

# Solketal

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Solketal (CAS 100–79–8) has low viscosity at room temperature (~11 cP) and freezing, boiling, and flash points of about –26 °C, 190 °C, and 80 °C, respectively. The density is 1.06 g/cm<sup>3</sup> and the vapor pressure is 107.32 mmHg. It has low toxicity, slight odor, and it is non-irritant for humans; due to these characteristics and to the renewable origin, it is considered an environmentally friendly substance. It is completely miscible in water and in most organic compounds, which endows its solvent capacity.

Keywords: glycerol valorization ; solketal ; continuous process ; heterogeneous catalyst ; Green Chemistry ; process intensification strategies

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## 1. Introduction

Owing to the high compatibility and miscibility of solketal, the major application is as a solvent in resins, paints coatings, and cleaning agents, also because it can influence film-formation and drying time <sup>[1]</sup>. Its low toxicity and solubility in body fluids enable it to be used also as a solvent in medicaments (i.e., driving agent), and as a precursor of other chemicals of medical interest <sup>[2]</sup>.

Nevertheless, the most-studied solketal application is as fuel additive. Malero et al. studied the benefits of adding oxygenated compounds in biodiesel and if the blends would be under the EN 14214 standard. Solketal has the positive effect of diminishing biodiesel viscosity and the negative effect of increasing fuel density, fundamental properties for the correct operation of the engine. Because of the amount of saturated fat in biodiesel, it presents poor cold properties, a problem proved to be aided by the addition of solketal in the fuel <sup>[3]</sup>. Giraldo et al. also attested the positive effect of using this ketal on diminishing the cloud point (the temperature at which wax crystals begin to form) and pour point (the temperature at which the fuel no longer flows) <sup>[4]</sup>.

Another parameter analyzed was the flash point ("the lowest temperature at which a volatile substance evaporates to form an ignitable mixture with air in the presence of an igneous source," according to Isac-García et al.), in which the addition of solketal decreased the properties' value <sup>[3][5]</sup>. Conversely, Alptekin registered higher flash point of the biodiesel blend and higher brake specific fuel consumption (measure of the fuel efficiency—rate of fuel consumption divided by the power produced) due to the low energetic efficiency of solketal. Despite that, CO<sub>2</sub>, CO, and THC (total hydrocarbon) emissions were lower <sup>[6]</sup>. Mota et al. tested the addition of solketal in gasoline and concluded that it improved octane number and reduced gum formation, results confirmed by Ilgen et al. <sup>[7][8]</sup>.

## 2. Solketal Synthesis

### 2.1. Solketal Synthesis

The ketalization reaction between acetone and glycerol is a process that adheres to the Green Chemistry principles because it is a condensation reaction, an example of atom economy, and it is a catalytic conversion <sup>[9][10]</sup>. According to Anastas and Warner, catalysis can improve energy efficiency, avoid the use of reactants in great excess, and enhance product selectivity <sup>[9]</sup>. The reaction produces two ketal species, one five-membered ring (solketal) and one six-membered ring (5-hydroxy-2,2-dimethyl-1,3-dioxane), with much higher selectivity for the first compound (99:1 molar ratio in recent studies) <sup>[11][10]</sup>. The reaction has a low equilibrium constant; therefore, it is thermodynamically limited. To obtain high conversion yields, it is necessary to shift the reaction in favor of product formation by either removing water or by adding acetone in excess <sup>[10]</sup>.

## 2.2. Solketal Production

The number of studies on solketal synthesis available in the open literature is substantial, with many new catalysts being explored. However, the number of studies on solketal production at an industrial scale grows at a much slower pace and the literature on large-scale methods for the production of solketal is rather scarce.

Solketal production plants are normally divided into Reaction Section and Separation Section. On a usual flowsheet, there is necessarily a reactor, the type depending on the catalyst and on the process, and a separation unit, usually a sequence of distillation columns. There can also be one or more mixers to homogenize the reactants and a heat exchanger to heat the compounds to the reaction temperature. Usually, a vessel is used to collect the products before they enter the separation section. The distillation columns are responsible for solketal purification and for the recovery of the eluent and unreacted reactants that can be recycled back to the column.

## 3. Conclusions and Future Prospects

Like almost all other sectors, the glycerol market was affected by the COVID-19 crisis mainly because many biodiesel plants have diminished production. Despite that, it was attested by the Independent Commodity Intelligence Services that glycerol supply is safe, and the shortcut was caused by logistic problems. Considering that relying on such chemical as raw material is advantageous due to its low cost, favorable physicochemical properties, and the environmental benefits of valorizing it. The main issue of the glycerol side-stream produced by the biodiesel industry is its inability to be absorbed by the traditional markets for pharmaceuticals and cosmetic applications. Thankfully, new uses for glycerol were discovered and, along with that, new treatment methods and even processes capable of using crude glycerol. Among the many subproducts of glycerol, solketal stands out due to its versatility and promising improvements in fuels when used as additive. Moreover, solketal does not require high-purity reactant, depending on how it is proposed to be produced.

New alternative catalysts have been studied to allow the use of crude or less treated glycerol and to diminish the cost of producing solketal. Additionally, new processes have been proposed to overcome the thermodynamic limitation inherent to this ketalization reaction. Nevertheless, the literature on the use of crude glycerol is still scarce, as well as on alternative technologies that can be applied at large scale to keep up with the glycerol production rate. The Process Intensification strategies proposed in the open literature for the production of solketal present great potential to be applied at industrial scale and an immensurable prospective environmental benefit. Besides enabling the reaction to achieve higher conversion, these strategies can diminish or even eliminate the need for downstream treatment, appointed by some authors as the most energy demanding step (consequently the costliest) <sup>[12][13][14]</sup>. Therefore, the most promising strategies are the continuous processes that result in purer product streams, as the Simulated Moving Bed Reactor, thoroughly investigated for the production of other chemicals <sup>[15][16][17][18][19][20]</sup>, Membrane Reactors <sup>[21][22][23][24]</sup>, and other hybrid reaction–separation technologies.

Unfortunately, these Process Intensification strategies are developed at a slow pace, and only few patents propose these strategies at an industrial scale. Additionally, there is a gap in the literature on studies that evaluate the environmental impacts of producing solketal, a common point for all the process mentioned in the present review. Considering that this indicator has been gaining strength, it is relevant that the studies perform a Life Cycle Analysis and provide these type of data to evidence if the proposed technologies are competitive from both economic and environmental aspects. This proves the research on solketal still has plenty of room for investigation.

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## References

1. Solketal: An EHS Friendly and Sustainable Solvent; IMPAG Switzerland: Zürich, Switzerland, 2017.
2. Esteban, J.; García-Ochoa, F.; Ladero, M. Solventless synthesis of solketal with commercially available sulfonic acid based ion exchange resins and their catalytic performance. *Green Process. Synth.* 2017, 6, 79–89.
3. Melero, J.A.; Vicente, G.; Morales, G.; Paniagua, M.; Bustamante, J. Oxygenated compounds derived from glycerol for biodiesel formulation: Influence on EN 14214 quality parameters. *Fuel* 2010, 89, 2011–2018.
4. Giraldo, S.Y.; Rios, L.A.; Suárez, N. Comparison of glycerol ketals, glycerol acetates and branched alcohol-derived fatty esters as cold-flow improvers for palm biodiesel. *Fuel* 2013, 108, 709–714.
5. Isac-García, J.; Dobado, J.A.; Calvo-Flores, F.G.; Martínez-García, H. Chapter 5—Determining physical and spectroscopic properties. In *Experimental Organic Chemistry*; Isac-García, J., Dobado, J.A., Calvo-Flores, F.G., Martínez-García, H., Eds.; Academic Press: Cambridge, MA, USA, 2016; pp. 145–175. ISBN 978-0-12-803893-2.

6. Alptekin, E. Emission, injection and combustion characteristics of biodiesel and oxygenated fuel blends in a common rail diesel engine. *Energy* 2017, 119, 44–52.
7. Mota, C.J.A.; da Silva, C.X.A.; Rosenbach, N.; Costa, J.; da Silva, F. Glycerin derivatives as fuel additives: The addition of glycerol/acetone ketal (solketal) in gasolines. *Energy Fuels* 2010, 24, 2733–2736.
8. Ilgen, O.; Yerlikaya, S.; Akyurek, F.O. Synthesis of solketal from glycerol and acetone over amberlyst-46 to produce an oxygenated fuel additive. *Period. Polytech. Chem. Eng.* 2016.
9. Anastas, P.; Eghbali, N. Green chemistry: Principles and practice. *Chem. Soc. Rev.* 2010, 39, 301–312.
10. Nanda, M.R.; Zhang, Y.; Yuan, Z.; Qin, W.; Ghaziaskar, H.S.; Xu, C. Catalytic conversion of glycerol for sustainable production of solketal as a fuel additive: A review. *Renew. Sustain. Energy Rev.* 2016, 56, 1022–1031.
11. Moreira, M.N.; Faria, R.P.V.; Ribeiro, A.M.; Rodrigues, A.E. Solketal production from glycerol ketalization with acetone: Catalyst selection and thermodynamic and kinetic reaction study. *Ind. Eng. Chem. Res.* 2019, 58, 17746–17759.
12. Al-Saadi, L.S.; Eze, V.C.; Harvey, A.P. Techno-economic analysis of glycerol valorization via catalytic applications of sulfonic acid-functionalized copolymer beads. *Front. Chem.* 2020, 7.
13. Dmitriev, G.S.; Terekhov, A.V.; Zhanaveskin, L.N.; Khadzhiev, S.N.; Zhanaveskin, K.L.; Maksimov, A.L. Choice of a catalyst and technological scheme for synthesis of solketal. *Russ. J. Appl. Chem.* 2017, 89, 1619–1624.
14. Da Silva, M.J.; de Ávila Rodrigues, F.; Júlio, A.A. SnF<sub>2</sub>-catalyzed glycerol ketalization: A friendly environmentally process to synthesize solketal at room temperature over on solid and reusable Lewis acid. *Chem. Eng. J.* 2017, 307, 828–835.
15. Constantino, D.S.M.; Faria, R.P.V.; Pereira, C.S.M.; Loureiro, J.M.; Rodrigues, A.E. Enhanced simulated moving bed reactor process for butyl acrylate synthesis: Process analysis and optimization. *Ind. Eng. Chem. Res.* 2016, 55, 10735–10743.
16. Faria, R.P.V.; Pereira, C.S.M.; Silva, V.M.T.M.; Loureiro, J.M.; Rodrigues, A.E. Sorption enhanced reactive process for the synthesis of glycerol ethyl acetal. *Chem. Eng. J.* 2014, 258, 229–239.
17. Pereira, C.S.M.; Gomes, P.S.; Gandi, G.K.; Silva, V.M.T.M.; Rodrigues, A.E. Multifunctional reactor for the synthesis of dimethylacetal. *Ind. Eng. Chem. Res.* 2008, 47, 3515–3524.
18. Minceva, M.; Gomes, P.S.; Meshko, V.; Rodrigues, A.E. Simulated moving bed reactor for isomerization and separation of p-xylene. *Chem. Eng. J.* 2008, 140, 305–323.
19. Ströhlein, G.; Mazzotti, M.; Morbidelli, M. Optimal operation of simulated-moving-bed reactors for nonlinear adsorption isotherms and equilibrium reactions. *Chem. Eng. Sci.* 2005, 60, 1525–1533.
20. Kawase, M.; Suzuki, T.B.; Inoue, K.; Yoshimoto, K.; Hashimoto, K. Increased esterification conversion by application of the simulated moving-bed reactor. *Chem. Eng. Sci.* 1996, 51, 2971–2976.
21. Dubé, M.A.; Tremblay, A.Y.; Liu, J. Biodiesel production using a membrane reactor. *Bioresour. Technol.* 2007, 98, 639–647.
22. Itoh, N. A membrane reactor using palladium. *AIChE J.* 1987, 33, 1576–1578.
23. De Falco, M.; Capocelli, M.; Giannattasio, A. Membrane reactor for one-step DME synthesis process: Industrial plant simulation and optimization. *J. CO<sub>2</sub> Util.* 2017, 22, 33–43.
24. Deshayes, A.L.; Miró, E.E.; Horowitz, G.I. Xylene isomerization in a membrane reactor: Part II. Simulation of an industrial reactor. *Chem. Eng. J.* 2006, 122, 149–157.