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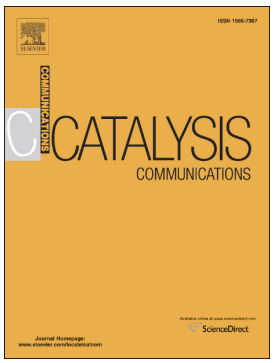

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Selective Conversion of Furfural into Value-added Chemical Commodity in Successive Fixed-bed Reactors

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Abstract

Successive hydrogenation of furfural in two fixed-bed reactors connected in tandem with Cu/SiO_2 and Ni/SiO_2 as the catalysts was achieved under atmospheric pressure. Various targeting products including furfuryl alcohol (yield: 98.8%), 2-methylfuran (yield: 95.1%), 2-methyltetrahydrofuran (yield: 96.2%) and tetrahydrofurfuryl alcohol (yield: 78.2%) could be obtained by variation of the reactor configurations.

Keywords: Hydrogenation, Furfural, 2-methylfuran, Furfuryl alcohol, Reactor configuration.

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1. Introduction

Currently, production of fine chemicals from biomass has attracted substantial attention.[1,2] For example, the selective conversion of biomass-derived furfural has become a research focus in recent years.[3] Furfural can be produced by the dehydration of the xylan and pentosans formed from the hydrolysis of hemicellulose. [4-6] Furfural is a representative compound for the investigation of the selectivity for hydrogenation of C=C and C=O groups with varied formulation of catalysts or reactor configuration.[7,8] Typically, hydrotreatment of furfural involves the hydrogenation and hydrogenolysis of the C=O group, the hydrogenation of the C=C group in the furan ring, the breaking of C-C bonds and so on. Generally, the Cu-based catalyst could be used for the hydrogenation of furfural to produce furfuryl alcohol (FOL) and 2-methylfuran (2-MeF) in a fixed-bed reactor at atmospheric pressure.[9-13] Ni-based catalyst, especially Raney nickel, is used for the hydrogenation of FOL and 2-MeF to tetrahydrofurfuryl alcohol (THFOL) and 2-methyltetrahydrofuran (2-MeTHF) in a batch reactor at high H_2 pressure. [14-18] The direct conversion of furfural to 2-MeTHF via one-step was also realized under atmospheric pressure over two-stage-packed Cu-Pd catalysts in a fixed-bed reactor.[19] However, via such process the separation of the 2-MeTHF from the water that is produced in the hydrogenation of furfural is difficult, as water and 2-MeTHF are azeotropic (the moisture content in commercial 2-MeTHF should be less than 300 ppm). On the other hand, the use of palladium-based catalyst make the process costly. Moreover, there may be differences in the lifetime for the two catalysts. In other words, when one kind of catalyst is deactivated, another non-deactivated catalyst has to be replaced together. To solve such issues, we designed a successive process for the conversion of furfural under atmospheric pressure, in which two fixed-bed reactors were used in series. Various

products such as FOL, 2-MeF, 2-MeTHF and THFOL could be obtained by variation of the reactor configurations.

2. Experimental

$Cu(NO_3)_2 \cdot 3H_2O$ (AR), $Ni(NO_3)_2 \cdot 6H_2O$ (AR), ammonia (AR) and urea (AR) were purchased from Shanghai Aladdin Bio-Chem Technology Co., Ltd. SiO_2 was purchased from Qingdao Ocean Chemical Industry Co., Ltd. Furfural and other chemicals were purchased from Sinopharm Chemical Reagent Co., Ltd.

The preparation method of Cu/SiO_2 was detailed as follows: Firstly, an aqueous solution of $Cu(NO_3)_2 \cdot 3H_2O$ (1.0 mol/L) was mixed with SiO_2 support (Silica gel type B). After that, under vigorous stirring, the mixed aqueous of urea (2.0 mol/L) and ammonia (5.0 mol/L) was dropped into the above mixed suspension at 100ºC. The amount of NH_4^+ was four times more than that of Cu^{2+}. After 1 h, the slurry was filtrated and washed with deionized water. After this, the precipitant was dried in air at 120ºC for 6 h. Subsequently, the obtained precursor was calcined at 550ºC in air and the Cu/SiO_2 catalyst was obtained. The preparation method of Ni/SiO_2 was similar to that of Cu/SiO_2. The difference was that the $Cu(NO_3)_2 \cdot 3H_2O$ was replaced by $Ni(NO_3)_2 \cdot 6H_2O$. The amount of NH_4^+ was six times more than that of Ni^{2+}.

The hydrogenation of furfural was performed in two series fixed-bed reactor. Before reaction, 10 % (*v*/*v*) H_2/N_2 was introduced into the reactor to reduce the catalysts. The reduction temperatures of the Cu/SiO_2 and Ni/SiO_2 catalysts (40~50 mesh) are 200 and 550ºC, respectively. After the reduction, furfural was continuously pumped into a preheater, while H_2 was also introduced into the preheater. Thereafter, the vaporized furfural and H_2 were mixed and introduced into reactors. The effects of

internal and external diffusion have been excluded (Table S1 and S2). The final products were condensed and trapped by N, N-dimethylformamide. The carbon balance could be greater than 99%. Isopropanol acted as an internal standard in the analysis of products. The products were analyzed by using a Shimadzu GC-2010 Plus chromatography equipped with a Rtx-5 capillary column.

X-ray diffraction patterns (XRD) were recorded on a PANalytical X'Pert PRO diffractometer using nickel-filtered Cu K α radiation. The bulk elemental analysis was carried out on a Philips Magix601 X-ray fluorescence (XRF) analysis apparatus. The N_2 adsorption-desorption isotherms were measured at 77 K on a Pioneer SSA–6000 physical adsorption instrument. Before N_2 adsorption, the samples were degassed in vacuum at 300ºC for 2 h. Temperature-programmed-reduction (H_2-TPR) was performed on a Vodo VDSorb–91x instrument. The catalyst (50 mg) was pretreated in Ar flow (50 mL/min) at 550ºC for 1 h. After that, a flow of 5 vol.% H_2/Ar (20 mL/min) was used as the reducing agent, and the temperature was increased from 50 to 700ºC for Cu/SiO_2 catalyst or 900ºC for Ni/SiO_2 catalyst at 20ºC/min. Water content in the products was measured on a Karl Fischer Moisture Titrator.

3. Results and discussion

A water separator and a desiccator were used and located in between of the two fixed-bed reactors (Figure 1). Cu/SiO_2 catalyst was employed in the first reactor and Ni/SiO_2 catalyst was employed in the second reactor. Desiccant was anhydrous calcium chloride. In this process, FOL, 2-MeF, THFOL and 2-MeTHF could be produced selectively by manipulating the experimental variables. For the purpose of production of 2-MeTHF, path 1 was preferred. The generated H_2O during the first step

could be almost completely removed by the water separator and desiccator. For the purpose to produce THFOL, path 2 was preferred because there was little water generated in the first step of the reaction. Interestingly, the yield of 2-MeTHF achieved 96.2% under an optimized conditions through path 1. Moreover, both Cu/SiO_2 and Ni/SiO_2 catalysts showed the excellent stability. From the perspective of industrialization, this process was also economical and could adjust target products, according to the need from market, conveniently. Furthermore, we also performed a detailed research of the Cu/SiO_2 and Ni/SiO_2 catalysts prepared by ammonia evaporation method and the influence of reaction conditions on the conversion of furfural.

The catalyst with good activity and stability was the key to achieve the high efficiency transformation of furfural. In the hydrogenation reaction, furfural was transformed into FOL on a Cu-based catalyst. FOL was subsequently converted into 2-MeF on the Cu-based catalyst or into THFOL on a Ni-based catalyst via hydrogenation. 2-MeF could also be hydrogenated into 2-MeTHF over the Ni-based catalyst. In industry, Cu-Cr catalyst was usually used for the conversion of furfural into FOL and 2-MeF. However, only about 100 gram products could be produced by 1 gram catalyst (Figure S3). The catalyst suffered from the quick deactivation because of the polymerization of furfural, sintering of copper or poisoning of the active sites by probably sulfur (about 40 ppm sulfur in furfural). Fortunately, the Cu/SiO_2 catalyst prepared by ammonia evaporation method had a large specific surface area and high dispersion of copper (Figure S1, S2 and Table S3). It showed excellent activity and stability in the hydrogenation of furfural into 2-MeF in the first fixed-bed reactor. The yield of 2-MeF was always above 92% during the 150 h stability test, and 2-MeTHF was the major by-product but with only 4% of yield (Figure 2). It could be estimated

that at least 270 gram 2-MeF could be produced by 1 gram Cu/SiO_2 catalyst.

Reaction conditions affected the distribution of the products (Table S4) and it could be found that the yield of FOL was 98.8% at the low temperature and low WHSV (T = 140ºC, WHSV = 0.50 h^{-1}). The Cu/SiO_2 catalyst was responsible for the hydrogenation of the HC=O bonds at the low temperature and could break (deoxygenation) HC=O bands at high temperature. However, Cu/SiO_2 catalyst was hardly active for the hydrogenation of the -C=C bonds in the furan ring. For the hydrogenation of C=C bonds, Pd-based and Ni-based catalysts exhibited good activity and selectivity. [20, 21] However, the cost of using Pd-based catalyst was high and hence Ni-based catalysts would be the better choice for the successive hydrogenation of 2-MeF or FOL in the second fixed-bed reactor.

The Ni/SiO_2 catalyst prepared by ammonia evaporation method also had large specific surface area, which helps to achieve the high dispersion of Ni (Figure S1, S2 and Table S3). It showed good activity and selectivity for the hydrogenation of C=C bonds (Table 1). The yield of 2-MeTHF was high (ca. 96.2%) through path 1. The water had a significant influence on the activity of the catalyst and the distribution of the product (Table S5). If the final target product was 2-MeTHF, the intermediate product in the first fixed-bed reactor should be 2-MeF. Accordingly, the production of 1 mole H_2O was accompanied by the production of 1 mole 2-MeF. The water would reduce the activity of the Ni/SiO_2 catalyst and cause the generation of 2-pentanol and 1, 4-pentanediol. The solubility of 2-MeF in water was about 0.3 wt% at 25ºC.[22] Therefore, 2-MeF and water could be easily separated into two phases (the upper phase was 2-MeF). In the water separator, 2-MeF could be brought into a desiccator (filled with anhydrous calcium chloride) by excess H_2 and then brought into the second fixed-bed reactor. The water content in 2-MeF could be lower than 0.5 wt%

after this treatment. It was known that the solubility of 2-MeTHF in water was about 15 wt% at 25ºC,[23] and 2-MeTHF and water are azeotropic. Therefore, nearly no water was introduced into the second reactor, which would make the subsequent purification of 2-MeTHF easier. Thus, the water content of less than 300 ppm in purified 2-MeTHF could be achieved at a low cost. If the final target product was THFOL, the intermediate product in the first fixed-bed reactor should be FOL. There was no much water in this process and the path 2 could be used. However, a small amount of water still led to the generation of 1, 4-Pentanediol.

From the view of industrial application, the stability was one of the most important factors determining applications of the catalysts. Figure 3 and 4 showed that both Cu/SiO_2 and Ni/SiO_2 catalysts had good stability for the production of 2-MeTHF and THFOL. There might be some difference in the lifetime between the Cu/SiO_2 and the Ni/SiO_2 catalyst in industrial operations. The Cu/SiO_2 catalyst, which was relatively inexpensive in the first fixed-bed reactor, could absorb sulfur to avoid the deactivation of Ni/SiO_2 catalyst in the second fixed-bed reactor. Therefore, only the Cu/SiO_2 catalyst was needed to be replaced if the Ni/SiO_2 still maintained the activity.

4. Conclusions

In summary, a highly efficient process for the catalytic conversion of furfural was developed by means of two fixed-bed reactors connected in series with Cu/SiO_2 and Ni/SiO_2 as catalysts, respectively. This strategy provided a successive hydrogenation of furfural to produce 2-MeTHF and THFOL with a high yield. Notably, the yield of 2-MeTHF and THFOL achieved were up to 96.2% and 78.2%, respectively. More importantly, both Cu/SiO_2 and Ni/SiO_2 catalysts exhibited excellent stability. In addition, the water separator between the first and the second reactor reduced the

difficulty for the separation of 2-MeTHF. This strategy could also be applied to other cascade reactions.

Acknowledgement

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Artwork

Table 1: The hydrogenation of furfural over the Cu/SiO_2 and Ni/SiO_2 catalyst in two series fixed-bed reactors.

Figure 1: The diagram of two fixed-bed reactors in series for the conversion of furfural.

Figure 2: The hydrogenation of furfural in the first fixed-bed reactor with the Cu/SiO_2 catalyst.

Figure 3: The hydrogenation of furfural to produce 2-MeTHF.

Figure 4: The hydrogenation of furfural to produce THFOL.

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Table 1 The hydrogenation of furfural over the Cu/SiO_2 and Ni/SiO_2 catalyst in two series fixed-bed reactors.

Reaction Conditions [a]					Conv. [%]	Yield [%]					
Entry	Path	T_1 [ºC][b]	T_2 [ºC][c]	$H_2/Furfural_{mol}$	Furfural	2-MeF	2-MeTHF	FOL	THFOL	2-Pentanol	1,4-Pentanediol
1	Path 1	200	100	10	99.9	20	79.3	0	0	0.6	0
2	Path 1	200	110	10	99.9	6.7	89.4	0	0	3.5	0
3	Path 1	200	120	10	99.9	0.9	96.2	0	0	2.7	0
4	Path 1	200	130	10	99.9	0.6	96.1	0	0	3	0
5	Path 1	200	140	10	99.9	0.4	95.3	0	0	4.4	0
6	Path 1	190	120	10	99.9	0.9	95.9	0	0	2.4	0
7	Path 1	180	120	10	99.9	0.9	95.6	0	0	2.8	0
8	Path 1	170	120	10	99.9	0.8	94.9	0	0	4.3	0
9	Path 2	160	120	10	99.9	1	13.1	9.1	70	2.9	3.8
10	Path 2	160	130	10	99.9	0.9	13.7	0	78.2	3	4.1

[a] Reaction conditions: atmospheric pressure; the mass of catalyst is 2 g, the flow rate of furfural is 4.6 g/h. [b] T_1 was the reaction temperature in the first fixed-bed reactor. [c] T_2 was the reaction temperature in the second fixed-bed reactor.

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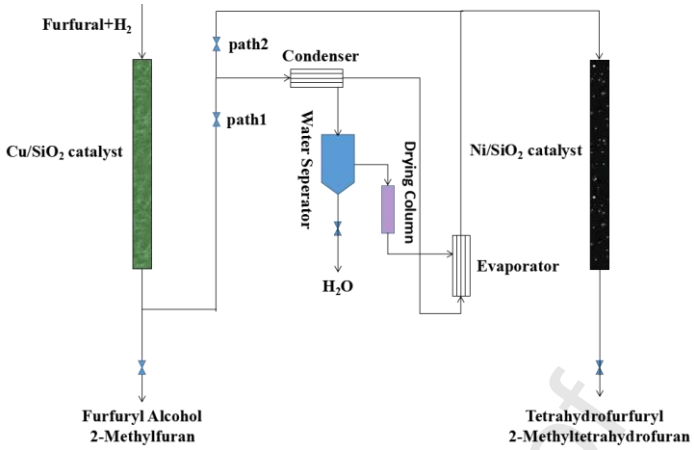

Figure 1 The diagram of two fixed-bed reactors in series for the conversion of furfural.

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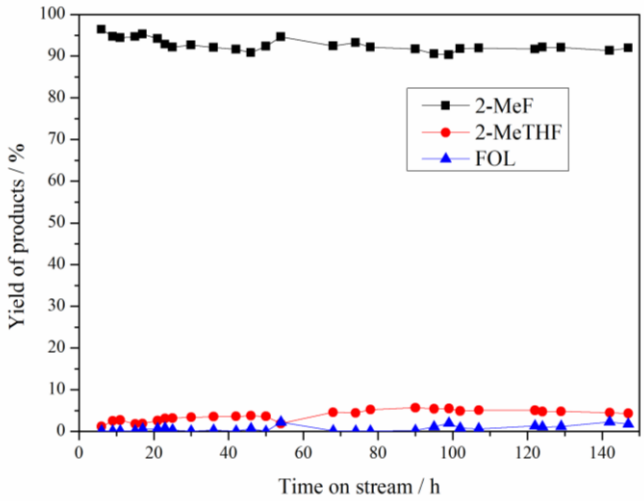

Figure 2 The hydrogenation of furfural in the first fixed-bed reactor with the Cu/SiO_2 catalyst. Reaction conditions: T = 200ºC, P = 1 atm, the mass of catalyst is 2 g, the flow rate of furfural is 4.6 g/h.

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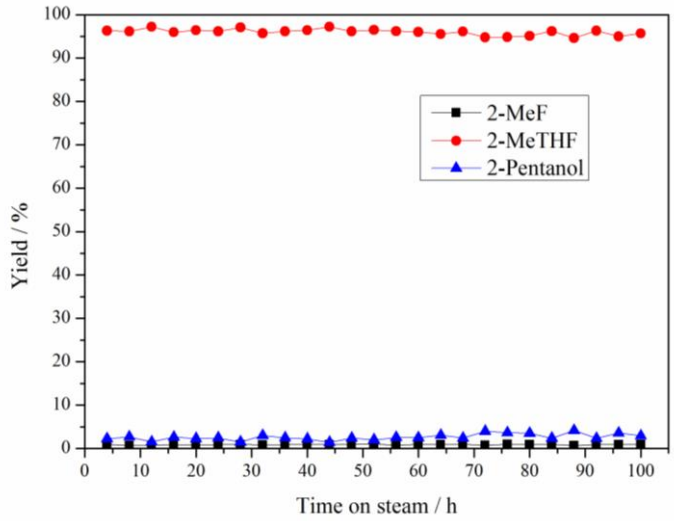

Figure 3 The hydrogenation of furfural to produce 2-MeTHF.

Reaction conditons:,T_1 = 200ºC, T_2 = 200ºC, P = 1 atm, H_2/Furfural$_{mol}$ = 10:1, the mass of catalyst is 2 g, the flow rate of furfural is 4.6 g/h.

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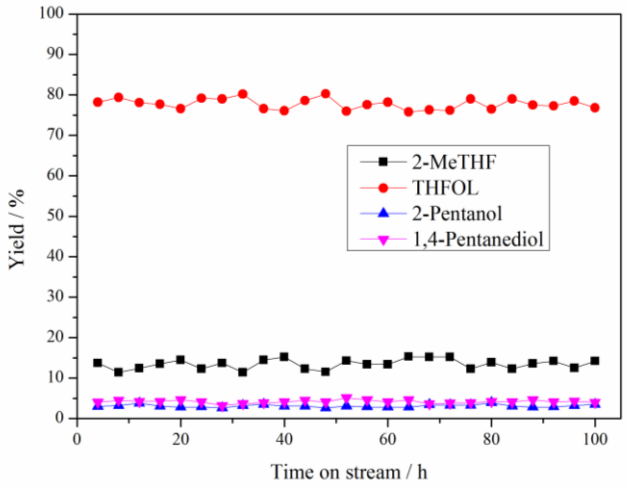

Figure 4 The hydrogenation of furfural to produce THFOL.

Reaction conditons: T_1 = 160ºC, T_2 = 130ºC, P = 1 atm, H_2/Furfural$_{mol}$ = 10:1, the mass of catalyst is 2 g, the flow rate of furfural is 4.6 g/h.

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Highlights

- A successive hydrogenation of furfural in two fixed-bed reactors was realized.
- Cu/SiO_2 and Ni/SiO_2 showed well activity and stability.
- Various products could be obtained by variation of the reaction strategy.

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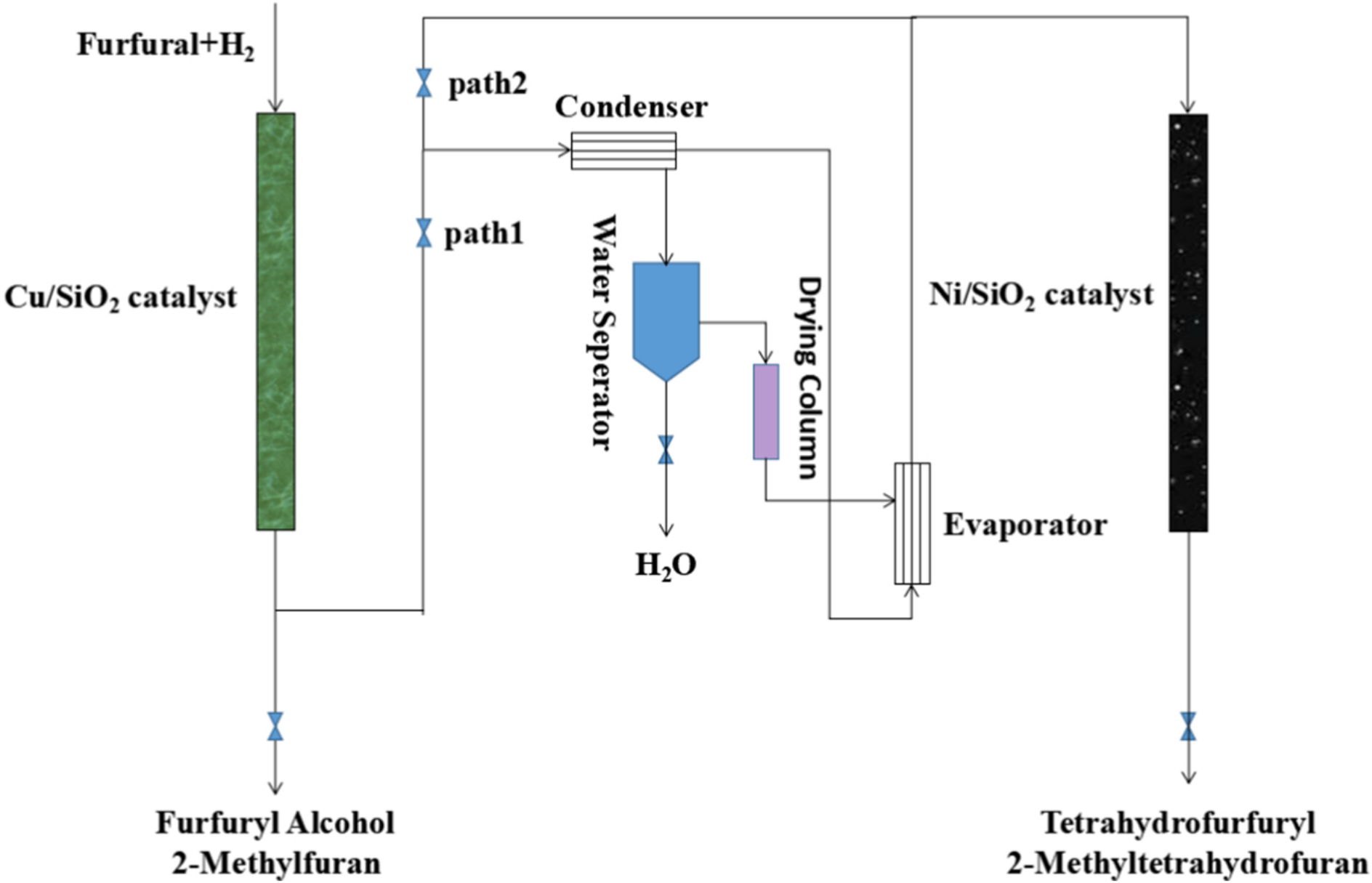
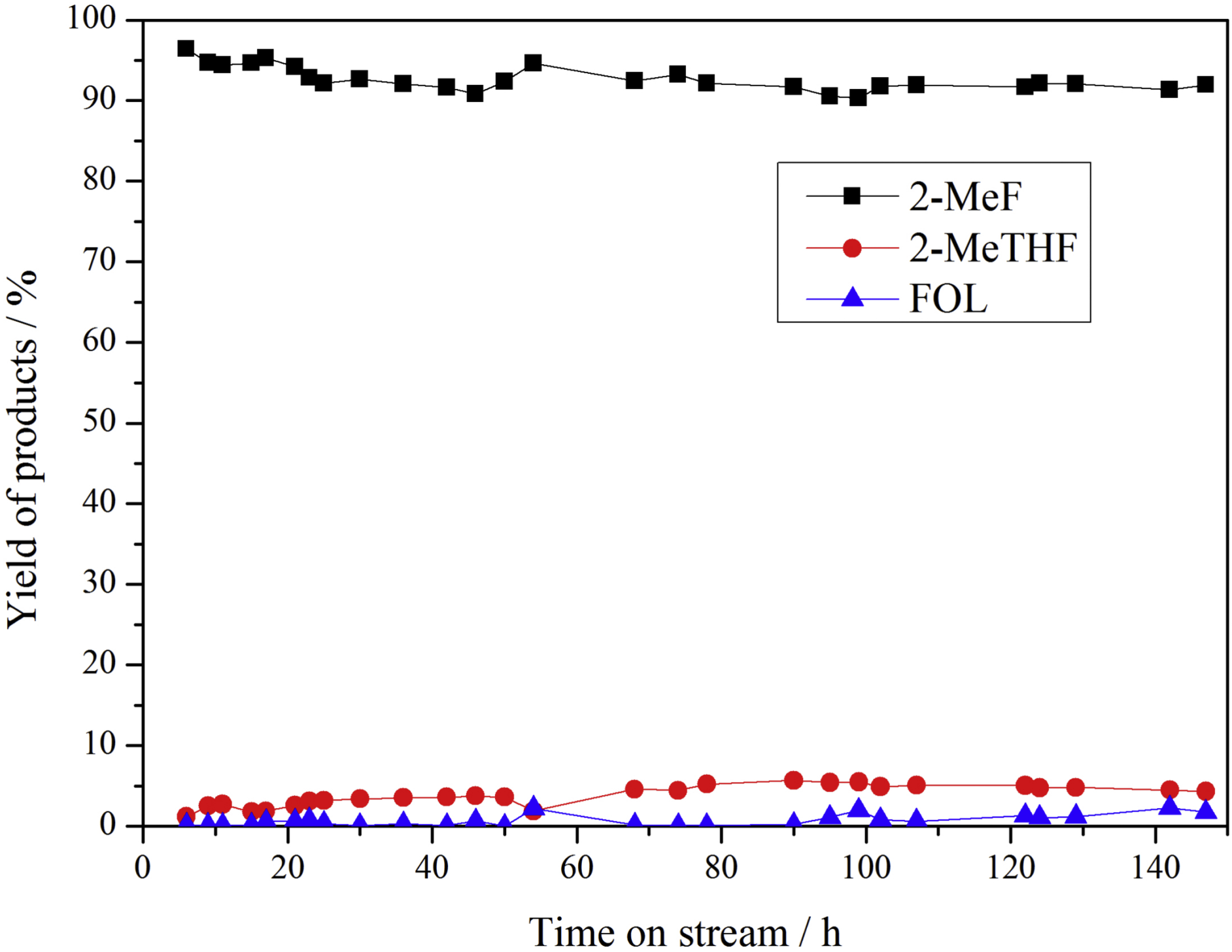

Furfural+H_2
path2
Condenser
path1
Water Seperator
Drying Column
Ni/SiO_2 catalyst
Cu/SiO_2 catalyst
Evaporator
H_2O
Furfuryl Alcohol
2-Methylfuran
Tetrahydrofurfuryl
2-Methyltetrahydrofuran

Figure 1


Yield of products / %
Time on stream / h
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2-MeTHF
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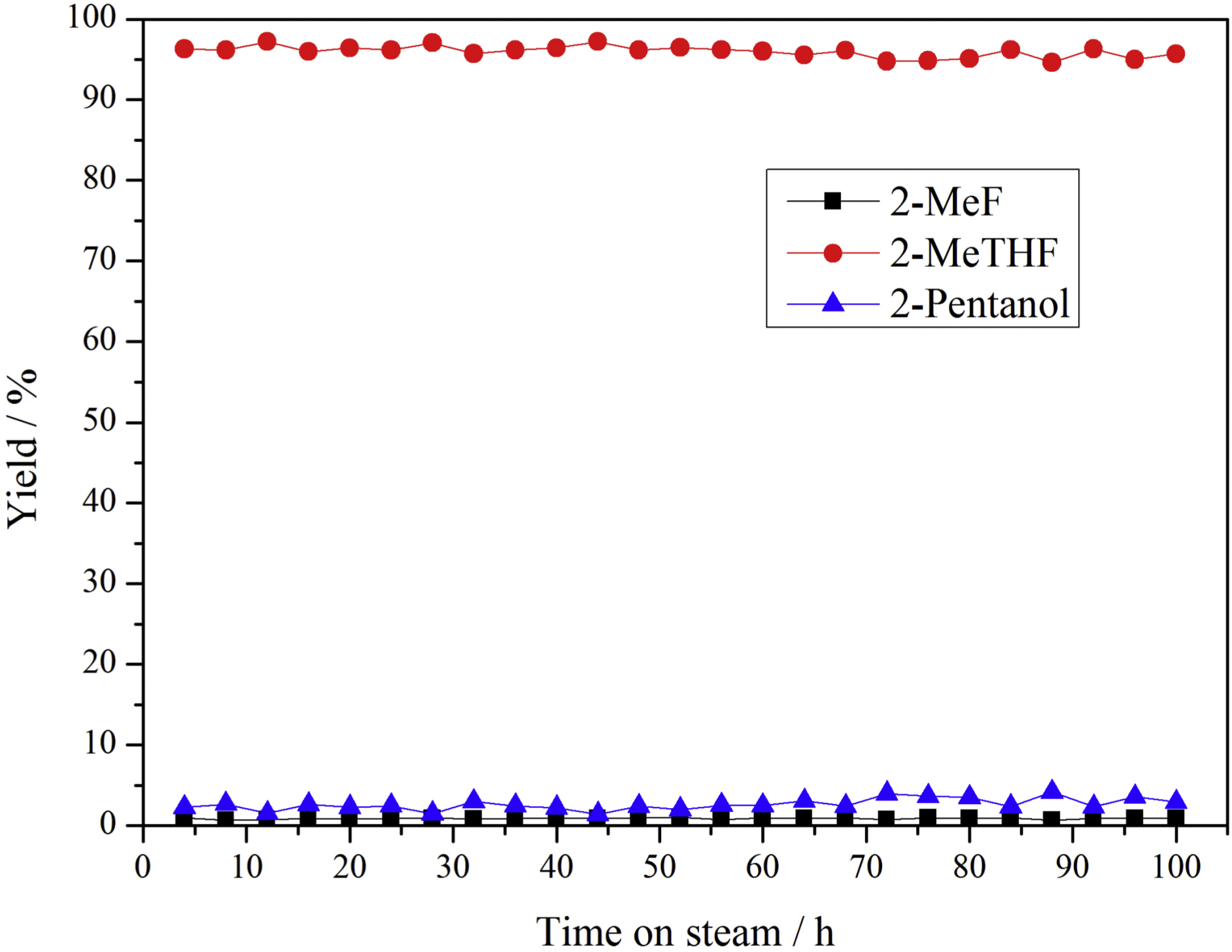
Figure 2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Time on steam / h
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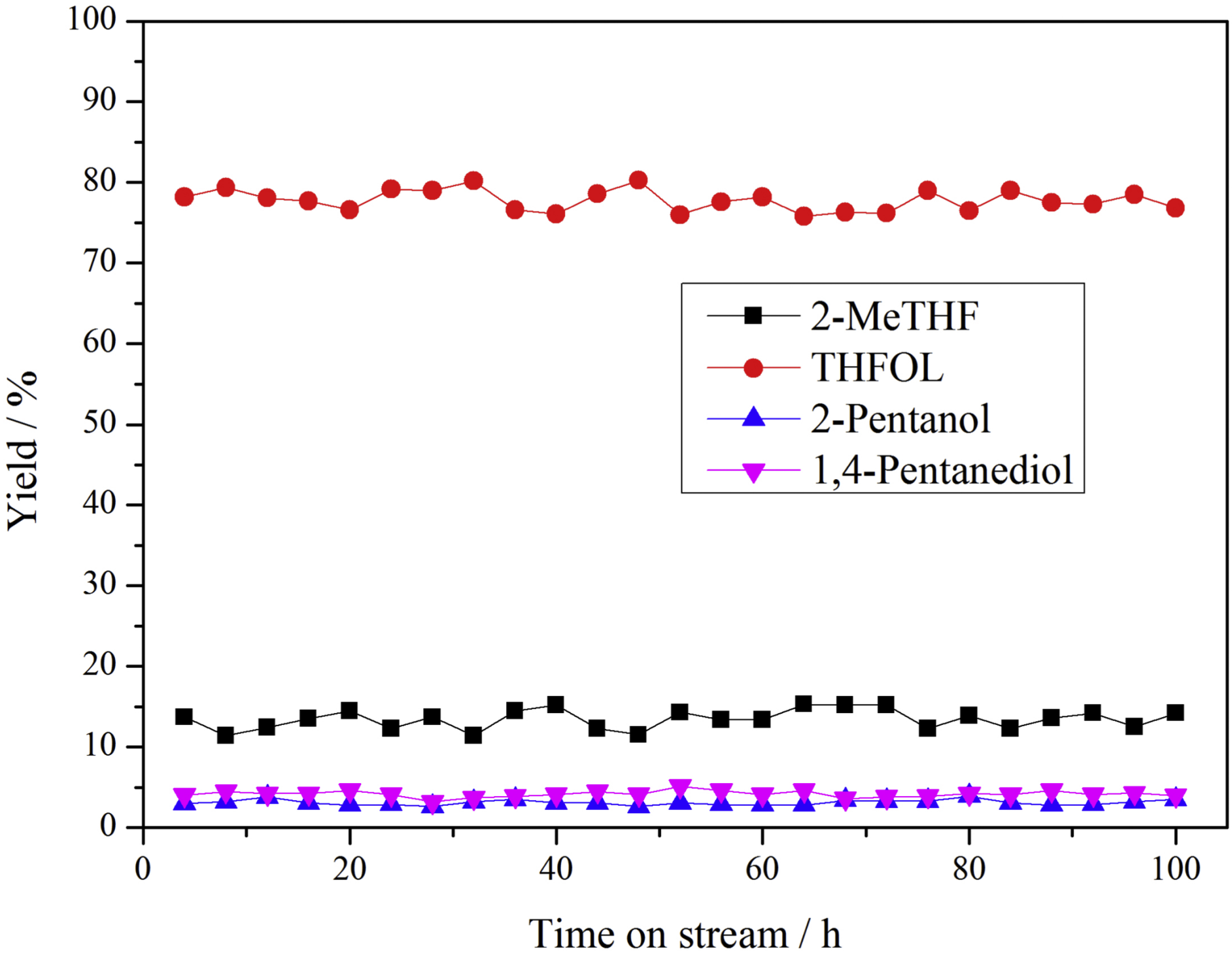
2-Pentanol

Figure 3


Yield / %
Time on stream / h
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THFOL
2-Pentanol
1,4-Pentanediol
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Figure 4