Fourth generation synthesis of solketal by glycerol acetalization with acetone: a solar-light photocatalytic approach.

Jesús Hidalgo-Carrillo*, Rafael C. Estévez-Toledano, Francisco J. López-Tenllado, Felipa M. Bautista, Francisco J. Urbano, Alberto Marinas*

Departamento de Química Orgánica. Instituto Universitario de Investigación en Nanoquímica (IUNAN). Universidad de Córdoba. Edf. Marie Curie (Annex). Campus de Rabanales, E-14071 Córdoba. España

*Corresponding authors.

Phone and E-mail addresses: +34 957218622, yimo@hotmail.com (J.Hidalgo-Carrillo), +34 957218622, alberto.marinas@uco.es (A.Marinas)

Abstract

Background: Biomass is the only renewable alternative to fossil fuels to produce chemicals. In this sense, glycerol is an important biomass-derived platform chemical obtained as a by-product during biodiesel generation. This paper reports for the first time the photocatalytic acetalization of glycerol with acetone to produce cyclic ketals, interesting chemicals with several applications such as solvents or (bio)fuel additives.

Methods: Commercial TiO_2 (Aeroxide® Evonik P25) was used as the photocatalyst and very mild reaction conditions (30°C, solar-simulated light) were utilized. The effect of glycerol/acetone ratio and catalyst concentration on both glycerol conversion and five-membered/six-membered ring acetal ratio was studied through factorial design of experiments. P25 concentration was in the 1-3 g/L range whereas acetone/glycerol molar ratio varied between 6 and 20.

Findings: All in all, the maximum conversion (89.6%) corresponded to 1.86g/L and acetone/glycerol ratio of 10.96. Selectivity to the 5-membered ring ketal (solketal) was over 92% in all cases. This procedure would constitute the fourth-generation synthesis of solketal by glycerol acetalization with acetone.

1.   Introduction

In the context of sustainability, we are currently facing the necessary transition from an economy largely based on fossil fuels (with their associated problems such as depletion or pollution) to another one based on renewables. The European Union promoted the development of biofuels, establishing an ambitious goal: a 20% of biofuel in the mixture with fossil fuels for the year 2020 and a 30% for the year 2030. Besides, the United States Department of Energy (DOE) has set among its objectives the replacement of the 30% of fossil fuel with biofuels, as well as 25% of the industrial organic chemicals by biomass-derived chemical compounds by 2025. Therefore, biomass valorization into fuels and chemicals is of paramount importance.

Biodiesel was one of the first options considered for being employed as biofuel. It is obtained as a mixture of ethyl and methyl esters of fatty acids (FAEE or FAME) from vegetable oils or animal fats through a transesterification reaction with a mono-alcohol, usually methanol, in the presence of an alkali catalyst. This biofuel exhibits some inherent advantages to substitute fossil fuels, such as the low toxicity and its biodegradable, renewable and biocompatible character. Furthermore, biodiesel can be easily integrated into the logistic of the global transportation system [1] and fits into the existing engines with little or no modifications needed [2]. However, during the biodiesel production, glycerol is obtained as a by-product, in a 10% by weight of the total biodiesel generated, constituting the main bottleneck of the process. To solve this problem, different approaches are being investigated. One option is the manufacture of biofuels that avoid the production of glycerol [3]. Another option is the use of glycerol as a platform molecule to produce fine chemicals or added-value products. In general, the added-value products are mainly obtained by reactions in the presence of heterogeneous catalysts, e.g. hydrogenolysis, dehydration, esterification, etherification, acetalization, etc, making

glycerol one of the most important biomass-derived platform molecules currently employed [4]. Among these options, the production of oxygenated bio-additives from glycerol has attained great attention [5]. These oxygenated additives can be classified in three groups: those obtained by glycerol acetylation, usually called as acetins, the glycerol ethers and the glycerol acetals and ketals, obtained by the reaction of glycerol either with aldehydes or ketones, usually formaldehyde or acetone, respectively. These additives are considered as a good option to replace those petroleum-based additives, such as the methyl tert-butyl ether (MTBE) and ethyl tert-butyl ether (ETBE) [6,7]. Among such glycerol-derived additives, the (2,2-dimethyl-1,3-dioxolan-4-yl)methanol, the so-called solketal, can be cited. Solketal is a colorless and odorless liquid, soluble in and with similar density to water (1.063 g/mL), possessing also a very low toxicity. Its use as fuel and biofuel additive has been recently reported by several research groups [7–9]. In addition to its use as oxygenated additive, solketal can also be employed as solvent to replace VOCs in several large-scale applications such as paints, or for preparation of diverse formulations and industrial goods such as inks, cleaning products, cooling agents, controlled delivery systems for drugs, pesticides, etc [10].

Three main approaches which corresponds to three different generations or technologies can be distinguished for the synthesis of solketal [11]. The first one is the production of solketal over homogeneous catalysts, mainly *p*-toluenesulfonic or sulfuric acid, using an organic solvent that improves the miscibility and the mass transfer between the organic and water phases. The second one contemplates the acetalization of glycerol with acetone over heterogeneous acid catalysts with a solvent, including reactions in continuous flow [12,13]. The third generation is the solventless production of solketal over heterogeneous catalysts, such as ion-exchange resins, zeolites, or mesoporous acid catalysts, just to cite some examples. Regardless of the acid catalysts used, either homogeneous or

heterogeneous, the reaction is controlled by the thermodynamic equilibrium. For the heterogeneously catalyzed reaction of glycerol with acetone, a reaction mechanism has been proposed [14] in which the formation of the 5-membered ring (2,2-dimethyl-1,3-dioxolan-4-yl)methanol, Solketal) is thermodynamically favored [15], although the 6-membered ring (2,2-dimethyl-1,3-dioxan-5-yl)methanol, DMDO) can also be obtained (Fig. S1).
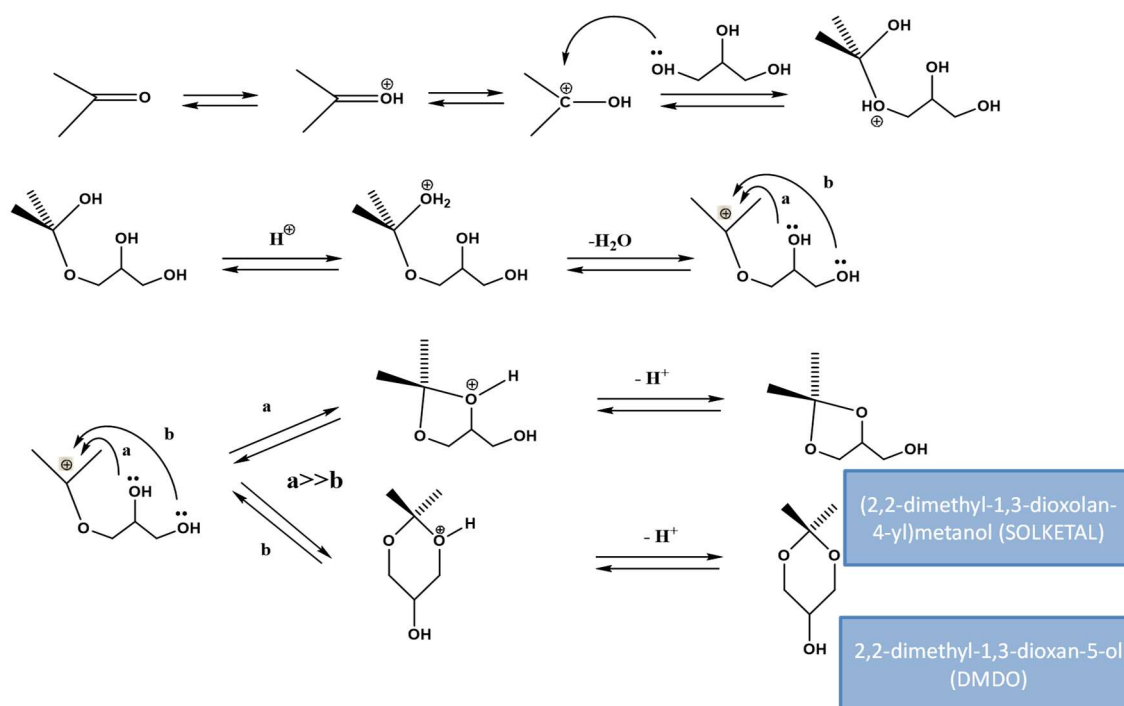

Fig. S1. Reaction mechanism of acid-catalyzed acetalization of glycerol with acetone (adapted from [14]).

In order to obtain a high solketal yield, the equilibrium must be shifted to the formation of acetals. To do so, different alternatives can be adopted, i.e. increase the reaction temperature, increase the acetone/glycerol molar ratio, remove the water that it is formed during the reaction, etc [8,11].

In the year 2004, de Lijser and Rangel [16] reported the photochemical reaction of carbonyl compounds with methanol. This reaction, homogeneously photocatalyzed, was presented as a sophisticated option of protecting carbonyl compounds by the formation of dimethyl acetates. The photocatalytic reaction of ethanol to obtain ethyl acetal was reported over a Pt/TiO$_2$ catalyst. This reaction consists in a cascade process in which the photo-dehydrogenation of ethanol yields acetaldehyde which is subsequently photo-acetalized with the ethanol in excess [17]. More recently, several researches report the protection of carbonyl compounds over several heterogeneous photo-catalysts, such as Eosin Y or graphitic carbon nitride, including in some cases the photo-acetalization of carbonyl compounds with 1,2-diols to produce 1,3-dioxolanes [18,19]. This photocatalytic reaction, carried out at room temperature, can be a suitable green alternative to the use of acid catalysts (Brönsted or Lewis) to produce these dioxolanes.

To the best of our knowledge, the present work reports for the first time the photocatalytic reaction of glycerol with acetone to yield 5- and 6-membered cyclic ketals. This process combines glycerol valorization with the use of solar energy, resulting in a green methodology to produce oxygenated bio-additives for (bio)fuels. Thus, regarding the above-mentioned methodologies, this photocatalytic process would constitute the fourth generation for the solketal production. The manuscript represents a proof of concept of a new synthetic route of solketal, a chemical compound of important applications, and may serve as inspiration for subsequent studies on different photocatalysts more active under visible light than TiO$_2$.

2. Experimental

2.1. Materials

Aeroxide® Evonik P25 was supplied by Evonik whereas glycerol was obtained from Panreac (Art Nr 141339). Acetone, solketal, Amberlyst®-15 (hereinafter referred as A-15) and DMPO were purchased from Sigma Aldrich (Art Nrs. 179124, 122696, 216380 and 92688, respectively).

2.2. Catalytic tests and spectroscopic studies

Photocatalytic experiments were performed in a 30mL double mouthed heart-shaped reactor under solar-simulated irradiation (Newport, Xe lamp) and air atmosphere. Light was focalized on the sample compartment through an optic fiber. Lamp power at the sample compartment as measured at <800 nm with an Ophir Starlite equipment was 106 mW·cm^{-2}. Further details on the experimental device are given elsewhere [20].

A multivariable experiment was designed to find the optimal reaction conditions, using the following variables: concentrations of a commercial TiO_2 catalyst (Aeroxide® Evonik P25, hereinafter referred as P25): 1, 2 and 3 g/L; acetone/glycerol molar ratios: 6, 13 and 20. The total liquid volume was kept constant at 5mL and reaction time adjusted to 24h. Catalyst suspension was continuously stirred at 800 rpm and the reactor was thermostated at 30°C.

For comparative purposes, A-15, a conventional acid catalyst consisting in a macro reticular based ion exchange resin with strongly sulfonic group, was also tested.

The products were analyzed by GC-FID (confirmation by MS), using 1,4-dioxane as an internal standard. The chromatographic separation program was: 60 °C for 6 min, heating rate of 20 °C·min^{-1} until 240 °C which was held for 10 min. The conversion of glycerol (X_G) and solketal selectivity ($S_{solketal}$) were determined by the following equations:

$$X_G\ (\%) = \frac{\text{mmol of glycerol converted}}{\text{initial mmol of glycerol}} \text{ x } 100$$

$$S_{solketal} (\%) = \frac{\text{mmol of solketal}}{\text{mmol of glycerol converted}} \text{ x } 100$$

It should be noted that in all cases, the only products coming from glycerol were the 5-membered cyclic ketal ((2,2-dimethyl-1,3-dioxolan-4-yl)methanol or solketal) and the 6-membered cyclic ketal (2,2-dimethyl-1,3-dioxan-5-ol or DMDO).

Experimental design matrices were constructed and the results were evaluated using the Statgraphics Statistical Computer Package "Statgraphics Centurion" version XV. The matrix design was randomized to eliminate the influence of any other non-observed co-variables on obtained results.

Diffuse Reflectance Infrared Fourier Transform (DRIFT) spectra were carried out on a FTIR instrument (Perkin Elmer Frontier) equipped with an "environmental chamber" (Harrick HVC-DRM). Catalyst samples were recovered by filtration, washed with 40mL water and dried overnight in an oven at 120˚C. Spectra were registered at 150˚C.

Radicals generated during the photocatalytic reaction were analyzed by EPR (Bruker EMX-Micro X-band spectrometer) operating at a frequency of 9.75 GHz. Spectra were recorded at room temperature in a 3 mm inner diameter quartz tube. Field frequency modulation, modulation amplitude, and microwave power were set to 100 kHz, 1 G, and 0.01544 mW, respectively. 5,5-dimethyl-1-pyrroline N-oxide (DMPO) was used as radicals spin-trapping reagent. A reaction mixture of acetone:glycerol (molar ratio 13:1) was suspended in 1g/L TiO_2 P25 and irradiated for 16h. DMPO (0.018M) was then added. After 10 minutes, the solution was filtered and EPR spectrum was recorded. For comparative purposes, EPR spin-trapping experiments of irradiated P25 suspensions (1g/L) in acetone and glycerol were also carried out.

3. Results and discussion

Initially, several control tests were carried out to confirm that the ketalization reaction of glycerol with acetone on P25 was photocatalytic. Those reactions were carried out at

30°C, using a catalyst concentration of 1g/L (P25 or A-15), an acetone/glycerol molar ratio of 13 and 24 h as the reaction time. Table 1 summarizes results expressed as glycerol conversion, the Solketal/DMDO molar ratio and the selectivity to solketal.

Table 1

 Preliminary tests on (photo)catalytic ketalization of glycerol with acetone.

Catalyst	Light irradiation (solar simulator)	Glycerol conversion (%)	Solketal/DMDO molar ratio	Selectivity solketal (%)
P25	No	0	0	0
A-15	No	59.4	55.8	98.2
P25	Yes	86.8	30.3	96.8
A-15	Yes	64.3	47.5	97.9
None	Yes	0	0	0

Reaction Conditions: 1.0 g/L catalyst; Acetone-to-glycerol molar ratio 13:1; 30°C, t= 24h.

Firstly, both P25 and A-15 were tested for conventional catalysis (no light). The former did not exhibit any activity, whereas the latter led to 59.4% conversion and 98.2% selectivity to solketal. In the presence of light, glycerol conversion on A-15 slightly increased (from 59.4 to 64.3%) whereas P25 exhibited 86.8% conversion and 96.8% selectivity to solketal. Finally, there was no photochemical reaction (light but no catalyst), thus confirming that reaction on P25 is photocatalytic.

Once verified that there was photocatalytic reaction on P25, the influence of acetone/glycerol ratio and catalyst mass on catalytic performance was studied through factorial design of experiments. Table 2 includes the designed matrix codes and the experimental values corresponding to the matrix values -1, 0 and 1. As commented above, three P25 catalyst concentrations 1, 2 and 3 g/L were used, and for the study of the influence of the acetone/glycerol molar ratio three different ratios 6, 13 and 20 were utilized. As can be seen, there are great differences concerning glycerol conversion,

spanning from 40.5% to 89.2% (runs 1 and 2, respectively). On the contrary, selectivity

to solketal is in all cases very high, over 92%.

Table 2
Results obtained for experimental design of glycerol acetalization with acetone on P25 at 30°C, t=24h under solar-simulated irradiation.

Run Nr	[catalyst] g/L	[catalyst] Matrix code	Molar ratio Acetone/ glycerol	Molar ratio matrix code	Glycerol conversion (%)	solketal/ DMDO molar ratio	Selectivity solketal
1	1	-1	20:1	1	40.5	13.4	93.0
2	2	0	13:1	0	89.2	39.5	97.5
3	1	-1	6:1	-1	71.5	22.3	95.6
4	1	-1	13:1	0	86.8	30.3	96.8
5	2	0	6:1	-1	75.4	27.3	96.4
6	2	0	20:1	1	47.0	14.0	93.3
7	3	1	20:1	1	44.0	12.1	92.3
8	3	1	6:1	-1	71.5	36.5	97.3
9	3	1	13:1	0	74.9	42.9	97.7

The data obtained were evaluated by ANOVA test at a significance level of 1%. Firstly,

glycerol conversion was studied, Fig. 1B representing the corresponding Pareto Chart. As

can be seen, within our experimental conditions, the catalyst concentration had no

significant influence on glycerol conversion whereas acetone to glycerol ratio had (see

the corresponding bars respectively below and over the vertical line). Moreover, in the

latter case the influence is negative thus meaning that the lower the acetone to glycerol
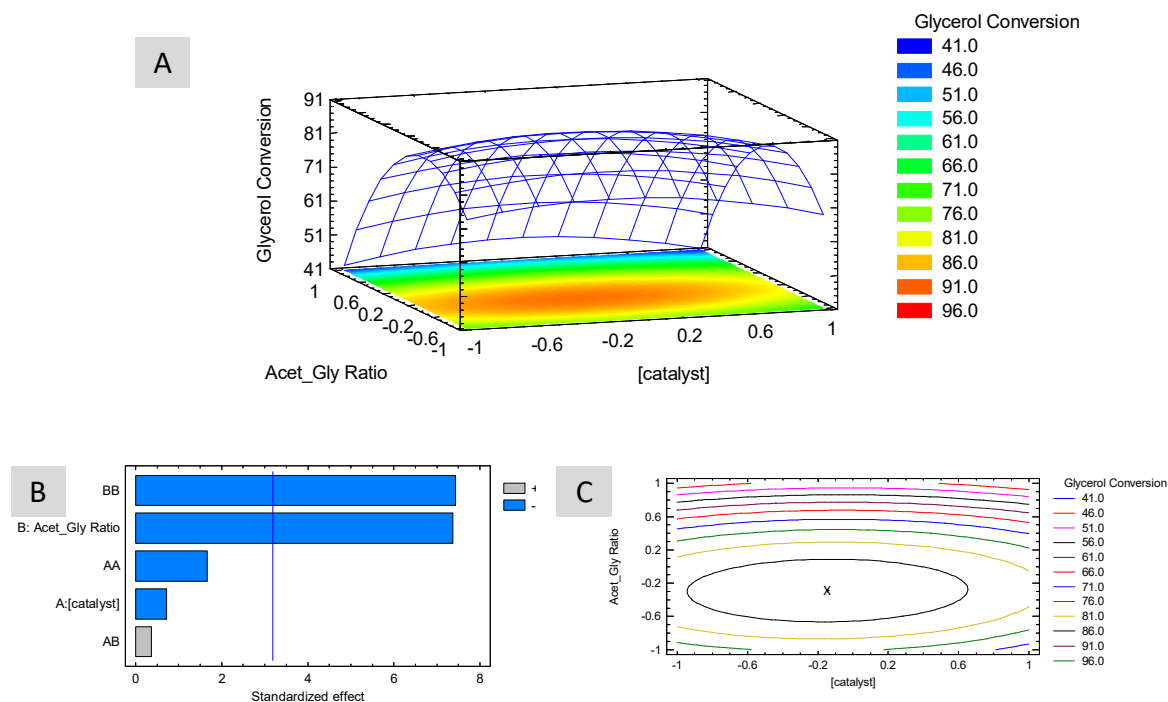
ratio, the higher the glycerol conversion.

Fig. 1. Glycerol photoacetalization with acetone on P25. Effect of catalyst concentration and acetone/glycerol ratio on glycerol conversion. Simulated response surfaces (A), Pareto chart (B) and Contour plot (C).

Table S1

Analysis of variance (ANOVA) test for response surface quadratic model and regression coefficients to describe the variability of the effects of glycerol conversion (R-squared=97.41%, R-squared adjusted for the degree of freedom =93.10%; estimation standard error =4.81%). Experimental and simulated (i.e. predicted) conversion values have also been included.

	Statistical parameters					Glycerol conversion %		
	Sum of squares	d.f.	F-Ratio	p-Value	Regr. Coeff.	Run Nr	Exp.	Simul.
Constant					87.41	1	40.5	42.5
A:[catalyst]	11.76	1	0.51	0.5277	-1.4	2	89.2	87.4
B:Acet_Gly ratio	1258.6	1	54.29	0.0052	-14.48	3	71.5	73.2
AA	64.22	1	2.77	0,1946	-5.67	4	86.8	83.1
AB	3.062	1	0.13	0.7404	0.875	5	75.4	76.6
BB	1281.9	1	55.29	0.005	-25.32	6	47.0	47.6
Total error	69.55	3				7	44.0	41.4
Total (correl.)	2689.1	8				8	71.5	68.6
						9	74.9	80.3

Fig. 1A represents the simulated response surface for glycerol conversion and Fig. 1C contains the contour plots. Fig. 1A confirms the results anticipated by Pareto chart as

regards the non-significant influence of catalyst concentration on the glycerol conversion. Nevertheless, on closer inspection, there is a slight increase from 1g/L to ca. 2g/L whereas subsequent increase up to 3g/L results in a drop. This decrease could be associated to the lower penetration of light into the solution for catalyst concentrations over 2g/L.

On the other hand (as also evidenced by Pareto chart), acetone/glycerol ratio has a significant influence on glycerol conversion, its value progressively increasing until one point from which further rise in the ratio results in a drop in the yield. This is the reason for the observed negative influence of acetone/glycerol ratio in Pareto Chart (Fig. 1B). The role of acetone is not only that of a reagent but also that of a solvent. It seems that a certain excess of acetone is necessary to homogenize the reaction mixture, lowering the high density of glycerol (1.26 g / L) and allowing a better dispersion of the photocatalyst in the reaction mixture. However, a high excess of acetone is detrimental to conversion. One possible explanation could be competition of acetone and glycerol by adsorption sites. Nevertheless, competitive studies carried out by our research group on hydrogen production through alcohol photoreforming evidenced the much higher adsorption of glycerol as compared to propan-2-ol on titania [21]. Moreover, once propan-2-ol had been converted to acetone, this chemical quickly desorbed from titania [22]. Another possible explanation is that, given that the total reaction volume is kept constant, once a minimum acetone content has ensured the homogenization of the mixture, decreasing initial glycerol density, a further increase in acetone content results in a decrease in reaction rate since glycerol concentration drops. Nevertheless, this deserves further studies. All in all, the maximum predicted conversion (89.6%) corresponds to 1.86g/L catalyst and acetone/glycerol ratio of 10.96. That point is marked with a cross in the contour plot. Having a look at the literature on solketal formation through conventional thermal acid catalysis, there are discrepancies on the optimum acetone/glycerol ratio with references

reporting 6:1 ratio [23] and other indicating values of 10:1 [24] or 12:1[25], more similar to our experimental photocatalytic results. Higher optimal ratios (e.g. 20:1[26]) have also been reported.

Table S1 summarizes results obtained from ANOVA test for prediction of glycerol conversion. Response surface obtained for glycerol conversion can be expressed according to equation 1:

Glycerol conversion= 87.41 – 1.40*[catalyst] – 14.48*(Acetone/glycerol ratio) – 5.67*[catalyst]^2 + 0.88*[catalyst]*(acetone/glycerol ratio) – 25.32*(Acetone/glycerol ratio)^2 **Equation 1**

Table S1 also depicts the observed (experimental) and predicted (from equation #1) values for glycerol conversion. As can be seen, there is quite a good correlation, with R^2=0.97 and an estimation standard error of 4.81%.

As far as the solketal/DMDO ratio is concerned, Fig. 2B shows the Pareto chart for the results presented in Table 2. Unlike Pareto chart for glycerol conversion, in this case both acetone/glycerol ratio and catalyst concentration have a significant influence, being negative and positive, respectively. In all cases (Table 2), solketal/DMDO ratio is over 12 which means that selectivity to the 5-membered ring ketal (solketal) is over 92%.

Fig. 2A and 2C depicts the simulated response surface for the solketal/DMDO ratio as well as the contour plots. As anticipated by Pareto chart, the higher the catalyst concentration the higher the solketal/DMDO ratio (i.e., positive effect in Fig. 2B). The optimum point (see the cross in the contour point) corresponds to 3g/L P25 and an acetone to glycerol ratio of 10.55 (solketal/DMDO=43.61, i.e. selectivity to solketal of 97.8%). Response surface for solketal/DMDO molar ratio can be expressed through equation # 2.

Solketal/DMDO molar ratio = 38.04 + 4.25*[catalyst] – 7.74*(acetone/glycerol ratio) – 0.71*[catalyst]^2 – 3.88*[catalyst]*(acetone/glycerol ratio) – 16.64*(acetone/glycerol ratio)^2 **Equation 2**
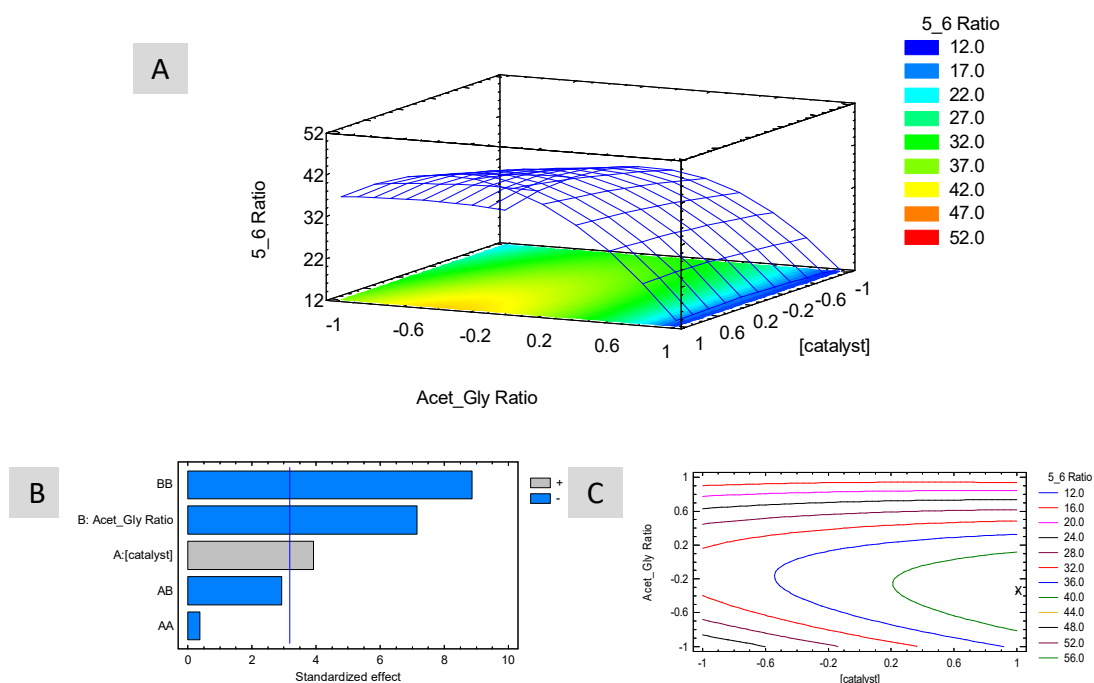

Fig. 2. Glycerol photoacetalization with acetone on P25. Effect of catalyst concentration and acetone/glycerol ratio on the five-membered/6-membered ring ratio. Simulated response surfaces (A), Pareto chart (B) and Contour plot (C).

Table S2 depicts the observed (experimental) and predicted (from equation # 2) values for solketal/DMDO molar ratio. Again, there is quite a good correlation, with R^2=0.98 and an estimation standard error of 2.65%.

Fig. S2 shows the overlap of the contour diagrams of glycerol conversion and solketal/DMDO ratio. The blue colored region represents the optimal zone for both variables. The zone is between 9 and 13 acetone/glycerol molar ratio (-0.6 and 0 in the figure) and catalyst concentration between 2.2 and 2.7 g/L (0.2 and 0.7 in x-axis).

Table S2
Analysis of variance (ANOVA) test for response surface quadratic model and regression coefficients to describe the variability of the effects of solketal/DMDO molar ratio (R-squared=98.09%, R-squared adjusted for the degree of freedom =94.90%; estimation standard error =2.65%). Experimental and simulated (i.e. predicted) Solketal/DMDO ratio values have also been included.

| Statistical parameters					Solketal/DMDO ratio		
	Sum of squares	d.f.	F-Ratio	p-Value	Regr. Coeff.	Run Nr	Exp.	Simul.
Constant					38.04	1	13.4	12.6
A:[catalyst]	108.46	1	15.42	0.0294	4.25	2	39.5	38.0
B:Acet_Gly ratio	359.91	1	51.16	0.0056	-7.75	3	22.2	20.3
AA	1.013	1	0.14	0.7296	-0.71	4	30.3	33.1
AB	60.14	1	8.55	0.0613	-3.88	5	27.3	29.1
BB	553.9	1	78.73	0.003	-16.64	6	14.0	13.7
Total error	21.11	3				7	12.1	13.3
Total (corr.)	1104.5	8				8	36.5	36.6
						9	42.9	41.6
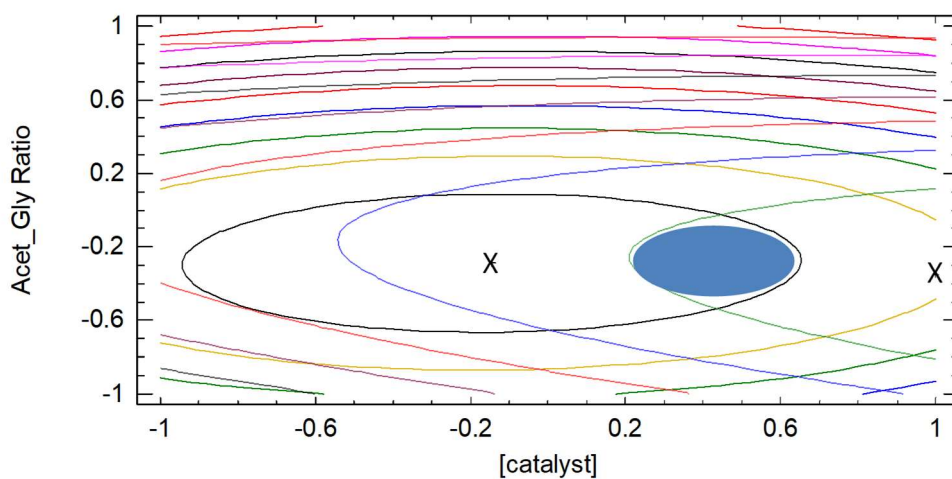
Fig. S2. Overlap of contour diagrams of glycerol conversion and solketal/DMDO ratio. The area in blue color corresponds to the optimal region for both variables.

To see if there is independence and normality of errors in the models, the Shapiro-Wilk test was carried out. The p values obtained for the model in Figure 1 (p = 0.5025) and for that of Figure 2 (p = 0.5450) confirm that the errors follow a normal distribution.

Likewise, for both cases the errors were represented against the standardized errors, and as can be seen (Figure S3) in both cases the points are close to the model line, thus confirming the null hypothesis of the independence and normality of the errors.
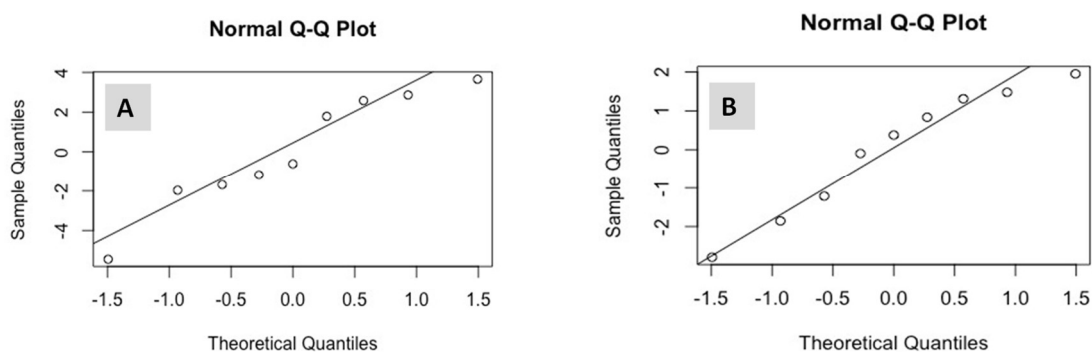

Fig. S3. Normal Q-Q Plot for the prediction models for glycerol conversion (A) and Solketal/DMDO molar ratio (B)

Table 3 compares results obtained in the present manuscript by photocatalysis with those reported in the literature using conventional heterogeneous acid catalysis under mild temperatures. Glycerol conversion obtained under photocatalytic conditions on A-15 was lower than that reported by other authors under conventional acid catalysis on Amberlysts (entries 3-5). Differences in the amount of catalyst and acetone/glycerol molar ratio used could account for that since the photocatalytic conditions do not influence the performance of A-15, as aforementioned (Table 1). Regarding photocatalytic results on P25, the values here obtained ($X_G= 87$, $S_S= 97$) are comparable or even higher than those achieved with other acid catalysts, such as zeolites (entries 6-8), sulfonated silicas (entries 9-10), Gallosilicates (entries 11-12) or heteropolyacids (entries 13-14).

Table 3

Values of glycerol conversion (X_G) and Selectivity to solketal (S_S) obtained on the solids here investigated and some other catalysts reported in the literature.

Entry	Catalyst	time (h)	catalyst (wt.%)[c]	Temperature (°C)	Acetone/ Glycerol molar ratio	X_G (%)	S_S (%)	Ref
1	P25[a]	24	0.8	30	13	87	97	This work
2	A-15[a]	24	0.8	30	13	64	98	This work
3	A-15[b]	2	3	30	6	85	84	[27]
4	A-36[b]	24	5	40	1.5	100	82	[28]
5	A-35[b]	4	5	40	6	88	86	[29]
6	NH_4-β zeolite[b]	1	5	28	2	80	78	[30]
7	HY zeolite[b]	1	5	28	2	80	78	[30]
8	IWW zeolite[b]	3	5	80	5	56	98	[31]
9	Sulfonated carbon silica (SCS)[b]	0.5	5	70	6	76	72	[32]
10	PSF-K-SiO_2[b]	1.5	5	25	10	86	98	[33]
11	XS-GaLac-B[b]	6	1	80	4	23	>95	[34]
12	Ga-P-5-Me[b]	2	2.7	50	4	29	85	[35]
13	$Sn_2SiW_{12}O_4$[b]	1	ND	25	4	97	>95	[36]
14	HPA-PMo[b]	-	5	70	6	100	98	[23]
15	Co_3O_4/SnO_2 (50:50)[b]	20	20	60	5	94	>90	[37]

[a] Experiments carried out under photocatalytic conditions.

[b] Experiments carried out under conventional acid catalysis.

[c] Determined as a function of the limiting reagent (glycerol).

To sum up, in the present workphotocatalytic solketal production was achieved on P25 under solar-simulated light with a 89.6% yield, the optimum catalyst concentration and acetone/glycerol ratio being 1.86 g/L and 10.96, respectively. These results are quite promising considering that the photocatalyst used, TiO_2 P25, is known to absorb 5% of solar light, only.

There are some discrepancies in the literature concerning the mechanism for photoacetalization reactions. On the one hand, Abdullah Khan et al [19] suggest that on illumination, some adsorbed protons are formed on the catalyst surface which are

responsible for acetalization of aldehydes through an ionic mechanism. On the other hand, Zhao et al [38] propose a radical mechanism initiated by proton abstraction from the alcohol.

In order to have some preliminary evidence on the reaction mechanism of solketal photoproduction, some additional experiments were performed. First, the reaction mixture (acetone:solketal 13:1, 1g/L TiO_2) was submitted to light irradiation for 14h, conversion to solketal being ca. 42%. The lamp was then switched off and the suspension stirred for 10 additional hours in the dark, conversion remaining the same. These experiments confirm that if produced, acid sites are *in-situ* generated upon illumination. Secondly, some DRIFT experiments were carried out, spectra being represented in Figure S4. Original P25 (trace a) exhibits some OH signals at ca. 3724, 3667 and 3631 cm^{-1} associated in the literature to isolated and bridging OH groups [39]. The same signals remain after *in-situ* illumination of the catalyst (trace b), their relative intensity slightly decreasing, probably as a consequence of the partial dehydration of the surface by some thermal effect (see the subtracted line). Adsorption of the reaction mixture (glycerol and acetone) on P25 results in an increase in OH signals (Fig. S4, trace c), probably due to contribution of hydroxyl groups in glycerol. Spectrum of the recovered catalyst after irradiation for 16h resulted in a further increase in surface hydroxyl groups (see the bands centered at ca. 3724 and 3660 cm^{-1} in trace d). This increase could be associated to the *in-situ* generation of hydroxyl groups, as proposed by Abdullah Khan et al [19] and/or to changes associated to the different alcohols formed during the reaction (i.e. transformation of glycerol into solketal).
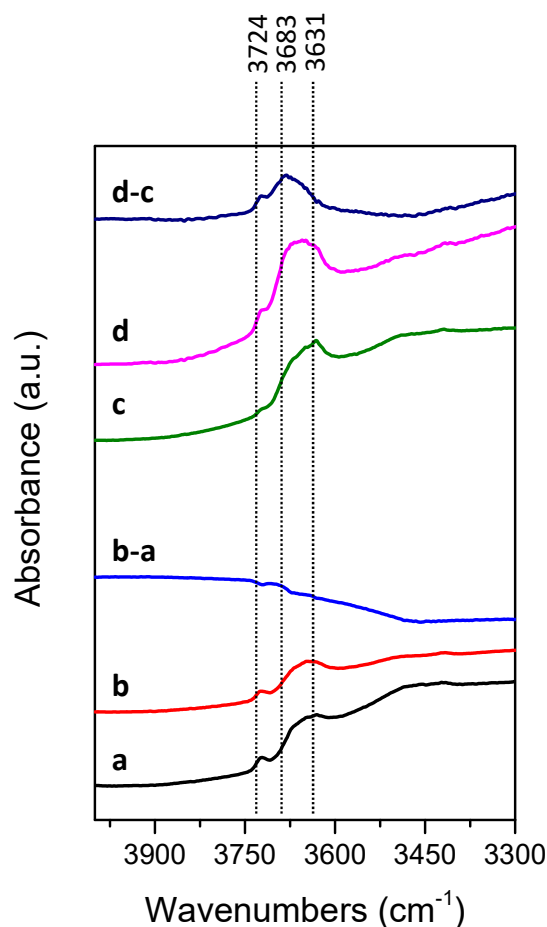
Fig S4. DRIFT spectra of P25 (a) in the dark, (b) illuminated, (c) after adsorption of the reaction mixture (acetone:glycerol 13:1) and (d) recovered after 16h of photocatalytic reaction. The corresponding substract spectra of (b)-(a) and (d)-(c) have also being included to better appreciate the changes.

Finally, some EPR studies were conducted, using DMPO as the trapping agent, the main results being summarized in Figure S5. Therefore, irradiation of either glycerol or acetone results in the generation of radicals. In the case of the reaction mixture, EPR profile resembles that of acetone. This is hardly surprising considering that the acetone:glycerol ratio was 13:1. Nevertheless, on closer inspection, the EPR of the reaction mixture after addition of DMPO exhibits some shoulders which could be associated to some new

radicals formed during the reaction. Thus, it is evident that radical species are formed in the reaction medium upon illumination, even though the coexistence of an ionic mechanism mediated by *in-situ* generated protons cannot be ruled out. This requires further studies.
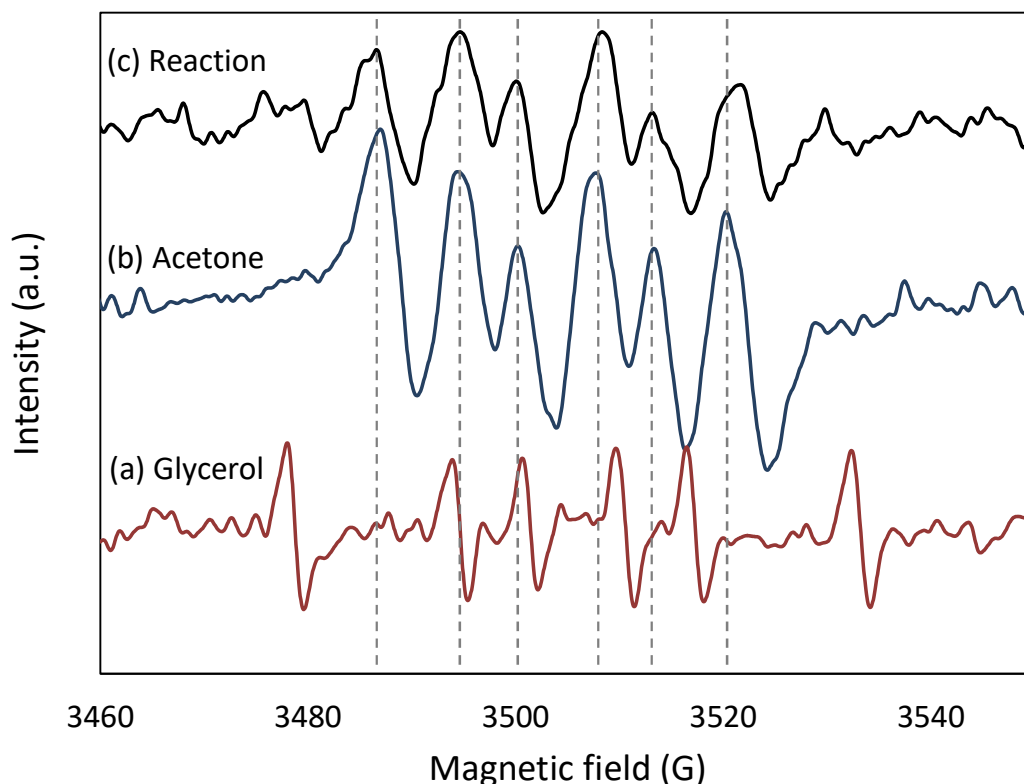

Fig S5. EPR spectra obtained upon illumination (solar simulator) of P25 suspensions in the presence of DMPO spin trap. (a) glycerol, (b) acetone, (c) acetone:gluycerol 13:1 mixture after 16h of irradiation with solar-simulated light.

All in all, considering EPR results, a tentative radical reaction mechanism for the photocatalytic synthesis of solketal is proposed in Figure 3. It is based on that proposed by Zhao *et al.* for the photocatalyzed reaction between a carbonyl compound and an alcohol [38]. Under solar-simulated radiation, the absorption of a photon generates an electron-hole pair in the semiconductor. Subsequently, glycerol is oxidized through its reaction with the photogenerated hole, forming the corresponding glycerol radical. This

extremely reactive radical species reacts with the carbonyl group of acetone, obtaining a new radical adduct which, subsequently and with the intervention of the electron generated in the semiconductor, is transformed into an anionic intermediate. The loss of a water molecule followed by the nucleophilic attack of a second hydroxyl group of glycerol finally leads to the five (solketal) or six-membered (DMDO) ring acetal, the production of the former being favorable [40].
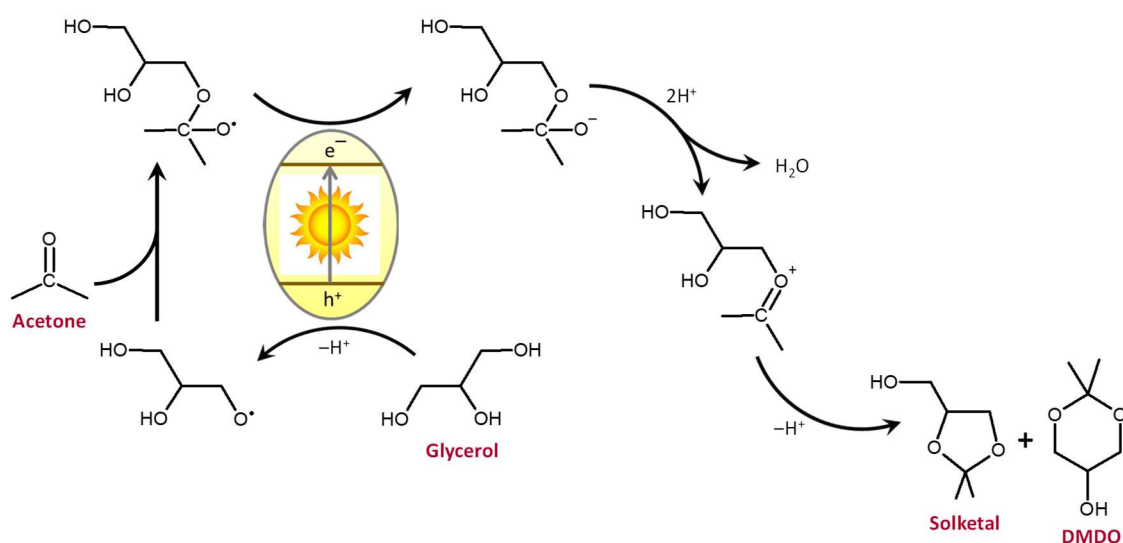

Fig. 3. Proposed reaction mechanism for photocatalytic acetalization of glycerol and acetone to produce solketal based on ref [38].

4. Conclusions and future prospects

Photocatalytic ketalization of glycerol with acetone to produce (bio)fuel additives, has been reported for the first time. The process can be achieved with high yield (89.6%) under mild reaction conditions (30ºC), by using a non-acid catalyst (Aeroxide® Evonik P25 TiO_2) and sun light. Selectivity to the 5-membered ring cyclic ketal (solketal) is over 92% in all cases, with the 6-membered ring ketal (DMDO) found as the only by-product. Considering that the catalyst used is P25, which only utilizes ca. 5% of sun light, there is ample room for improvement using some other visible-light active photocatalysts,

specially concerning reaction time. Moreover, performance of the photocatalytic reaction in flow conditions would be desirable. Further studies on the reaction mechanism are also required. All in all, this proof of concept has revealed as a new promising more sustainable solketal production approach.

CRediT authorship contribution statement

Jesús Hidalgo Carrillo: investigation, analysis, writing-original draft

Rafael C. Estévez-Toledano: investigation, analysis, writing-original draft

Francisco-J. López-Tenllado: investigation, analysis

Felipa M. Bautista: funding acquisition, project administration, supervision

Francisco J. Urbano: funding acquisition, project administration, conceptualization, supervision, review and editing

Alberto Marinas: funding acquisition, project administration, conceptualization, supervision, review and editing

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi XXXXXXX

References

[1]   Ridjan I, Mathiesen BV, Connolly D, Duić N. The feasibility of synthetic fuels in renewable energy systems. Energy 2013;57:76–84. https://doi.org/10.1016/j.energy.2013.01.046.

[2]   Knothe G, Razon LF. Biodiesel fuels. Prog Energy Combust Sci 2017;58:36–59. https://doi.org/10.1016/j.pecs.2016.08.001.

[3]   Estevez R, Aguado-Deblas L, Bautista FM, Luna D, Luna C, Calero J, et al. Biodiesel at the crossroads: A critical review. Catalysts 2019;9. https://doi.org/10.3390/catal9121033.

[4]   Bagheri S, Julkapli NM, Yehye WA. Catalytic conversion of biodiesel derived raw glycerol to value added products. Renew Sustain Energy Rev 2015;41:113–27. https://doi.org/10.1016/j.rser.2014.08.031.

[5]   Nda-Umar U, Ramli I, Taufiq-Yap Y, Muhamad E. An Overview of Recent Research in the Conversion of Glycerol into Biofuels, Fuel Additives and other Bio-Based Chemicals. Catalysts 2018;9:15. https://doi.org/10.3390/catal9010015.

[6]   Kulkarni RM, Britto PJ, Narula A, Saqline S, Anand D, Bhagyalakshmi C, et al. Kinetic studies on the synthesis of fuel additives from glycerol using CeO2-ZrO2 metal oxide catalyst. Biofuel Res J 2020;7:1100–8. https://doi.org/10.18331/BRJ2020.7.1.2.

[7]   Oprescu EE, Stepan E, Dragomir RE, Radu A, Rosca P. Synthesis and testing of glycerol ketals as components for diesel fuel. Fuel Process Technol 2013;110:214–7. https://doi.org/10.1016/j.fuproc.2012.12.017.

[8]   Nanda MR, Zhang Y, Yuan Z, Qin W, Ghaziaskar HS, Xu C. Catalytic conversion of glycerol for sustainable production of solketal as a fuel additive: A review. Renew Sustain Energy Rev 2016;56:1022–31. https://doi.org/10.1016/j.rser.2015.12.008.

[9]   Sankaranarayanan S, Jindapon W, Ngamcharussrivichai C. Valorization of biodiesel plant-derived products via preparation of solketal fatty esters over calcium-rich natural materials derived oxides. J Taiwan Inst Chem Eng 2017;81:57–64. https://doi.org/10.1016/j.jtice.2017.10.007.

[10]   Calvo-Flores FG, Monteagudo-Arrebola MJ, Dobado JA, Isac-García J. Green and Bio-Based Solvents. Top Curr Chem 2018;376:18. https://doi.org/10.1007/s41061-018-0191-6.

[11]   Talebian-Kiakalaieh A, Amin NAS, Najaafi N, Tarighi S. A Review on the Catalytic Acetalization of Bio-renewable Glycerol to Fuel Additives. Front Chem 2018;6. https://doi.org/10.3389/fchem.2018.00573.

[12]   Aghbashlo M, Tabatabaei M, Hosseinpour S, Rastegari H, Ghaziaskar HS. Multi-objective exergy-based optimization of continuous glycerol ketalization to synthesize solketal as a biodiesel additive in subcritical acetone. Energy Convers Manag 2018;160:251–61. https://doi.org/10.1016/j.enconman.2018.01.044.

[13]   Aghbashlo M, Hosseinpour S, Tabatabaei M, Rastegari H, Ghaziaskar HS. Multi-objective exergoeconomic and exergoenvironmental optimization of continuous synthesis of solketal through glycerol ketalization with acetone in the presence of ethanol as co-solvent. Renew Energy 2019;130:735–48. https://doi.org/10.1016/j.renene.2018.06.103.

[14]   Smirnov AA, Selishcheva SA, Yakovlev VA. Acetalization catalysts for synthesis of valuable oxygenated fuel additives from glycerol. Catalysts 2018;8:1–25. https://doi.org/10.3390/catal8120595.

[15]   Ozorio LP, Pianzolli R, Mota MBS, Mota CJA. Reactivity of glycerol/acetone ketal (solketal) and glycerol/formaldehyde acetals toward acid-catalyzed hydrolysis. J Braz Chem Soc 2012;23:931–7. https://doi.org/10.1590/S0103-50532012000500019.

[16]   De Lijser HJP, Rangel NA. Photochemical acetalization of carbonyl compounds in protic media using an in situ generated photocatalyst. J Org Chem 2004;69:8315–22. https://doi.org/10.1021/jo0485886.

[17]   Zhang H, Wu Y, Li L, Zhu Z. Photocatalytic Direct Conversion of Ethanol to 1,1-Diethoxyethane over Noble-Metal-Loaded TiO2 Nanotubes and Nanorods. ChemSusChem 2015;8:1226–31. https://doi.org/10.1002/cssc.201403305.

[18]   Zhou Q, Jia T, Li X-X, Zhou L, Li C-J, Feng Y-S. House bulb light-induced photochemical acetalization of carbonyl compounds catalyzed by Eosin Y. Synth Commun 2018;48:1068–75. https://doi.org/10.1080/00397911.2018.1434545.

[19]   Abdullah Khan M, Teixeira IF, Li MMJ, Koito Y, Tsang SCE. Graphitic carbon nitride catalysed photoacetalization of aldehydes/ketones under ambient conditions. Chem Commun 2016;52:2772–5. https://doi.org/10.1039/C5CC08344C.

[20]   Hidalgo-Carrillo J, Martín-Gómez J, Morales J, Espejo JC, Urbano FJ, Marinas A. Hydrogen Photo-Production from Glycerol Using Nickel-Doped TiO2 Catalysts: Effect of Catalyst Pre-Treatment. Energies 2019;12:3351. https://doi.org/https://doi.org/10.3390/en12173351.

[21]   López-Tenllado FJ, Hidalgo-Carrillo J, Montes V, Marinas A, Urbano FJ, Marinas JM, et al. A comparative study of hydrogen photocatalytic production from glycerol and propan-2-ol on M/TiO2 systems (M= Au, Pt, Pd). Catal Today 2017;280:58–64.

[22]   López-Tenllado FJ, Hidalgo-Carrillo J, Montes-Jiménez V, Sánchez-López E, Urbano FJ, Marinas A. Photocatalytic production of hydrogen from binary mixtures of C-3 alcohols on Pt/TiO2 : Influence of alcohol structure. Catal Today 2019;328:2–7. https://doi.org/10.1016/j.cattod.2018.10.001.

[23]   Ferreira P, Fonseca IM, Ramos AM, Vital J, Castanheiro JE. Valorisation of glycerol by condensation with acetone over silica-included heteropolyacids. Appl Catal B Environ 2010;98:94–9. https://doi.org/10.1016/j.apcatb.2010.05.018.

[24]   Li X, Zheng L, Hou Z. Acetalization of glycerol with acetone over Co[II](Co[III]xAl2−x)O4 derived from layered double hydroxide. Fuel 2018;233:565–71. https://doi.org/10.1016/j.fuel.2018.06.096.

[25]   Al-Saadi LS, Eze VC, Harvey AP. Techno-Economic Analysis of Glycerol Valorization via Catalytic Applications of Sulphonic Acid-Functionalized Copolymer Beads. Front Chem 2020;7. https://doi.org/10.3389/fchem.2019.00882.

[26]   Roldán L, Mallada R, Fraile JM, Menéndez M. Glycerol upgrading by ketalization in a zeolite membrane reactor. Asia-Pacific J Chem Eng 2009:279–84. https://doi.org/10.1002/apj.

[27]   Sandesh S, Halgeri AB, Shanbhag G V. Utilization of renewable resources: Condensation of glycerol with acetone at room temperature catalyzed by organic-inorganic hybrid catalyst. J Mol Catal A Chem 2015;401:73–80.

https://doi.org/10.1016/j.molcata.2015.02.015.

[28] Deutsch J, Martin A, Lieske H. Investigations on heterogeneously catalysed condensations of glycerol to cyclic acetals. J Catal 2007;245:428–35. https://doi.org/10.1016/j.jcat.2006.11.006.

[29] Nanda MR, Yuan Z, Qin W, Ghaziaskar HS, Poirier MA, Xu CC. A new continuous-flow process for catalytic conversion of glycerol to oxygenated fuel additive: Catalyst screening. Appl Energy 2014;123:75–81. https://doi.org/10.1016/j.apenergy.2014.02.055.

[30] Manjunathan P, Maradur SP, Halgeri AB, Shanbhag G V. Room temperature synthesis of solketal from acetalization of glycerol with acetone: Effect of crystallite size and the role of acidity of beta zeolite. J Mol Catal A Chem 2015;396:47–54. https://doi.org/10.1016/j.molcata.2014.09.028.

[31] Podolean I, Zhang J, Shamzhy M, Parvulescu VI, Čejka J. olvent-free ketalization of polyols over germanosilicate zeolites: the role of the nature and strength of acid sites. Catal Sci Technol 2020;10:8254–64.

[32] Nandan D, Sreenivasulu P, Sivakumar Konathala LN, Kumar M, Viswanadham N. Acid functionalized carbon-silica composite and its application for solketal production. Microporous Mesoporous Mater 2013;179:182–90. https://doi.org/10.1016/j.micromeso.2013.06.004.

[33] Zhou R, Jiang Y, Zhao H, Ye B, Wang L, Hou Z. Synthesis of solketal from glycerol over modified SiO2 supported p-phenolsulfonic acid catalyst. Fuel 2021;291:120207. https://doi.org/10.1016/j.fuel.2021.120207.

[34] Hussein H, Vivian A, Fusaro L, Devillers M, Aprile C. Synthesis of Highly Accessible Gallosilicates via Impregnation Procedure: Enhanced Catalytic Performances in the Conversion of Glycerol into Solketal. ChemCatChem 2020;12:5966–76. https://doi.org/10.1002/cctc.202001172.

[35] Vivian A, Soumoy L, Fusaro L, Fiorilli S, Debecker DP, Aprile C. Surface-functionalized mesoporous gallosilicate catalysts for the efficient and sustainable upgrading of glycerol to solketal. Green Chem 2021;23:354–66. https://doi.org/10.1039/d0gc02562c.

[36] da Silva MJ, Teixeira MG, Chaves DM, Siqueira L. An efficient process to synthesize solketal from glycerol over tin (II) silicotungstate catalyst. Fuel 2020;281:118724. https://doi.org/10.1016/j.fuel.2020.118724.

[37] Bewana S, Joe Ndolomingo M, Meijboom R, Bingwa N. Cobalt oxide promoted tin oxide catalysts for highly selective glycerol acetalization reaction. Inorg Chem Commun 2021;128:108578. https://doi.org/10.1016/j.inoche.2021.108578.

[38] Zhao Y, Shalom M, Antonietti M. Visible light-driven graphitic carbon nitride (g-C3N4) photocatalyzed ketalization reaction in methanol with methylviologen as efficient electron mediator. Appl Catal B Environ 2017;207:311–5. https://doi.org/10.1016/j.apcatb.2017.02.044.

[39] Li W, Du D, Yan T, Kong D, You J, Li D. Relationship between surface hydroxyl groups and liquid-phase photocatalytic activity of titanium dioxide. J Colloid Interface Sci 2015;444:42–8. https://doi.org/10.1016/j.jcis.2014.12.052.

[40] Rossa V, Pessanha YDSP, Díaz GC, Câmara LDT, Pergher SBC, Aranda DAG. Reaction kinetic study of solketal production from glycerol ketalization with acetone. Ind Eng

Chem Res 2017;56:479–88. https://doi.org/10.1021/acs.iecr.6b03581.