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Short communication

Efficient and selective conversion of glycidol to 1,2-propanediol over Pd/C catalyst

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ABSTRACT

The present work deals with the catalytic hydrogenolysis of glycidol to 1,2-propanediol. Reactions were carried out in a closed steel reactor using noble metal based heterogeneous catalysts (Pd, Rh, Pt) under hydrogen pressure (1–8 bars) in the temperature range of 25–140 °C. Pd/C shows the highest glycidol conversion (96%) under solvent free conditions after 24 h with high selectivity to 1,2-propanediol (93%). The effect of the solvent was also investigated and it was demonstrated that ethanol reduces drastically oligomer production enhancing selectivity up to 99% with a significant reaction time reduction (6 h). The Pd/C catalyst shows high recyclability and could be reused several times (9 cycles) without losses in activity and selectivity.

1. Introduction

The future of humanity is in the sustainable development which is strictly linked with the reduction of the use of non-renewable resources. This trend is nowadays highlighted by legislative interventions that favor or impose the use of bio-resources (see for example in European Directive 2009/28/EC about renewable energy and Horizon 2020 Program about research investments). In this framework a great industrial development has been obtained in the biodiesel production (22.5 billion liters were produced worldwide in 2012 [1]). The biodiesel is mainly produced by transesterification of triglycerides with methanol. A co-product of biodiesel is glycerol and today around 2 million of ton of glycerol are on the market. The glycerol glut has produced a reduction in glycerol price with a strong consequence on the economic sustainability of biodiesel production. However this situation has put on the market a new cheap raw material and a great number of new uses of glycerol has been proposed [2,3]. The production of propanediols (1,2 propanediol (1,2-PD) and 1,3 propanediol (1,3-PD)) by hydrogenolysis of glycerol has received particular attention [4–9]. The reaction of hydrogenolysis of glycerol is characterized by the necessity of high hydrogen pressure (1–25 MPa), high reaction temperature (400–500 K), and also by problems related with the selectivity (1,2-PD, 1,3-PD, 1 Propanol, 2 Propanol, ethylene glycol, ethanol can be formed in the hydrogenolysis reaction) [10,11]. Pd based catalyst has been successfully employed in glycerol hydrogenolysis to 1,2-PD both in the presence and in the absence of added hydrogen [12,13].

Generally, 1,2-PD is derived from propylene oxide [14], moreover, alternative synthetic routes have been investigated such as vapor phase catalytic hydrogenation of lactic acid [15]. 1,3-PD is currently produced from ethylene oxide (Shell route) or acrolein (Degussa–DuPont route) by catalytic routes.

Both 1,2-PD and 1,3-PD are value added products used in many applications therefore the synthesis of these chemicals from glycerol by using less harsh reaction conditions is a highly desirable target. In this scenario the use of alternative path to obtain the desired diols from glycerol seems to be a promising strategy. Indeed the hydrogenation of glycidol can give the desired diols in good yield under moderate reaction conditions. Glycidol can be obtained from glycerol by different ways (see Scheme 1) by decarboxylation of glycerol carbonate [10] or by basic treatment of monochlorohydrins [16].

Monochlorohydrins can be obtained by selective hydrochlorination of glycerol [17] or by hydrolysis of epichlorohydrin [18]. Despite glycerol carbonate is an interesting product for the industrial chemistry its practical application is still under development [19], on the contrary the production of epichlorohydrin from glycerol is now an important industrial reality [2].

The production of glycidol could be integrated in the epichlorohydrin plant also to solve the low reactivity of 2-chloro-1,3-propanediol in the formation of dichlorohydrins [16]. As a matter of fact the rate of conversion of this product to dichlorohydrins is very low and to avoid its accumulation a purge of the recirculation stream is necessary in the epichlorohydrin industrial plant. The purge stream is rich of monochlorohydrins that can be recovered by hydrolysis to glycerol or

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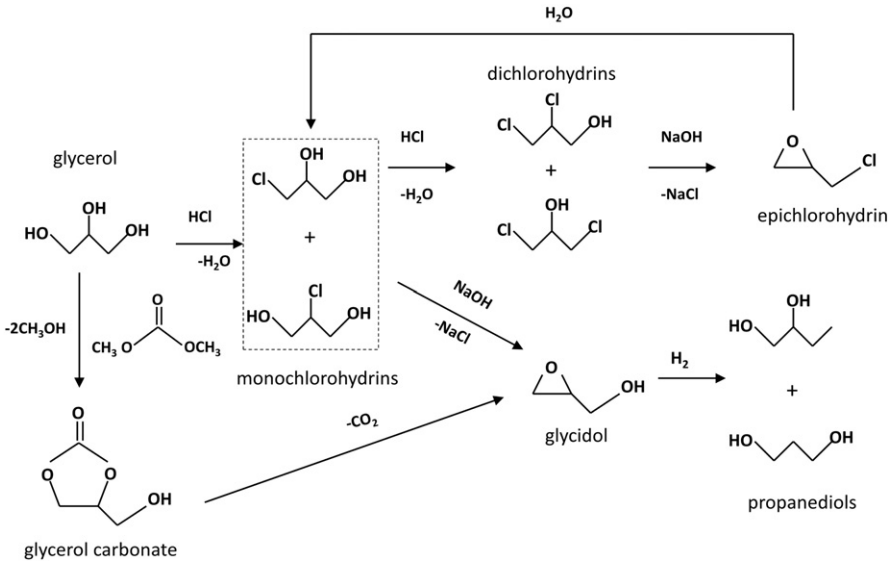

Scheme 1. Reaction pathway for glycerol conversion to epichlorohydrin.

in the new proposed process that can be converted to glycidol. It can be estimated that in an epichlorohydrin industrial plant (from the kinetics of the hydrochlorination reactions [16]) around 5% of glycidol in respect to production of epichlorohydrin can be produced by this way. This means, for example, that an industrial plant of 100,000 tons/y of epichlorohydrin can produce 5000 tons/y of glycidol, and consequently the same quantity of propanediols.

There aren't many data about glycidol hydrogenation, however in a patent application [20], it has been shown that the hydrogenation of glycidol can give place to high yield of 1,3 propanediol (50–65%) using mild reaction conditions 0.8–1.6 MPa, 373 K, metal based catalysts (Ni, Co, Ru) and solvents. Furthermore, a single reaction is reported by Sajiki et al. [21] where an efficient selective conversion (89% yield) of glycidol to 1,2-propanediol (selectivity100%) is obtained using Pd/C-ethylenediamine complex in methanol for 22 h at a hydrogen pressure of 1 bar using a glycidol/catalyst weight ratio of 10 (calculated TOF = 2.9 h^{-1}).

Noble metals based heterogeneous catalysts (Pd, Rh, Pt) are commonly preferred in hydrogenation reactions and in the reductive ring-opening of epoxides to the corresponding alcohols [22,23].

In this paper a systematic catalytic screening has been done to individuate the best catalyst for glycidol hydrogenation under solvent free conditions. Moreover the effect of reaction conditions (temperature, time, hydrogen pressure) and of the solvent (chloroform, toluene, tetrahydrofuran, ethanol, methanol, hexane, diethyl ether, dichloromethane) has been investigated.

2. Material and methods

2.1. Materials

The catalysts used in this work were purchased from Sigma-Aldrich (5% Rh/C, 10% Pt/C, 10% Pd/C, 0.5% Rh/Al_2O_3, 0.5% Pt/Al_2O_3, 0.5% Pd/Al_2O_3). Glycidol 96%, 1,2-propanediol 99.5%, 1,3-propanediol 98%, Al_2O_3 and activated charcoal were purchased from Sigma-Aldrich. All the solvents were distilled before reactions and the catalysts were not pretreated before reaction.

2.2. Catalytic reactions

Solvent free hydrogenation of glycidol was carried out in a pressure reactor (maximum operation pressure 8 bars) of 150 mL capacity equipped with a pressure gauge, safety valve, valves for gas inlet and outlet and a thermometer for temperature sensing. Glycidol (96% of purity, Sigma-Aldrich) was distilled before the experiments. Reactor was equipped with glass vials containing 5 mL of glycidol, an appropriate catalyst amount in order to obtain a glycidol/catalyst mass ratio of 100 and a magnetic stirrer. Experiments were carried out

Table 1
Glycidol hydrogenation under solvent free conditions[a].

Experiment	Catalyst/support	Conversion (%)	TOF[d] (h^{-1})	1,2-propanediol (%)	1,3-propanediol (%)	Oligomers (%)
1	No catalyst	13.8	–	<1	<1	>99
2	Rh/Al_2O_3[b]	65.1	4.1	74.5	<1	25.3
3	Pd/Al_2O_3[b]	59.0	3.9	79.6	<1	19.8
4	Pt/Al_2O_3[b]	37.8	4.5	56.9	<1	42.8
5	Rh/C[c]	95.2	6.3	21	1.8	77.2
6	Pd/C[c]	96.1	6.6	93.1	<1	6.7
7	Pt/C[c]	96.7	8.1	68.9	2.7	28.4
8	C[c]	89.6	–	<1	<1	99.0
9	Al_2O_3[c]	95.4	–	<1	<1	99.2

[a] Reaction conditions.
[b] 1.0 g of catalyst, 0.5 mL of glycidol, 8 bars H_2, 80 °C, 24 h.
[c] 0.5 g of catalyst, 5 mL of glycidol, 8 bars H_2, 80 °C, 24 h.
[d] TOF was calculated considering all the metal sites on the surface active in catalysis, in such a way the reported TOF is the lowest possible.

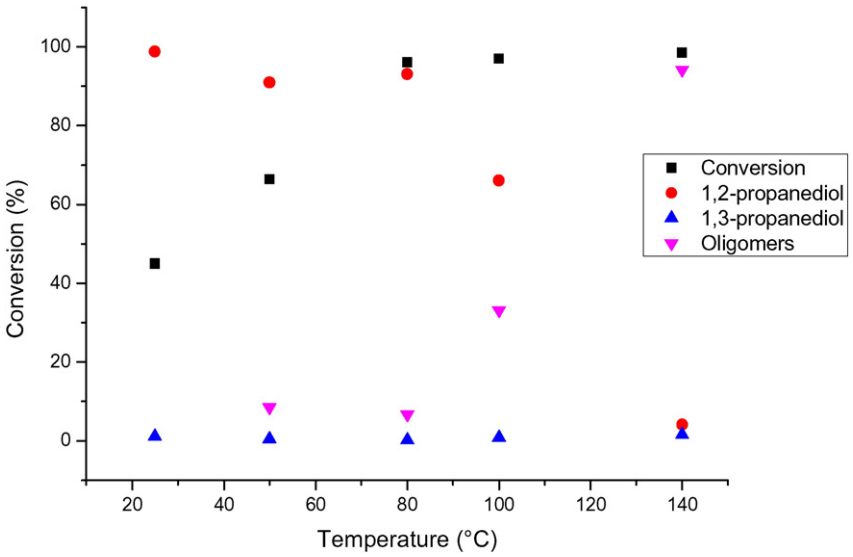

Fig. 1. Effect of temperature on glycidol conversion (reaction conditions: 0.5 g of Pd/C, 5 mL of glycidol, 8 bars H_2, 24 h).

under hydrogen pressure of 8 bars at 80 °C for 24 h. Catalyst was removed by filtration and the reaction products were purified on celite before GC-FID analysis.

Glycidol hydrogenation was also carried out using solvents in order to evaluate their effect on the reaction time and selectivity. In these experiments 5 mL of distilled solvent and 1 mL of purified glycidol and substrate were used and catalyst mass ratio was maintained at 100. Experiments were carried out at 80 °C for 24 h under magnetic stirrer (300 rpm). Products were purified on celite and solvent removed using a rotary evaporator before GC analysis. The samples were prepared for the analysis by diluting 0.1 mL of product sample to a final volume of 10 mL with ethanol in a glass vial.

Gas chromatographic analysis was carried out using a Thermo Trace GC equipped with a 30 m × 0.32 mm polar column Famewax. The initial oven temperature was initially 40 °C then programmed to 200 °C at 10 °C/min and held at 200 °C for 5 min with He flow rate of 1.2 mL/min and splitless injection mode was used. FID temperature was 250 °C while 230 °C for the inlet. The integrated areas were converted to weight percentages for each component present in the sample using the calibration curves prepared for all the components. The conversion and selectivity of glycidol were calculated on the basis of Eqs. (1) and (2):

$$\text{Glycidol conversion } [\%] = \frac{\text{moles of reacted glycidol}}{\text{moles of glycidol feed}} * 100 \quad (1)$$

$$\text{Glycidol selectivity } [\%] = \frac{\text{moles of defined product}}{\text{moles of reacted glycidol}} * 100. \quad (2)$$

The relative standard deviation of three replicates was lower than 4% in all cases.

3. Experimental

3.1. Results and discussion

3.1.1. Catalytic screening and reaction condition optimization

A preliminary catalytic screening in the hydrogenolysis of glycidol is performed in the presence of heterogeneous catalysts based on noble metals (Pd, Pt and Rh) commonly used for hydrogenation reactions

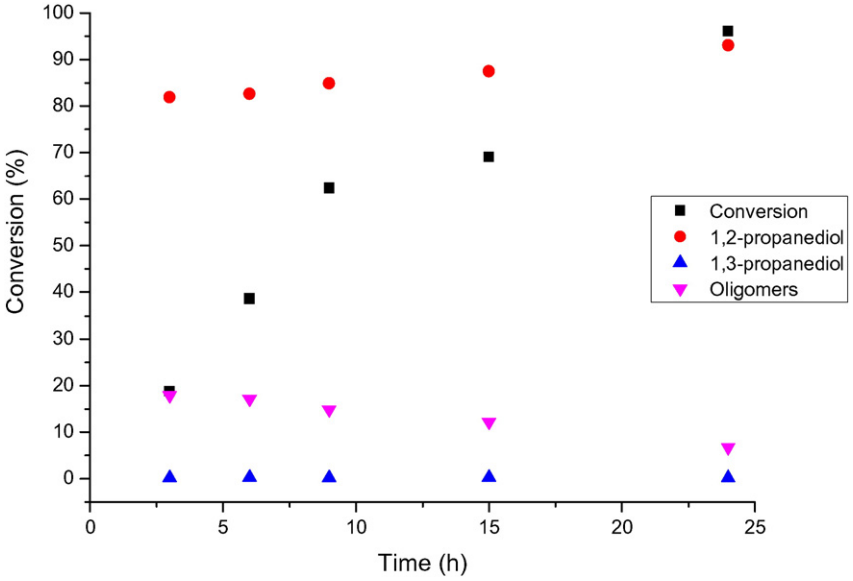

Fig. 2. Glycidol conversion using Pd/C catalyst (0.5 g Pd/C, 5 mL glycidol, 80 °C, 8 bars H_2).

Table 2
Glycidol hydrogenation using Pd/C[a].

Solvent	Conversion (%)	1,2-propanediol (%)	1,3-propanediol (%)	Oligomers
Tetrahydrofuran	93.2	95.6	0.7	3.7
Chloroform	52.5	28.7	0.7	70.6
Toluene	99.9	99.7	0.2	<1
Ethanol	99.2	99.2	0.4	0.4
Diethyl ether	99.7	98.9	0.8	<1
Dichloromethane	98.3	99.1	0.7	<1
Methanol	97.7	98.9	0.9	<1
Hexane	99.4	98.0	0.5	1.5

[a] Reaction conditions: 0.1 g of catalyst, 1 mL of glycidol, 5 mL solvent, 8 bars H_2, 80 °C, 24 h.

under solvent free conditions and the results are summarized in Table 1. Glycidol is conveniently hydrogenolyzed under a hydrogen pressure of 8 bars for 24 h at 80 °C. One can observe that the best results in terms of conversion and selectivity are obtained in the presence of the palladium and platinum based catalysts (entries 6 and 7). In particular, using 10 wt.% Pd/C the substrate is quantitatively converted, with high selectivity, to 1,2-PD, (93.1%). Notably, at this temperature the main byproduct is due to the oligomerization via epoxide opening of glycidol [24]. This reaction is catalyzed by the nucleophilic attack of both acid (charcoal) or basic (alumina) substrates (see entries 8 and 9) forming mainly dimers as evidenced by ^{13}C NMR analysis (see Fig. S3). Under these conditions, 1,3-PD is obtained only in very small amount with a maximum observed for the Pt/C catalyst (2.7%).

Owing the good performances in terms of conversion and selectivity to 1,2 PD of the 10% Pd/C we focus our investigation on this system, characterized by using XRD, TEM and BET analyses (See also Supporting information). Indeed, in order to evaluate the effect of temperature on the conversion and selectivity, the reactions were carried under solvent-free conditions at 25, 50, 80, 100 and 140 °C, under 8 bars of hydrogen pressure for 24 h. The effect of temperature on the conversion of glycidol to 1,2-PD is shown in Fig. 1 (See also Supporting information).

On one hand, the temperature has a significant effect on the overall yield of the 1,2-PD with an increase from 45% to 96% in the conversion passing from 25°to 80 °C maintaining a good selectivity toward 1,2-PD this range (around 90%). On the other hand, a further increase results in a severe loss of selectivity (66% at 100 °C and to 4% at 140 °C) with glycidol oligomers becoming the main product. In order to study the effect of the hydrogen pressure on the overall reaction the hydrogenations were carried out also at 1, 5 and 8 bars maintaining the temperature constant at 80 °C. As expected, the conversion of glycidol increased from 40% to 96% as the hydrogen pressure increased from 1 to 8 bars. It is worth noting that both the pressure (8 bars) and temperature (80 °C) requested for the efficient conversion of glycidol to 1,2-PD in the presence of 10wt.% Pd/C are decisively milder than those reported in literature (10–30 bars and 200 °C) for the direct conversion of glycerol to 1,2-PD. [5,25].

In addition the effect of the reaction time using Pd/C, under the optimized temperature of 80 °C and hydrogen pressure of 8 bars, was also studied in the range of 3–24 h. As evidenced in Fig. 2 the conversion increases up to a value of 96.0% after 24 h while selectivity toward 1,2-PD is retained.

3.1.2. The effect of the solvent using Pd/C

With the aim to reduce the formation of oligomers we also investigated the glycidol hydrogenolysis using Pd/C at 80 °C and 8 bars using various solvents as reaction medium. Therefore, the reactions were carried out in different solvents (chloroform, toluene, tetrahydrofuran, ethanol, methanol, hexane, diethyl ether, dichloromethane) for 24 h. Results of these experiments are reported in Table 2.

In all the used solvents, apart from chloroform where, probably, HCl impurities promote glycidol oligomerization, the conversion of glycidol is quantitative and at the same time a drastic reduction of the oligomer production is observed. Thus, under these conditions, the selectivity to 1,2-PD increased up to a value of 99%.

As reported in Fig. 2, glycidol oligomers under solvent free conditions, were formed in the first hours of reaction, and consequently the by-product production reduces the catalytic activity.

From an environmental point of view, based on its green characteristic [26], ethanol was chosen as solvent for a kinetic study. Besides, as shown in Fig. 3, the use of ethanol considerably shortens the reaction time (6 h vs. 24 h) to achieve the complete conversion of glycidol to 1,2-PD. Remarkably, the performances of our catalytic system are one order of magnitude higher than those reported in literature [21] in terms of productivity with a calculated TOF of 27 h^{-1}.

3.1.3. Recycling of the catalyst

The 10% Pd/C catalyst is stable and retains high efficiency in the hydrogenation of glycidol in ethanol during nine consecutive catalytic cycles maintaining good conversion (99%) and selectivity to 1,2-PD (96.9%) and resulting in a drop of the catalytic performance only at tenth cycle (89%) as shown in Fig. 4. The catalyst could be recovered

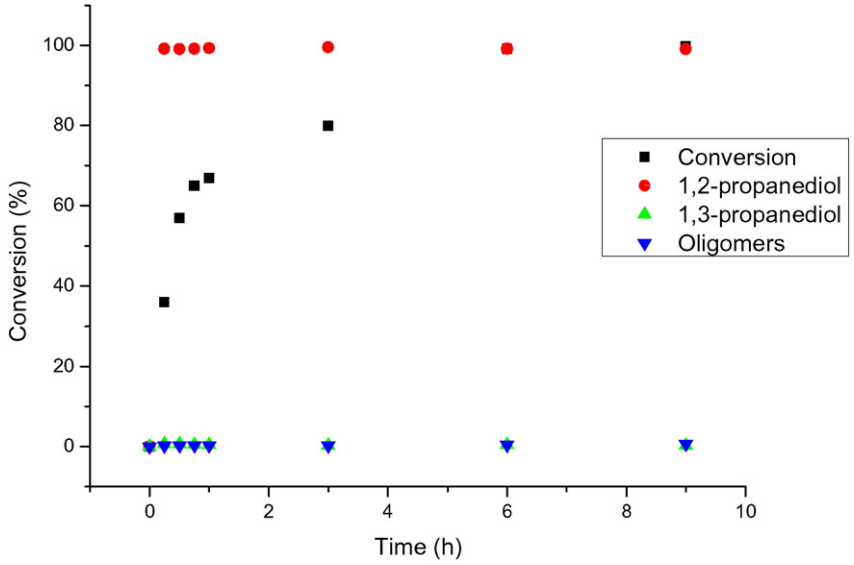

Fig. 3. Glycidol hydrogenation using Pd/C in ethanol (reaction conditions: 1 mL of glycidol, 5 mL of ethanol, 0.1 g of Pd/C, 80 °C, 8 bars H_2).

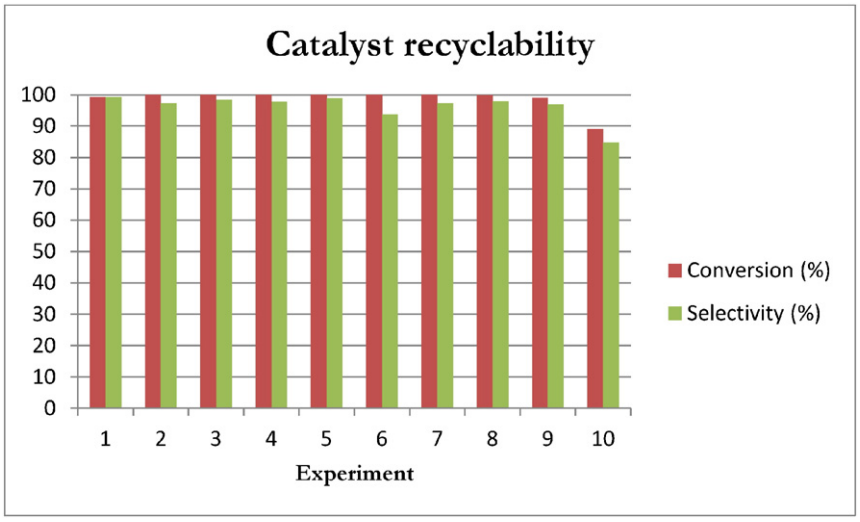

Fig. 4. Stability of the Pd/C catalyst (reaction conditions: 1 mL of glycidol, 5 mL of ethanol, 0.1 g Pd/C, 6 h, 80 °C, 8 bars H_2).

almost quantitatively following simple filtration of the catalyst, washing with EtOH and drying. For all the experiments performed, carbon balance based on the carbon content in the unconverted glycidol and in the hydrogenation products is systematically calculated and is in all cases higher than 95%.

4. Conclusions

In this work, a new, promising root to produce 1,2-propanediol through glycidol catalytic hydrogenation is reported. This synthetic strategy could be integrated in the epichlorohydrin plant solving the problem of low reactivity of 2-chloro-1,3-propanediol. For the first time, a systematic catalytic screening is conducted, using noble metal based catalysts, for the hydrogenolysis of glycidol. Results show that under solvent free conditions at 80 °C Pd/C is highly selective (93%) for the production of 1,2-propanediol at conversions of glycidol of 96%. The effects of the solvent, temperature, hydrogen pressure and the reaction time were also investigated giving useful insights for the reaction system optimization. As a matter of fact, solvent plays a crucial role inhibiting glycidol oligomer production with a consequential increase of the selectivity to 1,2-PD up to 99% and reduces the reaction time. In particular, using ethanol as solvent, glycidol conversion proceeds in only 6 h with a TOF value (27 h^{-1}). Finally, the Pd/C catalyst shows, under optimized reaction conditions, also high recyclability being reused several times without losses in activity and selectivity.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.catcom.2016.01.026.

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