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Solvolysis of benzyl phenyl ether in high-temperature aqueous methanol solution under high-pressure carbon dioxide

Monocyclic aromatic hydrocarbons (benzyl methyl ether, benzyl alcohol and phenol) were obtained by treatment of benzyl phenyl ether in aqueous methanol solution. The highest yield of monocyclic aromatic hydrocarbons was obtained in aqueous methanol solution with 0.2 methanol molar fraction under 17.7 MPa of carbon dioxide at 573 K. The alcoholysis to benzyl methyl ether did not proceed in pure methanol. High-temperature carbonated water is effective for the alcoholysis.





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# Solvolysis of benzyl phenyl ether in hightemperature aqueous methanol solution under high-pressure carbon dioxide

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Alcoholysis of benzyl phenyl ether to various aromatic compounds was studied in high-temperature aqueous methanol solution under high-pressure carbon dioxide conditions. The products formed included benzyl methyl ether, benzyl alcohol, phenol and toluene. As high as  $70.7 \pm 0.2\%$  yield of monocyclic aromatic hydrocarbon with 16.1  $\pm$  0.3% yield of benzyl methyl ether was obtained by treating benzyl phenyl ether with an aqueous solution with 0.2 molar fraction of methanol, under 17.7 MPa carbon dioxide for 1 h at 573 K.

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### Introduction

Lignin is a major component of lignocellulosic biomass and has a structure in which aromatic monomers are randomly bonded in various types of linkages. There are many reports on the catalytic decomposition of lignin to aromatic compounds by the cleavage of ether linkages in the lignin structure, using heterogeneous and homogeneous catalysts.<sup>1-10</sup> Because lignocellulosic biomass contains a lot of water, the partial decomposition of lignin in water is desirable for saving energy. Hydrolysis of the ether linkage of lignin proceeds in high-temperature water; however, the subsequent dehydration of these products having several hydroxyl groups immediately occurs to produce char due to repolymerization.<sup>11</sup> Not only the development of active catalysts, but also the optimization of reaction conditions such as solvents should be done.6,12 To obtain aromatic compounds with high yields from lignin in water, chemical transformation of lignin to small and stable molecules is needed. Hydrolytic cleavage of aromatic C-O bonds in aromatic ether molecules proceeded at around 473 K with gaseous hydrogen<sup>13</sup> and 2-propanol;<sup>14</sup> however, supported noble metal catalysts are dispensable. Alcoholysis of lignin, in which lower alcohol molecules react with the ether linkage in lignin to form the corresponding valuable aryl ethers, is a feasible way to obtain stable aromatic compounds in an aqueous solution.

However, acid catalysts are needed for alcoholysis. Güvenatam *et al.* showed that Lewis acid catalysts such as iron, copper, nickel and aluminium chloride were active in ethanol for the depolymerization of lignin model compounds to obtain monoaromatic hydrocarbons; however, the alcoholysis reaction did not proceed in ethanol solvent with Lewis acid catalysts.<sup>15</sup> It has been reported that the alcohol–water co-solvent (aqueous (methanol or ethanol) solution) was effective for the biomass direct liquefaction to fuel at a high temperature around 573 K (ref. 16) but it has not been reported for the production of chemicals without using heterogeneous catalysts.

High-temperature carbonated water, which could be obtained using high-temperature water under high-pressure carbon dioxide, is a green acidic solvent, because the neutralization of the system can be achieved merely by cooling and depressurization, without a base.<sup>17–25</sup> The types of ether linkages in lignin depend on the variety of wood and are classified in terms of  $\beta$ -O-4 (43–50%),  $\alpha$ -O-4 (6–8%),  $\beta$ -5 (9–12%), 5-5 (10–25%), 4-O-5 (4%),  $\beta$ -1 (3–7%) and  $\beta$ – $\beta$  (2–4%).<sup>1</sup> Among these linkages,  $\alpha$ -O-4 bonds could be dissociated with the lowest energy.<sup>26</sup>

Here, we studied alcoholysis of benzyl phenyl ether, which is a simple model compound having a lignin  $\alpha$ -O-4 bond, in water, methanol and aqueous methanol solution. We found that the alcoholysis to benzyl methyl ether in addition to hydrolysis proceeded in aqueous methanol solution and that the yield of benzyl methyl ether was enhanced in the presence of high-pressure carbon dioxide.

## Experimental

Benzyl phenyl ether (Tokyo Chemical Industry Co., Ltd), benzyl methyl ether (Wako Pure Chemical Industries), benzyl alcohol

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(Wako Pure Chemical Industries), phenol (Wako Pure toluene (Wako Chemical Industries), Pure Chemical Industries), anisole (NACALAI TESQUE, INC.), and n-butanol (Wako Pure Chemical Industries) were purchased and used without any further purification. The solvolysis reaction of benzyl phenyl ether was carried out in a batch reactor (inner volume: 6.0 cm<sup>3</sup>) made of a SUS316 tube.<sup>27,28</sup> After benzyl phenvl ether (0.10 mmol), water (3.0-0 mL (0.2-0 mol)), and methanol (0-3.0 mL (0-0.07 mol)) were loaded into the reactor, the air inside was removed with nitrogen gas. Carbon dioxide (8-12 MPa) was fed to the reactor at 323 K. The partial pressure of carbon dioxide in the reactor at 573 K was estimated to be 14.2, 17.7 and 21.3 MPa, based on the equation of Charles's law, corresponding to the initial pressure of 8, 10 and 12 MPa at 323 K, respectively. The reactor was then submerged in a sand bath at 573 K for a given reaction time and then submerged in a water bath for cooling quickly to ambient temperature after the reaction. The carbon dioxide gas in the reactor was removed by depressurization at room temperature. A mixture of the reactant and liquid products after the reaction was taken out from the reactor using *n*-butanol. The quantitative analysis of the reactant and liquid products was conducted by gas chromatography with a flame ionization detector (GC-FID) equipped with a DB-WAX capillary column (Agilent Technologies) using tetrahydrofurfuryl alcohol (Wako Pure Chemical Industries) as an internal standard. The products were identified by their retention time in the GC-FID analysis, compared with those for known materials: benzyl phenyl ether, benzyl methyl ether, benzyl alcohol, phenol, toluene and anisole. The conversion and yield of products were calculated as follows:

Conversion(%) =

(1 - (The amount of unreacted benzyl phenyl ether)/(The initial amount of benzyl phenyl ether)) × 100,

 $Yield(\%) = ((Mol of products formed) \times$ 

 $(The \,number\,of\, benzene\,ring\, in\, products))/$ 

 $((Mol\,of\,benzyl\,phenyl\,ether\,introduced)\times 2)\times 100.$ 

The recovery was calculated based on the number of benzene rings in the products as follows:

Recovery(%) = (Amount of benzene rings in products) +

- $2 \times ($ Unreacted benzyl phenyl ether)/
- $2\times$  (The initial amount of benzyl phenyl ether).

The experimental error was obtained by reproducing the same experiment two times.

### **Results and discussion**

# Solvolysis reaction of benzyl phenyl ether in aqueous methanol solution

Benzyl phenyl ether was treated in aqueous methanol solution for 30 min at 573 K in a batch reactor. The conversion and product yields as a function of the molar fraction of methanol are shown in Fig. 1. In water, benzyl phenyl ether was decomposed, and the conversion was as high as  $98.3 \pm 0.6\%$ . Benzyl alcohol and phenol were obtained; however, their yields were  $5.9 \pm 1.1$  and  $6.5 \pm 1.0\%$ , respectively. Güvenatam *et al.* studied the decomposition behaviour of benzyl phenyl ether in hightemperature liquid water and showed that benzyl phenyl ether underwent the acid-catalyzed hydrolysis of the ether bond to form benzyl alcohol and phenol, which are the main monocyclic aromatic products obtained at 573 K; however, the yields were very low.<sup>15</sup> He et al. also reported that the mono-aromatic oxygenated products formed were proved to undergo self- and cross-condensation reactions to form di-aromatic and highmolecular weight compounds.<sup>29</sup> We analyzed total organic compounds (TOC) in the recovered solution after the treatment



Fig. 1 Effect of the molar fraction of methanol on the conversion and the yields of aromatic products for the solvolysis reaction of benzyl phenyl ether. Benzyl phenyl ether conversion (a), aromatic product yield (b and c), conversion ( $\bullet$ ), benzyl methyl ether ( $\bullet$ ), benzyl alcohol ( $\blacksquare$ ), phenol ( $\blacktriangle$ ), toluene ( $\nabla$ ), benzyl methyl ether + benzyl alcohol + toluene ( $\blacklozenge$ ), temperature 573 K, reaction time 30 min, water : methanol = 3.0 : 0.0-0.0 : 3.0 (mL : mL), 0.2-0 : 0-0.07 (mol : mol).

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of benzyl phenyl ether in pure water for 30 min at 573 K, which is the subcritical condition of water : methanol = 3 : 0 in Fig. 1. 20% carbon yield was obtained in the solution, indicating that the decomposition of benzyl phenyl ether proceeded in liquid water at 573 K, followed by polymerization of the decomposition products to water-soluble compounds. We could not identify the water-soluble compounds in detail. Decomposition of benzyl phenyl ether proceeded in hightemperature liquid water; however, the subsequent repolymerization resulted in low yields of aromatic compounds.

In methanol at 573 K (supercritical conditions), the conversion was as low as  $10.0 \pm 4.7\%$  with the formation of several aromatic products such as benzyl methyl ether, benzyl alcohol, phenol, and toluene; however, the yields were also as low as  $0.4 \pm 0.2, 0.3 \pm 0.0, 4.7 \pm 0.0$  and  $3.4 \pm 0.1\%$ , respectively, while anisole was not detected. Similar results were reported by Yokoyama et al. who studied the reaction behaviour of benzyl phenyl ether in supercritical methanol and found that methanolvsis of benzyl phenyl ether hardly proceeded and toluene and phenol were formed by thermolysis.<sup>30</sup> Güvenatam et al. studied the decomposition behaviour of benzyl phenyl ether in methanol at 573 K (under supercritical conditions) and reported that toluene and phenol were obtained as monoaromatic compounds.15 Toluene would be formed through the hydrogenolysis of benzyl phenyl ether by hydrogen derived from methanol, which is a hydrogen donor solvent. Mauriello's group studied the catalytic conversion of aromatic ethers over Pd/C and Ru/C in hydrogen donor solvents (methanol, ethanol and 2-propanol) at 493 K and showed that hydrogenolysis to the corresponding aromatic products proceeded by hydrogen from the solvent in the first step of the conversion.14

In aqueous methanol solution, the conversion decreased with an increase in methanol molar fraction (Fig. 1(a)). Benzyl methyl ether, benzyl alcohol, phenol, and toluene were formed; however, anisole was not formed. Saturated cycloalkanes such as cyclohexanol were not formed, indicating that the reductive cleavage of benzyl phenyl ether did not proceed without supported metal catalysts. The yields of monocyclic aromatic hydrocarbons depended on the methanol molar fraction. The yields of benzyl alcohol, phenol and benzyl methyl ether increased with an increase in methanol molar fraction and became maximum at 0.2 molar fraction (2.0 mL water and 1.0 mL methanol at room temperature) and then decreased to zero at 0.5 molar fraction concentration of methanol. Fig. 1 shows that both methanol and water are needed for the methanolysis reaction to produce benzyl methyl ether. Toluene was not formed in water; however, it formed in aqueous methanol solution and the yield increased with an increase in the molar fraction of methanol, indicating that methanol worked as a hydrogen donor.

Scheme 1 shows the proposed reaction paths for solvolysis and hydrogenolysis of benzyl phenyl ether in an aqueous methanol solution. Hydrolysis of benzyl phenyl ether to benzyl alcohol and phenol proceeded in water (Scheme 1, path (a)). Benzyl methyl ether was not formed in the methanol solvent;



Scheme 1 Plausible reaction pathway for the decomposition of benzyl phenyl ether.

however, benzyl methyl ether was formed in an aqueous methanol solution. Reaction paths (a), (b) and (c) proceed in aqueous methanol solution. Acid catalysts are needed for the alcoholysis; then a probable explanation for the methanolysis in aqueous methanol solution is that protons derived from water provided Brønsted acid sites. We discussed later the role of protons in the section of high-pressured carbon dioxide (Scheme 2).

Benzyl alcohol was formed but anisole was not formed in aqueous methanol solution at 573 K. The benzyl cation is more stable than the phenyl cation; hence, anisole would not be formed. Also, the benzyl cation could react with methanol to produce benzyl methyl ether in aqueous methanol solution.

The yield of phenol was almost the same as the sum of benzyl methyl ether + benzyl alcohol + toluene (Fig. 1(c)), indicating that hydrolysis (Scheme 1(a)), methanolysis (Scheme 1(b)), and hydrogenolysis (Scheme 1(c)) reactions proceed under the conditions of the present work. In a control experiment, the effect of sulfuric acid on the solvolysis of benzyl phenyl ether in aqueous methanol solution was assessed and it was found that the methanolysis reaction of benzyl phenyl ether and its hydrogenolysis to toluene did not proceed at room temperature under acidic solution conditions (Table 1, entry 7).



Scheme 2 Plausible reaction scheme for methanolysis of benzyl phenyl ether in aqueous methanol solution in the presence of carbon dioxide.

Entry				Frounce yreius (70						
no.	Carbon dioxide pressure (MPa)	Carbon dioxide partial pressure (MPa) <sup>b</sup>	Temperature (K)	Benzyl methyl ether	Benzyl alcohol	Toluene	Phenol	Monocyclic aromatic hydrocarbon	Recovery (%)	Conversion (%)
1	I	I	523	$0.8 \pm 0.0$	$2.6 \pm 0.1$	n.d.	$3.6 \pm 0.2$	$7.0 \pm 0.3$	$95.2 \pm 0.9$	$11.9 \pm 1.3$
2	Ι	Ι	573	$4.9 \pm 0.4$	$12.5 \pm 0.8$	$0.9 \pm 0.1$	$18.9 \pm 1.3$	$37.3 \pm 2.6$	$78.3 \pm 2.6$	$59.0 \pm 0.0$
3		Ι	623	$4.6 \pm 0.8$	$8.0 \pm 0.6$	$9.2 \pm 1.4$	$27.2 \pm 0.8$	$48.9\pm0.8$	$57.9 \pm 0.1$	$91.0 \pm 0.7$
4	8	14.2	573	$9.4 \pm 0.6$	$17.2 \pm 0.3$	$0.4 \pm 0.1$	$28.3 \pm 0.1$	$55.2 \pm 0.1$	$96.2 \pm 6.3$	$59.1 \pm 6.4$
5	10	17.7	573	$8.2 \pm 0.8$	$14.6\pm0.8$	$0.3 \pm 0.0$	$24.3 \pm 1.5$	$47.4 \pm 3.1$	$92.3 \pm 1.8$	$55.1 \pm 1.3$
9	12	21.3	573	$11.3 \pm 0.2$	$15.1 \pm 0.2$	$0.2 \pm 0.1$	$27.7 \pm 0.1$	$54.4 \pm 0.3$	$95.7 \pm 7.5$	$58.7 \pm 7.2$
7 <sup>c</sup>			r.t.	n.d.	$0.2 \pm 0.0$	n.d.	$1.9\pm0.1$	$2.1 \pm 0.1$	$107.8 \pm 1.8$	$0 \pm 0.0$
7 6 5 4	8 10 	14.2 17.7 -1	573 573 r.t.	$9.4 \pm 0.6$ $8.2 \pm 0.8$ $11.3 \pm 0.2$ n.d.	$17.2 \pm 0.3$ $14.6 \pm 0.8$ $15.1 \pm 0.2$ $0.2 \pm 0.0$	$0.4 \pm 0.1$ $0.3 \pm 0.0$ $0.2 \pm 0.1$ n.d.	$28.3 \pm 0$ $24.3 \pm 1$ $27.7 \pm 0$ $1.9 \pm 0.5$	1 1 2 2	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	.1 $55.2 \pm 0.1$ $96.2 \pm 6.3$ .5 $47.4 \pm 3.1$ $92.3 \pm 1.8$ .1 $54.4 \pm 0.3$ $95.7 \pm 7.5$ 1 $2.1 \pm 0.1$ $107.8 \pm 1.8$

methanol = 2 mL : 1 mL. Monocyclic aromatic hydrocarbon = the total yield of anisole, benzyl methyl ether, toluene, benzyl alcohol and phenol.

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An aqueous methanol solution with 0.2 molar fraction of methanol was effective for the solvolysis of benzyl phenyl ether at 573 K, as shown in Fig. 1. We tested the temperature effect on the solvolysis yield in an aqueous methanol solution with 0.2 molar fraction of methanol. The reaction time shown in Table 1 is 15 min to study the initial reaction rate. The conversion increased; however, the recovery decreased with an increase in temperature, which would be caused by the decomposition of benzyl phenyl ether and the following polymerization. The solvolysis yield (benzyl methyl ether + benzyl alcohol) was 4% at 523 K and increased to 17% at 573 K; however, it decreased to 13% at 623 K, and then we focused on the study of benzyl phenyl ether solvolysis in aqueous methanol solution at a methanol molar fraction of 0.2, at 573 K. The reaction profile in aqueous methanol solution (Fig. 2 open key and dotted line) shows that the conversion increased from 59.0  $\pm$  0.0 to 87.7  $\pm$  3.9% with an increase in reaction time and became constant at 90%. Various aromatic products formed were benzyl methyl ether, benzyl alcohol, phenol, and toluene but anisole was not detected. The vields of benzyl methyl ether, benzyl alcohol, phenol, and toluene also increased with an increase in reaction time and were 8.4 ± 0.9, 14.8 ± 1.1, 27.0 ± 2.2, and 2.9 ± 0.2% at 60 min, respectively. The amount of phenol was almost the same as the sum of benzyl methyl ether + benzyl alcohol + toluene during the reaction (Fig. 2(c)), indicating that methanolysis (path (b) in Scheme 1) and hydrolysis (a), which are catalyzed by protons derived from high-temperature water, and hydrogenolysis (c) proceeded.

#### Effect of high-pressure carbon dioxide on solvolysis

The addition of carbon dioxide is highly beneficial for acid catalyzed reactions in high-temperature liquid water.17-25 Benzyl phenyl ether was treated in aqueous methanol solution under 17.7 MPa of carbon dioxide at 573 K (Fig. 2, filled keys and solid line). The conversion of benzyl phenyl ether increased with an increase in reaction time and the final conversion at 180 min in the presence of 17.7 MPa of carbon dioxide was 93.4  $\pm$  0.5%, which was almost the same as 87.7  $\pm$ 3.9% in the absence of carbon dioxide (Fig. 2(a)). Benzyl methyl ether, benzyl alcohol, phenol and toluene were formed as aromatic hydrocarbons, but anisole was not observed, which is the same result obtained without the addition of carbon dioxide. The amount of phenol was almost the same as the sum of benzyl methyl ether + benzyl alcohol + toluene (Fig. 2(c)), indicating that methanolysis, hydrolysis and hydrogenolysis proceeded in aqueous methanol solution under 17.7 MPa of carbon dioxide. Also, it is noteworthy that the aromatic compound yield at 60 min under 17.7 MPa of carbon dioxide  $(70.7 \pm 0.2\%)$  was higher than that in the absence of carbon dioxide  $(53.1 \pm 4.4\%)$ , indicating that the side reactions such as self- or cross-condensation were suppressed in the presence of high-pressure carbon dioxide. The addition of carbon dioxide was effective for the solvolysis of benzyl phenyl ether to aromatic compounds. Under high-pressure carbon dioxide, carbonic acid is formed, and the number of protons increased

Table 1 Decomposition of benzyl phenyl ether by an acid catalyst $^{arepsilon}$ 



**Fig. 2** Effect of high-pressure carbon dioxide on the solvolysis reaction of benzyl phenyl ether. 0 MPa (open symbol), 10 MPa (closed symbol), benzyl phenyl ether conversion (a), aromatic product yield (b and c), conversion ( $\bullet$ ,  $\bigcirc$ ), benzyl methyl ether ( $\bullet$ ,  $\bigcirc$ ), benzyl alcohol ( $\blacksquare$ ,  $\square$ ), phenol ( $\blacktriangle$ ,  $\bigcirc$ ), toluene ( $\blacktriangledown$ ,  $\bigtriangledown$ ), benzyl methyl ether + benzyl alcohol + toluene ( $\blacklozenge$ ,  $\bigcirc$ ), temperature 573 K, water : methanol = 2.0 : 1.0 (mL : mL), 0.11 : 0.02 (mol : mol).

by the dissociation of carbonic acid. Benzyl methyl ether was formed in high-temperature aqueous methanol and the yield was enhanced by the addition of high-pressure carbon dioxide, indicating that the methanolysis proceeded by protons. The plausible mechanism to produce benzyl methyl ether from benzyl phenyl ether in high-temperature aqueous methanol solution and/or in the presence of high-pressure carbon dioxide is shown in Scheme 2. Protons formed by the dissociation of water and by dissociation of carbonic acid would attack the oxygen atom in benzyl phenyl ether to produce a protonated intermediate followed by the formation of phenol and the benzyl cation. A methanol molecule could react with the cation to produce benzyl methyl ether and protons through a protonated intermediate.

The effect of carbon dioxide pressure on aromatic yields was also studied. Table 1 shows that the yields of aromatic compounds increased with an increase in carbon dioxide pressure (entries 4–6). It is reported that carbon dioxide dissolved in water produces carbonic acid and the amount of dissolved carbon dioxide and protons from carbonic acid increased with an increase in carbon dioxide pressure.<sup>21,22</sup> The number of protons increased with an increase in carbon dioxide pressure and the alcoholysis reaction of benzyl phenyl ether to benzyl methyl ether would be enhanced by the increased number of protons with an increase in carbon dioxide pressure.

#### Reaction pathway in aqueous methanol solution

The benzyl phenyl ether solvolysis reaction proceeded in aqueous methanol solution achieving more than 90% of conversion; however, the highest aromatic compound yield (sum of benzyl methyl ether, benzyl alcohol, phenol, and toluene) was  $70.7 \pm 0.2\%$  at 573 K. The stability of products during the solvolysis reaction was studied to understand the reaction pathways. Table 2 shows the results of aromatic compounds by the treatment with 0.2 molar fraction of methanol in aqueous solution under 17.7 MPa carbon dioxide for 60 min at 573 K.

The reactions were tested for 60 min to study the stability of substrate in aqueous methanol solution in the absence and presence of carbon dioxide. The reaction time in Table 2 is 60 min and is different from that in Table 1 (15 min). The reaction was tested two times and the average values are shown.

When benzyl methyl ether was treated in an aqueous methanol solution,  $12.4 \pm 3.5\%$  of benzyl alcohol was obtained and the recovered monomer yield (benzyl methyl ether, benzyl alcohol, phenol, and toluene) was as high as 88.7 ± 2.2% (Table 2, entry 1). The hydrolysis was found to be promoted and  $25.2 \pm 0.6\%$  of benzyl alcohol was obtained with a recovered monomer yield of 86.9  $\pm$  0.6% when 17.7 MPa of carbon dioxide was added in aqueous methanol solution (Table 2, entry 2). When benzyl alcohol was treated in aqueous methanol solution, dehydration between benzyl alcohol and methanol proceeded in aqueous methanol solution and  $9.5 \pm 0.6\%$ of benzyl methyl ether was obtained (Table 2, entry 3). The dehydration yield was improved to  $43.0 \pm 0.4\%$  by the addition of carbon dioxide (Table 2, entry 4). More than 95% of phenol was recovered in aqueous methanol solution both with and without 17.7 MPa of carbon dioxide (Table 2, entries 5 and 6), indicating that phenol is stable in high-temperature aqueous methanol solution.

The stability of the product mixture was also studied. The value of the recovered yield of mixtures of benzyl methyl ether + phenol and benzyl alcohol + phenol was high and benzyl phenyl ether was not formed (Table 2, entries 7–10). Scheme 3 shows the reaction pathways for hydrogenolysis, hydrolysis and methanolysis of benzyl phenyl ether in aqueous methanol solution under high-pressure carbon dioxide. Accordingly, benzyl alcohol and phenol are produced from benzyl phenyl ether in the presence of water due to hydrolysis. Benzyl methyl ether is produced by the reaction of benzyl phenyl ether and methanol (methanolysis) and the reaction pathway is promoted by the addition of carbon dioxide. Toluene and phenol are produced by hydrogenolysis, while the introduction of carbon dioxide promotes the methanolysis reaction and the

		Conditions		Product yields (%	()				
Entry no.	Substrate	Water : methanol (mL : mL)	Carbon dioxide partial pressure (MPa) <sup>b</sup>	Benzyl methyl ether	Toluene	Benzyl alcohol	Phenol	Benzyl phenyl ether	Monocyclic aromatic hydrocarbon
1	Benzyl methyl ether	2.0:1.0	0.0	$75.7 \pm 0.8$	$0.6\pm0.5$	$12.4 \pm 3.5$	$0.1 \pm 0.1$	n.d.	$88.7 \pm 2.2$
2	Benzyl methyl ether	2.0:1.0	17.7	$61.1 \pm 0.2$	$0.2 \pm 0.0$	$25.2 \pm 0.6$	$0.3 \pm 0.3$	n.d.	$86.9 \pm 0.6$
3	Benzyl alcohol	2.0:1.0	0.0	$9.5 \pm 0.6$	$0.2 \pm 0.0$	$89.4 \pm 0.5$	n.d.	n.d.	$99.1 \pm 1.0$
4	Benzyl alcohol	2.0:1.0	17.7	$43.0\pm0.4$	$0.1 \pm 0.0$	$51.8\pm2.4$	$0.3 \pm 0.3$	n.d.	$95.2 \pm 2.3$
5	Phenol	2.0:1.0	0.0	n.d.	n.d.	n.d.	$96.3 \pm 1.4$	n.d.	$96.3 \pm 1.4$
9	Phenol	2.0:1.0	17.7	n.d.	n.d.	n.d.	$98.2 \pm 1.1$	n.d.	$98.2 \pm 1.1$
7	Benzyl methyl ether + phenol	2.0:1.0	0.0	$73.9 \pm 1.6$	$0.1 \pm 0.0$	$12.2 \pm 3.5$	$95.5 \pm 1.8$	n.d.	$181.7 \pm 3.7$
8	Benzyl methyl ether + phenol	2.0:1.0	17.7	$59.7 \pm 0.3$	$0.1 \pm 0.0$	$26.3 \pm 0.1$	$91.3 \pm 1.0$	n.d.	$177.5 \pm 1.4$
6	Benzyl alcohol + phenol	2.0:1.0	0.0	$9.8 \pm 3.3$	$0.3 \pm 0.1$	$86.7 \pm 3.6$	$95.8\pm0.0$	n.d.	$192.7\pm0.2$
10	Benzyl alcohol + phenol	2.0:1.0	17.7	$39.3 \pm 2.1$	$0.1 \pm 0.0$	$56.8\pm2.8$	$94.5 \pm 2.7$	n.d.	$190.6 \pm 3.4$



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Scheme 3 Plausible reaction pathways for hydrogenolysis, methanolysis and hydrolysis of benzyl phenyl ether.

hydrolysis reaction, but it does not promote hydrogenolysis. Furthermore, benzyl alcohol reacts with methanol in the presence of carbonic acid to form benzyl methyl ether.

### Conclusions

Solvolysis of benzyl phenyl ether as a model compound having the lignin  $\alpha$ -O-4 bond was studied in water, methanol and aqueous methanol solution at 573 K, under high-pressure carbon dioxide in a batch reaction system. The following conclusions were obtained.

(1) The hydrolysis of benzyl phenyl ether proceeded in water at 573 K; however, the yield of benzyl alcohol and phenol was low.

(2) The methanolysis of benzyl phenyl ether did not proceed but hydrogenolysis to toluene and phenol occurred in methanol.

(3) Benzyl methyl ether, benzyl alcohol and phenol were obtained by the treatment of benzyl phenyl ether in an aqueous methanol solution. The highest yield was obtained in an aqueous methanol solution with 0.2 molar fraction of methanol at 573 K.

(4) The total yield of monocyclic aromatic hydrocarbons (benzyl methyl ether, benzyl alcohol and phenol) in aqueous methanol solution was enhanced by the addition of carbon dioxide under high pressure.

## Conflicts of interest

There are no conflicts to declare.

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Control solvolysis experiments for various substrates<sup>6</sup>

Table 2

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