Synthesis and Characterization of New Solketal Alkylesters Usable as Diesel Biobased Fuel Additives

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There are described experimental studies on the esterification of solketal, (the cyclic acetal produced from glycerol and acetone reaction), by transesterification reactions of the -OH group with methyl esters of C_3 *-* C_{10} *aliphatic acids (propionic, pentanoic, hexanoic, octanoic and decanoic). The goal was to obtain better additives for diesel and biodiesel fuels, as compared to solketal. The measured physical properties (especially density, viscosity and water solubility) of the synthesized solketal esters, closer to the corresponding ones for the diesel and biodiesel fuels, permit to suppose that these new compounds should be better additives for diesel type fuels, as compared with solketal. For three of these esters there were studied the liquid-vapor equilibrium at different temperatures, determining also the Antoine equation coefficients for the calculation of vapor pressure.*

Keywords: glycerol, solketal, solketal alkyl esters, biodiesel, vapor pressure

According to EU Directive 2009/28/ EC on the promoting of the use of energy produced from renewable sources, this quota will reach a minimum of 20% in each EU Member State by 2020 [1].

The Directive 2009/28/ EC seeks to ensure only the use of sustainable biofuels, generating a clean and net GHG economy, with no negative impact on biodiversity and land use.

Moreover, EU Directive 2003/30/ EC, on the promotion of the use of biofuels or other renewable fuels for transport, provides EU Member States with tax exemptions and reductions to promote the use of biofuels [2].

Defined broadly, biofuels are alternative fuels derived from renewable sources, that can contribute to the reduction of greenhouse gas emissions and to diminish the dependence on crude oil [3].

Among the biofuels, the biodiesel is a renewable fuel almost perfectly compatible with commercial diesel engines, having some advantages over conventional diesel, such as a high biodegradability, low toxicity and low toxic emissions. According to Directive 2009/28/ EC, biodiesel is defined as *the methyl ester obtained from vegetable or animal oils of diesel quality that can be used as biofuel.* These methyl esters, commonly called fatty acid methyl esters (FAME), are the products of the transesterification with methanol, of triglycerides from vegetable oils and animal fats in the presence of an acidic or basic catalyst. This process generates as by-product a quantity of glycerol equivalent to approximately 10% of the total mass of biodiesel.

The fraction rich in glycerol resulted from the esterification mixture and submitted to catalyst neutralization and a minimum separation steps, is called crude glycerol and has a purity of about 80%, the main contaminants being soaps, salts, methanol and water. By appropriate refining steps, from the crude glycerol is obtained a technical glycerol (minimum 90% purity), or, by advanced purification (vacuum distillation), a high purity (pharmaceutical) glycerol.

Under the circumstances of continuously growth of biodiesel production, the resulted glycerol amounts cannot be absorbed by the traditional consumers (pharmaceutical, cosmetics and food industry). This generated, in the last period of time, a surplus of glycerol bid on the market, which triggered a large research effort to discover technologies for its transformation into valuable products. As a consequence, an important number of technologies were proposed for glycerol valorization: hydrogenolysis to 1,2-propanediol and 1,3-propanediol;dehydration to acrolein or 3-hydroxy-propionaldehyde; etherification with olefins or alcohols; esterification with low molecular weight acids or transesterification with low molecular weight esters; acetalization with aldehydes and ketones; selective oxidation to produce a variety of compounds such as dihydroxyacetone, glyceraldehyde, glyceric acid, glycolic acid, hydroxypyruvic acid, mesoxalic acid, oxalic acid, tartaric acid; polymerization to polyglycerols and polyglycerol esters [4-6].

The glycerol valorization by such a transformation represents a promising and a viable economic alternative, as it is not only a new sustainable way to synthesize chemicals, but also a mean to increase the efficiency of biodiesel synthesis process, reducing finally the cost of biodiesel production.

Among the viable alternatives for the raw glycerol utilization there is its transformation into fuel additives, particularly by its acetalization with different aldehydes and ketones.

The acetalization reaction occurs in two reversible steps. In the first one the glycerol reacts with an aldehyde molecule leading to a hemiacetal, releasing a significant amount of heat. This reaction takes place relatively quickly even in the absence of catalyst, at room temperature. In the second step, another alcohol molecule reacts with the hydroxyl group of the hemiacetal forming the corresponding acetal and water. This second step is also an exothermic reaction but it takes place with an acceptable rate only in presence of an acid catalyst [7-10].

The reactions of aldehydes and ketones (including acetone) with glycerol were conducted in presence of various homogeneous and heterogeneous catalysts [21-26] leading to specific acetals and ketals. Acid catalysis is

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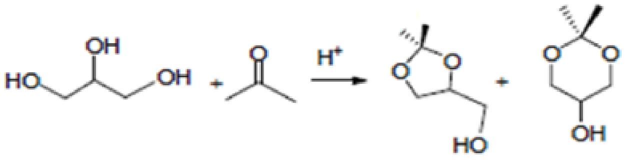
homogeneous when a strongly water-soluble or homogeneous acid is used (p-toluene-sulfonic acid is an example) and heterogenous when is used a solid acid catalyst, such as resins, zeolites or other acidified solids. The continuous extraction method can be used to achieve increased conversion and selectivity [15].

The glycerol-acetone acetalization (also called ketalization) gives two cyclic acetals, usually named ketals, both branched, having good combustion properties, namely (2,2-dimethyl-[1,3] dioxane-4-yl)-methanol (solketal a) and 2,2-dimethyl-[1,3]dioxane-5-ol (solketal b), in accordance with the following reaction scheme presented in the scheme 1.



Scheme 1. Reaction of solketal synthesis

The synthesis of solketal by the glycerol ketalization with acetone represents a viable route for efficient valorization of glycerol, leading to products with oxygenated structures, having good combustion properties and improving a number of biodiesel properties.

Some U.S. Patents [12-14] describe processes for the production of glycerol ketals usable as additives for diesel fuels. The described processes involve the reaction of purified glycerol with acetone, with or without solvent, using p-toluene-sulfonic acid catalysts or a series of strongly acidic resins (e.g. Amberlyst 15). The obtained acetals mixture is added in a proportion of 1-20% vol. in diesel, being partially soluble therein, an important feature for preventing storage separation. The presence of the acetals reducing the emission of particulate matter, especially in Diesel engines [11]. As a consequence, acetone-glycerol ketals were introduced as additives in the biodiesel formulations [16-20].

Ruiz et al. [27] describes a process for the valorization of glycerol and the mixture of glycerol/water by the formation of acetals. While p-toluene sulfonic acid is more active than Broensted acids such as zeolites and acidic resins for pure glycerol reaction, the synthesis of a hydrophobic zeolite with an optimal polarity / acid ratio leads to the formation of a better catalyst for the reaction of the water / glycerin mixture.

Maksimov et al. [28] investigated the activity of zeolite catalysts in the glycerol reaction with acetone. The authors used catalytic systems with different pore sizes, such as zeolite beta (6.6 × 6.7 nm pores), mordenite (6.5 × 7 nm pores), and zeolite HY (pores 7.4 × 7.4 nm) as well as systems based on polymer F-4SF (sulfonated tetrafluoroethylene- based fluoropolymer-copolymer**).** The activity of the catalysts was compared with that of the KU-2 (sulfonated cation exchanger) in H form, which is one of the most common catalysts for this reaction. The authors found that the activity of the zeolite catalysts is slightly lower than that of KU-2, for an acetone/glycerol ratio of 2:1. Catalysts based on beta zeolite were found to be the most suitable for the glycerol ketalization process.

Marton et al. [29] describes a study of acetone-glycerol ketals synthesis, using the molecular modeling. The molecular modeling tasks regarded elucidation of the mechanism and of the transition states involved in the reaction of acetone with glycerol, using benzene-sulfonic acid as a catalyst. The transition states for both steps are identified, the calculated low energy barriers confirming the reversibility of the involved reactions. In this case, the classical mechanism that is assuming the protonation of acetone is not confirmed by the Quantum Mecanics Study. Instead, a mechanism involving the assistance of glycerol molecule appeared more credible.

Solketal synthesis from glycerol and acetone in continuous processes were also reported [30-31]. The development of a fully continuous process for the synthesis of solketal using a reaction column with a fixed bed solid catalyst (acidic ion-exchange resin), is described by Clarkson et al. [30].

All of these studies confirm the efficiency of using solketal as a biofuel component or additive. However, the presence of the hydroxyl group in the solketal molecule is reducing its solubility in hydrocarbon fuels, inducing also some solketal physical properties quite different from those of biodiesel (FAME) or diesel fuel, as can be seen from the table 1.

Table 1

COMPARISON OF SOLKETAL PHYSICAL PROPERTIES WITH THOSE OF DIESEL FUELS

Product	Density D_{20} (kg/m^3)	Viscosity at 40°C (mm^2/s)	Solubility in water
solketal	1062-1066	11 (at 25°C)	miscible
biodiesel (FAME) acc. EN 14214	860-890	3.5-5.0	immiscible
Diesel, acc. EN 590	820-845	2.0-4.5	immiscible

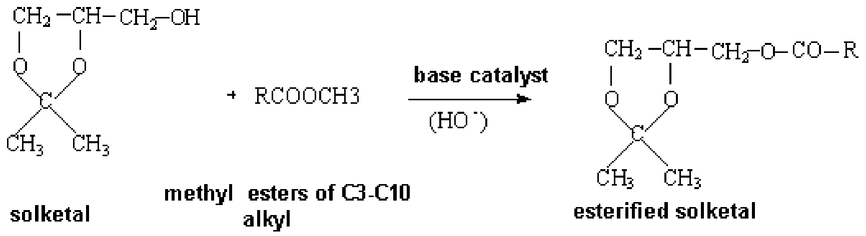
Perosa et al. [32] describe the acid-catalyzed synthesis and characterization of four fatty acids (C_8-C_{18}) esters of solketal and glycerol formal. The process consists in direct esterification of the four fatty acids with solketal in the presence of 5 wt % of para-toluene sulfonic acid (PTSA) as catalyst without solvents. Under these conditions, it was concluded that acid catalysis does not promote undesired acetal hydrolysis. High yields of isolated products were reported and all the synthesized compounds are stable. These new products contain different carbon-oxygen moieties that can in principle provide interesting properties as diesel fuel additives. However, high molar mass of resulted esters involves high viscosity and high melting points, making them unattractive for diesel fuels.

The aim of this study was to investigate the synthesis of lower molecular mass solketal esters, with C_3-C_{10} aliphatic acids (propionic, pentanoic, hexanoic, octanoic and decanoic), considered more compatible with diesel fuels. The proposed and tested process is based on the transesterification of the corresponding methyl esters of these acids with solketal in presence of a base catalyst. As a first check of the additivation properties of the solketal esters so prepared, their physical properties (particularly viscosity and water solubility) were compared to those of solketal and of diesel fuels. At our knowledge, no previous studies were published on this topic.

Experimental part

Materials and methods

Solketal (2,2-dimethyl-1,3-dioxolane-4-methanol, DL-1,2-Isopropylideneglycerol) was purchased from Sigma-Aldrich, having a purity of minimum 97%.Methyl esters of C_3 -C_{10} aliphatic acids, having a purity of 98-99%, were purchased from Sigma-Aldrich. The methanol (99 % purity) was purchased from SC Chimreactiv SRL. KOH pellets (purity of minim 90%) was purchased from Merck Schuchardt. All reagents and analytical grade solvents were commercially available and have been used as received.



Scheme 2. Solketal transesterification reaction

Since solketal is unstable in acidic medium, particularly in presence of water, the transesterification reaction was carried out in basic catalysis, using methyl esters of organic acids, according to the reaction described in scheme 2, following the method described by Stepan et. al. [33].

As catalyst, we used anhydrous potassium methoxide synthesized *in situ* from absolute methanol and KOH.

Analytical purity solketal (97%) was transesterified with the methyl esters of the following aliphatic acids: propionic acid, pentanoic acid, hexanoic acid, octanoic acid, decanoic acid. The corresponding solketal esters were synthesized, purified and characterized (solketal propionate, solketal pentanoate, solketal hexanoate, solketaloctanoate and solketal decanoate).

The synthesis process of the solketal esters comprises the following distinct steps: catalyst preparation, solketal-methylester transesterification, catalyst filtration and product purification by vacuum distillation.

As we performed batch experiments, the preparation of the catalyst was carried out in the installation used for transesterification step, consisting in a 4-neck reaction glass flask provided with electrically driven stirring, thermometer, descending condenser and an electrically heated cap (fig. 1).

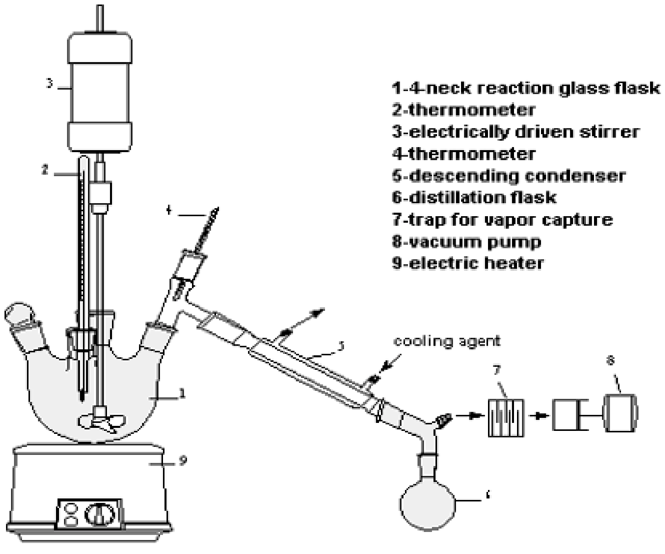


Fig. 1. Scheme of the installation used for the synthesis and purification of solketal esters

The condenser was fed with a cooling agent having the temperature -20°C. The agitation started and 90% potassium hydroxide pellets were dissolved in methanol. In the case of solketal propionate synthesis, due to its higher volatility, the setup was modified by replacing the condenser with a distillation column, provided at the top with condenser and reflux. The modification of the plant is necessary for a good separation of methanol from methyl propionate, based on the difference between their boiling points.

After complete dissolution of KOH, solketal was introduced into the flask (1) in the amounts described in Table 2 and the reaction mixture was heated to 100°C, when the liquid methanol excess was distilled off and collected in the flask (6). The potassium salt of solketal is thus formed, which is, in fact, the proper catalyst for the transesterification process. At the end of the heating period, the vacuum pump was connected, in order to completely remove the methanol and water traces from the system.

Further, the aliphatic methyl ester was added to the mixture in the flask (1), at the molar ratio methyl ester/ solketal shown in table 2. Then, the reaction mixture was heated under stirring, while maintaining the temperature in the range 120-140° C, under the vacuum generated by the vacuum pump (8). After a variable reaction time, depending on the ester used, a methanolic distillate was collected in the distillation flask (6), which can be re-used in the process.

The catalyst was then separated from the reaction mixture, by using a filtration funnel connected to a vacuum pump.

The crude product was purified in the next step, by vacuum distillation using the same installation as the transesterification step. The distillation head containing the excess reactant is separated and can be re-used in subsequent batches. The so obtained product, having the content in solketal esters over 95 wt.% is collected as distillate, a small amount of residue remaining in the flask. The purity of the final products was determined by GC-MS / MS analysis.

Product characterization

For the solketal esters synthesized above, density and viscosity determinations were performed to highlight the improvement of their characteristics as a diesel fuel component. The density was determined by using an appropriate pycnometer, pre-set and thermostated at 20 °C, and the viscosity was measured using a Hopler viscometer.

The composition of the transesterification products and of the used reagents, was analyzed using an Agilent Technology 7890A GC MS / MS Triple Quad chromatograph, equipped with a high polarity column having a cyanopropyl group grafted polysiloxane as stationary phase (SGE column BPX70: L = 50m; ID = 0.22 mm; Film φ = 0.25 μm), in the following operating conditions:

Injection Mode: Split 20: 1; Injection volume: 1μL; carrier gas Hydrogen (flow = 20 mL / min); Oven Temp.: 2100°C; Injector Temp.: 2500°C; Detector Temp: 2500°C.

VLE measurements

For the solketal esters of C_5-C_{10} aliphatic acids, the vapor-liquid equilibria were studied experimentally using a VLE 50 Fischer equipment produced by i-Fischer Engineering GmbH, Waldbuettelbrunn (Germany), allowing a pressure range of 10^{-3} - 50 bar (abs).

Results and discussions

Solketal esters synthesis

The main parameters of the transesterification process, as well as the results of solketal esters synthesis experiments (purity, yield based on solketal) are set out in

$C_x$alkyl radical	% KOH, relative to solketal	% Methanol, relative to solketal	Temperature/ reaction pressure°C/torr	Reaction time, h	Yield, %	Purity,%
x=3	1.3	8	85-90/700	6	93.6	98.25
x=5	1.4	9	135-140/100	5	94.2	97.01
x=6	1.5	10	135-140/80	4	92.5	97.35
x=8	1.5	10	135-140/60	5	92.9	98.17
x=10	1.8	12	140-145/30	6	91.2	87.92

Table 2
PARAMETERS USED FOR SYNTHESIS OF SOLKETAL ESTERS

crt nr.	Alkyl radical for esterification of solketal	C_x	Density D_{20} (kg/m^3)	Viscosity at 40°C (mm^2/s)	Solubility in water
1.	Propionate	C_3	1005.1	2.702	immiscible
2.	Pentanoate	C_5	1002.2	3.102	immiscible
3.	Hexanoate	C_6	994.6	3.220	immiscible
4.	Octanoate	C_8	971.7	3.865	immiscible
5.	Nonanoate	C_9	959.3	4.663	immiscible
6.	Decanoate	C_{10}	940.0	4.899	immiscible
7.	Solketal		1062-1066	11 (25°C)	miscible
8.	Biodiesel (FAME)*acc. EN 14214		860-890	3.5-5.0	immiscible
9.	Diesel fuel acc. EN 590		820-845	2.0-4.5	immiscible

**) Minimum content of methyl esters 96%.*

Table 3
PROPERTIES OF THE SYNTHESIZED PRODUCTS

table 2. The main properties of the synthesized products are presented in table 3.

The synthesis yield in respect with solketal was calculated by the relation:

$$h_e = \frac{n_e}{n_0}$$

n_e - amount of ester obtained from the synthesis (moles); n_0- amount of solketal used in synthesis (moles).

As observed from table 2, the described technology allows the synthesis of solketal esters of purity over 95%, by transesterification of solketal with the methyl esters of C_3-C_{10} aliphatic acids under basic catalysis. The synthesis yields in respect with solketal were also high, over 91 %, mostly over 92%.

Figures 2 and 3 present the results of GC/MS assays for one of the synthesized solketal pentanoate samples, which is considered representative for the set of experiments.

The results of GC/MS analysis for other solketal esters synthesized in our experiments are given in the supplementary material to this paper.

Based on data the presented in table 3, it can be admitted that, by the esterification of the OH group in solketal, compounds having densities and viscosity significantly closer to those of diesel fuel were obtained, as compared to those of the solketal.

VLE measurements

Table 5 presents the measured liquid-vapor equilibrium data for three of the solketal esters synthesized in this work.

The temperature dependences of vapor pressures for the three esters were correlated by the Antoine equation:

$$\log(p) = A - \frac{B}{C+T} \qquad (1)$$

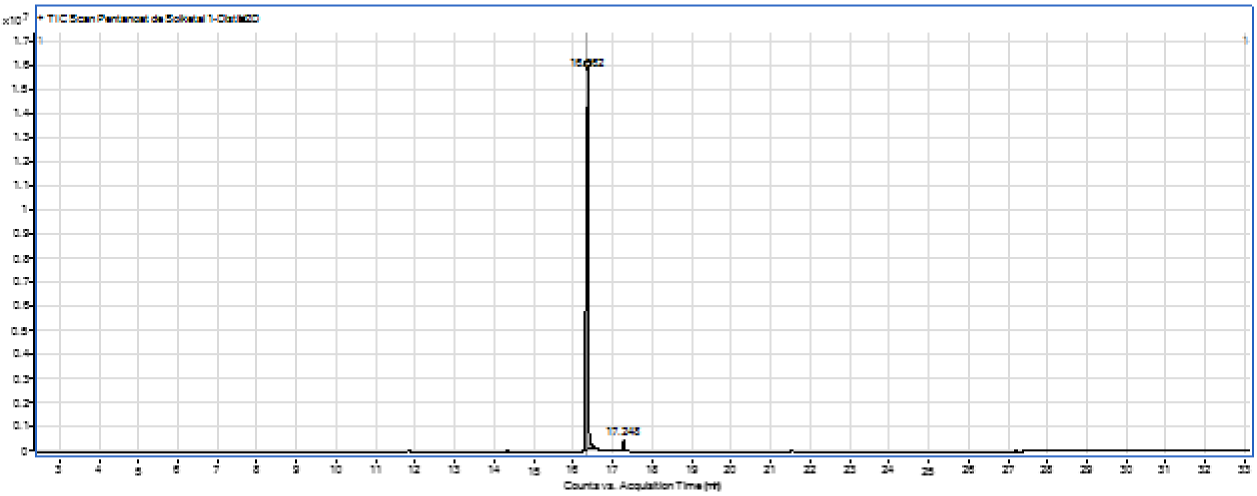
T - temperature, K; p - vapor pressure, mbar; A, B, C - parameters depending on the substance.

The parameters A, B and C for the three esters were estimated by using the nonlinear fitting tool of Matlab programming environment. The estimated parameter values are presented in table 6.

Figure 4 compares the experimental and theoretical data predicted by the Antoine equation for solketal pentanoate, as an example. It can be seen that the temperature dependence of vapor pressure is very well correlated by Antoine equation. The quality of the fit is equally good for the other two esters (solketal hexanoate and solketal decanoate). Also, confidence intervals were determined for a 95% probability. These are represented graphically as a band framing the Antoine equation curve. As seen, the interval of confidence is placed very tightly around the curve of calculated values, on the whole interval investigated.

Peak nr.	Substance	Retention time RT, min	Area sum, %
1	solketalpentanoate	16.362	98.28
2	methyl pentanoate	17.248	1.72

Table 4
CHROMATOGRAPHIC DATA OF SOLKETAL PENTANOATE



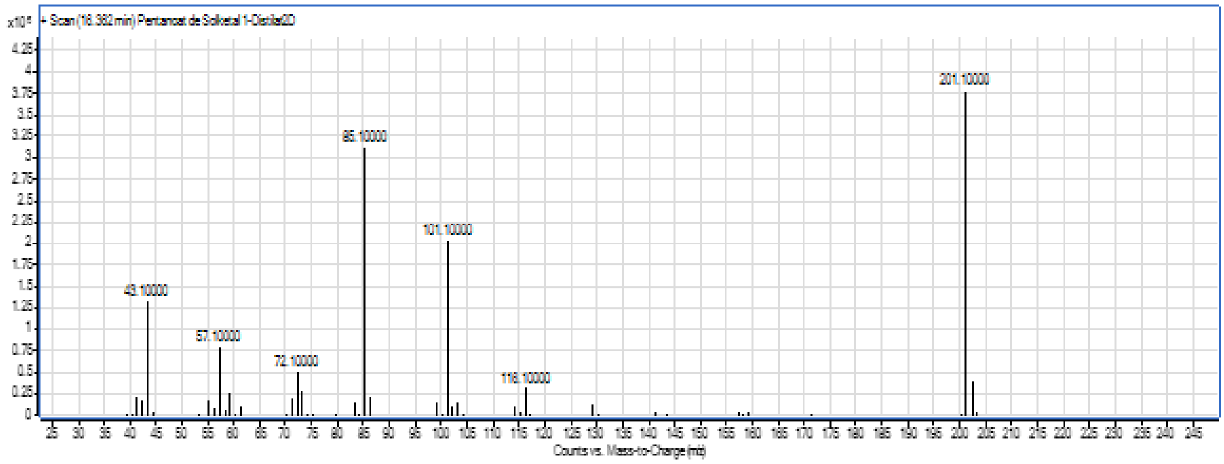


Fig. 2. Chromatogram and mass spectrum for solketal pentanoate

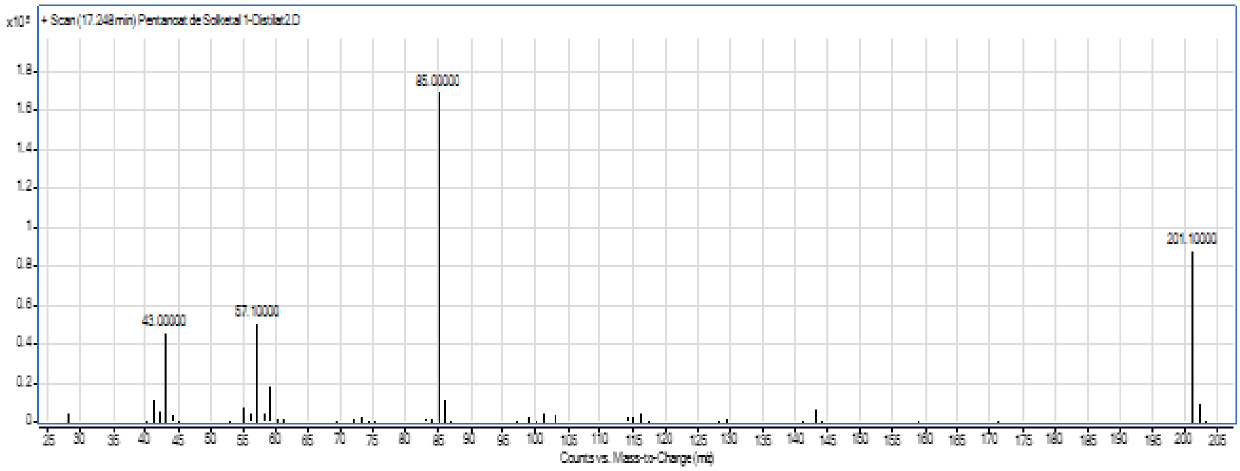


Fig. 3. Mass spectrum for methyl pentanoate (reagent)

Solketal pentanoate		**Solketal hexanoate**		**Solketal decanoate**	
P, mbar	*T, °K*	*P, mbar*	*T, °K*	*P, mbar*	*T, °K*
0.1	367.4	0.1	371.6	0.1	427.8
0.7	369.0	0.7	373.4	0.7	423.4
1.3	373.2	1.3	376.7	1.3	424.1
4.0	380.8	3.0	391.2	4.0	431.4
6.7	385.1	6.2	386.1	6.7	441.6
9.3	390.5	7.0	397.1	9.3	447.5
13.3	396.7	10.0	403.1	13.3	453.6
20.0	403.8	13.3	410.1	20.0	459.7
26.7	410.2	20.0	416.9	26.7	467.4
33.3	415.1	26.7	422.1	33.3	469.9
40.0	418.5	33.3	425.3	40.0	473.9
46.7	421.8	40.0	430.8	46.7	478.2
53.3	425.1	46.7	434.1	53.3	481.5
60.0	428.4	53.3	436.9	60.0	485.4
66.7	430.5	60.0	439.5	66.7	488.4
80.0	435.2	66.7	442.5	80.0	493.6
93.3	439.4	80.0	447.3	93.3	498.3
-	-	93.3	451.6	-	-

Table 5
MEASURED VAPOR PRESSURES
OF SOLKETAL ESTERS

Solketal Ester	**Antoine Coefficients (p in mbar; T in K)**		
	A	*B*	*C*
Solketal pentanoate	4.9	552.8	-251.5
Solketal hexanoate	5.2	674.8	-243.8
Solketal decanoate	4.1	334.3	-339.4

Table 6
ANTOINE COEFFICIENTS FOR SOLKETAL ESTERS

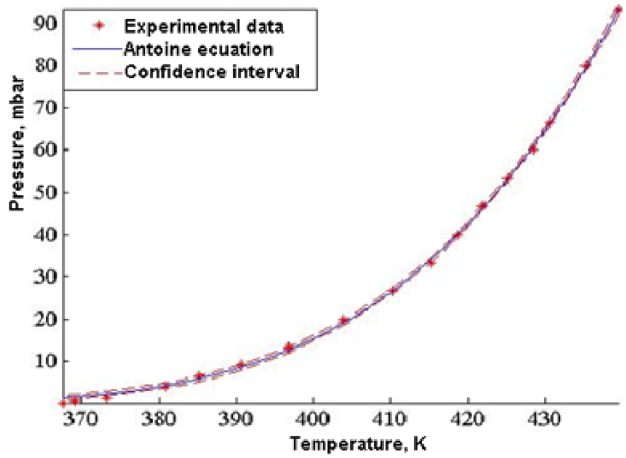


Fig. 4. Experimental and theoretical vapor pressures for solketal pentanoate

Conclusions

This work describes a procedure for base-catalyzed synthesis of several solketal esters with aliphatic acids C_3-C_{10} and their characterization. The basic medium insures the stability of solketal and a relatively high rate of reaction. The proposed method, based on the transesterification of the named methyl esters with solketal, led to high transformation yields (overs 91 % for all the esters synthesized). The determined physical properties of these solketal esters (particularly viscosity and water solubility) are closer to those of the diesel and biodiesel fuels, as compared with those of solketal. Consequently, these new solketal esters synthesized, could in principle provide interesting properties as diesel fuel additives, such as better lubricity, ignition and burning. So, the proposed solketal esterification technology, along with the already known solketal synthesis ones, could represent methods for glycerol valorization by its conversion into high quality additives for diesel and biodiesel fuels.

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