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Glycerol acetals and ketals as possible diesel additives. A review of their synthesis protocols

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ABSTRACT

With the rapid development of the biodiesel industry all over the world, a large surplus of glycerol has been created, so economic uses of glycerol for value-added products are critical for the sustainability of the biodiesel industry. One of the main interests in recent years for glycerin utilization is its conversion in acetals and ketals, with the potential to be used as fuel additives. Glycerol acetals and ketals can be synthesized through the acid-catalyzed reaction of glycerol with aldehydes and ketones, respectively. This paper reviews different approaches and techniques used to obtain glycerol acetals and ketals, regarding the reactor design, catalyst design and the effect of different parameters in the reaction system.

Contents

1. Introduction

Nowadays one of the global interests focuses on renewable energy sources due to fossil fuel depletion and environmental degradation. Biodiesel is considered as an attractive alternative to diesel fuels, because it is renewable, biodegradable, non-toxic and has almost the same properties as diesel fuel [1,2].

The market for biofuel expanded recently as it is used on increasingly large scales in the transport sector, especially for road vehicles, in aviation, to generate electricity, for cooking and in maritime transport [3]. In 2013, the global biodiesel production reached more than 110 billions of liters (see Fig. 1).

By 2022, the world production of bioethanol is estimated to reach 168 billion liters and the production of biodiesel, 141 billion liters, with the contribution of Renewable Fuel Standard (RFS2) in the United States, along with EU-RED. This will trigger a rise in the global production of bioethanol and biodiesel by 70 per cent until 2022, as compared to the average from 2010 to 2012. [4].

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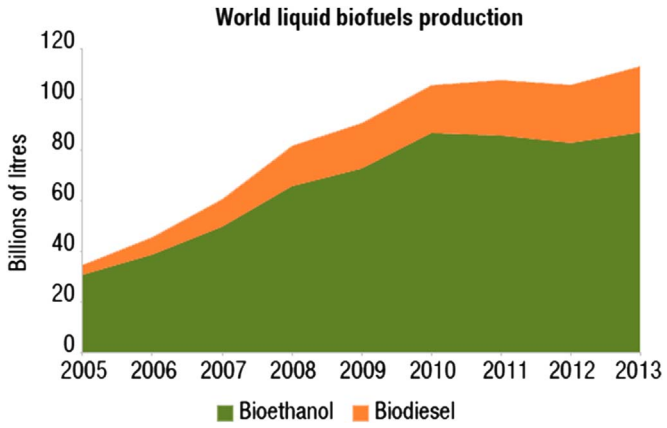

Fig. 1. Increasing production of biodiesel since 2005 to 2013 [3].

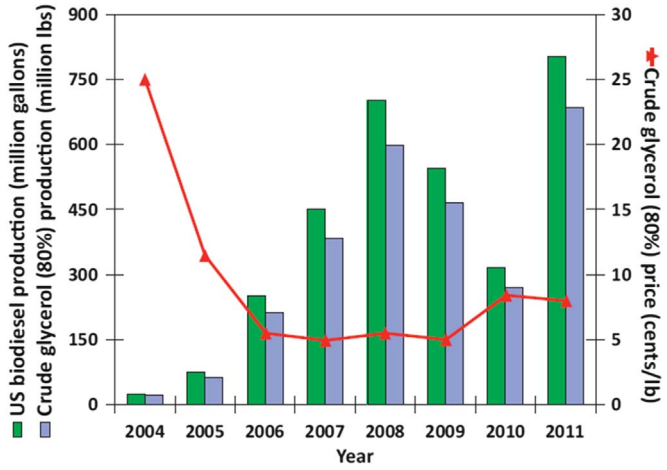

Fig. 2. Crude glycerol price trend [8].

Although biodiesel represents a renewable, convenient and environmental friendly alternative to fossil fuel, the economic feasibility of the biodiesel production must be improved. This can be done by acting on three elements of the process: the raw materials, the synthesis itself and the byproducts [5].

Biodiesel is produced by the transesterification of vegetable oils or animal fat with methanol, in base catalysis conditions [6].

As for the byproducts, glycerol is obtained at high concentration in a weight ratio of 1/10 (glycerol/biodiesel). Historically, disposal of crude glycerin has been by incineration: the byproduct has not historically been used as a raw material for secondary reaction [7]. As such, it could be especially advantageous to convert it to added-value products, especially because the growing market of biodiesel has generated a glycerol oversupply and consequently the glycerol commercial price fell down from 25 cents/lb in 2004, to less than a half in 2011, approximately 8 cents/lb, as seen in Fig. 2 [8].

One of the promising utilizations of low value glycerol is to be transformed into fuel additives. Among ethers and esters, glycerol acetals and ketals constitute excellent compounds for diesel and biodiesel blends [9]. They improve the octane number and the cold flow properties, reduce particulate emission and gum formation [10–13].

The paper has collected and analyzed data about the progress and research findings on glycerol acetals/ketals synthesis in the scientific literature. It focuses on aspects which include the reactor design, catalyst design and the effect of different parameters in the reaction system.

2. Reaction mechanism

To prepare glycerol acetal/ketal, the other component, aside glycerol, is an aldehyde or a ketone. Acetal formation is a reversible reaction via a two-step mechanism. Scheme 1 presents the general mechanism without specifying any reaction conditions. The first step is the formation of a hemiacetal, followed by the removal of water molecules. Acetal formation is strongly affected by electronic and steric factors, but it is generally accepted that the rate determining step is the formation of a cation from the protonated hemiacetal. In order to compensate for the low rate of hemiacetal formation, the reaction media must be sufficiently acidic to promote effective protonation of any hemiacetal formed and sufficiently polar to allow stabilization of the cationic intermediate [14].

For the inferior aldehydes and ketones, the equilibrium is shifted to the right.

Cyclic acetals or ketals are prepared by reacting a polyol with the appropriate aldehydes or ketones [16]. When glycerol is used as polyol, the 1,3 dioxane and 1,3 dioxolane structures are formed.

Cyclic ketals which result from the reaction of glycerol and ketones have a structure of 1,3 dioxolane (5 membered ring) and not a 1,3 dioxane (6 membered ring) due to the steric blocking of radicals and hydrogen atoms from positions 4 and 6 of the molecule, especially if taken into account that the C–O bond is shorter (1.43 Å) than the C–C bond (1.54 Å). Glycerol reacting to aldehydes results in 1,3 dioxane, with equatorial radical R [17]. The reaction mechanism for glycerol acetals/ketals synthesis is presented in Scheme 2.

Acetalization/ketalization of glycerol is highly dependent on the experimental conditions. The different conditions and performances reported in the literature for glycerol acetals/ketals synthesis are presented as follows.

3. Chemical conversion of glycerol to acetals and ketals

3.1. Catalyst design

Traditionally, the reaction of glycerol with aldehydes/ketones is carried out over mineral acids as catalysts like H_2SO_4, HCl, HF, H_3PO_4, and p-toluenesulphonic acid, etc [7,9,17,19,20] and over homogenous Lewis catalysts [18]. Recently, several studies were conducted regarding the use of heterogenous acid catalysts for acetalysation of different carbonyl compounds with glycerol: ion exchange resins, zeolites, montmorillonite, metal oxide based catalysts, activated carbons, mesoporous silicaheteropoly acids, mesoporous silicates with arylsulphonate group, rare-earth triflates, nanoparticles supported on multi-walled carbon nanotubes or ion liquids. When studying the influence of the catalyst on the reactant conversion, the research focused on the type of catalyst, acidity, porosity, catalyst loading, different techniques of catalyst preparation and its reusability. Many researchers studied only the influence of the catalyst loading, but there are also studies on different types of catalysts.

Starting with homogenous catalysts (strong mineral acids and lewis catalysts) which cause corrosion and environmental problems, and complicate the products' separation and purification, many studies were conducted with heterogenous catalysts that solve most of the shortcomings of homogenous catalysts. The efficiency and easy removal of the catalyst are not the only important aspects, but also the accessibility and the price of the catalyst and a good activity in mild conditions.

Ruiz et al. [18] studied the acetalization of glycerol with formaldehyde over three different types of acid catalysts: zeolites and organic resins - Bronsted acid, gold salts - Lewis catalysts and a