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New Applications for Soybean Biodiesel Glycerol

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1. Introduction

Glycerol (Fig. 1.1) is a viscous and polar substance that has long been known for its useful properties. As long ago as 1779, the Swedish scientist Karl Wilhelm Scheelle obtained glycerol from olive oil. In 1813, Michael E. Chevreul showed that glycerol was involved in the triglyceride structure, and called it glycerin, from the greek word that means sweet. The elucidation of its structure as a trihydroxylated alcohol was due to Wurtz in 1855. The name glycerin was changed to glycerol to indicate its alcohol nature. It is now common to refer to the pure chemical product as glycerol and refer to the commercial grades with varying glycerol content as glycerin (or glycerine). The first example of a chemical industrial application of glycerol is nitroglycerin which was synthesized by Ascanio Sobrero. In 1860 it was transformed into a safer and more convenient form of use by Alfred Nobel [Jerôme et al, 2008; Shreve & Brink, 1977; Kirk & Otmer, 1951].

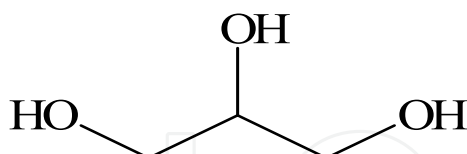


Fig. 1.1. Glycerol structure - 1,2,3-propanetriol

A large range of applications has been made possible due to its non-toxicity and biodegradability, mainly in cosmetic and food industries. As an additive in industry and in consumer goods it can be applied as a humectant, plasticizer, solvent or viscosifier, providing hydrodynamic lubrication [Kirk & Otmer, 1951]. In the polymer industry it is added as a stabilizer, plasticizer, and co-solvent in emulsion polymerization. Glycerol is also an important raw material for the synthesis of several valuable compounds. It was used as the basis for the first production of alkyd resins [Guner et al, 2006] while its partial fatty acid esters, the mono- and diesters of palmitic and stearic acids, have been widely employed as emulsifiers in processed foods. The cosmetics, pharmaceuticals and food industries account for at least 45% of glycerol production. Besides being the basis for nitroglycerin, which also finds application as a medicinal drug, glycerol is transformed in glycerol carbonate which is an intermediate in chemical synthesis and used as a gelation agent, in polyglycerols which are used in cosmetics,

in medical applications and in controlled drug release, to quote some well known glycerol derivatives and their useful applications [Berh et al, 2008; Guner et al, 2006].

The initial route to glycerol production was the hydrolysis or the saponification of triglycerides from vegetable oils or animal fats (Fig 1.2 and 1.3). This process results in crude glycerin containing approximately 88% glycerol in mass. The introduction of petroleum derived detergents brought a decline in soap production from vegetable oils which decreased the availability of glycerol. As a consequence, a synthetic route for glycerol was developed from the petroleum derivative propene, also known as propylene (Fig. 1.4), with large scale production starting in 1948, in the USA. The glycerol from both processes is purified by bi-distillation to guarantee a minimum of 99.5% purity and enable it to meet US pharmacopoeia (USP) specifications that regulate products for the cosmetics, pharmaceutical and food industries.

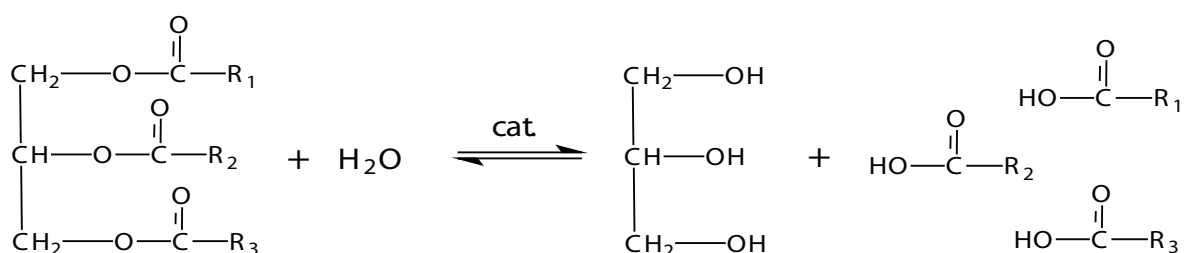


Fig. 1.2. Hydrolysis of a triglyceride showing the formation of glycerol and fatty acids

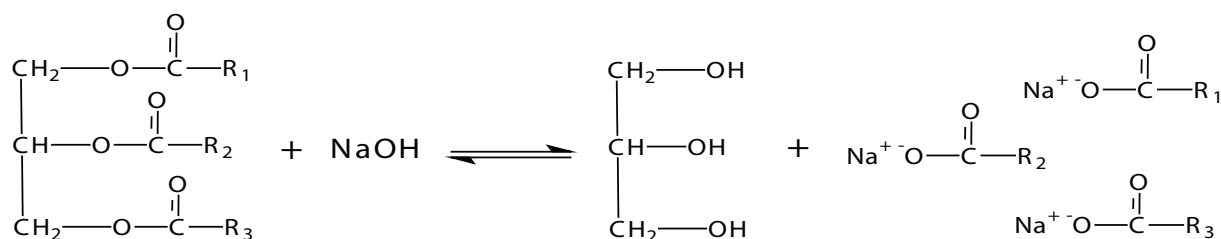


Fig. 1.3. Saponification of triglycerides showing the formation of glycerol and salts of fatty acids

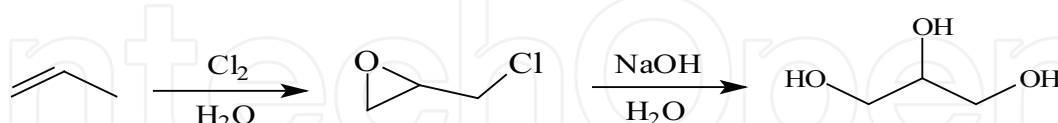


Fig. 1.4. Chemical reaction to obtain glycerol from propene, through several intermediates (Bell *et. al*, 2008).

The transesterification of triglycerides with methanol is the current route to biodiesel production, generating fatty acid methyl esters (biofuel) and glycerol (Fig. 1.5). It can be estimated that for each 100kg of biodiesel, around 10kg of crude glycerol are produced. Glycerol supply and demand have been kept in a reasonable equilibrium, with glycerol prices oscillating very little up to the start of the biodiesel production boom. In the last 10 years biodiesel production has had such an increase that glycerin supply has more than doubled whereas its demand has remained largely unchanged. This means that a surplus of glycerol is being added, consistently, to an otherwise stable market. As the increase of

biodiesel production is a worldwide trend, the quantity of crude glycerol being generated is considerable. Fig. 1.6 shows the enormous increase in glycerol supply after biodiesel production started all over the world.

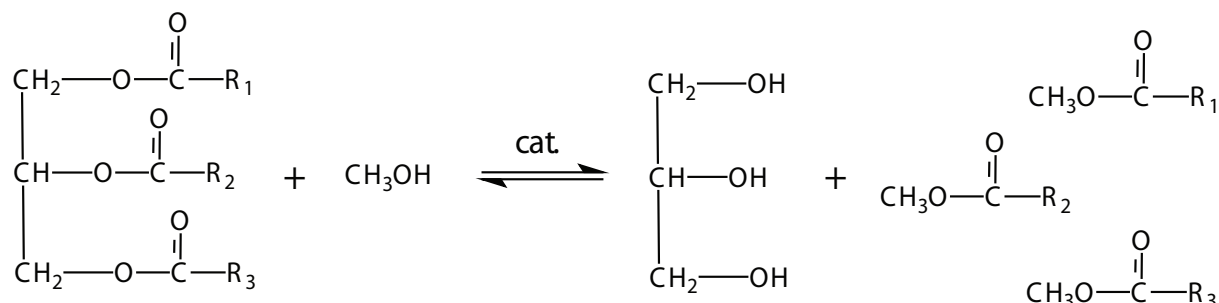


Fig. 1.5. Transesterification of triglycerides with methanol to form methyl fatty acid esters

Before considering crude glycerol for possible value-added products, it is necessary to purify it to a grade acceptable for most traditional applications. This is costly and generally not economically feasible for small to medium-sized plants. Several steps are necessary to free it of sodium salts and methanol and also of water, which needs to be treated before being discarded. This calls for large plants and investments to produce high quality and low price glycerol. The accumulation of glycerin and the difficulty to introduce its surplus in the market became a problem for some small biodiesel producers, and this led to solutions such as its discharge in rivers. It is clear that glycerin may become an environmental issue if adequate demand is not stimulated in the near future.

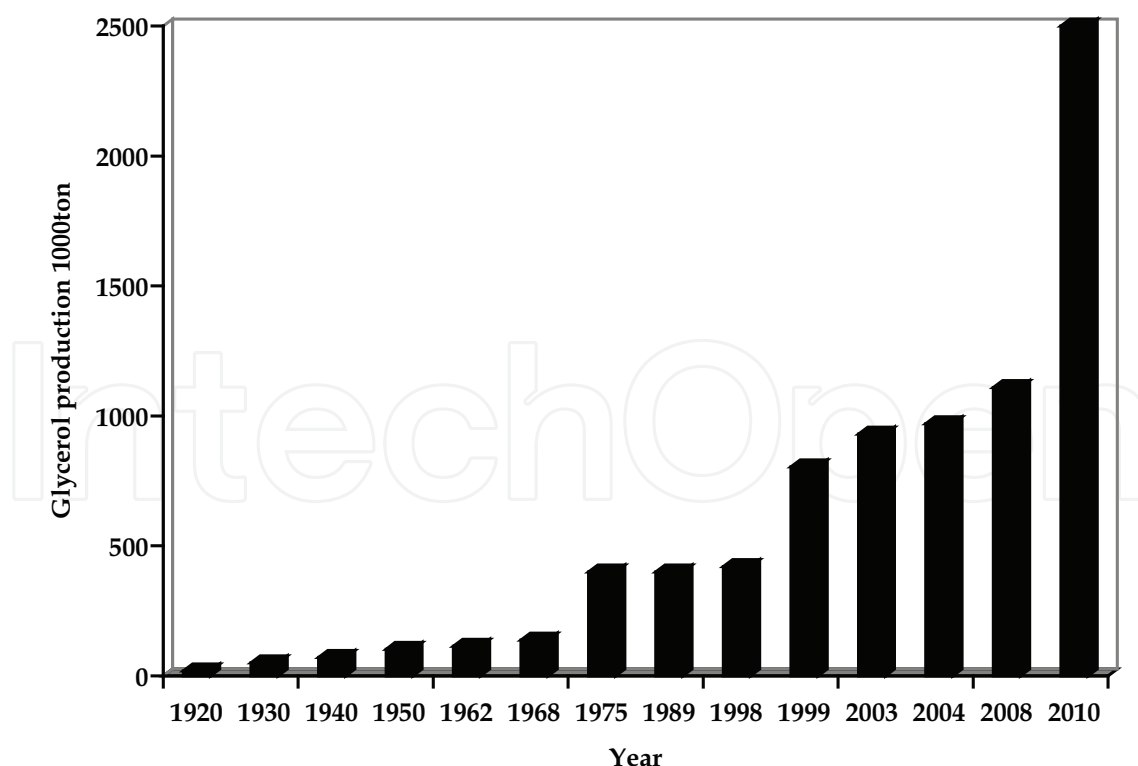


Fig. 1.6. Growth of glycerol production in the USA between 1920 and 1970 and the world production from 1975 compiled by the present authors from Shreve and Brinks, 1977 ; Kirk & Othmer, 1951; Sofiproteol, 2007.

1.1 Applications of glycerol and its derivatives: Literature review.

Alternative uses for the crude or partially purified glycerol are being pursued to make biodiesel more competitive in the growing global market. Research activities worldwide have started to focus on new applications for glycerol and its derivatives and also on processes to use glycerol as a raw material for the production of already known useful compounds.

Immediate use of glycerol as a low price substitute for polyhydroxylated alcohol (commonly abbreviated to polyols) was possible for some industrial segments, such as the paint industry, which benefits from its lubricating properties, or in cosmetic, food and pharmaceuticals industries to whose products it could be added to improve humectancy or sweetness.

The increasing price of crude oil motivated the chemical industry to search for alternatives routes for the synthesis of essential chemicals. The surplus glycerol was the main candidate for several products with a large market, in particular the monomers propylene glycol and epichlorohydrin, synthesis gas ($H_2 + CO$) and a number of other useful intermediates for the chemical process industries commonly prepared from petroleum derivatives.

1.1.1 New routes to well known products having glycerol as raw material

The investigation of processes which have glycerol as a raw material necessarily require knowledge of fundamental industrial processes such as hydrogenation, oxidation, hydrolysis, chlorination, etherification and esterification, among others. This knowledge has been the basis for the discovery and proposal of new processes for glycerol transformation into valuable products. Several literature reviews can be found that focus their presentation on these processes rather than on the product applications [Zhou et al, 2008; Jérôme et al, 2008; Berh et al, 2008].

In the last decade an important process, the aqueous phase reforming process (APR), was developed to produce the synthesis gas $H_2 + CO$ from glycerol which is an important source of hydrogen [Soares et al, 2006]. This is an alternative to the steam reforming processes of methane to prepare synthesis gas which, in its turn, is the raw material for the Fischer-Tropsch synthesis of liquid fuels; alkanes and low molecular alcohols [Suppes et al, 2005]. The development of a thermally efficient combination of the two processes resulted in the commercial production of methanol by Biomethanol Chemie Nederland [Simonetti et al, 2007]. This biomethanol can then be used in the biodiesel production. These developments made possible the economical utilization of glycerol in the production of hydrogen to be used as a fuel or as a reagent in chemical reactions.

Propylene glycol (propanediol) which has a high global demand is a monomer for the production of polyesters. It is also used as an anti-freeze fluid, and additive in cosmetics, food and pharmaceutical formulations to cite some of its uses. Its synthetic pathway has been through propylene (propene), a petroleum derivative, resulting in the formation of the isomers 1,2- and 1,3-propanediol and some ethylene glycol. It is now produced with a lower cost by the hydrogenolysis of glycerol over a copper chromite catalyst with 90% yield [Dasari et al, 2005; Shelley, 2007]. Further investigations led to a synthetic pathway for the selective preparation of 1,2-propanediol from glycerol by the Davy Process Technology [Pagliaro & Rossi, 2008]. The selective preparation of 1,3-propanediol is traditionally achieved by processes involving petroleum derivatives (dehydration of acrolein or ethylene oxide conversion), however biological process, where glycerol is the feedstock for the

fermentation process, has been proposed that can become a cheap alternative to corn syrup fermentation to produce one of the isomers preferentially [Shelley, 2007].

Another major resin ingredient compound that is already being prepared from glycerol, by its chlorination and epoxidation, is epichlorohydrin. This compound is a reagent in the synthesis of epoxy resins which are useful coating materials for marine appliances, in automotive industry and has many other applications [Guner et al, 2006]. Epichlorohydrin is traditionally prepared by propene chlorination, a process that involves one more step than the glycerol process. As glycerol used to be prepared from epichlorohydrin, the process is now reversed [Siano et al, 2006].

Yet another possibility for transforming glycerol into a value-added product is its conversion to acrolein, which is relied upon for many fine chemical products, and it is also the raw material for acrylic acid. Although its conversion from glycerol has long been known, for economic reasons the reaction has not been applied industrially; it is traditionally manufactured from propene. However, with the possibility of lower glycerol prices ahead, acrolein production from glycerol might be an elegant green alternative to the petrochemical route [Centi & Santen, 2007].

Polyglycerol is a useful derivative of glycerol which is extensively employed in controlled drug release and in cosmetics. It is comprised of several units of glycerol forming a branched ether structure with terminal hydroxyl groups. [Sunder et al, 1999; Marquez-Alvarez et al, 2004]

1.1.2 New applications for the glyceryl esters of fatty acids

A well known group of glycerol derivatives is that of mono- and diglycerides of fatty acids, usually abbreviated to MAG and DAG respectively, after the expressions monoacylglycerides and diacylglycerides. They are added to cosmetic and food formulations to prepare emulsions having components of different polarities that would otherwise separate in immiscible layers. The main glycerides are the palmitates, stearates and oleates (oleins). Their industrial production is accomplished through the direct esterification of glycerol with fatty acids or through the glycerolysis or hydrolysis of triglycerides, from vegetable oils or animal fat, which are processes that result in a mixture of mono- and diglyceryl esters [Corma et al, 2006]. An alternative route being studied is the enzymatic esterification of fatty acids with glycerol which is considered an environmentally friendly approach. Conditions for the enzymatic process are being searched to increase monoglyceride selectivity, with results of approximately 60% monoglycerides [Nandi et al, 2008; Freitas et al, 2010; Bogalhos et al, 2010]. These are good results considering that the directives of the World Health Organization for food emulsifiers require that these mixtures comprises at least 70% of both mono- and diglycerides with a minimum of 30% monoglyceride [Da Silva et al, 2000 and 2003]. To obtain MAG with a high purity for food additive usage, a purification step by distillation is required. The DAG derivatives are also a target, specifically the 1,3-isomers. These are being produced from vegetable oils and lipase by the Japanese company Kao, as a substitute for triglycerides oils for cooking due to their higher thermal stability [Watanabe et al, 2003]. A biosurfactant derived from glyceryl ester was produced by a fermentation process with a strain of *Pseudomonas aeruginosa* PA1 isolated from the water of oil production in Northeast of Brazil. They used different carbons sources (n-hexadecane, paraffinic oil, glycerol and babassu oil) and different nitrogen sources. The best results were achieved with glycerol as substrate [Santa Anna et al, 2001; Ciapila et al, 2006].

Monoglycerides are widely used as emulsifiers in food and cosmetic industries due to their active surfaces. As a consequence, their selective synthesis, by method other than the enzymatic approach, has been the object of several scientific papers in the search for a proper selective catalytic system [Abro et al, 1997; Pouilloux et al, 1999; Diaz et al, 2001, 2003, 2005; Marquez-Alvarez et al, 2004; Sakthivel et al, 2007; Jérôme et al, 2008]. Among the several heterogeneous catalysts studied, so far the best result has been 80% in selectivity at 93% conversion, using a specially tailored mesoporous material prepared by an environmentally friendly process [Karam et al, 2007]. Preparation of monoglycerides with high selectivity is a challenging issue still being investigated by researchers.

Importantly cosmetics and food markets are not increasing at the same rate as the glycerol production from biodiesel. Other markets that require compounds with lubricating and emulsifying properties could benefit from such esters derivatives. This could be the case for the fluids used for drilling wells which is a promising sector since glycerol technical grade could be used without further purification. Actually, glycerol is already a component of some formulations for water based drilling fluids in order to avoid gas hydrate formation in the well and to stabilize the water-sensitive formations, reactive shales, during drilling. [Fink, 2003; Youssif & Young, 1993; Hale & Dewan, 1989; Chenevert & Pernot, 1988; Pomerleau, 2009]. Since glycerol is a polar and highly water-soluble molecule, it cannot be used directly as an additive for boundary lubrication or as an emulsifier, while the monoglycerides, being amphiphilic molecules, can act as both. Only a few citations are found in the literature describing the use of glycerides in drilling fluids. Mueller *et al.* (2004) and Maker & Mueller (2009) developed water based drilling fluid formulations that use partial glycerides and oligoglycerides from fatty acids as lubricants. Al-Sabagh *et al* (2009) synthesized and evaluated glycerol oleates (mono-, di- and trioleate) as primary emulsifiers in oil based drilling fluids formulations. They have found that the fluid formulated with glycerol monooleate presented higher emulsion stability due to the surface activity properties of this molecule, related to its adequate hydrophilic-lipophilic balance (HLB). In the case of oil based drilling fluids where fatty acid methyl esters are the continuous phase, another problem is met related to its operation at low temperatures and high pressures, as found while drilling in deep waters. Under these conditions the drilling fluid may gellify, due to ester crystallization, which makes pumping difficult. Nascimento et al (2005) have shown the effect of several low mass esters on methyl palmitate and biodiesel crystallization behaviour and Albinante (2007) has found good results adding both partial oleins (MAG and DAG) to fatty acid methyl esters [Soares et al, 2009]. Thus, it is evident that drilling fluids represents an interesting niche to be explored for the application and development of glycerol derivatives.

One natural line of reasoning among researchers and those involved in fuel development in the search for other options for glycerol use was its conversion in oxygenated fuel additives. This would valorize the co-product of biodiesel and increase the fuel yield. Glycerol by itself can not be used as a diesel additive due to its high viscosity, its tendency to polymerize under combustion chambers conditions and, chiefly, because of its insolubility in diesel.

Given that ethers (eg methyl tertiary butyl ether) are already known to act as gasoline octane boosters, glycerol ethers (mainly tert-butyl glyceryl ether) were proposed and investigated as a fuel additive [Gupta, 1995; Klepacova et al, 2006]. In the case of gasoline it has been demonstrated that ethers from glycerol are capable of reducing particulate matter, hydrocarbons and carbon monoxide (CO) in emissions and acting as an anti-knock additive and an octane enhancer while, in biodiesel, they are capable of improving cold flow and reducing viscosity [Nouredini, 2001]. In spite of these properties a decrease in diesel and

biodiesel cetane number occurred as a consequence of the glycerol ethers branched chains [Spooner-Wyman & Appleby, 2003]. They are commercialized as gasoline additives in United States by CPS Biofuels [2010].

Other oxygenated additives are being considered as potential additives for diesel and biodiesel such as the higher glyceryl ethers, the glyceryl esters of acetic acid known as acetins, and acetals and ketals of glycerol with some patents being issued on their preparation processes [Rahmat et al, 2010; Melero et al, 2010]. This is the subject of another proposal to be presented in the following section.

1.2 Our proposals: Glycerol derivatives as fluid and fuels additives

The emulsifying and lubricating properties of glyceryl esters of fatty acids turn them into potential candidates to be applied as developed water additive to drilling fluids. This segment represents a large slice of a potential market for glycerol derivatives, solving, in part, the problem of providing a market for the glycerol excess.

Another potentially significant market to be explored for glycerol derivatives is the sector of fuels for transport. As described above, a product from glycerol is already commercialized as an octane booster for gasoline. Glycerol oxygenated compounds with properties adequated to improve diesel and/or biodiesel is another possibility to be discussed.

Additives for Drilling Fluids

Oil well drilling is performed by a complex apparatus that includes a drill pipe stem and a drill bit that perforates the formations with the aid of a drilling fluid. Drilling fluids are, in general, multi-phasic liquid systems, consisting of mixtures of solids in suspension, dissolved salts, and organic compounds dissolved or emulsified in water. These fluids play several important functions in the drilling process, including removal of the cuttings from the well, keeping the sides of the well stable, and transporting them up to the surface where they are eliminated. They are also responsible for the control of formation pressures, for sealing permeable formations, maintaining wellbore stability, minimizing formation damages and for transmitting hydraulic energy to the drilling tools to the bit. Another significant function of the drilling fluids is to lubricate the bit and the stem. It is a critical function, particularly while drilling directional wells, since the frictional forces between the drillstring and wellbore or casing are so significant that they can lead to several problems such as high torque and drag, which can lead to premature damage to the drilling tools, as a consequence of excessive wear and heat.

Drilling fluids may be air, water or oil based, depending on the nature of the continuous phase. In general, oil based fluids present lower coefficient of friction (COF) than water based fluids. However, most of the oil based fluids are not environmentally friendly and/or are considerably expensive, especially when compared with water. Thus, there is an imminent demand for new biodegradable and atoxic additives that perform as lubricants of high efficiency in water based drilling fluids.

In spite of the previously mentioned problems, oil based fluids have recently received great attention because of their high performance in drilling water-sensitive formations such as reactive shales and salt domes. Drilling these kinds of formations with water based fluids, in most cases, leads to wellbore instability problems. Reactive shales hydrate and swell in the presence of water and dome salt may dissolve significantly, both cases resulting in undesired enlargement of the well. An alternative is to work with oil based fluids. Since oil based fluids are inverted emulsions, there is no significant contact between water and the

formations, which prevents or at least minimizes wellbore instability. However, one of the main challenges in oil based fluids formulation is to obtain emulsions that persist over long periods of time. By definition, emulsions are thermodynamically unstable, because of the interfacial tension between oil and water, which increases the energy of an emulsified system, leading to emulsion breakage. Emulsions may be kinetically stabilized, for example through the use of emulsifiers, which reduce oil/water interfacial tension. There is a demand in the oil industry for high efficiency emulsifiers that are ecologically sound and have a low cost.

Molecules that have a polar segment (which has water affinity) and a nonpolar segment (which has oil affinity) show surfactant characteristics, due to their ability to adsorb at surfaces and interfaces. For this reason, these kinds of molecules are widely used as lubricant and emulsifiers. Since glycerol esters present such structural features they have a potential application in drilling fluids as lubricants and emulsifiers. Glycerol obtained from soybean biodiesel production seems to be an available and cheap resource for the production of these esters and their evaluation in drilling fluid formulation is one of our proposals.

Additives for Fuels

Compounds are added to fuel with different purposes that include the cleaning of several engine parts, the increase in combustion conversion and reduction in the emissions of undesirable or toxic substances. In diesel combustion a high level of particulates and nitrogen oxides (NO_x) are emitted. There are many techniques capable of improving combustion processes in diesel engines, such as the retarding of fuel injection, the recirculation of exhaust gas, a high pressure injection and an air intake supercharging. However due to the trade-off between the particulated matter (PM) and NO_x emissions, it is very difficult to have both reductions simultaneously [Wang et al, 2009]. One possible solution is to use oxygenated additives which are compounds capable of decreasing carbon monoxide (CO), NO_x and PM while improving the autoignition properties in diesel engines. The cetane number (CN) is the conventional term which characterizes the ignition quality and the flammability of diesel fuels. A high CN usually results in lower exhaust gas and smoke emissions, fuel consumption and engine noise, thus providing an overall better engine yield and drivability [Abu-Rachid et al, 2003].

A high cetane number depends on a high oxygen to carbon ratio and on the predominance of linear alkyl chains (high CH₂/CH₃). The capacity of some ether oxygenated additives to improve cetane number can be explained by the presence of an oxygen bridge that increase the reactivity of the hydrogen atoms in the hydrocarbon chain of the neighboring carbons contributing to the onset of combustion [Abu-Rachid et al, 2003; Marrouni et al, 2008]. For example, the comparison between CN values of dimethyl ether (DME) (55–60) and propane (–20) suggests that the 6 hydrogen atoms of the methyl groups of CH₃–O–CH₃ are much more reactive toward oxygen than the ones in CH₃–CH₂–CH₃. Table 1 compares CN of some compounds [Taylor et al, 2004].

This property led to the production of ether additives that are already commercialized as gasoline additives and stimulated further investigation on oxygenated compounds from glycerol. Three main classes of oxygenated glycerol derivatives have been developed and investigated in relation to their capacity to improve fuels properties. One such glycerol derivative is the commercialized glyceryl tert-butyl ether. Another group of ethers that has driven much attention are that of mono-, di- and triacetate of glycerol called acetins and, finally, the acetal or ketals of glycerol [Dubois et al, 2009; Melero et al, 2010].

Hydrocarbon	Cetane number	Oxygenated Compound	Cetane Number
Propane	-20	Dimethyl ether	55-78
Pentane	30	Diethyl ether	140-160
Octane	63,8- 65	Hexyl methyl ether	97
Nonane	72-74	Dibuthyl ether	91 – 100

Table 1. Cetane number of hydrocarbons and oxygenated compounds

These last proposals are based in the fact that the ketalization of glycerol hydroxyl groups retains the oxygen atoms in the molecular structure, while the esterification reduces its viscosity. The ketalization of glycerol with acetone yields the cyclic ether [3,3-dimethyl-2,4-dioxolan-4-yl] methanol (DDM), commercially known as solketal [Fig 2.1]. There are studies about the effect of a dioxolane ring on diesel emissions indicating reduction of particulate matter [Song et al, 2005; Boot et al, 2009]. In biodiesel, it has improved oxidative stability and low temperature properties [Melero et al, 2010]. This compound was the object of some patents. Delfort et al (2005) produced DDM and other analogous ketals derivatives to be used as diesel additives. Puche (2003) described a procedure to obtain a biodiesel with improved properties at low temperature, using DDM as component. Hillion et al (2005) described a method to produce biodiesel, ethers and soluble glycerol acetals. Miller et al (2008) presented an innovative procedure using reactive distillation to prepare biodiesel and DDM on the same process using acid catalyst, without a pre-separation of glycerol.

None of the above proposals contemplate a structure of a ketal-glyceryl ester. A compound containing both ester and ether groups could benefit from each group property. The ether group would be responsible for a better ignition whereas the ester group would provide a better lubricity. In this manner a single compound would provide both properties. In applying this concept to glycerol ketal, it is proposed that the glycerol hydroxyl be esterified with long chain fatty acids as the long hydrocarbon chains would then behave as a fuel just as in biodiesel. One could think of a fuel in a similar way to biodiesel in which the methanol had been changed by an alcohol prepared from the ketal-glycerol (DDM in this case). One such derivative has been proposed that uses the short chain acetic acid [Garcia et al, 2008]. Similarly to glycerol ethers, this ketal-glyceryl acetate compound is a volatile product and, consequently, it can only be added to diesel and biodiesel in low concentrations in order to not affect diesel and biodiesel volatilization behaviour. A glycerol derivative that could contribute to diesel and biodiesel performance would create a large market for this co-product.

This paper presents the preliminary studies on the evaluation of thermal properties of ketal-glyceryl esters of long chain fatty acids developed to perform as a biofuel additive and the study of their influence on the soybean biodiesel thermal properties. The paper also presents some results on the performance of glycerol esters in drilling fluids as lubricants for water based drilling fluids and as emulsifiers and anti-crystallization additives for oil based drilling fluids.

2. Methods

The synthetic routes for the preparation of several glyceryl esters and ketal-glyceryl esters both derived from fatty acids and their respective characterization methods are described. The techniques employed to essay their applications as lubricifiers, emulsifiers and anti-crystallization additives in drilling fluids and as a cetane enhancer additive in biodiesel are presented.

2.1 Preparation and characterization of glyceryl esters

The esterification reactions of glycerol with saturated and unsaturated carboxylic acids (octanoic, decanoic, dodecanoic and 9-(cis)-octadecenoic or oleic), catalyzed by p-toluenosulfonic acid, were conducted under a nitrogen atmosphere, at 125°C for 3 to 5h. The glycerol:acid molar proportion was 3:1 and 6:1 [Yaakoub, 2007]. A scheme for the esterification reaction is presented in Fig. 2.1.

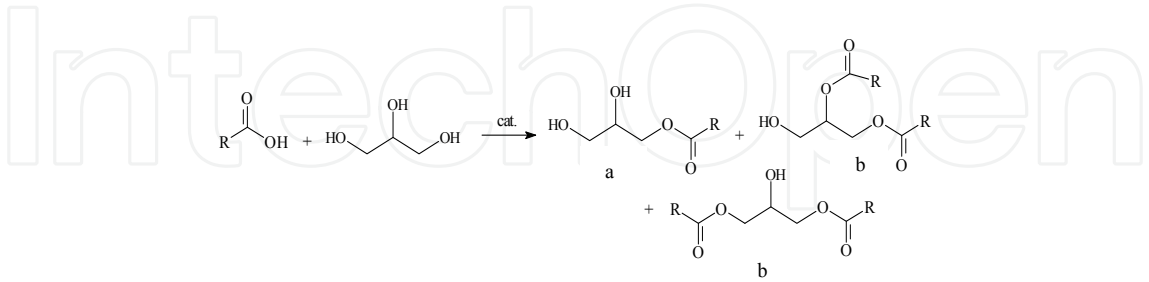


Fig. 2.1. Esterification of glycerol with carboxylic acids showing the products structures (a) monoglyceride (b) diglyceride. R represents a hydrocarbon chain having 9 to 17 carbon atoms.

The reaction mixture was washed with water to extract glycerol and ethyl ether was added to the organic phase containing the esters. After being dried with anhydrous magnesium sulfate, the solvent was evaporated and the product submitted to Fourier-transformed infrared (FTIR) and to ¹H e ¹³C nuclear magnetic resonance (NMR) analyses. By this reaction process both mono- and diglycerides were obtained as shown by FTIR that revealed ester carbonyl absorption bands (1745cm⁻¹), hydroxyl groups and the disappearance of acid carbonyls. Due to its nondestructive and noninvasive character, NMR spectroscopy provides the most convenient method for the determination of acyl positional distribution in glyceryl esters [Simova et al, 2003]. NMR allowed the quantitative determination of monoglycerides, diglycerides and acid conversion. Acid conversions for all reactions were found above 70%. The reaction performed at 6:1 resulted in higher monoglycerides proportions and the product of these reactions were used in application essays. These analytical results are presented in table 2.1.

Glyceryl Esters	Partial Ester distribution determined by ¹³ C- NMR		
	Mono	Di	Tri
Glyceryl octanoate	80.6	19.4	-
Glyceryl decanoate	77.5	18.7	3.8
Glyceryl laurate	78.5	21.5	-
Glyceryl Oleate	75.5	25.5	-
Glyceryl Oleate	60	40	-

Table 2.1. Glyceryl esters distribution as determined by ¹³ C- NMR.

2.2 Evaluation of glyceryl esters in drilling fluids

The glyceryl esters, containing mainly monoglycerides, were evaluated as lubricants in water based fluids formulations and as emulsifiers in oil based fluids formulations. First, the

general procedure for the drilling fluids formulations is described, followed by the specific techniques used to evaluate the additives for each of the desired properties. Finally, glyceryl oleate was evaluated as an anti-cristallizing additive for fatty acid methyl esters, used in ester oil based fluids.

2.2.1 Drilling fluids formulations

Several drilling fluids were formulated using the synthesized glyceryl esters as lubricants, in water based formulations, or emulsifiers in oil based formulations. The synthesized glycerides contained a minimum of 60% of monoglyceride, as presented in the section 2.1. Both water and oil based fluids were formulated in Hamilton Beach® shakers. The general compositions of the water and oil based fluids are respectively presented at Tables 2.2 and 2.3. At table 2.2, the lubricant component was either polyethyleneglycol 400 dioleate (a commercial lubricant for water based fluids) or the synthesized glyceryl esters. At table 2.3, the emulsifier component was either sorbitan monooleate (a commercial emulsifier for water-in-oil emulsions) or the synthesized glyceride.

Component	Amount	Function
Water	Up to 350 ml	Base
Xanthan Gum	2.5 g	Rheology modifier
Hydroxypropyl amide (HPA)	2.0 g	Filtrate control
PDADMAC ¹	3.0 wt%	Shale inhibition
Potassium Chloride (KCl)	3.0 wt%	Shale inhibition
Sodium Hydroxide (NaOH)	pH 9,0	pH control
Barite	28.0 g	Weight control
Lubricant	7.0g	Lubricant

¹ Polydiallyl dimethyl ammonium chloride, cationic polymer

Table 2.2. General water based fluids composition and the components functions

Component	Amount	Function
<i>n</i> -paraffin	157.5 g	Base
Brine (10wt% NaCl in water)	140.0 g	Dipersed phase
Emulsifier	11.78 g	Emulsifier
Tween® 80 ¹	2.22 g	Co-emulsifier
ECOTROL® ²	2.25 g	Filtrate control
Barite	28.0 g	Weight control

¹ polyoxyethylene sorbitan monooleate; ² polymeric additive produced by MI-SWACO

Table 2.3. General oil based fluids composition and the components functions

2.2.2 Lubricity measurements

Efficiency of the synthesized additives as lubricants in water based fluids formulations was evaluated through coefficient of friction (COF) measurements, in a Baroid Lubricity Tester

Model 212. In the experiments, a steel test block that simulates the well casing is pressed against a test ring by a torque arm. The torque is measured by intensity of current that is required to turn the ring at a constant rpm when immersed in the evaluated formulation. The applied rotational velocity and torque were, respectively, 60 rpm and 150 lb/inch, following the API procedure (RP 13B). Under these conditions, torque readings are related to COF by $\text{COF} = \text{torque reading}/135.5$, where COF is a dimensionless value. All the measurements in this work were performed at room temperature.

2.2.3 Determination of the relative stability of the emulsion

The efficiency of the synthesized additives as emulsifiers in oil based fluids formulations was evaluated through Electrical Stability (ES) tests. In these experiments, a pair of permanently spaced electrode plates is immersed in a fluid emulsion sample, and an increasing AC voltage is applied to the electrodes in a constant rate. The voltage at which the emulsion allows the current to flow is reported as relative emulsion stability (ES). High values of ES mean more kinetically stable emulsions, since a higher voltage is required to promote emulsion breakage. A commercial glyceryl oleate containing 50% of each partial ester was also essayed as emulsifier.

2.2.4 Evaluation of glyceryl ester as an anti-crystallizing agent

The anticrystallizing effect of a glyceryl oleate containing mono-, di- and triester in the proportion 60:37:3, respectively, was tested in an ester base drilling fluid consisting of a mixture of methyl fatty acid esters. These methyl esters were a commercial preparation obtained from Miracema, SA, Brazil, that will be named FAME to differentiate from other fatty acid methyl esters prepared to be used for other purposes. The FAME base fluid containing 5% of the additive in moles per weight and without the additive were both submitted to analysis in a Perkin Elmer, model 7, differential scanning calorimeter (DSC), for the determination of their temperatures of crystallization. These measurements were conducted in dynamic mode at a cooling rate of $10^{\circ}\text{C}/\text{min}$, from room temperature down to -35°C , in a nitrogen atmosphere. Isothermal measurements for the determination of the induction time for crystallization were conducted by visual inspection, at the bench, of the same solutions kept in a water-salt bath at -4°C .

2.3 Preparation and characterization of ketal-esters of glycerol

Preparation of the product of interest - (2,2-dimethyl-1,3-dioxolan-4-yl) methyl ester, product II shown in Fig 2.2-II, involved the ketalization of glycerol to (2,2-dimethyl-1,3-dioxolan-4-yl) methanol (product I shown in Fig 2.2-I) in a first step and the esterification of this intermediate in a second step. In the first step, a mixture of glycerol, propanone in excess, p-toluenesulfonic acid (catalyst) and chloroform were refluxed for 10h, while the water that was being formed was simultaneously removed by azeotropic distillation at 49°C . A Dean-Stark apparatus helped to separate the distilled solvent from the water so as to return it to the reaction flask. The ketal-glycerol (I) was isolated by: adding sodium carbonate to neutralize the catalyst, filtration of the catalyst and vacuum fractional distillation. The second step was the transesterification of product I with a mixture of methyl esters derived from palmitic (hexadecanoic), oleic (9-(cis)-octadecenoic) and stearic (octadecanoic) acids, for 6h at $125\text{--}140^{\circ}\text{C}$, in the presence of anhydrous sodium carbonate, to generate product II. This product was purified by filtration of the catalyst and distillation of

the excess of product I. The transesterification of methyl palmitate with product I was also conducted which produced (2, 2-dimethyl-1,3-dioxolan-4-yl) methyl palmitate (PDM).

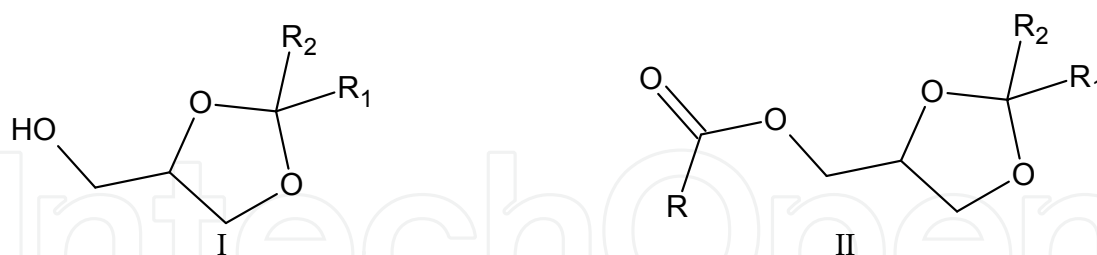


Fig. 2.2. Structure of intermediate I and product II (R =15-17 carbons; R₁, R₂ = CH₃)

These products were analysed by Fourier-transformed infrared spectrometry (FTIR) in a Nicolet, model Magma 750, by nuclear resonance spectrometry (¹H and ¹³C NMR) in a Bruker apparatus, Avance 200, at 200 and 50MHz, respectively, and by gas chromatography with mass detector (CG-MS) in a GC Agilent 5500. These analyses confirmed the formation of the ketals (I) and the ketal-esters (II). The FTIR spectra of the ketals (I) after distillation presented: the typical C-O band at 1090cm⁻¹, which differs from that of glycerol (1042cm⁻¹), an OH band at 3404cm⁻¹ relative to the non-reacted-hydroxyl, as expected, and the typical CH₃ bend vibration from the acetonyl radical at 1375cm⁻¹. The presence of a ketal C-O bond was signalled by the ¹³C-NMR spectra at 109.4 ppm. The FTIR spectra of ketal-glyceryl esters (II) showed typical ester bands at 1734cm⁻¹ and 1200cm⁻¹ and the absence of acid OH bands, while ¹³C- NMR spectra showed chemical shifts at 173.6 and 174.3ppm for ester carbonyls, besides that for ketal carbon at 109ppm. The carbonyl displacement at 174.3ppm was due to residual methyl ester from the transesterification step. The chromatographic analysis (with mass detector) also confirmed the presence of ketal-ester and residual methyl esters (Batista, 2008). Two product batches were prepared so as to contain the glyceryl-ketal esters and biodiesel in the proportions 65:35 (BDM65) and 25:75 (BDM25), respectively. A commercial biodiesel from soybean oil was used. These two mixtures were evaluated in relation to some fuel critical thermal properties.

2.5 Evaluation of ketal-glyceryl esters properties as fuel additives

The two products batches BDM65 and BDM25 containing ketal-glyceryl esters and biodiesel were evaluated in relation to the following thermal properties: temperature of crystallization at a cooling rate of 10°C/min in N₂ atmosphere and oxidation stability from 30 to 300°C in air atmosphere in a differential scanning calorimeter (Perkin-Elmer model 7); and distillation behaviour according to ASTM D1160. A sample of biodiesel and a sample of (2, 2-dimethyl-1,3-dioxolan-4-yl) methyl palmitate (PDM) were analysed under the same conditions.

3. Results

The glyceryl esters synthesized were essayed in relation to their performance: as a lubricant in water based drilling fluid, as an emulsifier in oil based drilling fluids and as an anti-crystallizing agent in ester (FAME) based drilling fluids. The ketal-glyceryl oleate was essayed in relation to its thermal properties that could affect those of biodiesel.

3.1 Glyceryl esters as lubricant for water based drilling fluid

Adsorption lubricants in an oil medium are widely known as surfactant molecules that adsorbs onto surfaces, minimizing the direct contact between those surfaces. In this lubricity model, the lubricant molecule must have a polar segment that strongly adsorbs onto the surface, and a long apolar chain, which interact their neighbours chains through weak Van der Waals forces, differently from the unlubricated surface, where strong interactions cause friction. However, in an aqueous medium this mechanism is difficult because even if the polar segment has good interaction with the surface, the apolar segment does not have a favorable interaction with water, leading to phase separation, instead of adsorption. The control of this equilibrium is a key challenge in the development of lubricants for aqueous systems.

In this work, the potential of synthesized glycerides are evaluated as lubricants in water based drilling fluids formulations. Table 3.1 presents the results obtained for the coefficient of friction (COF) measurements in formulations containing different lubricants at 2 wt%. The content of monoglycerides in these products is presented in table 2.1. All the systems containing the glyceryl esters presented considerably low COF values, when compared with the fluid without lubricant. In addition, their performance was even better than that obtained with the commercial lubricant used in aqueous formulations, polyethyleneglycol 400 dioleate.

Lubricant (2,0 wt%)	COF of fluids
Glyceryl octanoate (C8)	0.07
Glyceryl decanoate (C10)	0.06
Glyceryl laurate (C12)	0.08
Glyceryl monooleate (C18.1)*	0.04
Polyethyleneglycol 400 dioleate	0.18
Without Lubricant	0.23

* The glyceryl oleate evaluated as lubricants was the one with 74% of monoglyceride.

Table 3.1. Coefficient of Friction (COF) of the formulated water based fluids with different lubricants

Since the hydrophilic segment of the four evaluated glyceryl esters is the same, it would be expected that the efficiency of the products would increase together with the length of the hydrophobic segment, but this effect was not observed. As observed in Table 3.1, the additive that presented the best performance as lubricant in aqueous media was glyceryl oleate (C18.1), but no significant difference between the other glyceryl esters was observed. This behavior can be mainly attributed to the hydrophobic chain's length and to the additive's physical state. As glyceryl laurates (C12) and glyceryl decanoates (C10) are solid at room temperature, their dispersion is difficult, even with vigorous agitation of the Hamilton Beach shaker, resulting in a less effective performance. On the other hand, C8 and C18:1 are liquid at room temperature, which enables them to disperse easily within the media, and consequently cover the metal surface. The better results obtained by the oleates (C18:1) can be attributed to its longer hydrophobic segment, which leads to easier sliding between the covered surfaces. It is interesting to observe the role of the *cis* -insaturation

present in the structure of the C18.1 molecule on its potential as a lubricant. This configuration is responsible for the ester’s physical state in opposition to the trans isomer, glyceryl elaidate, which is a solid. In the case of the commercial lubricant, polyethyleneglycol 400 dioleate, even considering that it is liquid and presents the same hydrophobic chain as glyceryl monooleate, it does not have hydroxyls on the polar segment of its structure, which is a key structural parameter to promote the adsorption on the surface and consequently potential activity as lubricant.

3.1.2 Glyceryl esters as emulsifiers for oil based drilling fluids

Table 3.2 shows the electrical stability (ES) values obtained with the different formulations of paraffin based drilling fluids. In this study, the content of the glyceryl monooleate in relation to the dioleate was evaluated, as well as the nature of the emulsifier. It is observed that the commercial emulsifier sorbitan monooleate led to a lower ES value, while the synthesized glyceryl esters showed better results. In addition, the higher the amount of glyceyl monooleate in the composition of the oleic glyceride, the higher was the electrical stability presented by the fluid.

Emulsifier	% of monoderivative in emulsifiers	ES (Volts)
Sorbitan monooleate	-	489
Glyceryl laurate	-	593
Commercial Glyceryl oleate	50	484
Glyceryl oleate	60	638
Glyceryl oleate	74	746

Table 3.2. Electrical stability (ES) values of oil based drilling fluids formulated with different emulsifiers.

For a molecule to perform as an emulsifier it requires a specific structure where it presents a hydrophilic and a hydrophobic segment. Depending on the nature and the length of these segments, the molecule can promote a direct emulsion (oil-in-water) or an inverted emulsion (water-in-oil). Surfactants in which a hydrophilic nature predominates tends to form direct emulsions, while the predominantly lipophilic surfactants usually form inverted emulsions. The Hydrophilic-Lipophilic-Balance (HLB) is a key parameter that guides the choice of the appropriate surfactant to the target application. A high HLB surfactant is predominantly hydrophilic, whereas a low HLB surfactant is lipophilic in nature. As sorbitan monooleate is used as an emulsifier in inverted emulsions, due to its low HLB, its performance was compared to that of synthesized glyceryl esters. When comparing the structures of glyceryl monooleate with sorbitan monooleate it is observed that they have the same hydrophobic segments, but different hydrophilic segments. The ES results show that the glyceryl segment led to better emulsion stability. That is probably due to the fact that the glyceryl segment is less polar than the sorbitan segment, leading to a lower HLB, what would favour the emulsification in this case. Glycerin monolaurate showed a good performance even presenting a shorter lipophilic segment, suggesting that the nature of the

hydrophilic segment is in fact the key parameter. As discussed in previous sections, the selectivity of monoglycerides syntheses has to be optimized. When comparing the performance of products obtained in the esterification of glycerin with oleic acid where different monoderivatives yields were formed, we observe that better results were reached with systems that contained a higher amount of glyceryl monooleate and less glyceryl dioleate. This may suggest that the disubstituted product is excessively lipophilic, presenting a high affinity with the oil phase, which makes it migrate to this phase, instead of retaining it in the interface, and so minimizing its performance as an emulsifier of oil based fluid.

3.1.3 Glyceryl ester as an anti-crystallizing agent for ester based drilling fluids

The methyl esters of fatty acids (FAME) used as fluid base presented crystallization temperatures (T_c), at the present experimental conditions, at -6.4°C while by the addition of glyceryl oleate this temperature went down to -8.4°C . The effect of esters-additives prepared with monoalcohols and acids with up to 12 carbon atoms on the T_c of methyl fatty acid esters from soybean oil has already been registered to be able to decrease its T_c down to -7.6°C [Nascimento et al, 2005; Soares et al, 2009]. These same authors observed similar results for the ester-additives from di- and trihydroxylated alcohols other than glycerol. However the glyceryl oleate was able to decrease further the T_c of these methyl esters. Even more relevant was the data obtained for the induction time for crystallization as observed by the naked eye. A two fold increase in the induction time was observed for the FAME base fluid. The FAME crystallized after 30 minutes at -4°C without additive and upon its addition it delayed 50 minutes to start crystallization.

3.2 The ketal-glyceryl ester as fuel additive

The mixtures of biodiesel (B100) and the proposed additives (mixtures BDM65 and BDM25) were evaluated in relation to critical fuels thermal properties. The properties discussed are: the temperature of crystallization, the oxidation behaviour and the distillation range.

3.2.1 Temperature of crystallization

Temperature of crystallization (T_c) is one of the most critical properties of a biodiesel for, as crystallization starts, the viscosity increases leading to a higher pour point. In biodiesel this behaviour depends on the composition of methyl esters, specifically, on the percentages of methyl esters of stearic and palmitic acids [Knothe, 2005]. These are both solids at ambient temperature, and precipitate or form a gel, when their solutions are cooled, as it happens in biodiesel [Nascimento et al, 2005]. The calorimetric analysis (DSC) of biodiesel (B100) showed a crystallization onset at -6.9°C with two peak maxima at about -7.7°C and -15°C , which is typical of soybean-methyl-biodiesel at the present DSC experimental conditions. The products BDM65 and BDM25 presented a similar qualitative behaviour, but with less intense peaks, that means a smaller variation of enthalpy per gram, and a small increase in T_c . These data are shown in Table 3.3 for BDM65, which is the product containing the highest amount of ketal-glyceryl-ester. A higher crystallization temperature would be expected for the products containing ketal-glyceryl-esters, because of their greater average molecular mass. Corroborating with this expectation, the (2,2-dimethyl-1,3-dioxolan-4-yl) methyl palmitate (PDM), prepared in this work, presented a higher melting point (66°C) than methyl palmitate (30°C) and crystallized at 51°C . However, the palmitate derivative is

not the main component in these mixtures but the ketal-glyceryl esters prepared have a high contribution of unsaturated chain fatty acids as is common in biodiesel esters. This could explain the small effect of these additives on the Tc of the final mixture containing as much as 65% of ketal-glyceryl esters.

3.2.2 Oxidative stability of BDM Products

Another important characteristic to be considered in a soybean oil derived biofuel is its oxidative stability during storage. The process of oxidation of soybean oil or of its methyl esters, by the action of atmospheric oxygen, starts at the allyl carbon present in the chains of oleate, linoleate and linoleniate, which constitute about 80% of soybean oil biodiesel. Hydroperoxides formed at the initiation step can either react with other radicals, resulting in high molecular weight insoluble sediments and gums, or break apart to form carboxylic acids [McCormick et al, 2007]. In the present study this process would be of a concern because unsaturated chains are present. By differential scanning calorimetry (DSC), the product BDM65 presented oxidation onset at 143°C, BDM25 presented it at 127°C while B100 presented it at 128°C. This is a significant result indicating that the glycerol part of the structure did not enhance the oxidation process. Its presence in a higher amount, as in BDM65, seemed to work in the opposite direction helping to delay oxidation, while a smaller amount, as in BDM25 did not change the oxidative behaviour of B100.

Temperature of distillation (°C)			
Distilled			
Volume	10%	50%	90%
B100	188.6	192.9	357.9
BDM25	199	214.8	356.8

Table 3.3. Thermal properties of BDM mixtures containing biodiesel and ketal-glyceryl esters in different proportions measured by DSC.

3.3.3 Distillation range of BDM products

The distillation curve gives a pattern of the volatility of the components providing important information. The boiling range is directly related to viscosity, vapor pressure, heating value, average molecular weight, and many other chemical, physical, and mechanical properties. Any of these properties can be the determining factor in the suitability of the product in its intended application. Petroleum product specifications often include distillation limits based on data by the ASTM D1160. This test method covers the determination, at reduced pressures, of the range of boiling points for petroleum products that can be partially or completely vaporized at a maximum liquid temperature of 400°C. In the case of diesel, the distillation curve following ASTM 1160 is used to determine the cetane index by applying the distillation data to ASTM D4737. According to the Brazilian agency for fuel regulation (ANP), 90% of biodiesel B100 must distillate below 360°C. Table 1 gives the temperature of distillation determined by ASTM 1160 for a biodiesel (B100) and BDM25 at 10, 50 and 90% volume cuts as established by the referred method. The product BDM25 and B100 were inside the 90% limit, while a smaller percentage of BDM65 (87%) distilled below 360°C.

Temperature of distillation (°C)			
Distilled Volume	10%	50%	90%
B100	188,6	192,9	357,9
BDM25	199	214,8	356,8

Table 3.4. Distillation behaviour of biodiesel and BDM25, following ASTM 1160

These results showed that (2,2-dimethyl-1,3-dioxolan-4-yl)-methyl esters contributed to an increase in the final temperature of distillation, but that a maximum amount of 25% can be added to biodiesel in order to maintain its volatilization performance. If the BDM mixtures are diluted in diesel, for example mixed with B20, which is a diesel containing 20% biodiesel, these properties will also be diluted and will not affect the studied biodiesel thermal behaviour. It will be necessary, though, to test its performance under a higher amount of oxygen for longer times as they occur in the combustion chambers of compression ignition engines to investigate gum formation. This is a known problem detected in biodiesels that contain a certain amount of glycerol and partial glycerides.

4. Conclusions

Glyceryl oleates containing a minimum of 74% of monoglyceryl oleates have shown great potential for application as lubricants for water based fluids and as emulsifiers in oil based fluids, leading to excellent results, when compared to the commercially available additives. In addition, they are environmentally friendly and low cost, since they may be obtained from an abundant raw material which is the glycerin by product of biodiesel production. The evaluation of the thermal properties of mixtures of biodiesel and the ketal-glyceryl esters allows one to say that the substitution of methyl alcohol by a glycerol derivative in the structure of fatty esters has resulted in a product that is not detrimental to some critical biodiesel properties. The conversion of such a glycerol derivative into a product to be added to biodiesel could be a solution to the problem of utilising the excess of co-product glycerol. However it is not a “ready to use” product as some modifications must be made to compression ignition engines to avoid gum formation from the glycerol moiety.

5. Future research

Improvement in the synthesis of monoesters of glycerol must be focused on reaching higher selectivity in this product. It would be useful to have pure compounds to precisely establish the role of monoesters structures of polyhydroxylated alcohols as emulsifiers, lubricants and anti-crystallizing agents.

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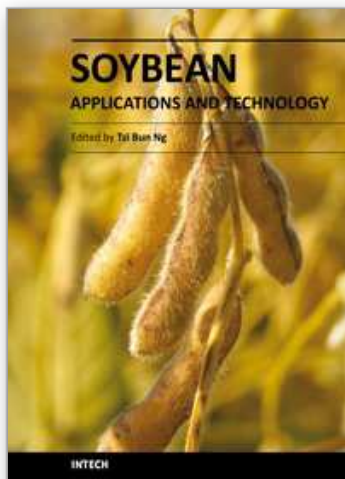
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