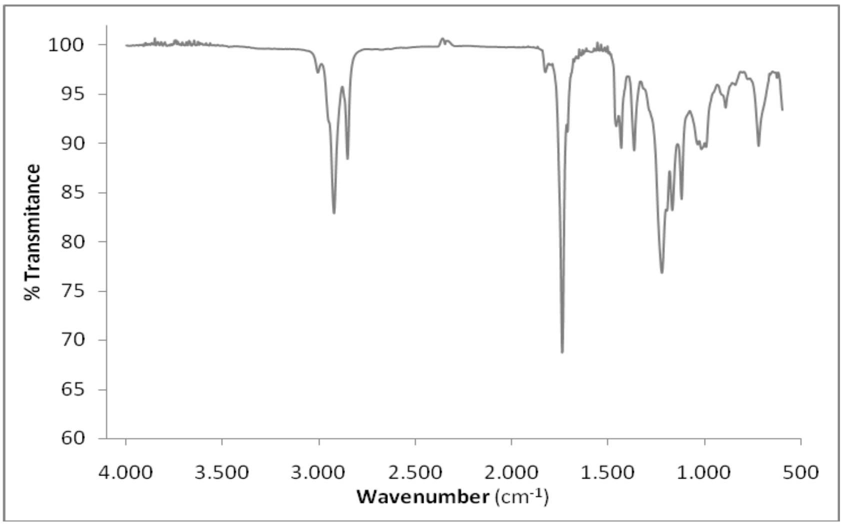

Figure 14 - FTIR spectra of SFAE from sucrose and FAME (4 FAME : 1 sucrose) using ATR method.

The FTIR spectrum obtained from the synthesis of SFAE from molasses and rapeseed FAME (1:4) is presented in the Figure 15, where the band at 3008 cm^{-1} corresponds to stretching frequencies of C-H in the carbon atoms with double bonds. C-H stretching bands were indentified at 2924 cm^{-1} and 2854 cm^{-1}, respectively, asymmetric and symmetric. At 1741 cm^{-1}, an ester band was identified. The bands at 1458 cm^{-1}, 1437 cm^{-1} and 1367 cm^{-1} were identified as C-H bending, methyl and methylene asymmetric and methyl symmetric, respectively. C-O stretching and cyclic ether stretching bands were identified at 1227 cm^{-1} and 1171 cm^{-1}, respectively. The band at 1018 cm^{-1} was associated with the vibrations of the cyclic structure. At 881 cm^{-1} and 723 cm^{-1}, were identified C-H bending out-of-plane band and $(CH_2)_n$ rocking vibrations, respectively.

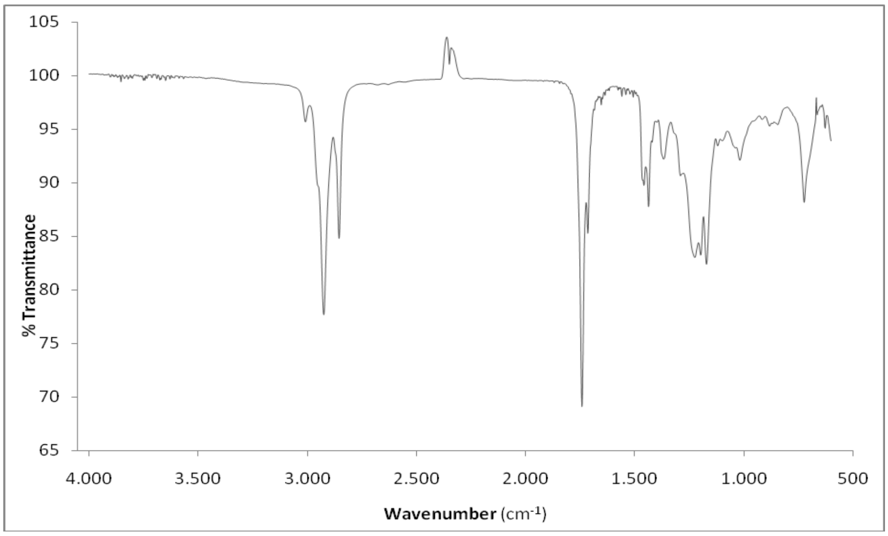

Figure 15 - FTIR spectra of SFAE from molasses and FAME (4 FAME : 1 sugar) using ATR method.

The FTIR spectrum obtained from the synthesis of SFAE from molasses and rapeseed FAME (1:1) is presented in Figure 16, where the band at 3008 cm^{-1} corresponds to the stretching frequencies of C-H in the carbon atoms with double bonds. C-H stretching bands were indentified at 2924 cm^{-1} and 2854 cm^{-1}, respectively, asymmetric and symmetric. At 1741 cm^{-1}, an ester band was identified. The bands at 1463 cm^{-1}, 1445 cm^{-1} and 1367 cm^{-1} were identified as C-H bending, methyl and methylene asymmetric and methyl symmetric, respectively. C-O stretching and cyclic ether stretching bands were identified at 1200 cm^{-1} and 1171 cm^{-1}, respectively. The band at 1019 cm^{-1} was associated with the vibrations of the cyclic structure. At 843 cm^{-1} and 723 cm^{-1}, were identified C-H bending out-of-plane band and $(CH_2)_n$ rocking vibrations, respectively.

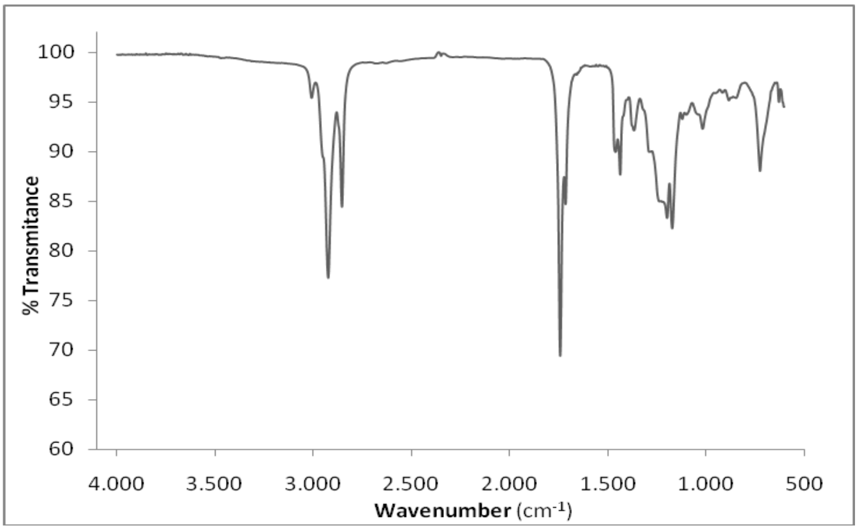

Figure 16 - FTIR spectra of SFAE from molasses and FAME (1 FAME : 1 sugar) using ATR method.

Figure 17 shows the FTIR spectrum of the SFAE obtained from glucose and lauric acid (1:1), where the bands at 2924 cm^{-1} and 2854 cm^{-1} correspond to the stretching frequencies of C-H, respectively asymmetric and symmetric vibrations. An ester band was identified at 1741 cm^{-1}. At 1433 cm^{-1} and 1372 cm^{-1}, were identified C-H bending bands, asymmetric and symmetric, respectively. C-O stretching and cyclic ether stretching bands were identified at 1224 cm^{-1} and 1129 cm^{-1}, respectively. The band at 1029 cm^{-1} was associated with the vibrations of the cyclic structure. At and 723 cm^{-1}, was identified $(CH_2)_n$ rocking vibrations.

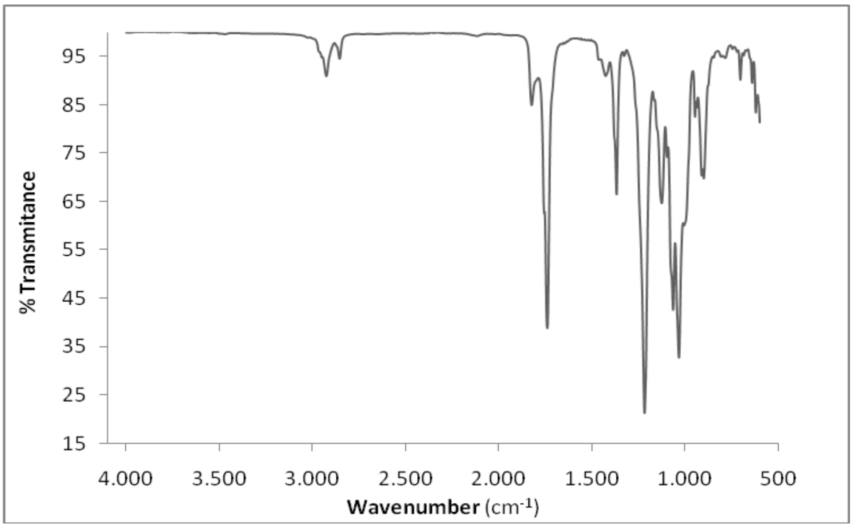

Figure 17 - FTIR spectra of SFAE from glucose and lauric acid (1 lauric acid : 1 glucose) using ATR method.

These four SFAE samples show a strong signal in the ester band, as expected. The different hydrophilic groups (glucose, sucrose and molasses) tested confers small deflections in some bands, namely, in the C-H bending, between the spectras, and substantial differences that allows to identify their origin.

As expected, the FTIR spectra of SFAE from rapeseed FAME exhibit unsaturations in the alkyl chains. Moreover, in the FTIR spectra of SFAE from lauric acid there are no bands associated with unsaturations. Furthermore, the small deflections and the difference in the signals strength of C-H bands between the spectras from FAME and lauric acid results from the difference in the length of the alkyl chains, C16 and C12, respectively.

3.2.2 – NMR

The proton NMR spectrum of the GFAE (Figure 32 and 33 – Appendix III) presented considerable difficulty in interpretation. The chemical shifts obtained from ^{1}H-NMR, using the conventional proton numbering, were: H1 (4.93); H2 (5.44); H3 (4.98); H4 (4.20); H5 (7.25); H6-a (4.02) and H6-b (4.18 ppm).

The obtained chemical shifts of carbon ^{13}C-NMR (Figures 34 and 35 – Appendix III) were the expected, 20.05 ppm for CH_3 and 13.52 ppm, 21.62 ppm, 23.09 ppm, 28.65 ppm and 30.88 ppm for CH_2, presented in the hydrophobic group (alkyl chain derivative from lauric acid), and 20.93 ppm and 21.62 ppm, respectively α and β, for CH_3 derivative from acetic acid. These results were consistent with the molecular structure of the product, namely the different chemical shifts obtained for the CH_2 presented in the alkyl group. For example, the maximum value obtained (30.88 ppm) corresponds to the CH_2 near the carbonyl group, thus the higher chemical shift.

COSY experiments allowed to indentify the connectivity for H1 to H2, H2 to H3, H3 to H4, H4 to H5. HSQC experiments allowed to indentify the connectivity for C1 to H1 (90.80 ppm), C2 to H2 (69.98 ppm), C3 to H3 (71.74 ppm), C4 to H4 (67.62 ppm), C5 to H5 (71.40 ppm) and C6 to H6 (61.42 ppm). These spectra are presented in Figures 36 and 37 (Appendix III), respectively.

These values were the expected, being consistent with the molecular structure of the product.

After peaks integration (^{1}H-NMR), presented in Figures 32 and 33 and identified with a green dash, it can be said that the proportion of α and β glucose was 1:2.27, and the sample presents the follow DE: 1.06 of lauric acid and 2.92 of acetic acid. Knowing that each glucose molecule has 5 OH groups, these results reveal that 1.02 of the OH remain free. This result was the expected, with the obtention of a DE approximately 1 (the aimed value), and demonstrate that 10 % excess of lauric acid was adequate. Although, it was expected that more hydroxyl groups has been substituted by acetyl groups, obtaining a lower value of free OH, 0.5 at most.

These NMR experiments did not allow to conclude on the exact structure of the product, that is, where the lauric acid was grafted in the glucose molecule. For that, other NMR experiments should be performed, such as HMBC (Heteronuclear Multiple Bond Correlation).

3.2.3 – HLB Number

The HLB numbers presented were not determined experimentally, but calculated using the Davies method, given by Eq. 7, with the following group contributions:

Table 7 – Values of group contribution for the Davies method used in the calculation of the SFAE HLB.

	Groups	***Value***
Lipophilic	CH CH_2 CH_3	0.475
Hydrophilic	Ester	2.4
	Ether	1.3
	OH	1.9

3.2.3.1 – Sucrose Fatty Acid Esters

In these calculation of SFAE, the hydrophilic components of the molecule are three ether groups and eight ester groups (hepta-acetyl + mono-FAE; hexa-acetyl + di-FAE; penta-acetyl + tri-FAE), for all examples. The lipophilic components of these SFAE molecules are: CH, CH_2 and CH_3. Furthermore, the number of the CH_2 groups contribution vary with the alkyl chain length, once all the examples are octa-esters, as shown in Tables 9 and 10.

Table 8 – Lipophilic components contribution for the SFAE from the coconut FAME, for different DE

	Mono	**Di**	**Tri**
CH	8	8	8
CH_2	13	23	33
CH_3	8	8	8

Table 9 - Lipophilic components contribution for the SFAE from the rapeseed FAME, for different DE.

	Mono-ester	**Di-ester**	**Tri-ester**
CH	8	8	8

CH_2	19	35	51
CH_3	8	8	8

The obtained values for SFAE from sucrose and FAME are presented in Table 11. The alkyl chain length used for these calculation was determined from a fatty acid distribution in the rapeseed oil and coconut oil, which values are 18 carbon atoms and 12 carbon atoms, respectively (Nelson 2003).

Table 10 - HLB values determined for SFAE from sucrose and FAME in different esterification degrees.

Degree of Esterification	Rapeseed	Coconut
Mono-ester	13.48	16.33
Di-ester	5.88	11.58
Tri-ester	-1.73	6.83

These were the expected values for the SFAE from sucrose and FAME derivative from rapeseed oil and coconut oil, revealing the HLB number variation with the DE and with the alkyl chain length.

Although, was obtained a negative value for the tri-ester from rapeseed FAME, which is apparently unreasonable. The HLB scale only admits positive values. So, Davies method and its values of group contribution cannot be applied for all surfactants, being unsuitable for non-ionic surfactants, such as SFAE, in extreme cases (Guo, Rong et al. 2006).

The HLB number varied with the DE, being the higher for mono-esters SFAE and the lower for tri-ester SFAE, in other words, the HLB number has decrease with the raise of DE. The alkyl chain length has a significant influence in the HLB number, with the results revealing, for the same degree of esterification, that the SFAE from rapeseed FAME has lower values than SFAE from coconut FAME. Then, the increase of alkyl chain length diminishes the HLB number, for the same esterification degree.

The maximum HLB value was mono-ester SFAE from coconut FAME, with 16.33, and the minimum HLB number was tri-ester SFAE from rapeseed FAME, with 1.13. The maximum HLB number expected for SFAE is the octa-acetyl sucrose, which corresponds to the maximum DE (8) and the minimum alkyl chain length, CH_3, and calculated as follows:

$$HLB_{octa-acetyl\ sucrose} = 7 + 8\times(ester) + 3\times(ether) + 8\times(CH) + 3\times(CH_2) + 8\times(CH_3) = 21{,}08$$

These examples of SFAE may be applied according to the surfactant HLB range and their applications, presented in the Table 3. Some of the possible applications are summarized in the Table 12.

Table 11 – Possible applications for the examples of Sucrose Fatty Acid Esters.

Degree of Esterification	Rapeseed	Coconut
Mono-ester	Detergent; O/W emulsifier	Solubilizer; O/W emulsifier
Di-ester	Wetting agent; O/W emulsifier	O/W emulsifier
Tri-ester	W/O emulsifier	Wetting agent; W/O emulsifier

3.2.3.2 – Glucose Fatty Acid Esters

In this calculation of GFAE, the hydrophilic components of the molecule are: one ether group and five ester groups (tetra-acetyl + mono-FAE), for all examples. The lipophilic components of these GFAE molecules are: CH, CH_2 and CH_3. As well in the SFAE, the number of the CH_2 contributions varies with the alkyl chain length, as shown in Table 13.

Table 12 - Lipophilic components contribution for the Glucose mono-FAE, for rapeseed and coconut FAME.

	Rapeseed	Coconut
CH	5	5
CH_2	17	11
CH_3	5	5

The values obtained for the HLB of glucose mono-FAE are presented in the following table.

Table 13 - HLB values for Glucose mono-FAE, for rapeseed and coconut FAME.

	HLB
Rapeseed	7.48
Coconut	10.33

As well as in the SFAE, the results revealed the influence of the alkyl chain length in the HLB number of the GFAE. As we can see, the HLB number is lower for the rapeseed FAME, which has a higher alkyl chain length then coconut FAME (18 carbon atoms against 12 carbon atoms). So, GFAE obtained from rapeseed FAME are less hydrophilic then GFAE obtained from coconut FAME.

Some of the possible applications for these two examples of GFAE are: wetting agent and O/W emulsifier, for rapeseed GFAE; and O/W emulsifier, for coconut GFAE. These possible applications are in accord to the surfactant HLB range and their applications, presented in Table 3.

The maximum HLB number expected for GFAE is the pent-acetyl glucose, which corresponds to the maximum degree of esterification, 5, and the minimum alkyl chain length, CH_3, and calculated as follows:

$$HLB_{penta-acetyl\ glu\cos e} = 7 + 5\times(ester) + 1\times(ether) + 5\times(CH) + 1\times(CH_2) + 5\times(CH_3) = 15{,}08$$

3.2.3.3 – SFAE *versus* GFAE

Comparing the HLB values for SFAE and GFAE, for the same conditions, the results revealed that with sucrose the final product was more hydrophilicity then with glucose. Taking the example of mono-FAE, the obtained HLB values are higher for sucrose then for glucose, which confers a higher hydrophilicity. These results are summarized in the following table.

Table 14 – Comparative HLB results for Sucrose and Glucose mono-FAE from rapeseed and coconut FAME.

	Rapeseed	***Coconut***
SFAE	13.48	16.33
GFAE	7.48	10.33

As can be seen, the difference between SFAE and GFAE, for the same FAME (rapeseed or coconut), is always 6 HLB units. The fact of sucrose being a disaccharide and glucose being a monosaccharide contributes for this difference. Moreover, sucrose has two more ether bounds then glucose (in particular the glycosidical linkage through their anomeric carbon atoms), which contribution for HLB is 2.6. Furthermore, sucrose has three more ester groups then glucose, which contribution is 7.2 for HLB, and has more three CH_3, two CH_2 and five CH then glucose, which contribution is -3,8. The sum of these contributions makes the 6 HLB units of difference.

This difference of 6 HLB units it is also observable between the octa-acetyl sucrose and penta-acetyl glucose, both in the maximum DE. Octa-acetyl sucrose has a HLB of 21.08 and penta-acetyl glucose has a HLB of 15.08.

3.2.4 – Emulsification: Preliminary Tests

The emulsification preliminary tests were performed to provide, in an easy way, the behavior of the synthesized products as W/O or O/W emulsifiers, this is, if the emulsions created with the SFAE were stable in W/O or O/W emulsions.

The emulsions stability was measured in a period of time, considering that an emulsion is stable when these periods were larger than 30 minutes. Unstable emulsions hold up only a few seconds. The results can be found in Table 16.

Table 15 - Emulsification behavior of the synthesized SFAE; variation with the stoichiometry.

Sugar	***DE***	***Emulsion***
Sucrose	3	W/O
Glucose	1	W/O
Molasses	3	W/O
Molasses	1	O/W

These results were the expected and in agreement with the HLB calculation presented in the previous point (3.2.3). As can be seen, the DE influences the behavior of the SFAE, such as the nature of the sugar.

For the same sugar, for example molasses, the results reveal that for higher DE (for example 3) the correspondent SFAE are a W/O emulsifier, and for lower DE (for example 1) the correspondent SFAE are an O/W emulsifier. These results are in agreement with the HLB calculation, presented previously, which reveals the influence of DE in the product application. Moreover, for higher DE lower the HLB number, being the correspondent SFAE suitable for W/O emulsions, and for lower DE the HLB number is higher, being the correspondent SFAE suitable for O/W emulsions.

In Figure 18, two emulsions are presented, on the left a W/O emulsion and on the right an O/W emulsion, using the same SFAE – from sucrose and rapeseed FAME, with a DE of 3.

Figure 18 - W/O and O/W emulsions using SFAE from sucrose and rapeseed FAME, with a DE of 3.

As can be seen, the stable emulsion was the left one, in other words, the W/O emulsion, which confirms that SFAE with a DE of 3 can be used as W/O emulsions, remaining stable for more than an hour.

The product synthesized from glucose and lauric acid does not behave as a good O/W emulsifier, as can be seen in Figure 19, despite of being a mono-ester. The emulsion on the left is a W/O emulsion, and on the right an O/W emulsion.

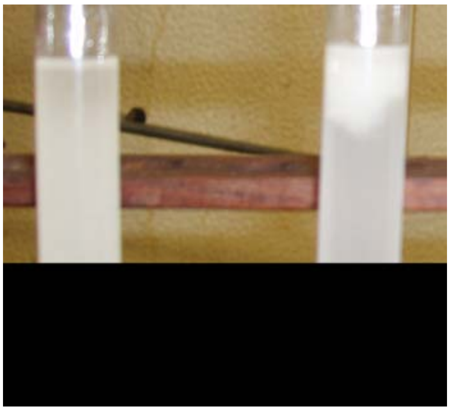

Figure 19 - W/O and O/W emulsions using SFAE from glucose and lauric acid, with a DE of 1.

This result was not in agreement with the HLB calculation for GFAE, which the HLB of 10.33 indicate a possible application as O/W emulsifier. The NMR experiments revealed a DE of 1 in, which gives a HLB of 10.33. As shown in Table 3, the HLB range to an O/W emulsifier is 8-18, where the value of 10.33 is included.

The laurate have not been further purified and some unconverted raw material can probably be the cause for a behavior different from the expected.

3.2.5 – Preliminary Tests by some of the BIOPRODUCTION Partners

A partner of this IP – BIOPRODUCTION – which tested some samples produced during this work was Ciba (UK).

One of the supplied samples (SFAE from sucrose and rapeseed FAME, with a DE of 3) was tested for their suitability as stabilizer in O/W emulsion preparation using a 100g/L of the insecticide cypermethrin. This preparation seemed oily and continuing the test becomes clear that the stabilizer was not working, with the resultant emulsion resembled curdled milk.

Afterwards, a W/O preparation was tried obtaining an acceptable emulsion, with a higher particle size than a normal 100 g/L cypermethrin would be (1.43 microns as opposed to 0.8 microns). The particle size graph is presented in Appendix IV (Figure 37).

Therefore, the emulsion was put on storage for two weeks at room temperature, at 54 ºC and in the fridge (about 5 ºC). After two weeks storage, the particle size were determined again and no growth was observed for any of the storage samples, and all the storage samples had slight settlements. The particle size graphs for these samples (two weeks at room temperature, at 54 ºC and at 5 ºC storage) are presented in Appendix IV (Figures 38, 39, 40).

Another partner, *P&G*, has informed, in a BIOPRODUCTIOM meeting, the successful use of the supplied sample in a preliminary test of detergency in a washing machine test process.

3.3 – Synthesis of the SFAE

In order to obtain a successful synthesis of the SFAE, different pathways were tested without good results. These pathways are summarized as follows.

In the first synthesis a solvent free synthesis of the SFAE was tried using pulverized sucrose and FAME, with the stoichiometry of four moles of FAME per mole of sucrose. The catalyst, titanium (IV) isopropoxide, was added (1% w/w) to the reactor after the temperature, inside the reactor, reached 80 ºC. This mixture was strongly stirred to promote a good contact between the molecules to react.

Methanol was expected as by-product, which would indicate the transesterification occurrence. As this did not happen, the temperature was gradually increased until the sucrose caramelizes at 140 ºC, approximately, and the N_2 flow was increased, as well as the stirring. Then, the reaction was stopped and a sample was gathered for a preliminary emulsification test, which confirmed the failure of this attempt, not obtaining a stable emulsion.

From this first attempt, it was clear the need of solvent in this reaction, once the antagonistic nature of sucrose and FAME molecules does not permit sucrose to dissolve in FAME. Thus, several solvents were tested to dissolve sucrose and FAME, being DMSO the chosen, despite its high boiling temperature. Only three solvents can well dissolve sucrose, H_2O, DMSO and DMF. Water cannot be used in this reaction as it hydrolyzes SFAE.

Furthermore, to improve the SFAE synthesis other catalysts were tested, such as imidazole and DABCO, and reduced pressure applied to promote the methanol removal. None of these catalysts proved efficient reaction.

The second synthesis was carried out like the first one, using pulverized sucrose and FAME (1:4), but this time with a solvent, DMSO. The catalyst used was imidazole (1 % w/w), added to the reactor when the temperature, inside the reactor, has reached 80 ºC. Once more, methanol was not obtained until sucrose caramelizes, at 150 ºC, approximately. The preliminary emulsification test confirmed the failure of this attempt, not obtaining a stable emulsion.

This attempt reveals that DMSO has low capacity to dissolve both sucrose and FAME, with the separation of the two phases after stop the stirring. Increase the amount of solvent may improve, but more solvent has to be removed, increasing the production cost. It was also thought the use of a co-solvent to dissolve both sucrose and FAME, such as ionic liquids, however they are expensive.

The ionic liquids act not only as solvents, but also as catalysts – phase transfer catalysis (PTC) – being environmental friendly, promoting reactions between immiscible reagents, increasing reaction rates, product selectivity and decreasing the energy consumption (Cai, Yi et al. 2009).

A third synthesis was tried using again sucrose and FAME (1:4), and DMSO as solvent. In this attempt, another catalyst was tested, crystalline DABCO, but likewise the two other syntheses, no methanol was recovered, even with the increase of temperature until the sucrose caramelizes, approximately at 150 ºC. Being so, a new alternative have been thought, a two step synthesis.

In this new pathway, the first step consisted in the total acetylation of sucrose (or glucose or molasses) and a second step, the transesterification (or ester-ester exchange) of the octa-acetyl sucrose with the FAME. This pathway is summarized in Figures 20 and 21.

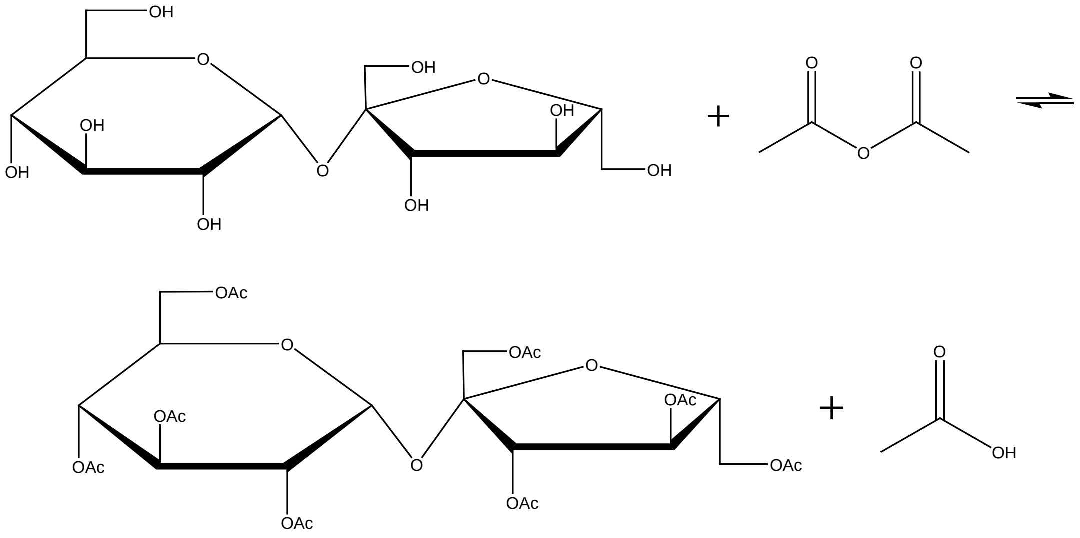

Figure 20 - First step: octa-acetylation of the sucrose.

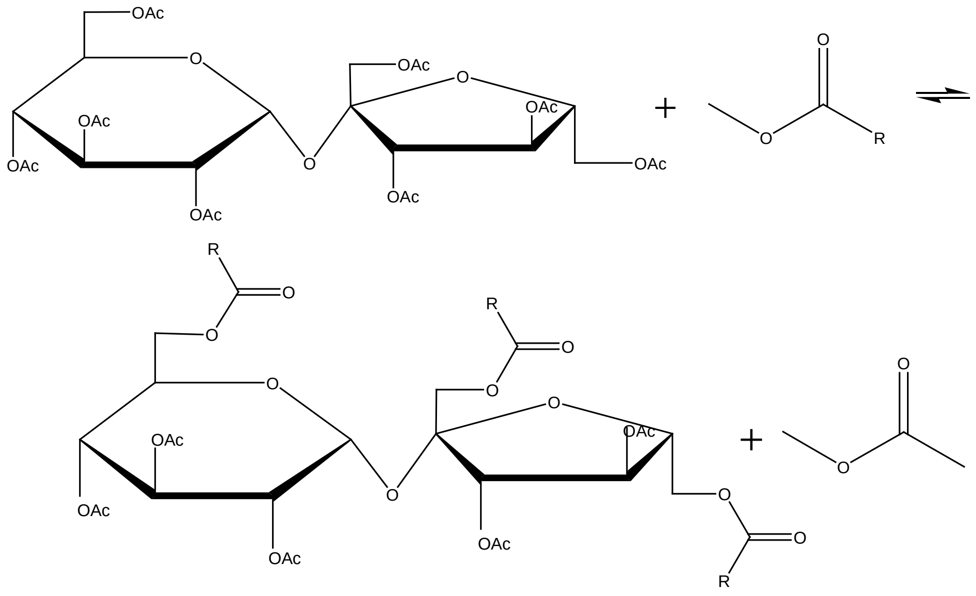

Figure 21 - Second step: transesterification of the octa-acetyl sucrose with FAME (R indicates an alkyl group).

The fourth synthesis was carried out by using this two steps methodology. In the first step, sucrose was octa-acetylated with acetic anhydride, in 20 % excess, using sodium acetate as catalyst, at 70 ºC. As alternative, it was also thought using pyridine or DMAP, but these compounds are toxic and the final product could not be applied to food and cosmetics without a complete removal, which raises the production cost.

In the second step, octa-acetyl sucrose react with rapeseed FAME (1:4), at 80 ºC, applying reduce pressure and using scandium triflate as catalyst (1 %, weight). A volatile by-product was recovered at a temperature of 40 ºC, approximately, in the head of the distillation arm. This temperature matches the boiling point of the azeotrope formed by methanol and methyl acetate, which is 36.7 ºC at 52.87 kPa, with the molar fraction of 0,6986 (Gmehling and Bolts 1996). At atmospheric pressure the boiling point of this azeotrope is 54 ºC with a mass fraction of 0.81 (Smallwood 1996).

The product of this synthesis was tested as an emulsifier in a preliminary test of emulsification, with the obtention of a stable W/O emulsion. This result demonstrates that this synthesis process was promising.

In the following syntheses other lanthanide triflates were tested, namely praseodymium and gadolinium triflate, different saccharides, such as glucose and sugar cane molasses, lauric acid and FAME from coconut oil, and also different DE, which allowed to obtain different products for several applications. The emulsification preliminary tests were promising, demonstrating that the produced SFAE can be applied as emulsifiers.

SFAE produced using molasses is less expensive, but the final product has intense color, which does not satisfy the requisite of not producing a dark color product.

The first syntheses were carried out in 1 L capacity reactors. Then, a scale-up to 4 L reactors was made, with success. This is a promising result that allows to foreseen a successful scale-up to a pilot scale, but more optimization studies must be done.

III – Synthesis of Functionalized Methacrylates (Preliminary Tests)

1 – Introduction

1.1 – Methacrylic Ester Polymers

Methacrylic ester monomers are a versatile group of monomers whose chemical properties are determined by the nature of the side-chain group, R, in the molecular structure (Mark 2004), which is the following:

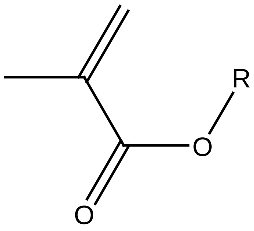

Figure 22 - Molecular structure of a methacrylic ester. R represents a side-chain group.

The physical and chemical properties of the polymer also depend on the R group, the molecular weight and the tacticity of the polymer (Mark 2004).

The difference between the methacrylic monomers and acrylic monomers is the methyl group in the α position of the vinyl group, which gives stability, hardness and stiffness to the polymers formed from methacrylic ester monomers (Barbour 2000; Mark 2004).

Methacrylic esters monomers can be copolymerized with either methacrylic or acrylic esters monomers to form a greater variety of acrylic copolymers. Moreover, this ability to form copolymers among these two monomers allows the creation of polymers with a great range of properties, from tacky adhesives to hard powders and rigid sheets (Lovell and El-Aasser 1997; Barbour 2000; Mark 2004).

1.1.1 – Production

The most common production process of commercial methacrylic ester polymers is by free-radical initiators, such as peroxides and azo compounds. Photoinitiation and radiation-induced are alternatives for this polymerization. The polymerization of methacrylic monomers is highly exothermic, involves an increase in the density of the forming polymeric material and produce, mainly, atactic polymers, due to the symmetric nature of the radical species (Lovell and El-Aasser 1997; Barbour 2000; Mark 2004).

At constant temperature, there is a first-order dependence of the polymerization rate on monomer concentration and a one-half-order dependence on initiator concentration (Matyjaszewski and Davis 2002; Mark 2004).

Other production process is bulk polymerization, which is used primarily for the production of cast sheets of PMMA. Three main types of bulk polymerization are practiced commercially: batch cell casting, continuous casting, and continuous bulk (Mark 2004).

In this polymerization an auto-acceleration, known as the *Trommsdorf* or gel effect, is observed at 20-50 % conversion, approximately. This phenomena is attributable to an increase in viscosity as the monomer is converted to polymer. Once the viscosity reaches the critical point, the termination begins to slow down below the rate of propagation. Therefore, the overall rate of polymerization increases, as well as the rate of heat generated from the reactor. (Mark 2004).

The molecular weight of the product formed after the gel-effect point is higher than the product formed previously, due to the slowing in termination. Moreover, the molecular weight is limited only by the diffusion of monomer to the growing radical chain end (Mark 2004).

1.1.2 – Properties

1.1.2.1 – Glass-transition temperature

Glass transition often takes place over a large range of temperatures and is manifested in a polymeric material as an embrittlement when expose to a range from high to low temperatures (Barbour 2000; Mark 2004).

Methacrylic ester polymers are relatively soft and flexible, as rubbery materials, above the T_g, and hard and brittle, as glass-like materials, below the T_g (Mark 2004).

The T_g of a given type of polymers is affected by tacticity of the polymer backbone. Moreover, T_g decrease in the follow order: syndiotactic > atactic > isotactic (Barbour 2000; Mark 2004).

There are a variety of techniques to measure the T_g, such as differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA). These two methods are currently the most commonly accepted (Barbour 2000; Mark 2004).

1.1.2.2 – Chemical Properties

Comparatively, methacrylic ester polymers have more chemical resistance than the methacrylic esters, which are less susceptible to hydrolysis than acrylic ester polymers (Mark 2004).

There are significant differences in the chemical resistance of different forms of PMMA. The syndiotactic form of PMMA is the most chemically inert, with the hydrolysis rate for syndiotactic PMMA lower than for isotactic. Radical polymerization form more syndiotactic PMMA, which benefits the stability (Mark 2004).

Chemical species which will degrade PMMA include lower esters (ethyl acetate, isopropyl acetate), aromatic hydrocarbons (benzene, toluene, xylene, phenols), cresol, carbolic acid, aryl halides (chlorobenzene, bromobenzene), aliphatic acids (butyric acid, acetic acid), alkyl polyhalides (ethylene dichloride, methylene chloride), high concentrations of alcohols (methanol, ethanol, 2-propanol), and high concentrations of alkalies and oxidizing agents (Mark 2004).

1.2 Free-Radical Initiators

Chemical substances that, under certain conditions, initiate chemical reactions by producing free-radicals are denominated free-radical initiators. Thus, radicals are reactive chemical species possessing a free electron, unbonded or unpaired. Generally, have small lifetimes, typically half-life times less than 10^{-3} (Lovell and El-Aasser 1997; Matyjaszewski and Davis 2002; Mark 2004).

Initiators contain, at least, one labile bond that cleaves homolytically when sufficient energy is supplied to the molecule. This amount of energy must be greater than the bond dissociation energy (BDE) of the labile bond (Mark 2004).

Commercially, the principal initiators used to produce free-radicals are peroxides and azo compounds. The emerging technologies use N-alkoxyamines as free-radical initiators or employ group (or atom) transfer facilitated by transition metals (Matyjaszewski and Davis 2002; Mark 2004).

Atom transfer radical polymerization (ATRP) is one of the most efficient synthetic methods for the preparation of polymers with controlled chain topology, composition, microstructure and functionality. In the last decade, ATRP has been intensively studied in the polymer chemistry field. A novel approach combines ATRP with crosslinking for the production of homogeneous networks (Yamamoto, Pietrasik et al. 2007; Qiang Yu 2008).

1.2.1 – Formation and Use

There are three general processes for supplying the energy necessary to generate radicals from initiators (Matyjaszewski and Davis 2002; Mark 2004):

- Thermal processes;
- Microwave or Ultraviolet radiation;
- Electron transfer processes (redox).

The radical reaction mechanism involves three steps: initiation, propagation and termination. In an initiation reaction, a initiator becomes a radical. In a propagation reaction, a radical reacts to form a covalent bond and generate a new radical. In a termination reaction, two radicals interact forming a covalent bond and the reaction stops (Lovell and El-Aasser 1997; Matyjaszewski and Davis 2002; Mark 2004). This mechanism can be described as follows:

1. Initiation:

$$I \rightarrow I^{\cdot} \tag{1}$$

2. Propagation:

$$I^{\cdot} + M \rightarrow I - M^{\cdot} \tag{2}$$

$$I - M^{\cdot} + {}_{n}M \rightarrow I - M_{n} - M^{\cdot} \tag{3}$$

3. Termination:

$$2I - M_{n} - M^{\cdot} \rightarrow I - M_{n} - M - M - M_{n} - I \tag{4}$$

$$2I - M_{n} - M^{\cdot} \rightarrow I - M_{n} - M' + I - M_{n} - M'' \tag{5}$$

where, I is the initiator, $I^{\cdot}$ is the radical intermediate, M is the vinyl monomer, $I\text{-}M^{\cdot}$ an initial monomer radical, $I\text{-}M_n\text{-}M^{\cdot}$ a propagation radical, and M' and M'' the polymers end groups.

The most common propagation reactions are atom abstraction, β-scission and addition to carbon-carbon double bonds or aromatic rings, and the most common termination reactions are coupling and disproportionation (Mark 2004).

Radicals are largely employed in the polymer industry to transform vinyl monomers into polymers and copolymers. Two other important commercial uses of initiators are in polymer crosslinking and polymer degradation. Thus, crosslinking is a commercial important reaction of thermoplastics and elastomers (Matyjaszewski and Davis 2002; Mark 2004).

In a crosslinking reaction, an atom abstraction (usually hydrogen) occurs, followed by coupling of two polymer radicals to form a covalent cross-link – termination (Mark 2004):

$$P - H + I^{\cdot} \rightarrow I - H + P^{\cdot} \tag{6}$$

$$2P^{\cdot} \rightarrow P - P \tag{7}$$

where, $P\text{-}H$ is a polymer with covalently attached hydrogen, $I^{\cdot}$ is the initiating radical, and $P\text{-}P$ is a cross-linked polymer.

1.2.2 – Activation Parameters

In the obtention of radicals, thermal processes are commonly used to break labile initiator bonds. The amount of thermal energy necessary varies with the environment, and there are three important factors, known as the activation parameters: temperature (T), activation energy (E_a), and the frequency factor (A_3). The Arrhenius equation (Eq. 11) associates the activation parameters with the initiator decomposition rate (k_d), where R is the gas constant (Lovell and El-Aasser 1997; Matyjaszewski and Davis 2002; Mark 2004).

$$k_d = A \times e^{(-E_a/RT)} \tag{Eq. 11}$$

The increase of temperature increases the initiator decomposition rate. Thus, when a single labile bond is broken, the frequency factor is high, and when multiple bonds are broken, the activated complex is restricted, the frequency factor is low and the initiator decomposition rate is reduced, with no change in E_a. Generally, slower rates of decomposition of the initiator intend higher activation energy values (Mark 2004).

1.2.3 – Organic Peroxides

Organic peroxides are compounds possessing one or more oxygen-oxygen bonds, with the general structure ROOR or ROOH. When a sufficient energy is supplied, this oxygen-oxygen bond is cleaved to produce two radicals, as follow (Mark 2004):

$$ROOR' \rightarrow RO^{\cdot} + {}^{\cdot}OR'$$

Figure 23 – Initiator decomposition with the formation of two radicals.

The rates of decomposition of organic peroxides can be increased by specific promoters, which significantly decrease the energy necessary to break the oxygen-oxygen bond, but usually result the generation of only one useful radical. These accelerated decompositions occur bellow the normal temperature of application of the peroxides (Mark 2004).

Dialkyl peroxides, such as dicumyl peroxide, are the most commonly used crosslinking agents for polyolefins (Johnston 2003).

1.3 – Coating

Coatings are used in several applications, such as decorative, protective, and/or functional purpose on many kinds of surfaces (Barbour 2000; Mark 2004).

Traditionally, coatings evolutionary response to new performance requirements has been slowly due to the difficulty in predicting product performance. Recently, the research in this area has been increased, allowing more rapid response to the needs for change (Barbour 2000; Mark 2004).

Since 1965, with the restriction of VOC (volatile organic compound) emissions, the rate of technical changes has increased. Moreover, other factors, such as the cost of energy for heating curing ovens, requiring lower temperature for curing, gradual limitation in the regulation of the use of potentially toxic materials, and increased performance requirements, also contribute for this research enlargement (Mark 2004).

A film can be defined as a solid under determined conditions by stating the minimum viscosity at which flow is observable in the specified time interval. Most coatings are applied as liquids and converted to solid after application (Barbour 2000; Mark 2004).

A way to form films is to dissolve a polymer in solvents at the needed concentration for application, then apply the coating and allow the solvent to evaporate. As solvents evaporate, viscosity and T_g increases, and free volume decreases (Mark 2004).

Coatings based on solutions of lower molecular weight thermosetting resins needed less solvent. After application, the solvent evaporates and causes crosslinking reactions. For obtaining good properties, average functionality has to be greater than two and the amount of mono-functional resin should be minimal. These systems present a problem in the relationship between stability during storage and time and temperature required to cure a film after application (Barbour 2000; Mark 2004).

Generally, it is desirable to store a coating for many months without a significant increase in viscosity. Moreover, after application, it is desirable to have crosslinking reactions precede rapidly at the lowest possible temperature. Reaction rates depend on concentration, and are reduced by dilution with solvent and increase as solvent evaporates. Crosslinking reactions, after solvent evaporation, are initially faster than during storage. To minimize the temperature required for curing, it is desirable to select a system for which the crosslinking reactions rate depend strongly on temperature (Mark 2004; Youngjae Yoo 2009).

2 – Experimental

2.1 – Synthesis of the Functionalized Methacrylates

2.1.1 – Raw-Materials

The following materials were used in the production of the functionalized acrylates:

i. MMA

A sample of MMA was kindly offered by *Paraglas*. The grade of this sample was 99 %, satisfactory for synthesis.

ii. Polyol

The three polyols tested in this work were ALCUPOL F-2831, ALCUPOL F-5611 and QUIMIPOL PT 1000, kindly offered by CPB. In the following table some properties of these conventional polyols are showed.

Table 16 - Some properties of the polyols tested in this work (Soditas).

	F-2831	***F-5611***	***PT 1000***
MW (Da)	6000	3000	1000
Hydroxyl Number (mgKOH/g)	28	56	-
Viscosity (@ 25 ºC; cp)	1100	470	-
Functionality (OH)	3	3	3

iii. Titanium (IV) Isopropoxide

Produced from *Merck*, this catalyst has 98 % purity, 284.25 g.mol^{-1} molecular weight, and a specific volume of 0.96 g.cm^{-3}.

iv. Initiators

During curing reaction, two initiators were tested: benzoyl peroxide (50 %), from *Dinis dos Santos, Lda*., and methyl ethyl ketone peroxide (MEKP), from CPB.

v. Accelerators

Cobalt octoate (10%), from *Dinis dos Santos, Lda*., and N,N-dimethylaniline (DMA), from CPB, were the accelerators used for the cure of MMA and TMMA.

vi. Linseed Oil

Purchased from *Quimidroga Portugal, Lda*., was used for reticulation tests with MMA.

2.1.2 – Experimental Apparatus

The experimental set-up designed for this synthesis is presented in Figure 12 (chapter II, sub-chapter 2.1.2).

2.1.3 – Reaction Design

The synthesis of functionalized methacrylates was achieved by the transesterification of MMA with conventional polyols, typically PEG or PPG with 6000, 3000 and 1000 Da (*vide* Figure 24). Each polyol molecule has three free OH available to react with MMA, but the stoichiometry used was 5:1 (MMA:polyol), which ensure the complete conversion of the polyol.

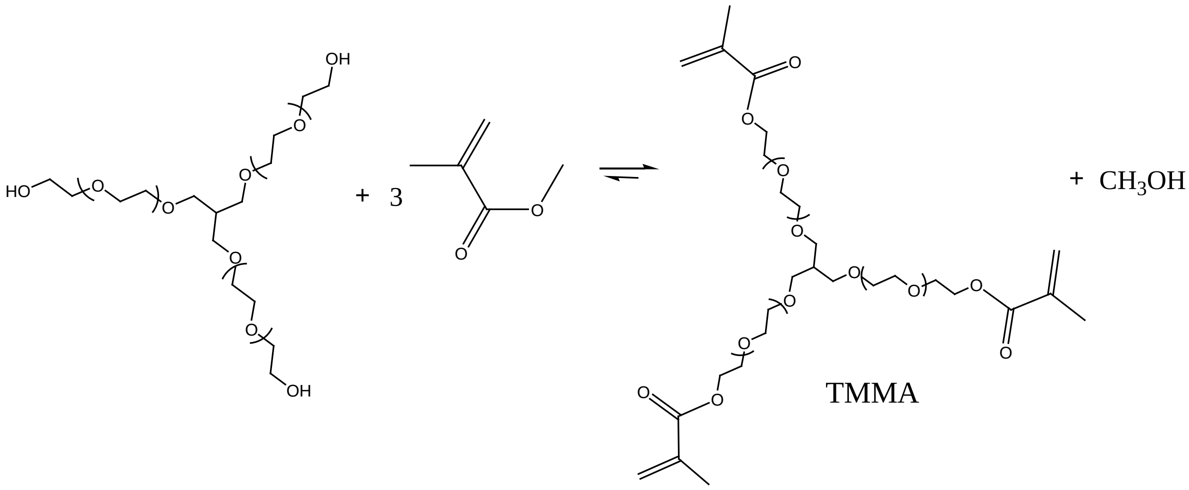

Figure 24 - Schematic of the transesterification reaction from MMA with a conventional polyol.

Before loading the raw-materials in the reactor, the heating system was turned on and when the temperature reaches 110 ºC, the catalyst (1 %, weight) was introduced in the reactant mixture. The catalyst, Titanium (IV) isopropoxide, was only introduced in the mixture after the temperature reaches 110 ºC to avoid the hydrolysis of this catalyst.

These reactions start at different temperatures, for each polyol. Thus, the synthesis with the 6000 Da molecular weight polyol started at 180 ºC, the 3000Da molecular weight polyol started at 145 ºC, and the 1000 Da molecular weight polyol started at 120 ºC. It was at these temperatures that the assembling of methanol started and the color of the mixture becomes pale yellow, but translucent too.

These syntheses were carried out in a 1 L and 2 L glass vessels with a connection to a distillation arm, which allow removing the by-product (methanol) and extending the equilibrium to the formation of more functionalized acrylates. A tube with N_2 flow was immersed into mixture to promote the methanol removal. The stirring was stronger as possible, typically 500 rpm.

Since the reaction begins a condensate appears in the top of the distillation arm, being collected in a vessel at the end of distillation arm (Figure 12). At this point, the thermometer at the top of the distillation arm displays 70 ºC, which is higher than the methanol boiling point. Being so, methanol drags some MMA. Thus, a great excess of MMA is essential.

The terminus of this reaction was reached when the condensation of the methanol stops, even with the increase of N_2 flow and increase of temperature to 210 ºC. For a 1 L batch, using 600 g of Alcupol F-2831 and 50 g of MMA, this reaction runs for 4 hours.

During these syntheses, the MMA can start to polymerize, due to the high temperature and the presence of atmospheric O_2 (free-radical). A signal of this polymerization is the increase of viscosity of the mixture, displayed by the torque of the mechanic stirrer. When the torque increases significantly, it is necessary to introduce an inhibitor, such as hydroquinone. The amount needed of inhibitor is 0.01 % (weight).

2.2 – Curing of Functionalized MMA

The product was only characterized by gel time. Two curing systems, initiated by free-radical initiators, were tested at different temperatures (room temperature, 40 ºC and 60 ºC); a redox system consisting of MEKP and cobalt octoate; and a system consisting of benzoyl peroxide and DMA.

The two curing systems were applied on the functionalized acrylates and the accelerator amount varied in order to obtain a reasonable gel time. The gel time was measured on Gelnorm® (Gel Instruments AG) that detects sharp change in viscosity at the gel point by moving a probe up and down into the sample.

3 – Results and Discussion

3.1 – Characterization of Functionalized Methacrylates

The first gel time experiments were carried out testing two different curing systems – benzoyl peroxide + DMA, and MEKP + cobalt octoate – in order to polymerize the monomer MMA, at room temperature. The amount tested for each curing component was 2 % (w/w), and the amount of MMA was practically the same in each test.

Benzoyl peroxide and DMA reveals to be the best curing system to polymerize MMA in an acceptable time. The other curing system, MEKP and cobalt octoate, did not polymerize MMA. An acceptable time lies between 30 minutes and 6 hours.

In the second set of experiments the amount of DMA necessary to the polymerization of MMA was tested. Three experiments were carried out using the same amount of MMA, approximately 14 g, 2 % of benzoyl peroxide and 5 %, 10 % and 15 % of DMA, at 40.9 ºC. The results were the following:

Table 17 - Gel time results of MMA, varying the amount of DMA, at 40.9 ºC.

Experiment	***% DMA***	***Gel Time*** *(hours)*
2A	5	17
2B	10	24
2C	15	> 24

It was concluded that the amount of DMA, in this curing system, should not overtake 5 %. In experiment 2C, using 15 % of DMA, the polymerization was very slow (more than one day). In experiment 2B, using 10 % of DMA, the polymerization was slow too, practically one day. These two experiments shown that the amount of DMA should be the minimum as possible, once that a DMA excess affects negatively the polymerization. Being so, experiment 2A reveals to be promising, besides the polymerization had been yet a little slower.

In the third set of experiments, the reticulation of MMA with linseed oil was tested, which has an iodine index higher than 110, and using the curing system composed by 2 % of benzoyl peroxide and 5 % of DMA, at 60 ºC. The results were the following:

Table 18 - Reticulation results of MMA with linseed oil, varying their proportions, at 60 ºC.

Experiment	**% MMA**	**% Linseed Oil**	**Gel Time** (hours)
3A	75	25	Not polymerize
3B	50	50	Partial polymerization
3C	25	75	Partial polymerization

After varying the proportion of MMA and linseed oil, as presented in Table 19, and obtained an approximate total weight, it was verified that linseed oil and MMA do not reticulate in proportions that MMA percentage is bigger than linseed oil percentage (experiment 3A). For equal proportions of MMA and linseed oil (experiment 3B), the polymerization was only partial, observed only in the tube bottom. In proportions that linseed oil percentage is bigger than MMA percentage (experiment 3C), the polymerization was partially too, but occurs less slowly. Moreover, in experiments 3B and 3C, was observed an oily liquid float in the tubes top.

Being so, the reticulation using this curing system occurs more favorably for proportions of linseed oil higher than MMA. Although, these results were not as promising as expected. Different formulations had to be tested and even test different curing systems.

The synthesized products (TMMA) were tested to be applied in coatings with rubber. In fact, a set of experiments was conducted in order to verify if rubber inhibits the polymerization of these products. These experiments were carried out with granulated rubber (from *Recipneu*), 10 %, using MMA functionalized polyol with 3000 Da (TMMA-2) and 1000 Da (TMMA-3), and the curing system composed by 2 % of benzoyl peroxide and 5 % of DMA, at room temperature. The results were the following:

Table 19 – Gel time results for the polymerization of TMMA and the effect of rubber.

Experiment	***Product***	***Rubber***	***Gel Time*** *(min)*
4A	TMMA-2	×	10
4B		√	15
4C	TMMA-3	×	12
4D		√	16

It was concluded that rubber does not inhibit the polymerization of the synthesized products (TMMA). The obtained gel time shows a little difference between the experiments with (√) and without (×) rubber. Moreover, the obtained polymers were completely translucent. This result was very promising for the application of TMMA in the coating of rubber.

After verifying that rubber does not inhibits the polymerization of TMMA-2 and TMMA-3, a film formation was tested using two glass plaques and the curing system composed by 2 % of benzoyl peroxide, 5 % of DMA, and TMMA-2 or TMMA-3, at room temperature. These two films were not obtained due to the fact that TMMA-2 and TMMA-3 did not polymerized when dispersed in the glass plaques surface, after properly mixtured.

The mixture dispersion on the plaques strongly increases the interface with air, which has oxygen in their composition, and the curing system becomes less efficient. Being so, it was necessary minimize the contact of the mixture with the atmospheric oxygen, which inhibits the radical polymerization.

Liquid and solid paraffin were added before disperse the curing mixture in the glass plaques with the purpose of minimize the contact between the mixture and atmospheric oxygen, although the films were not obtained again. So, it is necessary to change formulations and seek more efficient curing systems.

IV - Conclusions and Future Trends

The SFAE process synthesis and the production of crude samples, which were the main objectives of this work, were, as expected, accomplished. The results obtained in the emulsification preliminary test and the results obtained from BIOPRODUCTION partners, as well the product characterization by FTIR and NMR, also support this statement.

FTIR spectra from the different synthesized SFAE revealed both the presence of esters and bands associated with carbohydrates, which confirm the obtention of SFAE. Moreover, the FTIR spectra from SFAE synthesized from rapeseed FAME reveals the presence of unsaturated alkyl chain.

NMR experiments performed in the characterization of glucose mono-laurate reveal a DE of 1.06 of lauric acid, 2.92 of acetic acid and 1.02 of free OH. These results allow to conclude about the performance of this synthesis, which was as expected, obtaining a glucose mono-ester from lauric acid.

The HLB number of SFAE was calculated, using the Davies method, for different DE (mono-, di- and tri-) of sucrose and glucose with rapeseed and coconut FAME. The HLB number varies with the DE, diminishing with the increase of DE. The alkyl chain length also influences the HLB number. For the same DE, the increase of alkyl chain length diminishes the HLB number.

In these calculations, the maximum HLB value was 16.33, for mono-ester SFAE from coconut FAME, and the minimum HLB value was -1.73, for tri-ester SFAE from rapeseed FAME. This negative value is unreasonable, making the Davies method unsuitable for SFAE, in particular for extreme cases.

Some of the possible applications for these SFAE, synthesized using rapeseed and coconut FAME, are:

- Mono-ester - O/W emulsifiers;
- Di-ester - O/W emulsifiers;
- Tri-ester - W/O emulsifiers.

Comparing the HLB values of SFAE from sucrose and glucose, the results revealed that HLB values are higher for sucrose then for glucose, conferring a higher hydrophilicity. Moreover, it was noticed a difference of 6 units between SFAE and GFAE, for the same DE. This difference is owing to the fact that sucrose has two more ether bounds, three more ester groups and more three CH_3, two CH_2 and five CH.

Regarding emulsification preliminary tests, it was verified that the DE and the nature of the saccharides influences the behavior of the SFAE, as expected. The results demonstrate that an increase of the DE turns the SFAE more lipophilic, and SFAE synthesized using sucrose revealed to be more hydrophilic than SFAE synthesized using glucose, which is in agreement with the HLB calculation.

These emulsification preliminary tests revealed that three of the synthesized SFAE were able to be applied in W/O emulsions, and one of the synthesized SFAE was able to be applied in O/W emulsions.

The product synthesized from glucose and lauric acid demonstrates not be a good W/O emulsifier, despite being a mono-ester and the HLB calculation indicates a possible application as O/W emulsifier. A contaminant, not identified in the FTIR spectra, has influenced the product HLB.

Ciba has tested some SFAE samples and reported promising results. A SFAE sample reveals to be suitable to use in W/O preparations. Moreover, this sample reveals to create stable W/O emulsions at both hot and cold environments, and also after two weeks storage.

P&G has tested a SFAE sample in a preliminary test of detergency, in a washing machine, and reported successfully.

From all the used catalysts in the synthesis of SFAE, lanthanide triflates were the ones who had better performance, allowing this synthesis at low temperature and so minimize the sugar degradation.

A scale-up from 1 L to 4 L was successfully achieved. This is a promising result for trying a larger production scale. Although, more tests should be made before trying this scale-up.

A main objective of the BIOPRODUCTION project was to produce a non-ionic surfactant from renewable and economical raw-materials. This objective was accomplished with the production of SFAE from sugar cane molasses and rapeseed FAME, which are obtained from renewable raw-materials, plenty available and low-priced.

Moreover, this SFAE production allows the obtention of versatile products, suitable in several applications, due to the capacity to vary the DE and also employ different saccharides. Therefore, SFAE has a promising probability as raw material for detergents.

The main objectives were accomplished, but this work could continue to be developed. The product characterization could be more complete, namely in their physical properties, such as surface tension, moisturing power and foamy power. The product purification should be developed to perform these tests, regarding the customers and environmental requirements.

More developments could be made in the pilot scale, seeking a more efficient process in energetic terms. Thus, kinetic studies should be performed to optimize the process and then scale-up to an industrial scale.

According to the results obtained in the functionalized methacrylate synthesis, we may conclude that the curing system composed by benzoyl peroxide and DMA was better than the curing system composed by MEKP and cobalt octoate. Moreover, DMA influence the polymerization time, being more desirable an amount as less as possible.

It was verified that TMMA can be applied in rubber coatings, as rubber does not inhibits the polymerization of TMMA products, although the film formation was not obtained. Perhaps, the used curing system should not be applied in film formations, since that atmospheric oxygen has a larger interface to diffuse inside the curing mixture, which may preclude the polymerization.

The reticulation of MMA with linseed oil was tested and the results showed that the amount of oil should be greater or equal than the MMA, otherwise the reticulation not occurs.

These were preliminary tests and different formulations have to be tested and even seeking more efficient curing systems. For a better characterization of this product, TMMA, the T_g should be measured, which allows the obtention of important properties related to T_g and compare with similar products. Other properties should be measured, such as, adhesion; abrasion and photoinitiated oxidative degradation, to better characterize this product.

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Appendix

Appendix I – FAME production process

Before starting the transesterification reaction it is necessary to measure the acidity value of the vegetable oil. A routine method consists in titrating a sample of the vegetable oil (1 g, approximately, in 100 mL of acetone) with a solution of potassium hydroxide (0.1 M), using phenolphthalein as indicator. If the acidity value were upper than 0.5 it is necessary to proceed with an esterification to lower the acidity value to 0.5.

The follow equation was used to calculate the acidity value.

$$Acidity\,value = \frac{3611 \times V_{tittrate}}{sample\,mass} \qquad \text{(Eq. 11)}$$

FAME production was carried out in a 2 L glass vessel, using a mechanic stirrer and a reflux condenser. To obtain FAME it is necessary to proceed with a transesterification reaction, as shown in the Figure 25, in which each fat molecule react with three methanol molecules, giving three FAME molecules and glycerol.

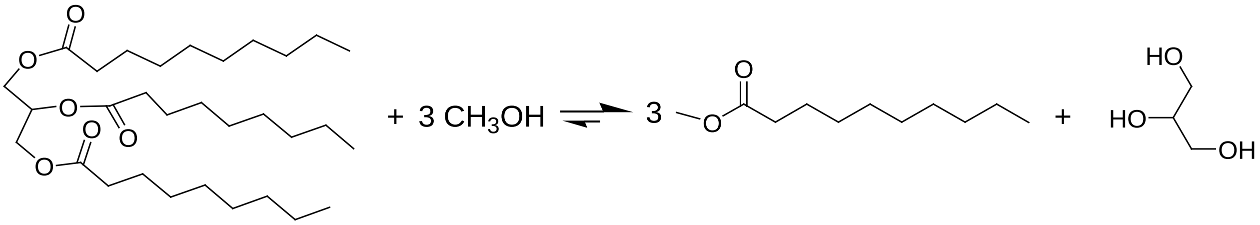

Figure 25 - Transesterification reaction of vegetable oil with methanol.

The typical stoichiometry for this reaction is 6 mole of methanol per mole of fat. This excess of 100 % is necessary to maximize the reaction conversion. To catalyze the reaction is used 0,6 % (w/w) of sodium methoxide in an alcoholic solution (30 % in methanol).

After the transesterification reaction is necessary to purify the product, proceeding with the distillation of the methanol in excess and then washing. This washing is a three step process, which begins with a first wash using water (10 % of the product volume), then a second wash with acidified water (0,01 M and 5 % of the product volume), and a final wash with water (15 % of the product volume).

Appendix II – FTIR spectra of the raw-materials

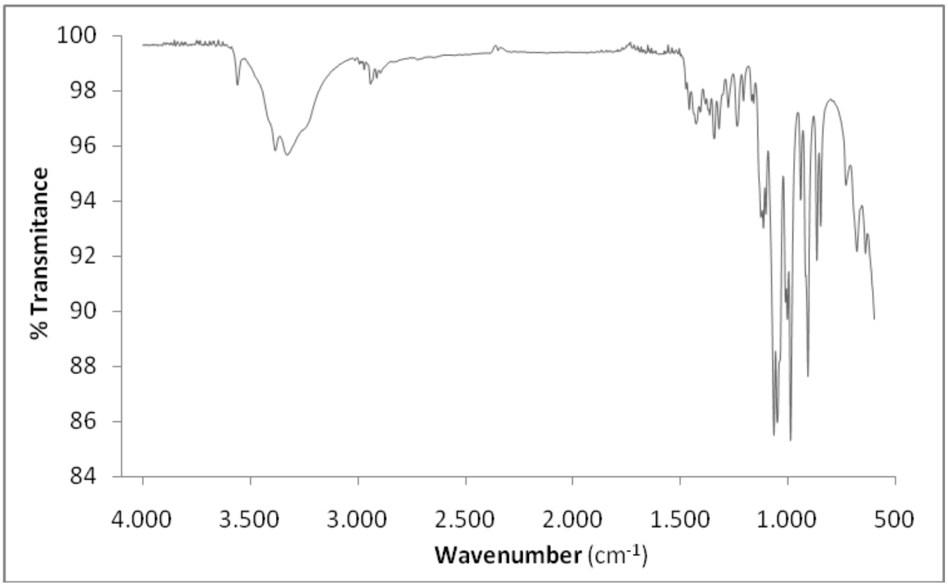

Figure 26 - FTIR specta of sucrose using ATR method.

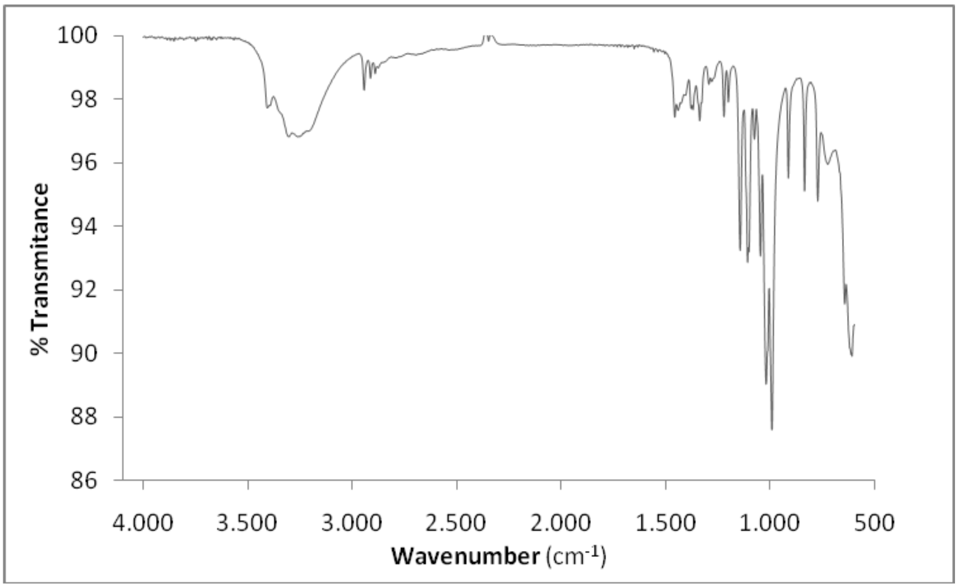

Figure 27 - FTIR spectra of glucose using ATR method.

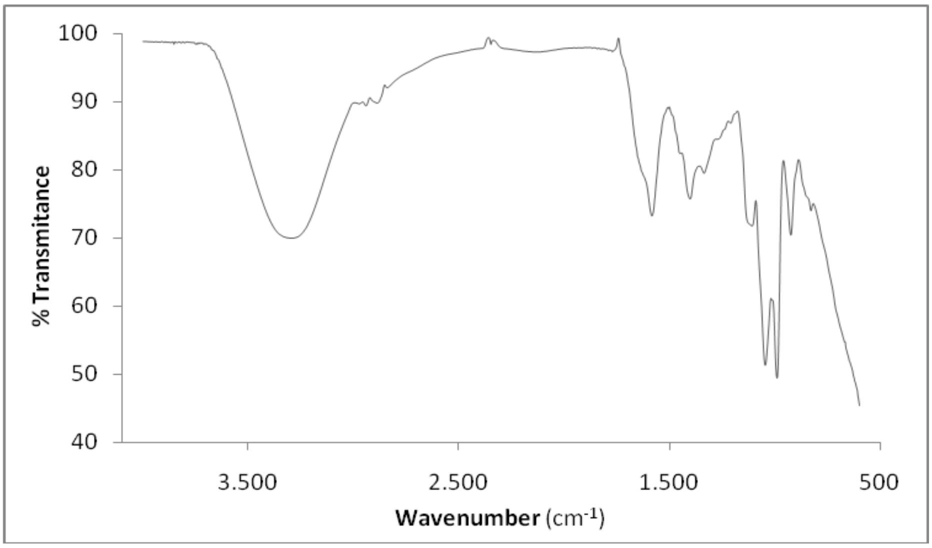

Figure 28 - FTIR spectra of sugar cane molasses using ATR method.

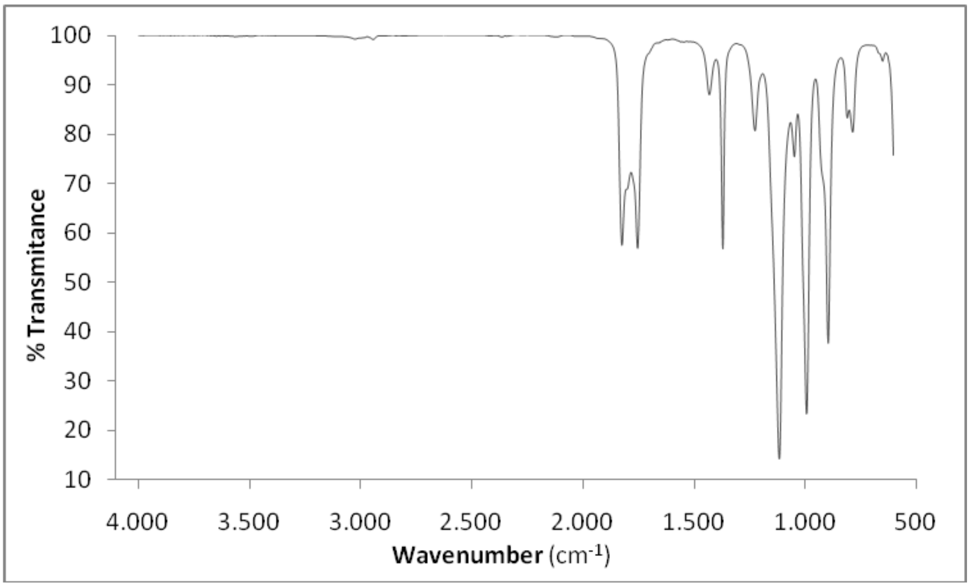

Figure 29 - FTIR spectra of acetic anhydride using ATR method.

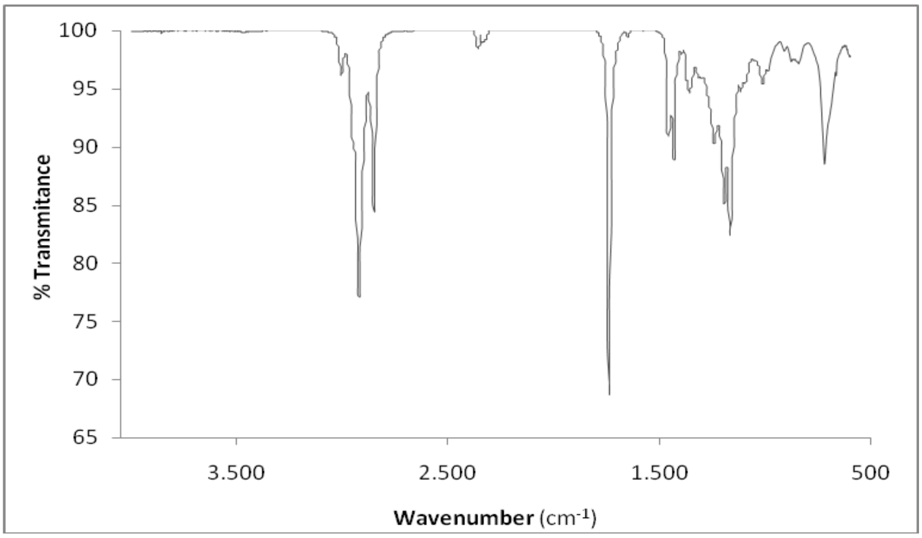

Figure 30 - FTIR spectra of FAME from rapeseed using ATR method.

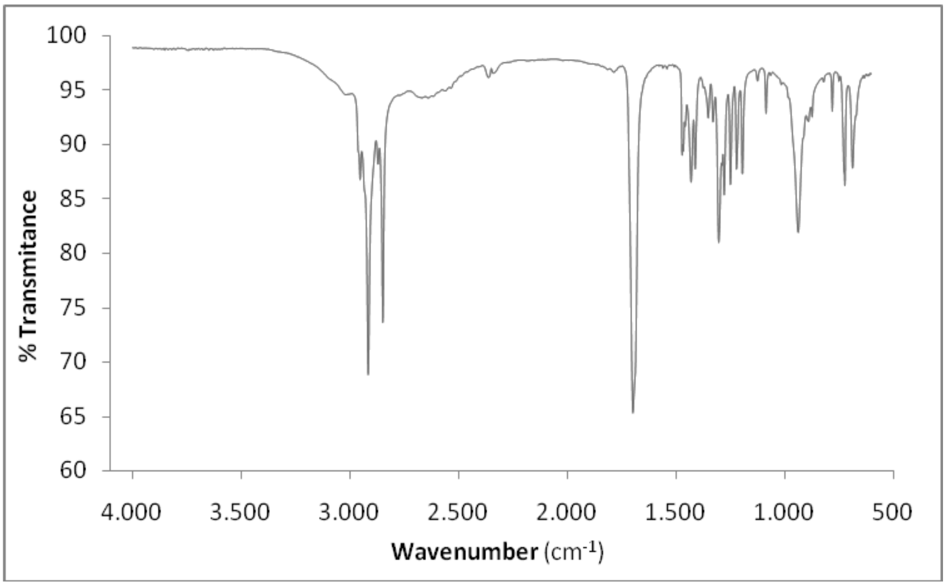

Figure 31 - FTIR spectra of lauric acid using ATR method.

Appendix III – NMR spectras of mono-dodecanoylglucose

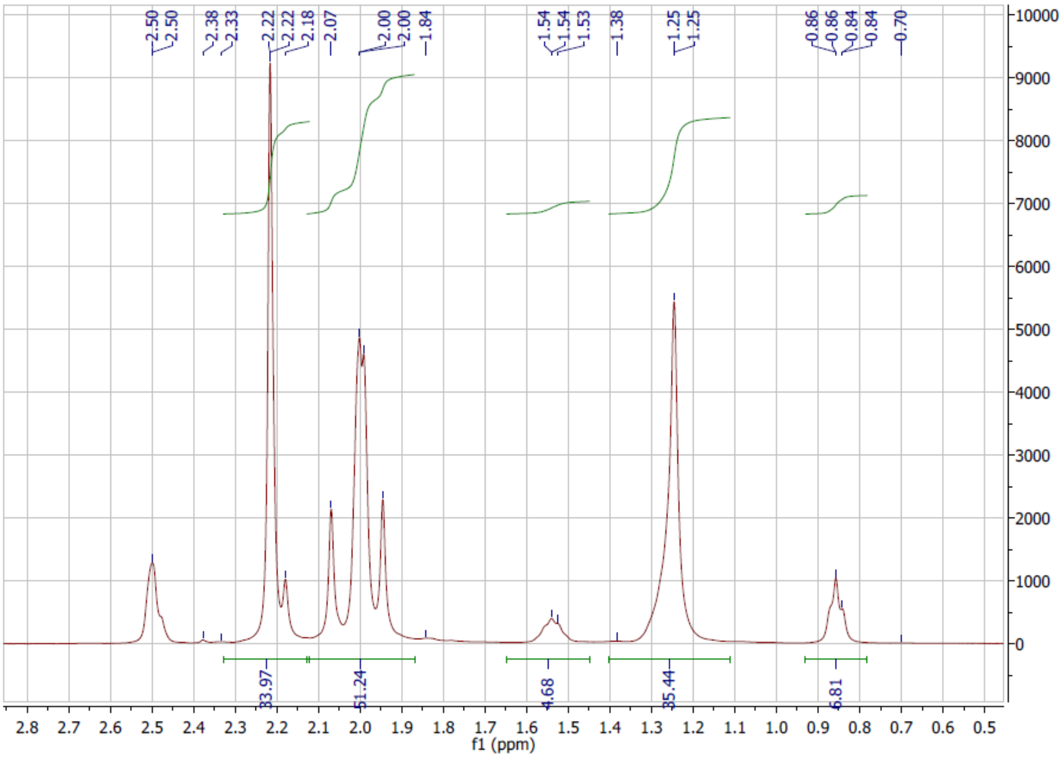

Figure 32 – ^{1}H-NMR shift (δ) data for GFAE, from 0,45 to 2,85 ppm.

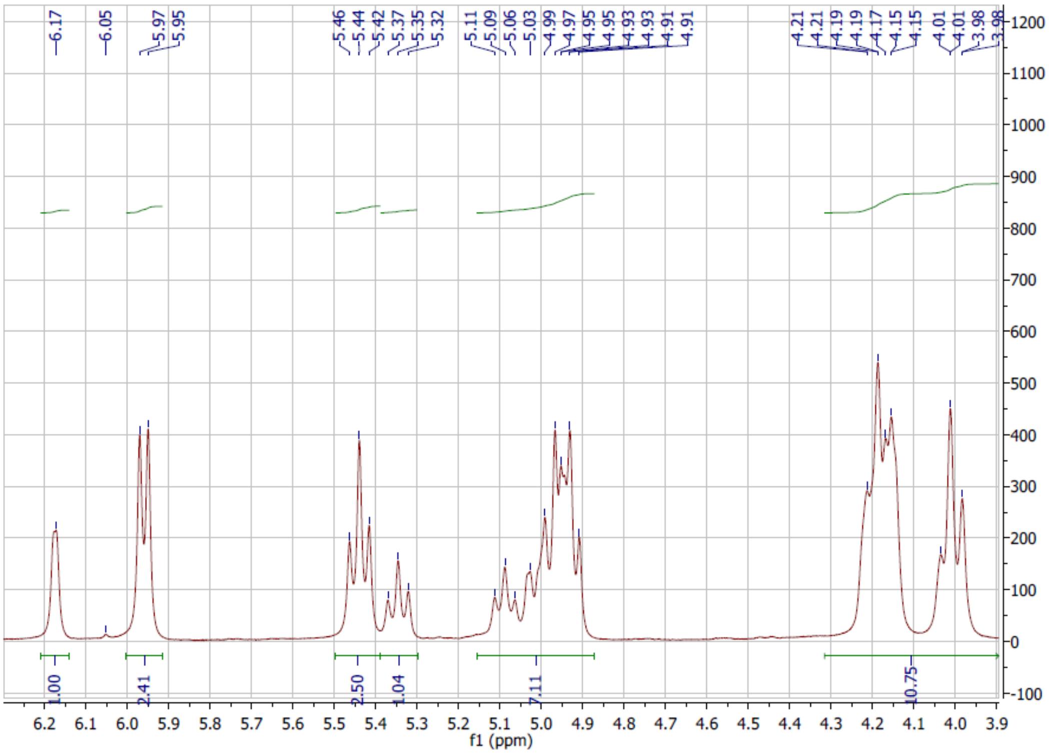

Figure 33 - ^{1}H-NMR shift (δ) data for GFAE, from 3,9 to 6,3 ppm.

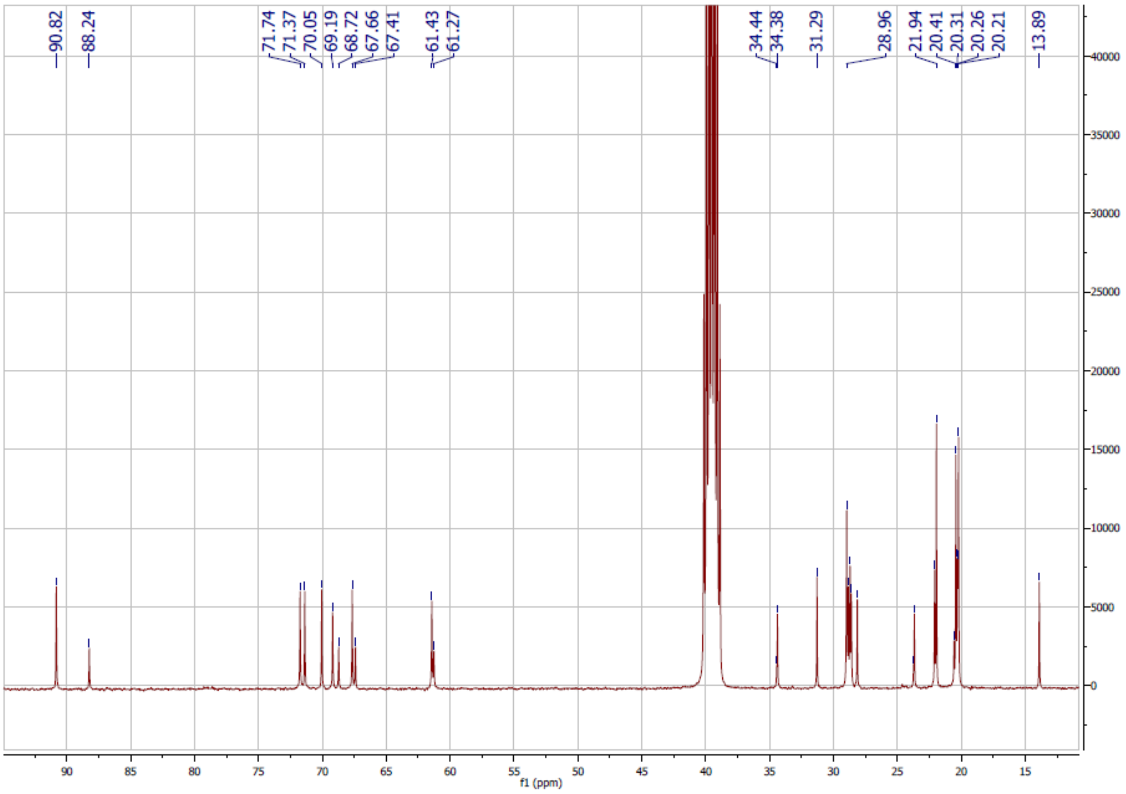

Figure 34 – ^{13}C-NMR shift (δ) data for GFAE, from 10 to 95 ppm.

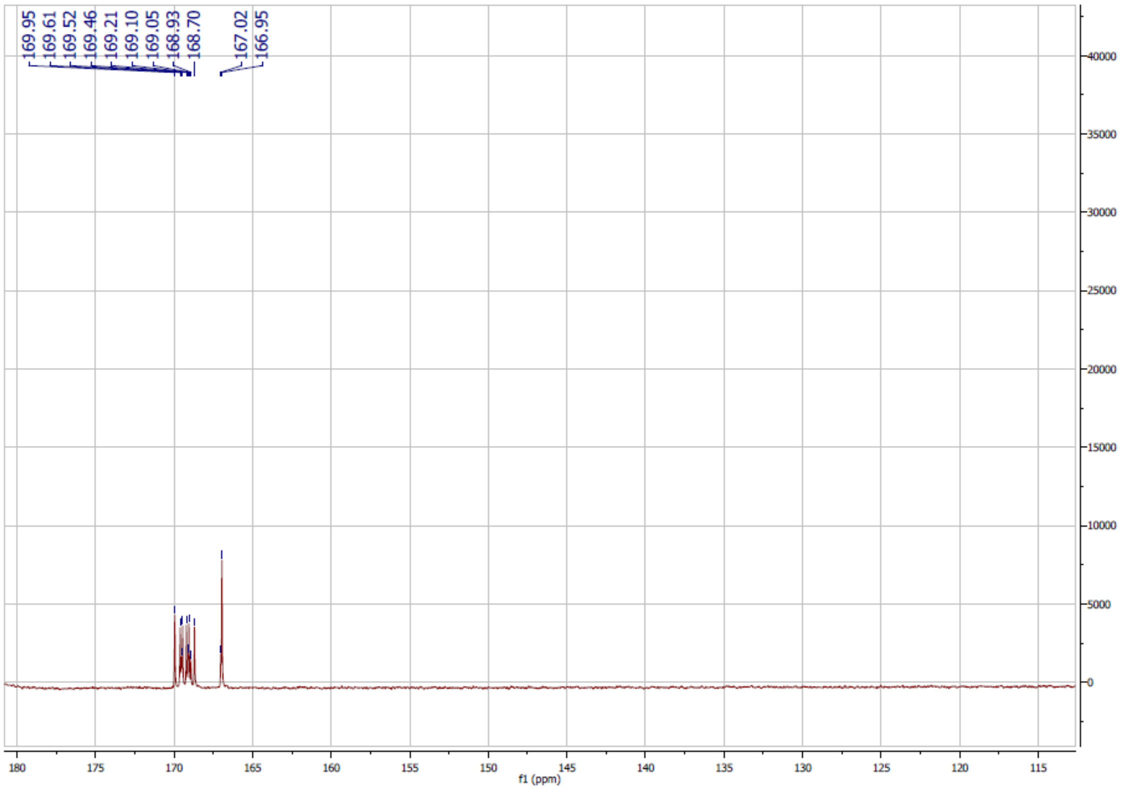

Figure 35 - ^{13}C-NMR shift (δ) data for GFAE, from 110 to 180 ppm.

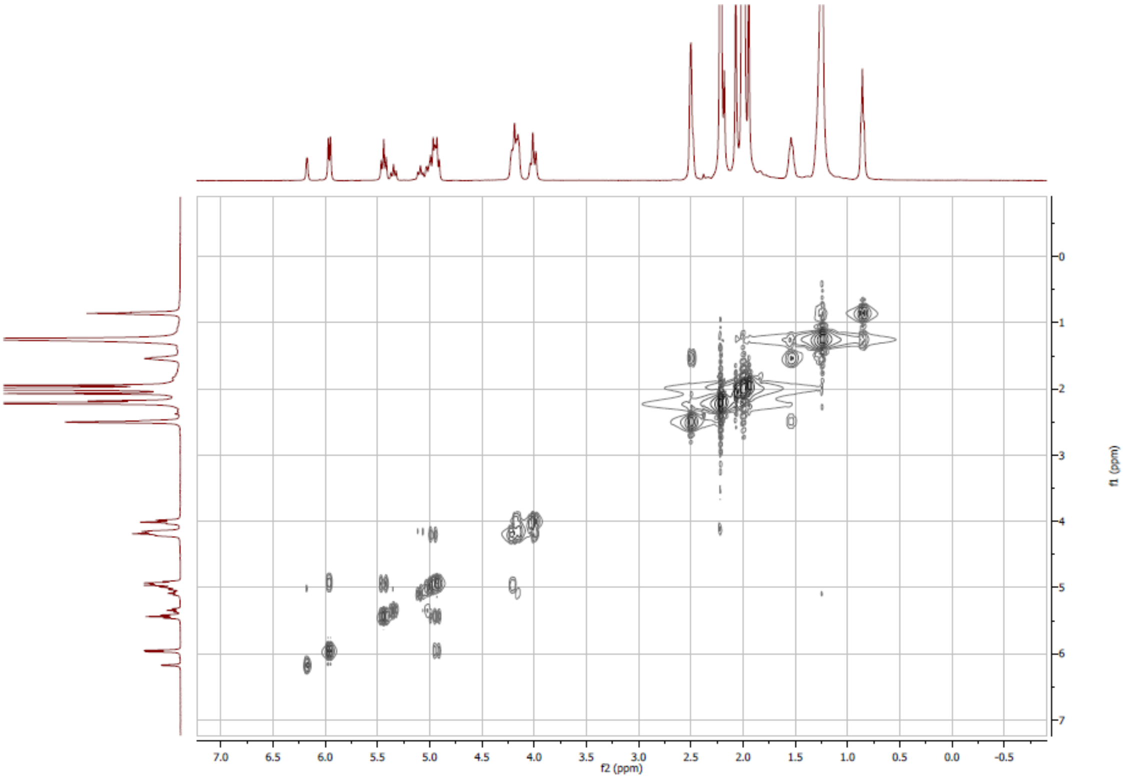

Figure 36 – 2D-NMR COSY shift (*δ*) data for GFAE.

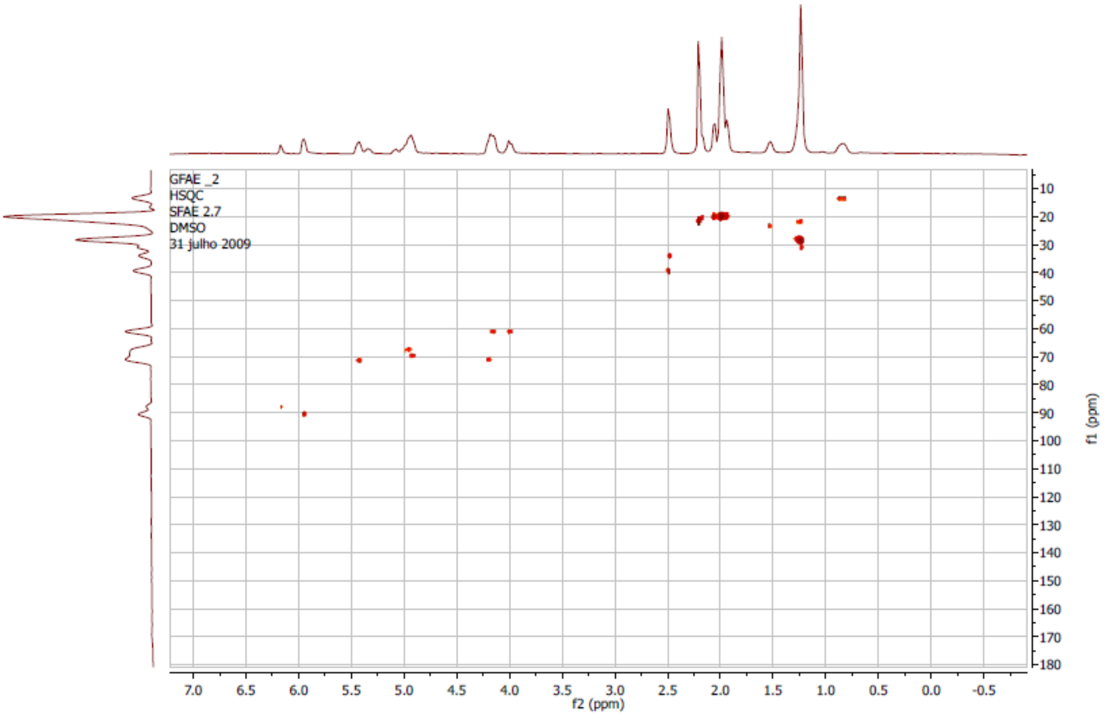

Figure 37 - 2D-NMR HSQC shift (δ) data for GFAE.

Appendix IV – Results obtained from Ciba

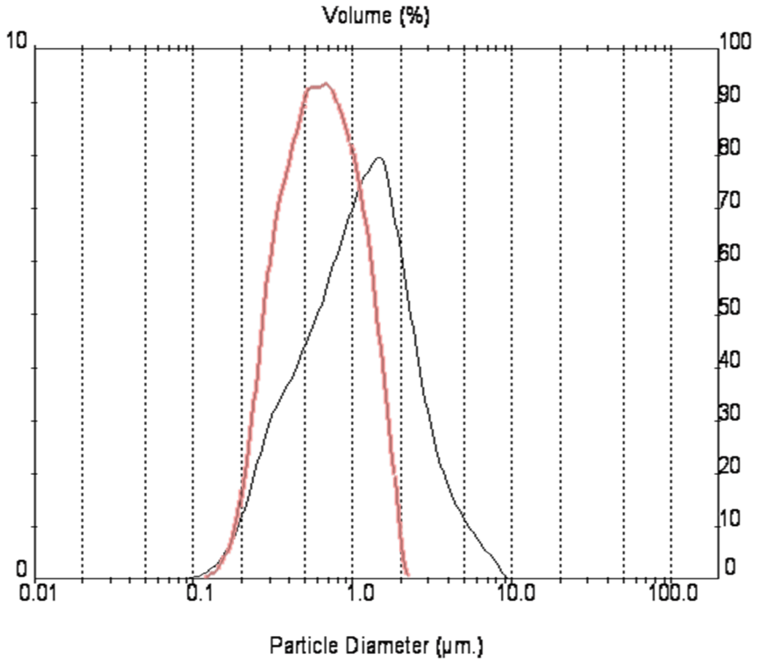

Figure 38 – Comparison between standard preparation (cypermethrin) and SFAE, where the dark track represents SFAE and the red track represents the standard preparation.

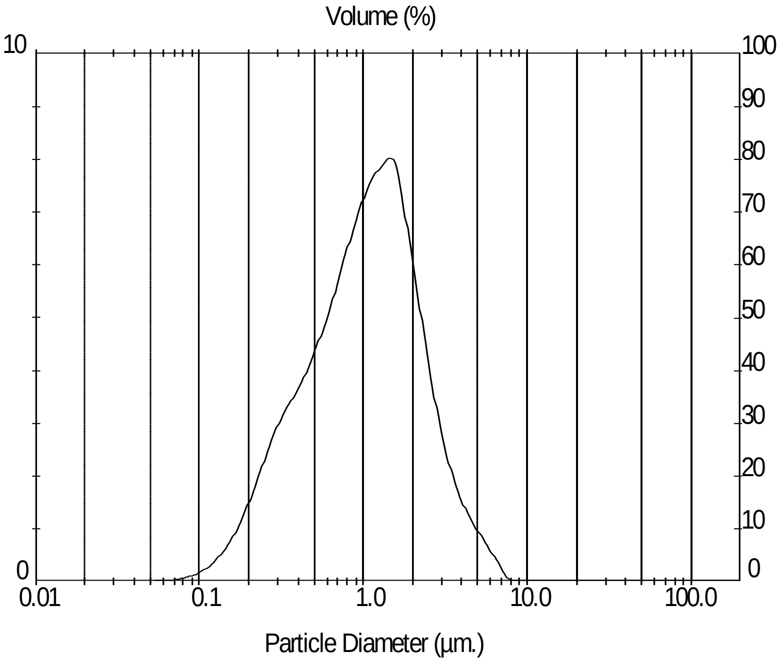

Figure 39 – Particle size graph for SFAE, in oil phase, after 2 weeks in ambient storage.

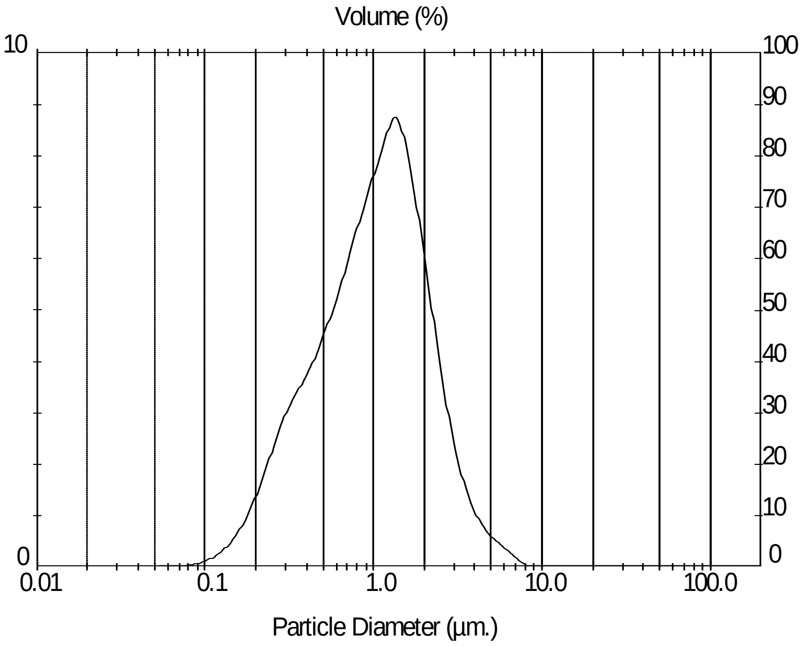

Figure 40 - Particle size graph for SFAE, in oil phase, after 2 weeks storage at 4 ºC.

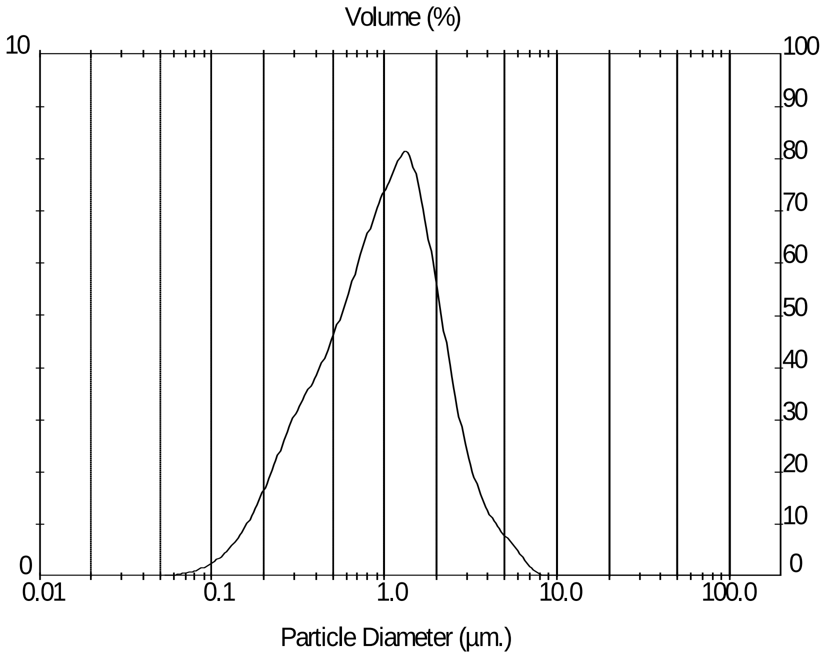

Figure 41 - Particle size graph for SFAE, in oil phase, after 2 weeks storage at 54 ºC.