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Process design and optimization for etherification of glycerol with isobutene

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HIGHLIGHTS

- A new process for the production of glycerol ethers is proposed.
- Dimerization of isobutene is considered in the new process.
- Latest kinetic and liquid–liquid equilibrium data are used.
- Optimization based on economic analyses is implemented.
- Isobutene cost greatly dominates the production cost of glycerol ethers.

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ABSTRACT

Surplus glycerol from biodiesel production can be transformed to valuable fuel additives through etherification with isobutene. Our previous work has studied the kinetics and thermodynamics of this reaction. In the present work, a novel process design is proposed. An optimization problem is also formulated to minimize the cost of production of the di-*tert*-butyl ethers and tri-*tert*-butyl ether of glycerol. The resulting mixed-integer nonlinear program enables simultaneous determination of values of key decision variables including number of column trays, feed tray location of column, volume of reactor, process flowrates etc. The optimal design leads to a minimal production cost of glycerol ethers of 1.201 $/kg, which is dominated by the cost of isobutene.

1. Introduction

The development and commercialization of biodiesel has rapidly expanded worldwide in recent years, driven by sustainability and environmental considerations. Glycerol is the main byproduct in biodiesel production that cannot be used as a fuel additive, because of its low solubility and poor thermostability. On the other hand it can be converted to a variety of high value chemicals (Zhou et al., 2008; Zheng et al., 2008; Izquierdo et al., 2012; Behr et al., 2008; Ayoub and Abdullah, 2012; Tan et al., 2013; Quispe et al., 2013). *tert*-Butyl glycerol ethers are among the most promising ones. Glycerol (G) reacting with isobutene (IB) or *tert*-butyl alcohol forms mono-*tert*-butyl ethers of glycerol (ME), di-*tert*-butyl ethers of glycerol (DE) and tri-*tert*-butyl ether of glycerol (TE). DE and TE, the so-called high-ethers, are potential fuel additives. When they are added into biodiesel or diesel (5–15 wt%), not only the particulate matter and greenhouse gas emissions in combustion are reduced (Kesling et al., 1994, 1995; Frusteri et al., 2013; Beatrice et al., 2013; Asdrubali et al., 2015), but also low-temperature properties (pour point and cold filter plugging point) and the viscosity of the biodiesel are improved (Melero et al., 2010). Also, their high octane number makes them an alternative oxygenate additive to gasoline (Karinen and Krause, 2006), as a substitute for methyl-*tert*-butyl ether (MTBE) and ethyl-*tert*-butyl ether (ETBE). As such their market potential is significant.

Although *tert*-butyl alcohol is soluble with glycerol and cheaper than isobutene in the current market (Chang et al., 2014; Ozbay et al., 2012; Celdeira et al., 2014), *tert*-butylation of glycerol using isobutene has drawn more consideration because of higher glycerol conversion and product selectivity. Most of the research in this area has focused on finding active and selective catalysts and optimizing the reaction conditions (Frusteri et al., 2013; González

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et al., 2013; González et al., 2014; González et al., 2014; Zhao et al., 2013; González et al., 2013; González et al., 2012; Frusteri et al., 2012; Zhou et al., 2014; Singh et al., 2015). Three kinds of processes have been proposed, the ARCO process (Vijai and Berwyn, 1995), the Behr and Obendorf process (Behr and Obendorf, 2002) and the Di Serio et al. process (Di Serio et al., 2010). They differ in the methods for the recycle of unreacted glycerol and isolation of ME from the other products. The flowsheets of the three processes are illustrated in Supplementary material. In the ARCO process (Vijai and Berwyn, 1995), partially reacted glycerol, isobutene and products enter into a decanter. The heavier phase containing glycerol, ME and acid catalyst is recycled back to the reactor. The light phase is fed to a stripping column to recover isobutene, followed by a water wash column to obtain high-ethers. A large amount of glycerol and ME in the wastewater is not recovered, resulting in waste of materials.

Behr and Obendorf (2002) developed a process consisting of a three-step reactor cascade. The fresh glycerol is used to extract ME in the reaction product, instead of being fed to the reactor directly. The extract stream containing glycerol and ME is recycled to the reactor, and the raffinate stream is passed to a flash tank to recover unreacted isobutene. The bottom product of the flash tank enters into a vacuum distillation column to isolate DE and TE from other impurities including ME and Glycerol. Cheng et al. (2011) modified this process by changing the three-step reactor cascade to one reactor to reduce capital costs, replacing the flash tank with a multistage stripping column to ensure a complete recovery of the unreacted isobutene, and recycling the bottom product of the vacuum distillation column to the extraction column instead of to the reactor to avoid reverse reaction. In this configuration, the vacuum distillation column used for purification of DE and TE operates under extreme conditions and steams out a large amount of distillates with high boiling points.

Di Serio et al. (2010) proposed a process using biodiesel to extract ME, DE and TE from the etherification products. The extract is washed by water to remove ME and obtain biodiesel containing DE and TE. Combining the properties of high-ethers and their application, this process produces a mixture of biodiesel high-ethers instead of “pure” high-ethers.

The concept of the Behr and Obendorf process has been employed in subsequent studies. Vlad et al. (Vlad et al., 2013) optimized the process with a low-purity isobutene feeding. Martín and Grossmann (2014) integrated the production of biodiesel (FAME or FAEE) with glycerol ethers. The integration increases the production of biofuel by 20%, with a production cost of almost 3 times that of producing biodiesel alone, due to the high price of isobutene. They concluded that a key factor for improving economics is to reduce the cost and improve the availability of isobutene. Also they found that it is economically promising to produce isobutene from biomass containing glucose (Martín and Grossmann, 2014). Thus, they designed an integrated process for the production of biodiesel, bioethanol, isobutene and glycerol ethers from algae (de la Cruz et al., 2014). An affordable production cost for biofuel was obtained. In summary, although optimization and economic analyses of specific process designs have been performed using simplified process models (Vlad et al., 2013; Martín and Grossmann, 2014) or based on sensitivity analysis (Cheng et al., 2011), there is no definitive evaluation of the economic feasibility of this etherification route for glycerol conversion.

Our previous work has investigated the reaction kinetics (Liu et al., 2013) and liquid–liquid equilibrium (Liu et al., 2014) of etherification of glycerol with isobutene. This paper aims at the design and optimization of a process for this etherification reaction. We initially propose a process flow sheet inspired by the existing processes, but also modified to avoid waste of raw materials or extreme operating conditions. The dimerization of isobutene detected in experiment (Liu et al., 2013) is also considered in the reaction and separation sections of the process. Detailed mathematical models are formulated for each unit operation in the process. Kinetic and liquid–liquid equilibrium data obtained from our previous experimental study are used, which is very important for the accuracy of the models. An optimization problem is formulated to seek an optimal process configuration minimizing the production cost of glycerol ethers. Finally, the effect of raw material prices on the process economics is studied.

2. Process design

The reaction system contains three consecutive etherification reactions and one dimerization, shown in Fig. 1. Mono-*tert*-butyl ethers of glycerol (ME), di-*tert*-butyl ethers of glycerol (DE) and tri-*tert*-butyl ether of glycerol (TE) are produced continuously. A side reaction forms dimers of isobutene (DIB). TE and DE are the desired products. Thus the production process mainly considers the reaction, the recycle of unreacted glycerol (G), isobutene (IB) and intermediate ME, and the isolation of DIB from the products.

The proposed process is schematically illustrated in Fig. 2. The reactions take place in a CSTR under pressure, catalyzed by NKC-9. ME should be recovered and recycled back to the reactor to be further converted to high-ethers. Extracting ME from the reaction products using glycerol proved to be effective in the study of Behr and Obendorf (Behr and Obendorf, 2002). Thus an extraction column (E1) is placed after the CSTR, and fresh glycerol is used as the solvent. Glycerol in the raffinate of E1 (stream 9) is washed by water in another extraction column (E2). Isobutene in stream 15 can be recovered relatively easily due to its low boiling point compared with other components. Both the Behr and Obendorf

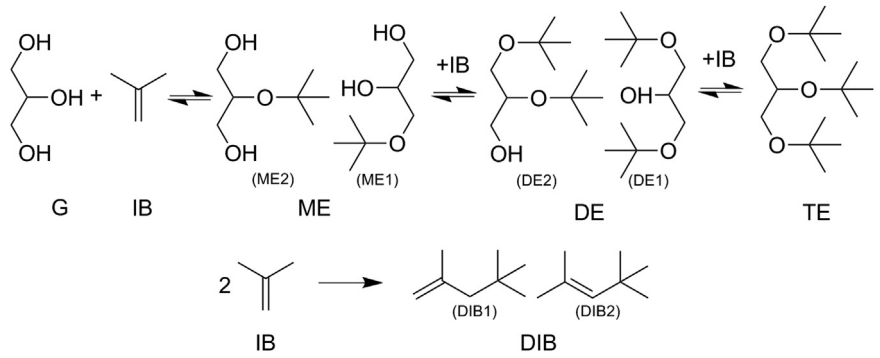

Fig. 1. Reaction pathway of the etherification process.