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Heterogeneous catalytic conversion of glycerol to oxygenated fuel additives

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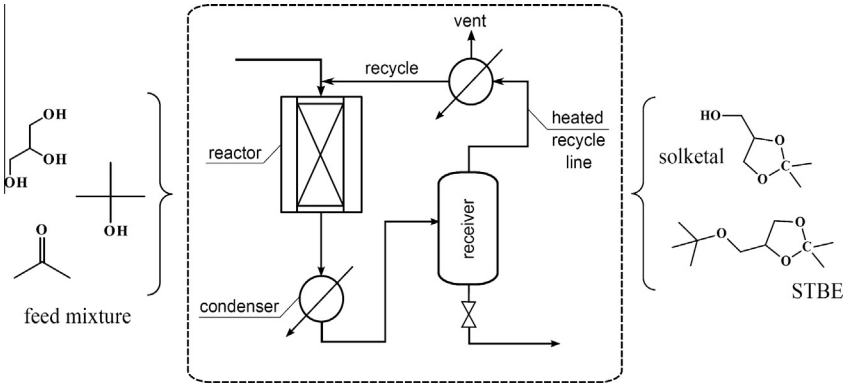
HIGHLIGHTS

- Reaction of glycerol with *tert*-butyl alcohol and acetone in flow reactor.
- Zeolite-BEA converts glycerol completely into the mixture of solketal and STBE.
- Yield of STBE in 1-mono-GTBE ketalisation depends inversely from temperature.
- The introduction of solketal into hydrocarbon oil improves its antiwear properties.
- Solketal is the most effective antiwear agent from all the ethers formed.

GRAPHICAL ABSTRACT



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ABSTRACT

Glycerol alkylation with *tert*-butyl alcohol and ketalisation of glycerol 1-mono-*tert*-butyl ether with acetone, as well as the combined ketalisation–alkylation process, has been studied in a fixed-bed flow reactor. It has been shown that a continuous, one-step process for the quantitative conversion of glycerol into a mixture of ethers can be accomplished under mild conditions (atmospheric pressure and temperatures of 40–70 °C) over a zeolite BEA catalyst. Furthermore, the effects of the glycerol ether additives on the antiwear properties of low-viscosity base oil have been characterised.

1. Introduction

The progressive increase in the world production of biodiesel confronts, among others, two important issues: the improvement in the performance characteristics of biodiesel and the comprehensive processing of bioglycerol, which is a byproduct of the manufacture of fatty acid methyl esters. Compared with petroleum fuel, biodiesel increases the emission of nitrogen oxides during engine operation and experiences low-temperature pumpability problems. Many ways to utilise bioglycerol have been proposed; they are primarily aimed at the manufacture of petrochemicals

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and the intermediates that are produced from propylene, propylene oxide, or 1,2- and 1,3-propanediols as feedstocks [1,2]. Moreover, the problems with sustained bioglycerol utilisation and the quality improvement of biodiesel fuel blends can be resolved simultaneously because the bioglycerol processing method herein suggests that glycerol can be used to manufacture additives for motor fuels [3].

Glycerol acetals can be easily synthesized and are used as additives for alternative and petroleum fuels or their blends [3–11]. In particular, ethers are known to reduce the emission of hazardous substances during fuel combustion [12]. 2,2-Dimethyl-4-hydroxy methyl-1,3-dioxolane (known as solketal, the acetone ketal of glycerol) is quite a promising additive for fuels and lubricants. It has been recently shown [13] that solketal can be obtained with 100% selectivity and a 95% yield by performing the reaction in subcritical acetone on Purolite® PD 206 cation-exchange resin. When added to motor gasoline (including bioethanol–gasoline fuel), solketal increases the octane number of the fuel and reduces gum formation [7]. In diesel and biodiesel or their blends, acetals reduce the exhaust emissions of nitrogen oxides, carbon monoxide and soot, and they improve cold flow properties but noticeably decrease the oxidation stability [1,4]. In addition, glycerol acetals including solketal exhibit antiwear properties when added to motor fuels or lubricating oils [14].

Glycerol ethers of monohydric alcohols also improve the properties of diesel and biodiesel fuels. The production of glycerol *tert*-butyl ethers (GTBEs) was thoroughly investigated in a number of studies [15–21] and summarised in a review [22]. Ozbay and coworkers [23] have recently reported the results of the reaction of glycerol with *tert*-butanol (TBA) on various industrial solid acid catalysts in batch and flow reactors. Behr et al. [1] presented a flow chart of GTBE production by glycerol alkylation with isobutylene. The feasibility of GTBE production by reactive distillation was also described [24].

It should be noted that the abovementioned glycerol *tert*-butylation experiments were performed in order to evaluate the activity of the catalyst in the particular reaction, glycerol conversion and the products distribution. The literature indicates that GTBE production industrial process was developed by Behr and Obendorf [25,26]. The authors used a cascade of stirred batch reactors and p-toluenesulfonic acid as the catalyst. Moreover, there is information that an industrial plant (500.000 ton of GTBEs per year) was opened in 2010: Behr [25] quoted that there is a patented industrial process developed by ARCO Chemical Technology. Thus, the industrial synthesis of GTBEs seems to have been already developed and realized on the industrial scale.

The possibility of the involvement of GTBE mixtures into motor fuels remains debatable. The main problem is associated with the hydrophilicity of the ethers because the glycerol monoethers exhibit good miscibility with water and the diethers are amphiphilic liquids. The synthesis of tri-*tert*-butyl ethers is fraught with great difficulties because the formation of a structure of this type is impeded by significant steric hindrance. The ways to apply the GTBE mixtures have already been considered in [1], and such mixtures do not have an unambiguously favourable effect on the properties of formulated motor fuels. Mono- and diethers of glycerol do not possess the optimal volatility for their blending with gasoline [2]; however, when mixed with biodiesel, they significantly improve its low-temperature and environmental properties [2,4,6].

We believe that it is better to use GTBE as a minor fuel additive together with the major components, STBE and solketal. In this scenario, the aforementioned problems would not be so acute.

In [27], we reported success in acetone ketalisation of glycerol in a flow reactor, yielding a mixture of solketal and 2,2-dimethyl-5-hydroxy-1,3-dioxane, the solketal isomer differing in the number of atoms in the cyclic moiety. Moreover, glycerol ketalisation was reported to be realized in a flow reactor with the use of methanol as a co-solvent [11]. Because these ketals bear a hydroxyl group in their molecules, it is reasonable to convert it into an alkoxy substituent. A ketal molecule modified in this manner should exhibit higher hydrophobicity, oxidation stability, and heat of combustion.

Monbaliu et al. [28,29] reported the effective production of solketal *tert*-butyl ether (STBE), including its synthesis in continuous flow systems. STBE was obtained by glycerol ketalisation followed by solketal O-alkylation with isobutylene; sulphuric acid was used as a catalyst. STBE is known as a promising motor fuel additive. The introduction of STBE at a concentration of no more than 5% into diesel leads to a reduction in nitrogen oxides, carbon monoxide, and soot emissions [2]. When added to gasoline, STBE presumably exerts an octane-boosting effect (solketal has a blending octane number of 98) [7].

The synthesis of solketal ethers by reacting solketal with benzyl alcohol [30] or olefin oxides [31] has been previously described. The published method for the two-step synthesis of STBE from glycerol involves the acetone ketalisation of glycerol as the first step, followed by alkylation of the product solketal with isobutylene [28,29].

The aim of this work was to study the synthesis of STBE in one stage in a flow system and to outline the basic parameters of its effective production process. The use of isobutylene as an alkylating agent causes problems associated with impeded mass transfer, the amenability of isobutylene to side reactions in the presence of strong acid catalysts, and the need to use a compressor to pump the olefin. Therefore, we chose *tert*-butyl alcohol as the alkylating agent.

The efficiency of an industrial-scale process always decreases with an increasing number of stages. Therefore, we focused on developing a one-step process for glycerol conversion into substituted derivatives. Because STBE can be produced from either solketal (by alkylation with TBA) or glycerol 1-mono-*tert*-butyl ether (mono-1-GTBE) by ketalisation with acetone, the following processes were investigated in a flow system:

1. glycerol alkylation with TBA;
2. acetone ketalisation of 1-mono-GTBE; and
3. combined alkylation–ketalisation of glycerol with a mixture of alcohol and ketone.

2. Materials and methods

2.1. Materials

The catalyst used in the study was commercially available zeolite beta (Zeolyst International, Kansas City, Kansas, USA) CP811Tl in the H^+-form ($SiO_2/Al_2O_3 = 40$; 0.05% Na; specific surface area, 725 m^2/g; acidity, 0.81 $mmolH^+/g$; pore volume, 0.58 cm^3/g; pore diameter, 0.69 nm). The powdered catalyst was tabletted (compacting pressure of 3 t/cm^2), ground, and sieved to select a fraction of 0.63–1.60 mm.

The reactants were glycerol, acetone, and *tert*-butyl alcohol (Aldrich, USA). All chemicals were used without further purification.

2.2. Equipment

Flow reactor experiments were performed on a unit with a "structured-regime reactor" that was specially designed for running such processes (Fig. 1). The design of the unit included a heated plug-flow reactor with a fixed catalyst bed and a heated receiver–vaporiser connected to the reactor inlet by a separate heated line. This design allows unreacted acetone and *tert*-butanol to be continuously distilled off and recycled into the