

## SYNTHESIS OF NEW ACETALS AND KETALS OF GLYCEROL AS DIESEL ADDITIVES

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*Multiple experiments of glycerol ketalization / acetalization with aldehydes / ketones at laboratory scale on discontinuous plants were performed, to convert glycerol into viable biodiesel component. For the ketalization / acetalization of glycerol, 3 aldehydes (acetaldehyde, butyraldehyde and furfuryl aldehyde) and 3 ketones (acetone, methyl-isobutyl ketone and cyclohexanone) were used under acidic heterogeneous catalysis conditions. All ketalization processes have been found to take place with high conversion of glycerol (over 90%).*

*From a technical and economical point of view, the synthesis of the solketal by ketalization of glycerol with acetone appears to be suitable for scale-up to functionalize glycerol as a biodiesel component.*

**Keywords:** glycerol; acetals; ketals; additives; biodiesel

### 1. Introduction

It is well known that nowadays, oil is still the main source of fuel used in transport, heating and hydrocarbon sources for the petrochemical industry. However, oil is a fossil fuel and more and more experts expect the reserves to be exhausted over the next 20-60 years. The International Energy Agency's World Energy Outlook (IEA, 2017) estimates that the era of oil is not yet over and the demand for fossil fuels will still grow with appreciable speeds in the next period.

Moreover, there is more evidence that the climate of the planet is changing due to the global warming generated by the greenhouse effect produced by massive greenhouse gases (GHG) emissions (especially CO<sub>2</sub>). The temperature on Earth is rising and the ice in the area of the poles begins to melt; all these changes are attributed to the greenhouse effect shown above. It has been estimated that 82% of the anthropogenic CO<sub>2</sub> emissions in the last decades were generated by the increasing incineration of fossil fuels. Consequently, it is obvious that alternative sources of energy, especially renewable ones, are necessary to diminish the global greenhouse effect.

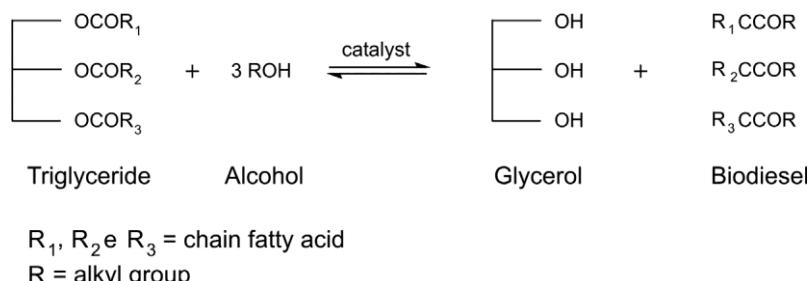
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In the field of renewable fuels production, the production of blends of methyl esters of fatty acids (biodiesel), prepared by transesterification processes of vegetable and animal fats has been widely spread lately.

The transesterification process of triglycerides is conducted in the presence of basic catalysts, typically sodium or potassium hydroxide. The general reactions of the biodiesel fuel synthesis process are presented in Scheme 1 [1].



Scheme 1. Global chemical equation for transesterification of triglycerides

Glycerol resulted as a by-product of this process represents about 10% (mass) related to the main product, the biodiesel fuel. Since the economic efficacy of these processes, and consequently the price of the obtained fuel depends on the rate of utilization of glycerol, efforts are currently being made towards the development of technologies for its transformation into products having high value.

Because of increasing the number of Biodiesel companies worldwide, an increase in glycerol production is expected in the next years, much over the current possibilities for its valorization (in the field of cosmetics, pharmaceuticals, detergents, etc.). At present, in Romania, although there are many industrial producers of Biodiesel (typically small-sized companies with limited financial capabilities), they do not have proper technologies for processing the glycerol resulted from the process. Therefore, it is either discharged into the environment, or it is sold to processors on the foreign market.

To avoid saturation of the global glycerol market, it is essential to turn it into industrial applications. An interesting method for the valorization of glycerol is its conversion to soluble in hydrocarbon-based fuels derivatives. Among the variety of glycerol derivatives, ketals and their ethers have great potential to be used as additives in fuels and biofuels [2-7]. Adding ethers to fuels can improve the cold flow properties, ignition properties and cetane number of fuels [8-10], while the use of glycerol acetals on biodiesel can improve viscosity, melting point and particulate emissions [11].

However, not all glycerol ketals/acetals can be used as additives for diesel or biodiesel. Some acetals have low ignition points and, therefore, they are not suitable for use as diesel additives.

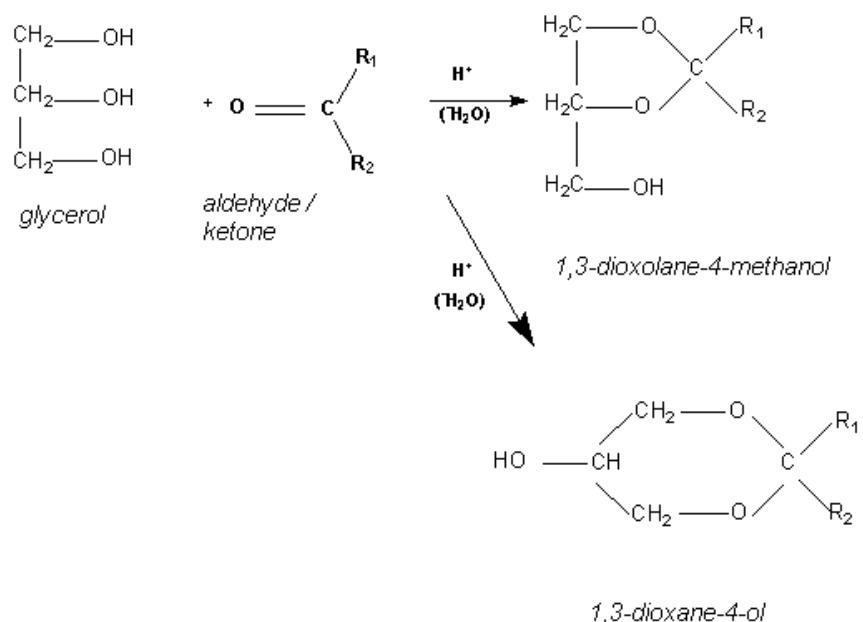
Several properties of these acetals or ketals derived from glycerol with some aldehydes or ketones, subsequently derivatized by various processes, according to Delfort et. al., [12-15], are presented in Table 1. The studies described in this work aimed to synthesize cyclic ketals and acetals of glycerol with a few rigorously chosen aldehydes and ketones, in order to transform glycerol into biodiesel components (additives), in a process viable from technical and economic point of view.

*Table 1*  
**Main properties of glycerol derivatives synthesized and tested for combustible characteristics**

Characteristics of glycerol derivatives				
Acronym	Name of main products	Obtained by reaction of glycerol with:	O content (%)	Density (kg/m <sup>3</sup> )
GBA	Glycerol Butyl Acetal	Butyraldehyde	33.6	1055
GBAC	Carbonate of Glycerol Butyl Acetal	Butyraldehyde Diethylcarbonate	36.4	1100
GEA	Glycerol Ethyl Acetal	Di Ethoxy 1.1 Ethane	36.7	1076
GFTBE	Glycerol Formal Tert-Butyl Ether	1) Formaldehyde 2) Isobutene	30.4	995
GFEA	Glycerol Formal - Ethyl Acetal	1) Formaldehyde 2) Diethoximethane	40.8	1060
GF-O	Glycerol Formal Oleate	1) Formaldehyde 2) Me Ester of rapeseed	16.5	959
GF-L	Glycerol Formal Laurate	1) Formaldehyde 2) Me Ester C <sub>12</sub> -C <sub>16</sub>	21.2	970
GTBE	Glycerol Tert-Butyl Ether	Isobutene	25.0	917
diGTBE	di-Glycerol Ter Butyl Ether	1) Glycerol condensation 2) Isobutene	25.9	959
GTBEC	Glycerol Ter Butyl Ether Carbonate	1) Isobutene 2) Diethylcarbonate	28.3	960
GPAC	Carbonate of Glycerol iso Propyl Acetal	1) Acetone 2) Diethycarbonate	39.8	1140
RME	Rapeseed Methyl Ester	-	11.3	880

## 2. Experimental Section

The experiments were carried out batchwise, on a laboratory scale setup. The transformations occur according to the reactions described in Scheme 2:



Scheme 2. Reactions for glycerol acetalization / ketalization

Depending on the nature of R1 and R2 radicals, the acetals / ketals of glycerol described in Table 2 were synthesized.

Table 2.

Carbonyl compounds used for the ketalization / acetalization of glycerol

Nr. crt	R1	R2	Carbonyl reagent
aldehydes:			
1	H	methyl	ethanal, acetaldehyde
2	H	propyl	butanal, butyraldehyde
3	-	furfuryl	furfuryl aldehyde, furan-2-carbaldehyde
cetones:			
4	methyl	methyl	acetone
5	methyl	isobutyl	methyl-isobutyl ketone
6	-	cyclohexyl	cyclohexanone

## 2.1 Chemicals

### Aldehydes

Three aldehydes - ethanal (acetaldehyde), n-butanal, furfuryl aldehyde - and three ketones - acetone, methyl isobutyl ketone and cyclohexanone - were used.

- n-Butanal, Supplier: S.C. OLTCHIM s.a. Râmnicu Vâlcea, n-butyraldehyde content: 99,04%

- Ethanal or acetaldehyde, supplier: Fluka, concentration > 99.5% (GC)

### Ketones

- Acetone: reagent p.a., supplier Chimopar S.A., acetone content, (GC) min. 99%

- Methyl-isobutyl ketone, supplier: Fluka, ketone content (GC): min. 99.0%

- Cyclohexanone, supplier: Chimopar S.A, ketone content (GC): min. 99.2%

### Glycerol

Supplier: S.C. Chimreactiv S.R.L. , Characteristics :

- purity: min. 99.5% (GC)
- density: 1.26 g / cm<sup>3</sup>

### Catalysts

Reactions were carried out under heterogeneous catalysis using strongly acidic, macroporous ion exchange resins such as Purolite 275 and Amberlyst 35, as catalysts with the characteristics presented in Table 3.

Table 3.

Main physico-chemical characteristics of the catalysts used in reactions

Characteristics	Purolite CT 275	Amberlyst 35
Structure of the polymeric core	macroporous polystyrene crosslinked with divinylbenzene	macroporous polystyrene crosslinked with divinylbenzene
Appearance	spherical granules	spherical granules
Functional groups	sulfonic acid	sulfonic acid
Ionic form on delivery	H <sup>+</sup>	H <sup>+</sup>
Water retention coefficient, %	51-59	51-57
Drying capacity, eq / kg	5,20	4,90
Pore volume, ml / g	0.4-0.6	0.35
Specific area, m <sup>2</sup> / g	20-40	50
Average pore diameter, Å	400-700	300

## 2.2 Equipment

The installation for the synthesis and purification of glycerol acetals / ketals consists in several setups where the various stages of the process were carried out, according to the scheme of operations presented below.

The acetalization / ketalization of glycerol was performed for most laboratory experiments in a 4-necked glass flask fitted with electrically driven stirring, thermometer, drip funnel, Dean-Starck hatch, reflux cooler and an electrically heated cap.

Subsequent processing of the reaction mixture involves separation of the solid catalyst and purification of the glycerol acetal / ketal. Resin catalyst filtration was done through a Büchner funnel assembled with a filtration collector vessel, coupled with a vacuum pump, protected with a cooled vapor trap.

The separation of the excess reactants and of the solvent, as well as the vacuum distillation of the final products, were done in an installation similar to that for synthesis, consisting of a 4-necked flask, equipped with an electrically operated stirrer, a thermometer, a downward condenser and an electrically heated cap. The condenser was provided with a distillation flask for collecting the distillate and was connected to a vacuum pump protected with a cooled hatch for vapor capture.

### **2.3. Procedure**

The experiments of acetalization / ketalization of glycerol with carbonyl compounds were carried out under similar conditions except for a few non-significant aspects, depending on the structure of the radicals corresponding to Scheme 1 and Table 2.

For purposes of illustration, there is further shown how to perform experiments for the synthesis of glycerol-acetone ketal (solketal).

#### ***Working procedure for the synthesis of solketal***

In a laboratory installation consisting of a 4-neck glass flask equipped with electrically operated stirring, drip funnel, thermometer, electrically heated cap, Dean-Stark water separator, assembled with a condenser, as shown in fig. 2, 368 g of glycerin were fed. Stirring was started and 20 g of strong sulfonic acid catalyst (Purolite CT 275) was fed over glycerol. Stirring was continued for 10 minutes. 302 g (5.2 moles) of acetone was fed through the dropping funnel at 45-50 °C for one hour. The reaction mass was heated with stirring while maintaining reflux for 3 hours.

140 g of condensate 1, consisting of water with acetone was distilled off. 302 g (5.2 moles) of acetone was fed through the dropping funnel for 10 minutes. The reaction mixture was heated under stirring while maintaining to reflux for 3 hours. Further, 180 g of condensate 2, made up of water with acetone was distilled off. Subsequently, 232 g (4 mol) of acetone was fed through the dropping funnel over 10 minutes. The reaction mixture was heated with stirring while maintaining reflux for 3 hours. The reaction mixture was cooled, and the catalyst was filtered off, to be re-used for subsequent batches.

328 g of condensate 3, consisting of water with acetone was distilled off. From the glycerol reaction with acetone, about 90% of solketal was obtained. The reaction yield based on glycerol was  $\eta = 89\%$ . The flax product was further purified by vacuum distillation, resulting in a product containing > 97% solketal, determined by the GC-MS-MS analysis shown below.

#### 2.4. Analytical characterization

The samples periodically taken off from synthesis were diluted with acetonitrile using the Workbench Model 7696 A automatic sample preparation device, purchased from Agilent.

The analyzes were performed on an Agilent Technology 7890A GC MS / MS Triple Quad chromatograph, on a high polarity column having a cyanopropyl-grafted polysiloxane stationary phase.

The operating conditions of the chromatograph were:

- SGE column BPX70: L = 50m; ID = 0.22 mm; film  $\varphi = 0,25 \mu\text{m}$
- oven temperature: 210°C
- injector temperature: 250°C
- detector temperature: 250°C
- carrier gas: hydrogen; flow = 20 mL / min
- injection mode: split 20: 1
- injection volume: 1 $\mu\text{l}$

#### 4. Results and discussion

Table 4 presents the results of laboratory experiments for the synthesis of acetals / ketals of glycerol.

*Table 4.*  
**Results of experiments for glycerol ketals / acetals synthesis in a batch system**

Nr. exp.	Carbonyl reagent	Mol. ratio glycerol / carbonyl	Catalyst	Reaction time (h)	Way to achieve the experiment	Glycerol conversion, %
1	butyraldehyde	1:1.5	Purolite CT 275	8	azeotropic distillation with excess BA	94
2	acetaldehyde	1:1.5	Purolite CT 275	5	azeotropic distillation with benzene	91
3	acetone	1:3.5	Purolite CT 275	9	water entraining with excess acetone (in 3 rounds)	89
4	metyl isobutyl ketone	1:1.5	Amberlyst 35	10	azeotropic distillation with benzene	93

5	cyclohexanone	1:1.5	Amberlyst 35	5	azeotropic distillation with benzene	94
6	furan-2-carbaldehyde	1:1.1	$\text{SO}_4^{2-}$ / $\text{TiO}_2$ – $\text{La}_2\text{O}_3$	5	azeotropic distillation with benzene	91

The progress of the reactions was determined by measuring the conversion of glycerol over time, using GC-MS assay. Fig. 1 shows the conversion of glycerol over time for several carbonyl reactants.

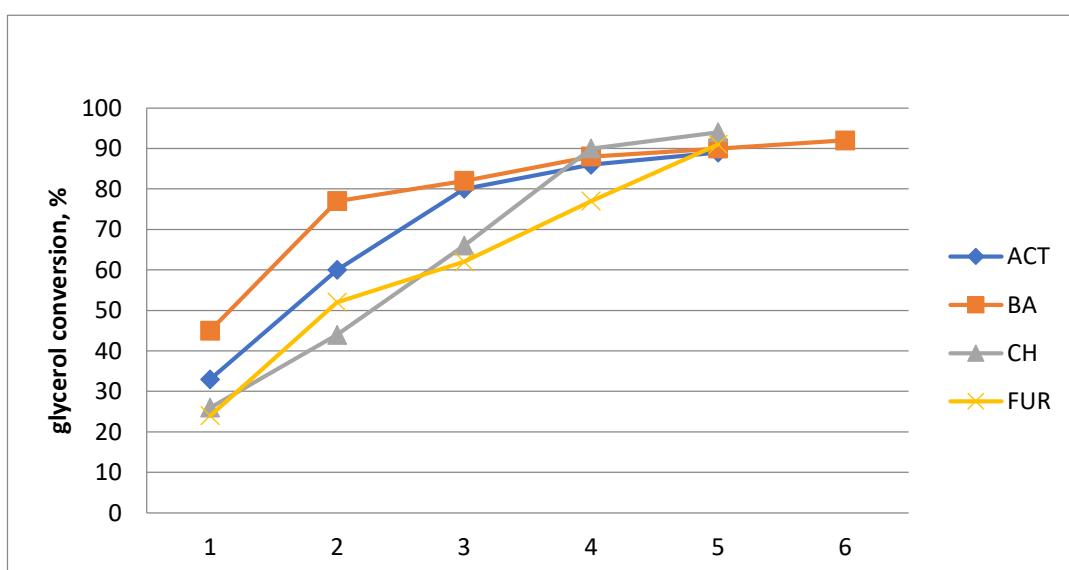


Fig. 1. Conversion of glycerol over time for several carbonyl reagents: ACT-acetone; BA-butyraldehyde; CH- cyclohexanone; FUR- furan-2-carbaldehyde

The chromatogram of the glycerol ketal with acetone, named solketal, together with the mass spectra of the compounds identified using the analytical system, are shown below in Table 5 and fig. 2, 3 and 4.

Table 5  
Peak areas at solketal GC analysis

Peak Number	RT	Area	Area %	Height	Area Sum %
1	6,758	138501	1.19	60486	1.32
2	10,053	11622865	100	4409616	96.47
3	11,457	269061	2.31	100779	2.20

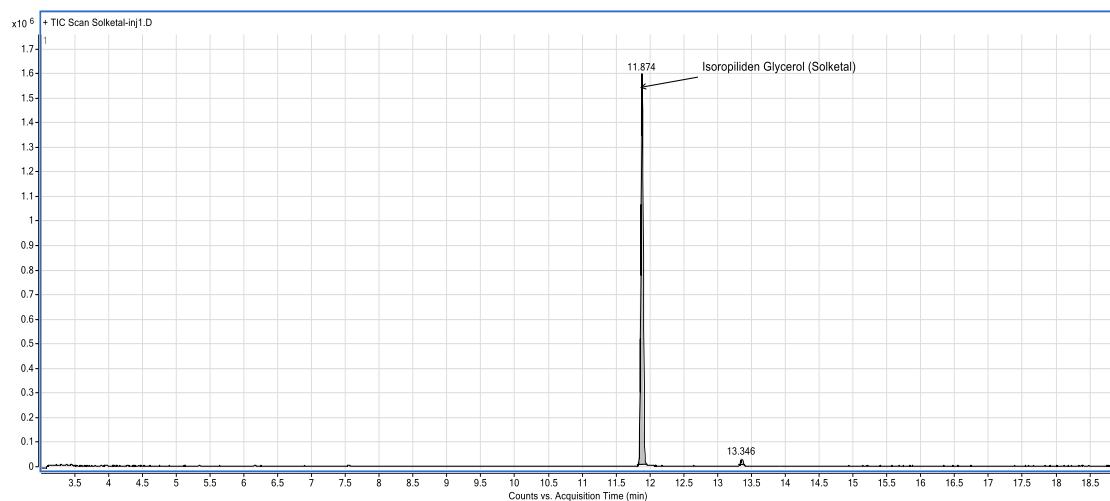


Fig.2 Chromatogram of solketal

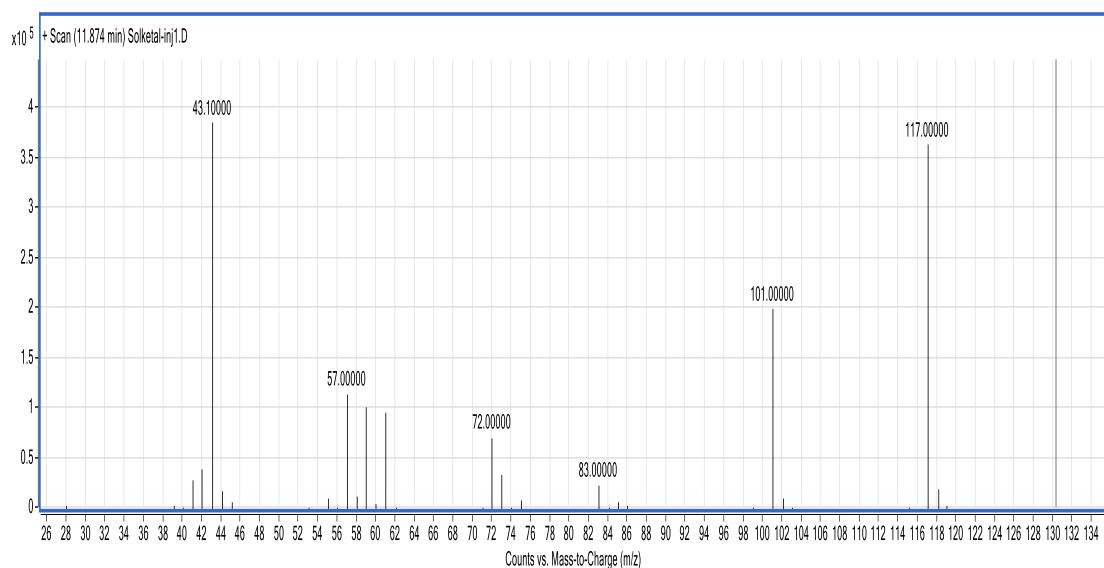


Fig. 3. Mass spectrum of 1,3-dioxolane as reaction product

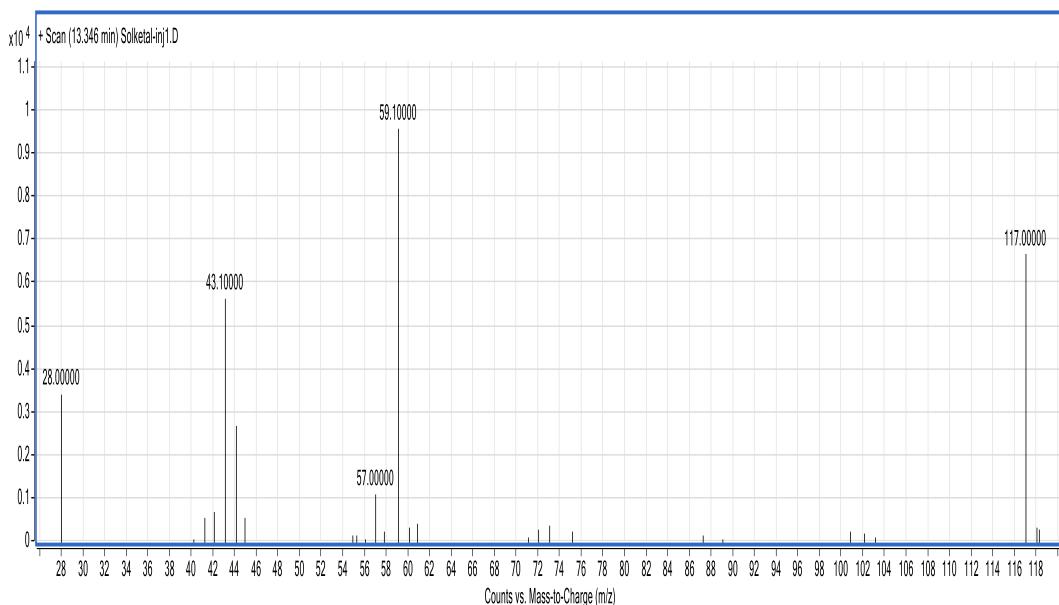


Fig. 4. Mass spectrum of the 1,3-dioxane as reaction product

## 5. Conclusions

A series of laboratory-scale experiments have been carried out on a discontinuous installation for glycerol ketalization / acetalization using a series of aldehydes / ketones as carbonyl reagents, in order to transform it into a biodiesel component. For the ketalization / acetalization of glycerol, 3 aldehydes (acetaldehyde, butyraldehyde and furan-2-carbaldehyde) and 3 ketones (acetone, methyl isobutyl ketone and cyclohexanone) were used in acidic heterogeneous catalysis.

It has been found that all ketalization processes result in a similar, high (generally over 90%) conversion of glycerol.

From a technical and economic point of view, taking into account the raw material price and the overall conversion of glycerol, it appears that the synthesis of the glycerol ketal with acetone (solketal) seems viable for scaling-up, in order to transform glycerol into the biodiesel component / additive.

## Acknowledgment:

The authors acknowledge the financial support of POSCCE project ID 652, code SMIS – CSNR 12594, „New possibilities of integrating sustainable biodiesel production. Recovery of glycerol esters and omega acids ( $\omega$  BIOGLYVAL)”

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