



Catalytic conversion of glycerol for sustainable production of solketal as a fuel additive: A review



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ABSTRACT

The exponential growth of biodiesel industries all around the world has produced a large amount of glycerol as a byproduct, which must be valorized for the sustainability of the biodiesel industry. Ketalization of glycerol with acetone to synthesize solketal—a potential fuel additive is one of the most promising routes for valorization of glycerol. In this article, state-of-the-art of glycerol ketalization is reviewed, focusing on innovative and potential technologies towards sustainable production of solketal. The glycerol ketalization processes developed in both batch and continuous reactors and performance of some typical catalysts are compared. The mechanisms for the acid-catalyzed conversion of glycerol into solketal are presented. The main operation issues related to catalytic conversion of crude glycerol in a continuous-flow process and the direct use of crude glycerol are discussed.

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Abbreviations: pTSA, p-toluenesulfonic acid; Ar-sBA-15, Arenesulfonic acid-functionalized mesostructured silica; PW, Tungsto-phosphoric acid; SiW, Tungsto-silicic acid; PMo, Molybdo-phosphoric acid; SiMo, Molybdo-silicic acid; CMR, Continuous microwave reactor; FM, Fluidic modules; WHSV, Weight hourly space velocity; Pr-SBA-15, Propylsulfonic acid-functionalized mesostructured silica; Ar-SBA-15, Arenesulfonic acid-functionalized mesostructured silica; HAR-SBA-15, Hydrophobised arenasulfonic acid-functionalized mesostructured silica; MPV, Meerwein–Ponndorf–Verley reduction; G, Glycerol; A, Acetone; F, Vacant adsorb sites; S, Solketal; FTIR, Fourier Transformation Infrared Spectroscopy; CTAB, Cetyltrimethyl ammonium bromide; TEOS, Tetraethyl orthosilicate; Zr-TUD-1, Three dimensional mesoporous Zirconium containing catalyst; Hf-TUD-1, Three dimensional mesoporous Hafnium containing catalyst; Sn-MCM-41, Mesoporous tin containing catalyst with mobil composition of matter number 41; Sn-MCM-1, Mesoporous tin containing catalyst with mobil composition of matter number 1; A/G, Acetone to glycerol molar ratio; Pr-SO₃H-SiO₂, Silica bonded-propylsulfonic acid; T-SiO₂, Silica bond-tosic acid; SAC-13, Nafion silica composite

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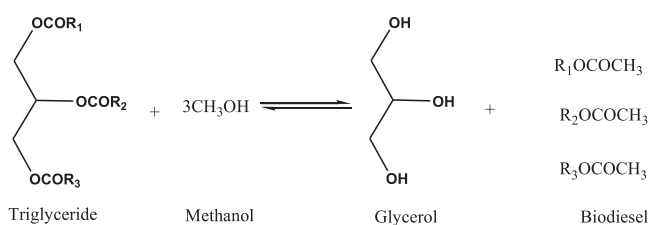
1. Introduction

The depletion of non-renewable fossil fuels and their environmental impacts are among the main factors that have drawn increasing attention towards biofuels, mainly bio-ethanol and biodiesel. Biodiesel is mainly produced by the transesterification of animal fats or vegetable oils (triglyceride) with a mono-alcohol (usually methanol) in presence of alkalis as shown below (Scheme 1) [1–3]. This biodiesel can be used directly or after blending with fossil-based diesel fuel.

In the transesterification process, glycerol is formed as the principal byproduct. It is estimated that 10 wt% amount crude glycerol is generated for each amount of biodiesel produced [4]. With the continued increase in the production of biodiesel, an excessive amount of glycerol is expected to accumulate. It is predicted that by 2020 the global production of glycerol will be 41.9 billion liters [5]. The crude glycerol produced from biodiesel industry contains impurities such as water, inorganic salts (sodium or potassium salts), methanol, fatty acids, and esters etc. [6–8], hence it is commonly treated as the waste stream of biodiesel industry. It is economically viable for the large biodiesel producers to refine this waste stream for the industrial applications, whereas for small biodiesel producers, they are unable to leverage the treatment costs and instead they pay for glycerol removal. Due to the excessive amount generated, the current crude glycerol price is as low as 0.04–0.09 \$/lb [9]. The predicted rapid growth of biodiesel production will further lower the glycerol price once it enters into market [10]. Therefore, new and economical ways of using glycerol must be developed to increase the value of crude glycerol to enhance the sustainability of biodiesel industries.

That being said, glycerol has diverse applications in different fields especially in the pharmaceuticals, food, cosmetics, and polymer industries [11–13]. The versatility of glycerol is mainly due to its physical and chemical properties. The presence of three hydroxyl groups in glycerol makes it completely soluble in water and alcohols whereas insoluble in hydrocarbons. Furthermore, the inter and intramolecular hydrogen bonds due to the presence of hydroxyl groups lead to the high boiling point of glycerol (290 °C) at ambient pressure and high viscosity (1.412 Pa s) at room temperature [14].

On the other hand, catalytic and biological conversion of glycerol offer a tremendous potential to produce value-added chemicals such as propanediols, acrolein, dihydroxyacetone, glyceric acid, tartaric acid, epichlorohydrin, hydrogen, syngas, ethers, esters, etc. [15–21]. Therefore glycerol can be considered as a platform chemical. A selection of these possibilities were reviewed recently [12,22,23]. Production of cyclic acetals and ketals from glycerol with aldehydes and ketones, respectively, is believed to be one of the most promising glycerol applications as fuel/chemical intermediates [24–27].



Scheme 1. Glycerol as byproduct during biodiesel production.

The ketalization reaction between glycerol and acetone is given in Scheme 2, where solketal (2, 2-dimethyl-1, 3-dioxolane-4-methanol or 1,2-isopropylidenglycerol) is formed as the condensation product over an acid catalyst. Solketal can be used as a fuel additive to reduce the particulate emission and to improve the cold flow properties of liquid transportation fuels [28]. It helps to reduce the gum formation, improves the oxidation stability, and enhances the octane number when added to gasoline [29]. Maksimov et al. reported its use as a versatile solvent and a plasticizer in the polymer industry and a solubilizing and suspending agent in pharmaceutical preparations [30].

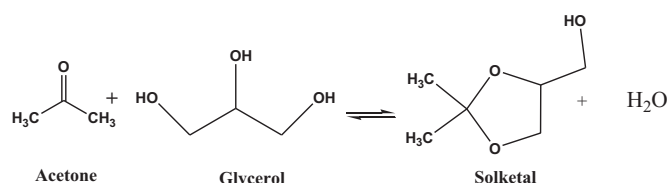
This review paper mainly over-views the state-of-the-art of the sustainable production of solketal by catalytic reaction of glycerol with acetone. Different types of processes and catalysts developed and their performances are compared. Fundamentals of reaction mechanisms for the acid-catalyzed conversion of glycerol into solketal are presented. The main operation issues related to catalytic conversion of crude glycerol in a continuous-flow process and the direct use of crude glycerol are discussed.

The review article aims to (1) introduce various applications of solketal in different industries including polymer, pharmaceutical and cosmetics, food, and fuel industries, (2) highlight some major challenges for industrial production of solketal, and (3) demonstrates promise of some new processes for utilization of crude glycerol as feedstock for the production of solketal.

2. Recent progress in the reaction processes

2.1. Historical context

It is well-known that ketals can be prepared by the reaction of an alcohol with a ketone in presence of an acid catalyst. Based on the public sources of literature, Fischer first prepared the solketal from acetone and glycerol in a batch reactor catalyzed by hydrogen chloride [31]. 25 years later Fischer and Pfahler reported ketalization of glycerol using hydrogen chloride and anhydrous sodium sulfate in a similar process [32]. Later, in 1948, Renoll and Newmann published their work on the synthesis of solketal in a three neck flask with reflux equipped with a sealed mechanical stirrer [33]. The authors chose petroleum ether as the reaction medium and p-toluenesulfonic acid (pTSA) monohydrate as the catalyst to achieve a high yield of solketal (87–90%). After the reaction, the products were separated by distillation under reduced pressure; however the reaction time was very long (21–36 h). These early studies on the synthesis of solketal remained without further advances until the end of the 20th century when massive amount of cheap glycerol was produced from biodiesel industry.



Scheme 2. Ketalization reaction between glycerol and acetone.

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