Supplementary information for the revised manuscript ijcre-2015-0198R1

Supplementary information:

**Synthesis of Butyl Acetate in a Membrane Reactor**

**in a Flow-Through Mode**

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1. Characteristics of the pervaporation membrane

The water flux equation is listed as:

 Eq. 1

The separation factor equation is listed as:

 Eq. 2

Where *J* and *α* are water flux (g/m2•h) and separation factor, respectively, *m* is the mass of the permeation solution (g), *S* is the effective area of pervaporation membrane (m2), *t* is the separating time (h), *YA* and *YB*are the contents of A (water) and B (n-butyl alcohol, acetic acid and butyl acetate) in the permeation side, *XA* and *XB*are the contents of A (water) and B (n-butyl alcohol, acetic acid and butyl acetate) in the feed liquid.

To understand the pervaporation membrane performance, the mixed solution including n-butyl alcohol (19.22 wt%), acetic acid (15.58 wt%), butyl acetate (56.45 wt%) and water (8.75 wt%), which is equal to the content of reaction mixture when the conversion is 65.2% under the ratio of n-butyl alcohol to acetic acid of 1:1. The temperature of pervaporation is 343 K. The component contents (n-butyl alcohol, acetic acid and butyl acetate) in the permeation side were determined by GC. The water flux and separation factor are described by Eq. 1 and Eq. 2. The water flux and separation factor and the contents in the permeation side were shown in Table S1. The water flux and separation factor are 96.12 g/m2•h and 629.36, respectively, indicating the pervaporation membrane possessed a good performance of water removal.

Table S1. The water flux and separation factor and the contents in the permeation side of pervaporation membrane

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| substances | acetic acid | n-butyl alcohol | butyl acetate | water |
| the contents in the permeation side (wt%) | 1.62% | 0.008% | 0.002% | 98.37% |
| water flux (g/m2·h) | 96.12 | | | |
| separation factor | 629.36 | | | |

2. Theoretical conversion and activation energy

From the thermodynamic parameters shown in Table S2, the equilibrium constant K298 at 298 K can be got from Eq. 3.

 Eq. 3

The equilibrium constant K363 at 363 K can be got from Eq. 4.

 Eq. 4

The concentrations of each component at 363 K can be gained from Eq. 5.

 Eq. 5

Based on the following thermodynamic parameters [Xiancai Fu, Physical chemistry, Higher Education Press, 5th edition, 2005], the theoretical conversion was calculated under the reaction temperature of 363 K and initial acetic acid/n-butyl alcohol molar ratio of 1:1 by Eq. 3, Eq. 4 and Eq. 5. The thermodynamic parameters are shown in Table S2.

The theoretical conversion is 68.0%. The experiment result is 65.2% under the same conditions, close to the theoretical value.

Table S2. The thermodynamic parameters of each component (298.15 K)

|  |  |  |
| --- | --- | --- |
| Component | HfØ(KJ.mol-1) | GfØ(KJ.mol-1) |
| CH3COOH | -484.50 | -389.90 |
| CH3CH2CH2CH2OH | -325.81 | -160.00 |
| CH3CH2CH2CH2OCOCH3 | -528.82 | -309.72 |
| H2O | -285.83 | -237.13 |

To consider the effect of reaction temperature on the kinetic model, the Arrhenius equation is listed as:

 Eq. 6

The plots of lnK can be used as a function of the reciprocal temperature:

 Eq. 7

The dependence of the reaction constants on reaction temperature is described by the Arrhenius equation [Eq. 6 and Eq. 7]. The activation energy of the reaction under a temperature range of 348-363 K was calculated and summarized in Fig. S1. For the esterification reaction, through the conversions we calculated the equilibrium constants. The plot of lnK vs. 1/T can be represented by a straight line. The activation energy was 25.05 kJ/mol from the slope of the line. The figure is expressed as follow.



Fig. S1. Activation energy for the esterification in the temperature range of 348-363 K.