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# Ternary solubility of mono- and di-tert-butyl ethers of glycerol in supercritical carbon dioxide

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ABSTRACT

Using a continuous flow apparatus, the ternary solubility of mono- and di-tert-butyl ethers of glycerol (MTBG and DTBG, respectively) in supercritical carbon dioxide was measured at the temperatures of 313.15, 333.15, and 348.15 K; a pressure range of 80–200 bar; and an expanded gas flow rate of 180 ± 10 mL min$^{-1}$ at average laboratory temperature of 300.15 K and pressure of 0.89 bar. The ternary solubility of the ethers at the constant temperatures of 333.15 and 348.15 K increased with increasing pressure up to the crossover point (i.e., 152 bar for MTBG and 170 bar for DTBG). MTBG exhibited a higher solubility than DTBG in scCO$_2$. The experimental data for the ternary solubility of MTBG and DTBG were correlated using the Bartle equation.

## 1. Introduction

The growing concern for global warming, as one of the most important scientific issues since the dawn of the present century, has motivated research on renewable energy sources with lower CO$_2$ emissions. While the modern society still depends to a large extent on such fossil fuels as petroleum products and natural gas, the feasibility of using renewable energy is gaining increasing attention the world over. Among these new energy sources, biodiesel appears to be one of the most promising and feasible over the short term. Its production and use has been stimulated in many countries, especially in Europe. Biodiesel is generally produced by transesterification of vegetable oils with methanol or ethanol under basic catalytic conditions with glycerol as a by-product [1,2]. For each 90 m$^3$ of biodiesel produced from transesterification of vegetable oils, approximately 10 m$^3$ of glycerol is produced [3]. Increasing production of biodiesel will naturally result in glycerol supplied to the market in excess of the demand. In Europe, for example, the growing use of biodiesel has caused glycerol prices to decline so that many plants that produce glycerol from petrochemical raw materials are finding it increasingly uneconomical to continue operation [1]. This situation calls for new glycerol applications to save the market. One possible application of glycerol is the production of alkyl ethers of glycerol by etherification with tert-butyl alcohol (or isobutylene) in the presence of an acid catalyst. In this process, a mixture of mono-, di-, and tri-tert-butyl ethers of glycerol (MTBG, DTBG, and TTBG, respectively) is produced (Fig. 1) [4]. Addition of these ethers to the final diesel fuel increases its quality but decreases its particulate matter emission, carbon oxides, and carbonyl compounds in the exhaust gases. Moreover, glycerol ether oxygenates can reduce diesel fuel cloud point when combined with biodiesel [5]. DTBG and TTBG are used as oxygenating additives to diesel fuels because of their good miscibility with diesel fuel; MTBG, on the contrary, has a low solubility in diesel fuel and must be separated from the DTBG and TTBG mixture [6].

Supercritical fluid extraction (SFE), compared to conventional extraction methods, has a great potential as an efficient and clean alternative for separating these isomers. Supercritical carbon dioxide (scCO$_2$) is the most intensively used solvent in SFE due to its low critical point ($P_c = 73$ bar, $T_c = 304$ K), non-toxicity, inertness, and non-flammability, while remaining an inexpensive and environmentally acceptable substance [7]. Solutes solubility data in scCO$_2$ are important not only for selective separation of different compounds from a complex mixture, but also for tailoring chemical reactions toward a specific product [8]. In the production process of ethers, mostly a mixture of MTBG and DTBG is produced, which requires a subsequent separation process. In this study, the effects of pressure, temperature, and sample weight on the ternary solubility of MTBG and DTBG in scCO$_2$ were studied. The counter current separation of the isomers using scCO$_2$ is the subject of another study currently in progress in our research laboratory.

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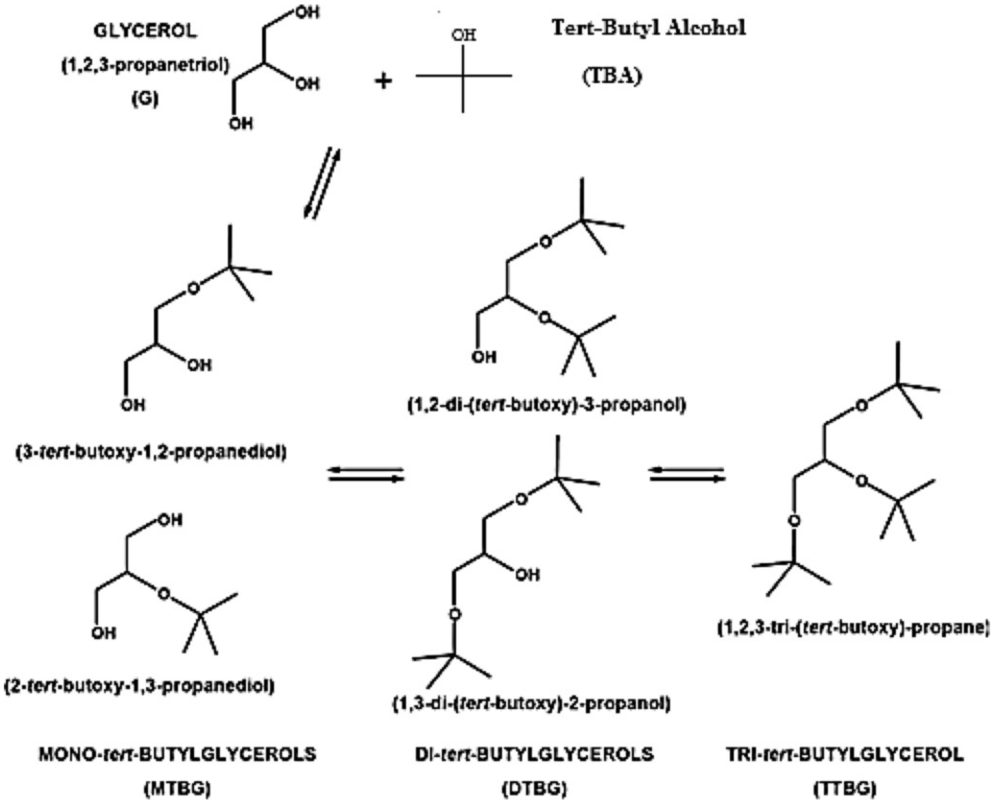

**Fig. 1.** Main reaction products in the glycerol etherification with tert-butyl alcohol [4].

## 2. Experimental

### 2.1. Materials

Absolute ethanol was purchased from Temad Co., Tehran, Iran (purity > 99%); $CO_2$ with a mass purity of 99.95% from Zamzam Co. Ltd. (Isfahan, Iran); Amberlyst 15® from Merck Co., Germany; and tert-butyl alcohol with a mass purity of 99% from Fluka, U.S.A. Glycerol and 1-hexanol (purity > 98%) were obtained from Hopkins & Williams, England, and Riedel-de Haën, Germany, respectively.

### 2.2. MTBG and DTBG synthesis

Since no chemical company was found to supply MTBG and DTBG on the market, they were synthesized via previously reported methods [4–6] and then purified. It was found that drop addition of tert-butyl alcohol to the reaction medium worked better for the synthesis of MTBG and DTBG. So tert-butyl alcohol (257 g) was manually added dropwise to a mixture of glycerol (20 g) and Amberlyst 15® (1.5 g) and refluxed for 12 h. Water formed during the reaction was removed continuously by Dean-Stark. The products were identified by comparing mass spectra taken by a GC–MS (model TU-P-55-17A, Shimadzu Co., Japan) and reported mass spectra [2]. A GC-FID was used to establish the purity levels of MTBG and DTBG in the mixture as 55.03% and 40.90%, respectively. Only a small percentage of TTBG formed (<4%) during the synthesis.

### 2.3. Apparatus

Solubility measurements were performed using a continuous flow apparatus as shown in Fig. 2. Liquid $CO_2$ was passed through a Peltier cooled reciprocating $CO_2$ pump head set (model PU-2080, JASCO, Japan) at 269.15 K. The accuracy of the set liquid-$CO_2$ flow rate was within ±2% and its flow-rate stability was within ±0.5%. It was experimentally verified that, prior to each experiment, the system had to be kept at the desired temperature and pressure for 5 min (under static conditions) in order to reach equilibrium. Immediately after the equilibrium had been reached, the saturated $scCO_2$ was depressurized via a back pressure regulator (model BP 1580-81, JASCO, Japan) at a low but constant flow rate of $180 \pm 10\,mL\,min^{-1}$. In other respects, the system was identical to that reported elsewhere [9].

### 2.4. Procedure

In each measurement, $1.0 \pm 0.1$ g of the sample was poured into the 1st equilibrium cell, which was filled with glass wool both to lower the cell dead volume and to increase the contact surface. The 2nd equilibrium cell of the same volume as the 1st (i.e., 10 mL) was only filled with glass wool not only to prevent the physical transfer of the solute but also to enhance the reproducibility of solubility measurements. A dip tube was connected to the inlets of the 1st and 2nd cells to transfer $scCO_2$ to the bottom of the cells. For ternary solubility measurements, the dissolved solutes after exit from the back-pressure regulator were trapped in a vial filled with absolute ethanol ($V = 1$ mL) and cooled in a salt–ice–water slurry. After adding 0.5 mL of an internal standard solution at a concentration of $2.000\,g\,L^{-1}$ 1-hexanol in ethanol to the vial, its content was transferred to a 5 mL volumetric flask and the volume was made up and analysed by GC-FID.

Ternary solubility levels were measured at 313.15 K and 110 bar for various flow rates of $scCO_2$ ranging from 180 to $500 \pm 10\,mL\,min^{-1}$ and for various static times from 5 to 25 min. Constant solubilities of MTBG and DTBG (i.e., $3.67 \pm 0.27$ and $1.53 \pm 0.08$) were interpreted as achieving saturation and equilibrium conditions. Therefore, a flow rate of as low as $180 \pm 10\,mL\,min^{-1}$ and a static time of 5 min were kept in all