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Fuel-based ethanol dehydration process directly extracted by gasoline additive

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ABSTRACT

To reduce the heavy energy consumption of the conventional dehydration process of bioethanol production from biomass fermentation broth, this work aims to develop a fuel-based ethanol dehydration process directly extracted by gasoline additive. Methyl *tert*-butyl ether (MTBE) is screened and validated as an available entrainer of heteroazeotropic distillation from gasoline additives by analyzing and determining residue curve maps on the basis of simulation and experimental method. Two fuel-based ethanol separation processes with MTBE as entrainer, i.e. direct-cycle scheme and three-column scheme, are proposed and optimized by using ASPEN PLUS. It indicates that the proposed dehydration process with MTBE as entrainer can significantly reduce the energy and entrainer consumption, and the product can be directly used in gas pool. The techno-economic evaluation indicates MTBE scheme with 8000 ton/year ethanol production presents lower capital and utility costs than isooctane scheme.

1. Introduction

Due to the more and more serious energy and environmental concerns, renewable sources of energy and fuels become viable and realistic alternatives in the energy market [1]. Bioethanol obtained from crops and lignocellulosic biomass is considered as one of the most promising renewable fuels. A major advantage of bioethanol as fuel, over other fuel alternatives, is that it can be easily integrated in the existing fuel pool as a 5–25% mixture with gasoline, which does not need any modification of current engines. Moreover, due to the higher content of oxygen in ethanol, it has been used as an oxygenate added into gasoline pool, which not only leads to a more efficient combustion, but also improves the antiknock properties [2,3]. Currently, fuel ethanol accounts for around 73% of worldwide ethanol yields [4], which contributes to about 13% reduction in the greenhouse gas emissions. In the future, it expects that much higher amount of ethanol will be used as motor fuel, with increasing fivefold in the proportion of biofuel used in the world transport from 1% in 2009 to 6% in 2020 [5,6].

According to the current international bioethanol standards, the maximum allowed water content in fuels is 0.6 mol% (EN 15376, Europe), 1.2 mol% (ABTN/Resolução ANP No. 36/2005, Brazil) or 3.2 mol% (ASTM D 4806, USA). Ethanol is mainly produced by microbial fermentation currently only working directly with sugars converted from two major components of plants such as starch and cellulose. A common feature of these technologies is the production of diluted bioethanol, in the range of 5–12 wt% ethanol, that needs to be further concentrated and dehydrated. Therefore, two energy demanding separation steps are required to reach the purity target, mainly due to the presence of the binary azeotrope ethanol–water with 95.63 wt% ethanol (89.5 mol%). This azeotrope with a boiling point of 78.1 °C cannot be further purified by traditional distillation.

The first step is typically an ordinary distillation to concentrate bioethanol close to its azeotrope with water. The second step is more complex and of high interest, as it requires further dehydration of ethanol to the required product. Several processes based on the technologies of reactive distillation, azeotropic distillation, extractive distillation, adsorption and membrane have been developed for producing absolute ethanol in an efficient way [7–9]. In spite of different technologies, most of the energy consumption in bio-ethanol dehydration occurs in removing water from the azeotropic mixture [10–12]. One novel approach is direct dehydration by reactive distillation, where water can completely react with ethylene oxide and finally pure ethanol and ethylene glycol can be obtained [13]. The new technology is energy efficient and profitable; however, due to strong interactions of chemical reaction, heat and mass transfer, the separation process will be complicated and highly sensitive to operating variables. Hence, more investigation for both the reaction and distillation is required before its further application.

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In large-scale industrial processes, heteroazeotropic distillation has been widely applied for separating the binary azeotropic mixtures into their pure components by introducing an entrainer into the system. The entrainer results in a liquid–liquid phase splitting region which makes the process more economical and efficient [14,15]. A typical example of ethanol dehydration process by heteroazeotropic distillation technology is the process using benzene as entrainer [13]. Due to a small amount of benzene remained in the solution, absolute alcohol produced by this method is now considered not suitable for consumption, as benzene is carcinogenic. Instead, more environment-friendly entrainers such as cyclohexane, n-dodecane, glycerol and ethylene glycol are used to replace the toxic benzene [16,17]. Moreover, isooctane, the new gasoline additive used in the USA, was investigated as the entrainer to produce fuel ethanol for gasoline use, and the proposed process may result in less energy consumption and facility investment [18–20]. However, since isobutane is used as alternative of other gasoline additives mainly in the USA, more applicable entrainer among other gasoline additives widely used worldwide is desired.

Ethers such as methyl *tert*-butyl ether (MTBE), ethyl *tert*-butyl ether (ETBE), diisopropyl ether (DIPE) and *tert*-amyl methyl ether (TAME) with high octane value are the most widely used gasoline additives to improve fuel combustion efficiency for decades [21], and they are dominating the world market. If the entrainer derives from these gasoline additives, the product (mixture of ethanol and gasoline additive) can be mixed immediately with gasoline, which will simplify the separation process and reduce the energy consumption. This work aims to develop a more efficient fuel-based ethanol dehydration process by screening available entrainer from gasoline additives. The goal of the proposed process is to obtain the mixture of ethanol and the gasoline additive, rather than pure ethanol, which can be blended directly with gasoline without further separation. For this purpose, the entrainer is first screened and verified by determining the residue curves. The dehydration process based on the selected entrainer is then proposed and optimized. Moreover, in order to investigate the economic feasibility of the new dehydration process, the techno-economic evaluation was conducted to analyze the capital and utility investment of MTBE and isooctane processes. According to the production capacity of the existing bio-ethanol distillation plant, the economic analysis was calculated on the basis of fuel-ethanol production of 8000 ton per year [7].

2. Theory and methods

2.1. Residue curve map

As a conceptual design tool for ordinary distillation and special distillation processes, residue curve map (RCM) represents a collection of residue curves of the liquid residue composition with time as the result of a simple, one stage batch distillation [22]. Different residue lines result from starting compositions lined on the curve. RCM is used to preliminarily estimate feasible product regions for distillation of ternary mixtures. For azeotropic systems, the distillation boundaries separate the map into different distillation regions [23]. A feasible product can be determined for each distillation region, which guides to directly figure out the proper feed composition. Therefore, the RCM has been used for feasibility analysis of distillation processes with non-ideal and azeotropic mixtures [15,24,25].

2.2. Validation of RCM model

In order to validate the reliability of the RCM model and verify the accuracy of activity model and its parameters for distillation simulation, experiments were carried out to determine the MTBE–water–ethanol residue curves in different distillation regions.

2.2.1. Materials

Methyl *tert*-butyl ether (MTBE) with purity of >99.9%, ethanol with purity of >99.5% and acetone with purity of >99.5% were obtained from Aladdin Chemistry Co., Ltd., Shanghai. Deionized water was used as the solvent throughout the experiment.

2.2.2. Apparatus and procedures

The apparatus for determining the liquid residue composition with time mainly consists of a 500 mL three-necked flask, 300 mL condenser-west tube and 500 mL stand-up flask. The three-necked flask was placed in the oil bath with thermostat heaters and magnetic stirrers. The temperature was controlled by oil bath (Huber, Germany) with the accuracy of 0.1 °C. Two mercury thermometers with accuracy of 0.01 °C were used to observe the liquid temperature and gas phase temperature, respectively.

About 300 g mixture of MTBE–ethanol–water with certain concentration was weighted on an electronic balance (Sartorius, ±0.0001 g) and put into the three-necked flask. The system was controlled at the specific temperature with oil bath. About 1.5 g liquid sample was withdrawn by injection syringe with time and then transferred to the glass bottle equipped with rubber septum directly which refrained the sample from volatilizing and contacting with water. The water content in sample was determined by Karl-Fischer method (Mettler-toledo, V20). The ethanol content was determined by gas chromatography (Agilent, 7890), which employed a 2 m × 3 mm column packed with Porapak Q 80/100 and a thermal conductivity detector (TCD). The oven temperature was 140 °C and the argon (99.999%) flow rate was 50 mL/min. The temperature of the detector was 130 °C, and the current for the TCD was 70 mA. The method of internal standard (acetone) was used to improve the precision of quantitative analysis of ethanol content. After determining the content of ethanol and water, the MTBE content could be calculated.

3. Results and discussion

3.1. RCMs of gasoline additives–water–ethanol

Based on Aspen Plus, RCMs and liquid–liquid equilibrium (LLE) diagrams of the ternary mixture of ethanol, water and candidate gasoline additive were calculated by employing the UNIQUAC property method (the missing parameters of UNIQUAC were estimated by UNIFAC method), the binary interaction coefficients are listed in Table 1. Note that, unless particularly stated, in all triangular RCMs of this work the residue curve is arrowed orienting from the lowest boiling point (unstable node), then bending around the middle boiling point (saddle), and finally ending at the highest boiling point (stable node) of the bounded region. As high purity ethanol is desired as product, it cannot be saddle in the map. Instead, the ethanol point should be an unstable or a

Table 1
Binary interaction coefficients ($\Lambda_{i,j}$) for UNIQUAC model (at 298.15 K).

$\Lambda_{i,j}$[a]	Ethanol	Water	MTBE	ETBE	DIPE	TAME
Ethanol	1.0000	1.0463	0.3450	0.2724	0.3132	0.3219
Water	0.6438	1.0000	0.0812	0.5480	0.0744	0.1084
MTBE	1.3246	0.9855				
ETBE	1.3309	0.3665				
DIPE	1.2710	0.9055				
TAME	1.3160	0.7645				

[a] $\Lambda_{i,j}$ is calculated by $\Lambda_{i,j} = \exp(a_{ij} + b_{ij}/T + c_{ij} \times \ln T + e_{ij} \times T + d_{ij}/T)$; the parameters ($a_{ij}$, b_{ij}, c_{ij}, e_{ij} and d_{ij}) are listed in Tables S1 and S2.