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Production of biofuel additives by esterification and acetalization of bioglycerol

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ABSTRACT

The current transition from petrochemical resources to biomass-derived platform molecules is in great demand for the development of synergies, scientific innovations and breakthroughs, and steep changes in the infrastructure of chemical industries. This article is focused on new opportunities for the production of biofuel additives from bioglycerol, which is obtained as waste and/or by-product from the current biodiesel industries. Here, we summarize the recent relevant processes for the production of biofuel additives from bioglycerol over various acid catalysts in two different pathways: (i) the esterification of bioglycerol with acetic acid, levulinic acid and other acids, and (ii) the acetalization of bioglycerol with acetone, furfural, benzaldehyde and other carbonyl compounds. It is evident that the synthesis of biofuel additives through esterfication and acetalization of bioglycerol is an important research area with imperative prospects for industrial applications.

1. Introduction

Currently, the world is facing a number of interdependent challenges: the excessive use of petrochemicals has created severe problems in relation to climate change, local economic dependencies, ecological impact, and sustainability [1–8]. The diminishing of petroleum reserves and growing environmental concerns have motivated researchers for newer approaches to the production of advanced biofuels from biomass as a feedstock. Biomass provides an ideal alternative to fossil resources [1,4,7]. In fact, biomass is the only sustainable source for organic molecules and has been suggested as the ideal comparable to petroleum for the production of biofuels and chemicals [1–4]. It is an abundant, widespread, and inexpensive energy resource resulting from organic substances, which include agricultural residues, forest resources, perennial grasses, woody crops, wastes, algae, etc [9–11]. As a consequence, biomass-derived fuels have attracted attention as alternatives to fossil fuels because of their environmentally benign and renewable nature. In recent years, a significant number of platform molecules have been synthesized from biomass for the production of commodity chemicals and biofuels. Glycerol is one of the most promising renewable platform chemicals for the production of a broad range of commercially significant fine chemicals and biofuel additives. Therefore, the development of new technologies for producing biofuels from sustainable resources has been encouraging biomass utilization to become an important area of research [1,12].

Consequently, glycerol cannot be added to fuel because at high temperatures its polymerization takes place and thereby blocks the engine. In addition, it is partly oxidized to form the toxic acrolein. On the other hand, a major concern of using glycerol as a fuel additive is its very hygroscopic nature and hence has a strong tendency to be contaminated with water. Conversely, glycerol oxygenate products are reported to be excellent fuel additives on the

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basis of their anti detonant and octane number improving properties. Glycerol can be converted to various fuel additive units through various reaction pathways like esterification, acetalization, etherification, transesterification, hydrogenolysis, and carbonylation [13–22]. The transformation of glycerol into highly oxygenated fuels by esterification and acetalization reactions is of special interest since they are economically viable for the synthesis of glycerol by-products from biodiesel processes.

Esterification of glycerol with acetic acid produces highly important oxygenated biofuel additives, which are generally called as acetins namely, monoacetylglycerol (MAG), diacetylaglycerol (DAG), and triacetylglycerol (TAG). Individually, each acetylated product has its own potential applications in various fields. MAG is used as a food additive, solvent for dyes, and as a tanning agent and is used in the manufacture of explosives [23]. Diacetyl glyceride conjugated with different amino acids shows potential applications in pharmaceutical and food formulations [24]. MAG and DAG are used in the medicine and cosmetic industry and as raw materials for the production of biodegradable polyesters [25]. TAG can be used as a fuel additive to enhance the octane number in gasoline [26]. On the other hand, glycerol esterification with levulinic acid (LA) produces acetylated products which are used as monomers for the synthesis of polymers [27]. Also, esterification with other carboxylic acids such as oleic acid, lauric acid, propionic acid, and butanoic acid with bioglycerol produces acetylated products, which are useful in several industries [28]. The acetalization of glycerol with carbonyl compounds and its derivatives produces highly oxygenated compounds, such as 5-membered and 6-membered cyclic compounds. These highly oxygenated acetals/ketals are used as versatile biofuel additives for diesel fuel. In addition, a remarkable reduction in harmful emissions, unregulated aldehydes and particulate matter can be achieved by adding the glycerol acetals/ketals to the standard diesel fuel [4,15,29].

Generally, esterification and acetalization of glycerol are performed over homogeneous mineral acids such as HCl and H_2SO_4 as well as other strong acids like *p*-toluenesulfonic acid [25]. However, the use of these mineral acids is usually limited by several technical and environmental drawbacks such as catalyst separation, use of expensive and toxic reagents, product purity, reactor corrosion, and generation of large amounts of waste [30]. In addition, the costs for the disposal of hazardous substances and related pollution are above the inflation rate in many countries. Hence, the challenge is to replace them with highly efficient heterogeneous solid acid catalysts which are easier to separate from the products, stable at high temperatures and less toxic. Additionally, they have been found to offer better selectivity towards desired products compared to homogeneous catalysts [31]. Solid acids significantly differ from homogeneous catalysts in terms of acidity, surface area, and cost of production. Also, it is economically feasible because of the reusability of the catalyst for both batch and continuous processes [32,33]. Recently, a large number of heterogeneous solid acid catalysts have been developed including hydroxylated magnesium fluorides, sulfated activated carbon, SO_3H-functionalized ionic liquids, mesoporous silica with sulfonic acid groups, zeolites, Amberlyst, heteropolyacids, and promoted metal oxides for valorization of bioglycerol to value added products [4,7,15,32,34–37]. In the present article, we report the high production of biofuels by the esterification and acetalization of bioglycerol over highly effective solid acid catalysts from the literature including our catalysts. Presently, we have focused our attention on the production of glycerol esters, acetals, and ketals over various promising solid catalysts.

2. Esterification of bioglycerol with carboxylic acids

2.1. Esterification of bioglycerol with acetic acid

The esterification of glycerol with acetic acid provides three important oxygenated products, namely, MAG, DAG and TAG (Scheme 1). The esterification of glycerol with acetic acid was performed over a wide variety of heterogeneous solid acid catalysts and the obtained results are presented in Table 1. Among the reported catalysts, Amberlyst-70 exhibited a high catalytic performance of glycerol esterification with acetic acid at 378 K reaction temperature and 4 h reaction time [38]. The Amberlyst-70 catalyst exhibited 100% glycerol conversion and the product selectivities of MAG, DAG, and TAG were found to be ~2.5, 51.7, and 45.8%, respectively (Table 1, entry 1). Zhu and co-workers [39] reported a series of silver-exchanged phosphotungstic acid (Ag_1PW) catalysts for the esterification of glycerol with acetic acid at 393 K. Among them, the Ag_1PW catalyst showed excellent glycerol conversion (96.8%) with 48.4, 46.4 and 5.2% selectivity of MAG, DAG and TAG, respectively (Table 1, entry 2). It is mainly due to the presence of a high amount of acidic sites and outstanding water tolerance of the Ag_1PW catalyst. Recently, Reddy et al. [15] reported promising MoO_3, WO_3 and SO_4^{2-} promoted SnO_2-based acid catalysts for the esterification of glycerol with acetic acid. The SO_4^{2-}/SnO_2 catalyst exhibited superior catalytic activity and high product selectivity toward DAG and TAG compared to other catalysts (Table 1, entry 6). The high catalytic activity of the SO_4^{2-}/SnO_2 catalyst was mainly attributed to the presence of a large amount of acidic sites with ample super acidic sites. Also, zirconia based catalysts were reported for esterification of glycerol with acetic acid and the obtained results are presented in Table 1. The un-promoted ZrO_2 and $TiO_2–ZrO_2$ catalysts exhibited lower glycerol conversion than the promoted catalysts such as $WO_x/TiO_2–ZrO_2$ and $MoO_x/TiO_2–ZrO_2$ (Table 1, entries 7, 8, 9). The low catalytic activity of un-promoted catalysts could be explained by the less number of acidic sites associated with weak acid strength [13].

In recent times, the glycerol acetylation with acetic acid was also studied over the mesoporous KIL-2 supported sulfated zirconia catalyst [40]. It was reported that mesoporous KIL-2 supported zirconia samples are more active when compared to that of pure zirconia. With increasing ZrO_2 amount, KIL-2 supported catalysts showed enhanced catalytic performance to produce valuable fuel additives (i.e., MAG and TAG). SO_4^{2-}/ZrKIL-2 catalyst exhibited higher glycerol conversion and better selectivity towards