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### Oil formation from glucose with formic acid and cobalt catalyst in hot-compressed water

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Abstract—Liquefaction of glucose into oil was examined in hot-compressed water at 300 °C and 30 or 60 min in a tumbling batch reactor. The effects of alkali (KHCO<sub>3</sub>), a hydrogenating agent (HCO<sub>2</sub>H), and a cobalt catalyst (Co<sub>3</sub>O<sub>4</sub>) were studied. Also the combinations of these additives were investigated. HCO<sub>2</sub>H and KHCO<sub>3</sub> showed a positive effect on oil formation. Co<sub>3</sub>O<sub>4</sub> was found to be an advantageous additive as well, increasing the oil formation from glucose, but the stability of this catalyst under reaction conditions was quite low.

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### 1. Introduction

Biomass refinery processes must be developed in the next few decades because only biomass is a sustainable carbon resource, and its use is required to replace petroleum and other fossil fuels. These changes are necessary to develop a sustainable society and to reduce global warming caused by CO<sub>2</sub> emissions. Possible processes for getting energy from biomass are both direct and indirect gasification. The latter is a two-step process of liquefaction of biomass following gasification of the liquefaction products, as, for example, ethanol or bio-oil. Advantages of indirect gasification are the avoiding of the transport of biomass along large distances to large gasification facilities as well as fewer problems because of using 'clean fuels' for gasification. Salts, especially, can cause several problems during gasification, and bio-oil contains almost no salt. Direct biomass gasification has been widely studied, and several processes for the gasification of biomass of different water content have been reported.<sup>1</sup>

Although biomass liquefaction has several advantages such as less transport effort, and thus, in effect, the preservation of biomass, the state-of-the-art of liquefaction processes for biomass, in particular for biomass with high water content, are still insufficiently well developed. Living plants contain more than 80 wt % of water. Biomass feedstocks with such high water content are usually called 'wet biomass' and must be dried for further processing. Dry biomass that includes only few percent of water can be converted into a bio-oil by flash pyrolysis; however, flash pyrolysis is not useful for wet biomass with water content of several tens of percent because the vaporization of water requires much energy. The most popular process of wet biomass liquefaction (biomass conversion into liquid fuel) is ethanol production by fermentation, which has a separation step in which water is removed from the products (i.e., an ethanol-water mixture). This separation demands much energy and leads to a loss of total energy efficiency, much like that encountered in the drying of biomass.

An alternative process for wet biomass liquefaction is to convert biomass into oil in the presence of water. To

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avoid evaporation an increased pressure is necessary. The oil should have a low oxygen content and should be liquid under ambient conditions, because in this case, the hydrophobic oil spontaneously separates from water. The best-known method to concentrate wet biomass into oil is the so-called 'hydrothermal upgrading' or HTU process originally developed at Shell Research B.V. (Amsterdam). At 300–350 °C and 15–20 MPa, the biomass reacts into gaseous products and oil within  $5-15 \text{ min.}^2$ 

To get oil from biomass, elimination of oxygen atoms from biomass is required because biomass such as cellulose  $(C_6H_{10}O_5)_n$  has a high oxygen content. One way to remove oxygen from an organic compound is dehydration (-H<sub>2</sub>O), with the resultant formation of double bonds. However, the dehydration process also causes a depletion of hydrogen in the organic compound (H/ C < 1) by formation of unsaturated compounds. The double bonds may polymerize leading to high-molecular-weight compounds and coke formation. The other ways of the oxygen elimination are decarbonylation (-CO) and decarboxylation (-CO<sub>2</sub>). Under decarboxylation two oxygen atoms with one carbon are removed from the feedstock, and under decarbonylation only one oxygen atom per carbon atom is removed. Previously, other researchers had reported that (1) the oil liquefaction of biomass was examined at 200–350 °C,<sup>2–11</sup> (2) the oil liquefaction is sensitive for the concentration of biomass,<sup>9,11</sup> and (3) it is enhanced by alkali catalvsts.<sup>2-8,10,11</sup> The main reason for the enhancement of the oil liquefaction by alkali was assumed to be increasing decarboxylation. However, the crude oil from biomass is mainly aromatic  $(C/H \approx 1)$ ,<sup>1,7,8</sup> and thus it has high viscosity.

Recently, Huber et al.<sup>12</sup> reported that a biomassderived compound was converted into alkane-like oil through a new oxygen atom removal reaction, a dehydration/hydrogenation process (D/H process) in hotcompressed water around 250 °C. Here, the dehydration of a sugar such as glucose must first be promoted in the direction of furan compound formation. The furan compounds then couple with small carbonyl compounds to produce, via retro-aldol condensation of the sugar, a furan with a side chain. Thus, to form the side chain, the retro-aldol condensation must also occur. Finally, the double bonds of the furan with the side chain react with hydrogen to form single bonds. By this way the aromatic furan ring is opened to form a straight-chain alkane. This new concept is quite reasonable because both reactions, the dehydration  $(-H_2O)$  and the hydrogenation  $(+H_2)$ , are employed to get alkane-like (H/C > 2) oil from carbohydrate (C:H:O=1:2:1). Thus, to get good quality oil, hydrogenation is needed. Formic acid is known to be an active hydrogenation agent in hot-compressed water,<sup>13</sup> and it is applied to improve the oil formation in this study.

However, we considered that the effective progress of the D/H process has an inconsistency. That is, to progress, the D/H process, both the dehydration and the retro-aldol condensation of sugar must occur, while the control of these two reactions is difficult because the best conditions for one of these reactions are detrimental to the other. Sasaki et al.<sup>14</sup> reported that the retro-aldol condensation of glucose is favored at higher temperature and lower pressure, and the dehydration of glucose is preferred at lower temperature and higher pressure. The other reports show that the retro-aldol condensation is increased under basic conditions,<sup>15,16</sup> and that the dehydration is promoted under acidic conditions.<sup>16–19</sup>

We herein suggest a new concept for oil liquefaction of cellulosic biomass  $(C_6H_{10}O_5)_n$  to solve these inconsistencies: the cellulosic material decomposes into a monomer unit of biomass such as glucose and then further converts into small fragments without loss of water via the retro-aldol condensation.<sup>20-22</sup> Finally the small pieces having C-O or C=O bonds such as alcohols, acids, aldehydes, and ketones must be connected by losing an oxygen atom to form hydrocarbons. So far, it has been revealed that (1) the hydrolysis of cellulosic biomass to a monomer unit such as glucose rapidly occurs without catalyst in hot-compressed water, and (2) glucose further decomposes into a small aldehyde and acids under alkali conditions. What must be clarified is how to couple these small C-O or C=O compounds to alkanelike hydrocarbons  $(-CH_{2}-)$ . One of the possibilities is to use a Fischer-Tropsch (FT) type reaction, because the FT reaction enables  $C \equiv O$ . C = O. and C = O compounds to combine into the alkane-like hydrocarbons. To enhance the FT type reaction, a catalyst is needed. Effective catalysts for the FT type reaction are well known to be Fe, Ni, Co, and Ru catalysts. An Fe catalyst is inexpensive and has a high activity for the water-gas shift reaction. The active species on Fe catalyst for the FT type reaction,  $FeC_x$ , is well known to be deactivated by steam. A Ni catalyst has been used to gasify biomass in hot-compressed water around 200-400 °C, and it was found to be useful to produce  $CH_4$  or  $H_2$ .<sup>23–25</sup> Thus, the candidates for the FT type reaction for making oil consisting of long-chain alkanes in hot-compressed water at 200-400 °C are Co- and Ru-based catalysts. A Ru catalyst was employed to gasify biomass in hot-compressed water and was shown to be effective above 350 °C.<sup>26-29</sup> Some researchers have studied the effect of water on the CO reaction in the presence of Co catalyst (the FT type reaction<sup>30</sup> and CO oxidation<sup>31</sup>). From these studies it was revealed that the water reduces the catalytic activity (methanation<sup>30</sup> and CO oxidation<sup>31</sup>), while water improves C-C propagation on the FT type reaction.<sup>30</sup> Ding et al.<sup>32</sup> reported that a metal oxide of Co might be used as a catalyst in hot-compressed water media because of its high stability in this medium. Thus, Co

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is expected to support the formation of C–C bonds from C=O and C–O compounds in hot-compressed water. The FT type reaction also requires hydrogen. As stated above, formic acid is an active hydrogenating compound in hot-compressed water, <sup>13</sup> and it is expected to improve oil formation from biomass.

In this study, cellulosic biomass liquefaction to oil was examined. Cellulosic material was found to rapidly decompose into its monomer and oligomers in hot-compressed water.<sup>33</sup> Thus, to gather basic knowledge, glucose was employed as a model compound to study the effect of reaction time, formic acid (HCO<sub>2</sub>H), a co-catalyst (Co<sub>3</sub>O<sub>4</sub>), and alkali (KHCO<sub>3</sub>) on oil formation.

### 2. Experimental

All reagents and catalysts were obtained from E. Merck: glucose monohydrate (starting material); formic acid (used without further purification); potassium hydrogencarbonate (used as alkali); and  $Co_3O_4$  (the metal oxide catalyst).

The experiments were conducted in an Inconel 625lined, tumbling batch autoclave.<sup>34</sup> Glucose (20 g) and a catalyst [2 g of KHCO<sub>3</sub> (2 g) and/or a solid catalyst (1 g)] were carefully mixed, and the feedstock was adjusted to a total of 200 g by adding pure water. For HCO<sub>2</sub>H addition, HCO<sub>2</sub>H (2 g) was poured into the glucose solution. The internal volume of the autoclave was 1 L. The maximum pressure and temperature of the reactor were 50 MPa at 500 °C. The reactor was heated by a heating cartridge, and the control of temperature was within  $\pm 5$  °C. A tube in which three thermocouples were fastened for temperature measurement was located inside the reactor. Loading of the solution in the reactor was achieved by another tube. The heating rates and the final temperature were adjusted by a temperature controller connected with the thermocouples, and the pressure was measured by an analog manometer. The signals were continuously recorded by a six-channel recorder (Logoprint 100, Jumo Messund Regeltechnik M. K. Juchheim GmbH & Co.). A disadvantage of this large reactor is the long time needed for heating up and cooling down. Advantages are the relative large product samples, enabling a large number of analytical samples to be taken and the possibility of mixing. The latter two properties are the reasons for why this reactor was chosen to explore these new research fields.

The glucose or glucose-catalyst solution or suspension was loaded in the evacuated autoclave through a valve. After the mixture was loaded, the autoclave was purged by N<sub>2</sub> to remove air in the reactor. Then the temperature controller was adjusted to the desired heating rate (3 °C/min) and to the final temperature (300 °C). After the reactor had reached the final temperature, the experiment was continued for 60 min at the reaction temperature. Table 1 shows the experimental conditions. The symbol Y in Table 1 indicates the additive (HCO<sub>2</sub>H,  $Co_3O_4$ , and KHCO<sub>3</sub>) that was added in the experiment. The compositions 1, 2, and 5-7 are the experiments performed without the hydrogenating agent (HCO<sub>2</sub>H). These experiments were conducted to study the effect of KHCO<sub>3</sub> and Co<sub>3</sub>O<sub>4</sub> on the oil formation. The compositions 3, 4, and 8–10 are the experiments performed in the presence of HCO<sub>2</sub>H to understand the effect of HCO<sub>2</sub>H on the oil formation. The compositions 1 and 3 are experiments performed at 30 min reaction time at the final temperature. Table 1 also lists the values of pressure inside the reactor at the reaction temperature (300 °C) and the final reaction time (30 or 60 min).

After cooling, the amount of gases formed was measured by a gas meter. The water solution was forced out of the reactor by compressed air. Some researchers have used acetone for recovery of the oil because the oil from biomass is sometimes defined as acetone-soluble.<sup>7,9</sup> Therefore, we also used acetone as the solvent to recover the produced oil in this study. Acetone was loaded into the reactor, and the reactor was tumbled for a few minutes to dissolve the formed oil. The acetone–oil solution was also forced out of the reactor by compressed air. The aqueous solution was filtered, and samples of the gaseous, liquid, and solid phases were analyzed. The experimental error, here mainly determined by reproducibility, was roughly 1% of the given values.

Gas analysis was conducted by two gas chromatographs. To measure the H<sub>2</sub> content, an HP 5889A gas chromatograph was used. The carrier gas was nitrogen, the column was a Porapak Q column (80/100 Porapak Q by Supelco, 1.83 m in length), and the detector was a thermal conductivity detector. Analysis of all other gases was carried out by an HP 6890 instrument with column switching: the first column was an 80/100 Hayesep Q (2 m long, Resteck), and the second column was a

Table 1. Experimental conditions

Composition	t (min)	HCO <sub>2</sub> H	KHCO <sub>3</sub>	Co <sub>3</sub> O <sub>4</sub>	$p (MPa)^{b}$
1	30	_	_	_	8.47
2	60	_		—	8.53
3	30	Y <sup>a</sup>	_	_	8.74
4	60	Y	_	_	8.89
5	60	—	Y	—	8.48
6	60	—		Y	8.61
7	60	_	Y	Y	8.6
8	60	Y	Y	_	8.74
9	60	Y	_	Y	8.8
10	60	Y	Y	Y	8.89

<sup>a</sup>Y = additive present.

 $^{b}p$  = pressure at the reaction temperature and the final reaction time.

60/80 Molesieve 5 Å (4 m long, Resteck). The two columns, as well as a thermal conductivity and a flame ionization detector, were connected in series. The second column was bypassed by a six port valve for analysis of CO<sub>2</sub> and hydrocarbons. The carrier gas of the HP 6890 was helium. Determination of the residual total organic carbon (TOC) content in the liquid effluent was performed by a commercial TOC analyzing method (Hach Lange). The total amounts of phenolic compounds (which are called 'phenols' in this study) were quantified by a UV-vis spectrometer (Cadas 200 spectrophotometer, Hach Lange). Two different SPME-GC applications were used for the qualitative and quantitative determination of organic compounds.<sup>34</sup> The amounts of organic acids and furfurals were measured by LC with a UV-vis detector (L-4250, E. Merck). The columns attached to the LC were an Aminex TMHPX-87 H column (Bio-Rad) for organic acids and an RP-18 column (E. Merck) for furfurals. The weight of oil was measured after evaporating the acetone and water. The residue was analyzed by a commercial CHNOS elemental analyzer (Vario EL III, Elementar). Although the precision of the analyzer detector is 0.1% (max.) relative, we learned by experience that the accuracy of the results is only 15% (max.) relative. The reasons are the small sample weight of 2 mg, problems faced during sampling, inhomogenities of solid materials, etc.

During evaporation, polymerization usually occurs, changing the oil to a black, oily-looking solid. This polymerization should not change the CHO ratio, but a further identification in view of the identification of single compounds is not possible.

The definition of each yield is as follows:

 $H_2$  yield, mol %

$$= \frac{2 \times (\text{Produced H}_2, \text{mole})}{\text{H atom in the starting glucose, mole}} \times 100 \quad (1)$$

CO and CO<sub>2</sub> yield, mol %

$$= \frac{\text{CO or CO}_2, \text{mole}}{\text{C atom in the starting glucose, mole}} \times 100$$
 (2)

TOC yield, mol %

=

$$= \frac{\text{C in the water solution, mole}}{\text{C atom in the starting glucose, mole}} \times 100 \quad (3)$$

Oil yield, wt % = 
$$\frac{\text{oil, g}}{\text{the starting glucose, g}} \times 100$$
 (4)

Products yield in water solutions, wt %

$$= \frac{\text{Products, g}}{\text{the starting glucose, g}} \times 100$$
(5)

Loss of Co<sub>3</sub>O<sub>4</sub>, wt %

$$= \frac{\text{Co in the recovered solution, } g}{\text{Co in the starting } \text{Co}_3\text{O}_4, g} \times 100$$
(6)

The products analyzed in the aqueous solution were phenols, 5-hydroxymethyl-2-furaldehyde (HMF), fural-dehyde (FU), 2-methylfuraldehyde (MF), acetic acid, and glycolic acid.

### 3. Results and discussion

### 3.1. General observations

The experimental error, here mainly determined by reproducibility, is roughly 5% of the given values (except the oil composition). The pH values shown in Table 2 were measured after the reaction at room temperature. The gaseous products were mainly CO, CO<sub>2</sub> and H<sub>2</sub>. The quantified products in the recovered water solution were phenols. HMF, FU, methanol, ethanol, acetic acid, and glycolic acid. The yields of FU, methanol, and ethanol were always low and are therefore not reported here. In the presence of HCO<sub>2</sub>H, CO<sub>2</sub>, and H<sub>2</sub> were produced from the HCO<sub>2</sub>H. A small amount of CO may be formed; however, the decarboxylation of HCO<sub>2</sub>H is predominant in hot-compressed water.<sup>35,36</sup> The conversion of HCO<sub>2</sub>H was always >90%. The yields of  $H_2$  (Eq. 1) and  $CO_2$  (Eq. 2) from  $HCO_2H$  were both about 7% at 100% conversion of HCO<sub>2</sub>H. The differences in the yield of CO<sub>2</sub> with HCO<sub>2</sub>H compared to that without HCO<sub>2</sub>H under the same experimental conditions (compositions 1 and 3, compositions 2 and 4, compositions 5 and 8, compositions 6 and 9, compositions 7 and 10) were always 5-6% and reasonable. However, the differences of the H<sub>2</sub> yield were always <4%. Thus, consumption of H<sub>2</sub> produced from HCO<sub>2</sub>H occurred because  $H_2$  and  $CO_2$  should be formed in the same amount from  $HCO_2H$ . So this is a clear indication that HCO<sub>2</sub>H is a hydrogenating agent.

Table 2. Additional experimental results

Composition	pH <sup>a</sup>	Phenols (wt %)	HMF (wt %)
1	3.20	0.13	0.00
2	3.70	0.15	0.08
3	3.60	0.12	0.35
4	3.70	0.14	0.16
5	4.50	0.20	0.03
6	4.10	0.16	0.07
7	5.00	0.17	0.03
8	4.80	0.17	0.11
9	4.40	0.18	0.10
10	5.10	0.18	0.07

<sup>a</sup> pH at room temperature after the reaction.

### 3.2. Time profile of the reaction with and without HCO<sub>2</sub>H

To study the reaction course briefly, the time profile of the reaction was examined with and without HCO<sub>2</sub>H. Figure 1 shows the time profile of the yields of CO<sub>2</sub>, TOC, and oil without HCO<sub>2</sub>H. The yields of CO<sub>2</sub> increased with the increase in reaction time. In contrast, the oil yield decreased with time. Figure 2 displays the time profile about the yields of acetic acid and glycolic acid because the yields of these organic acids are remarkably high compared with the other products. The yield of acetic acid, as well as the yields of oil (Fig. 1) also decreased with an increase in time. Acetic acid is well known to be stable even in supercritical water.<sup>29</sup> Thus, the conversion of acetic acid must be increased because of the coupling reaction with a reactive species, not by acceleration of the self-decomposition into CO<sub>2</sub> and CH<sub>4</sub>. Thus, without an additive, a longtime reaction is not suitable for oil formation. The formation of phenols is not significantly influenced by the presence of formic acid or the other additives. The HMF content is increased in the presence of formic acid (Table 2). A brief reaction scheme for glucose is shown in Figure 3. Glucose decomposes into small fragments through C–C splitting and into a ring compound through dehydration.<sup>20,21</sup> A ring compound is then com-



Figure 1. Time profile of the yields of  $CO_2$  (mol%), TOC (mol%), and oil (wt%) in the absence of additive.



Figure 2. Time profile of the yield of the organic acids in the absence of additive.



Figure 3. Schematic diagram of glucose reaction in hot-compressed water.

bined with a small fragment (aldehyde and acid) through condensation to form oil.<sup>22</sup> The oil produced polymerizes easily to form an acetone-insoluble tar and charred mass.

Figure 4 shows the yield of CO<sub>2</sub>, H<sub>2</sub>, TOC, and oil in the presence of HCO<sub>2</sub>H. As mentioned above, by adding HCO<sub>2</sub>H, the yield of H<sub>2</sub> increased (see Fig. 7 compared with Fig. 11); however, the increase of H<sub>2</sub> does not agree with the amount of H<sub>2</sub> formed by the conversion of HCO<sub>2</sub>H. This means that hydrogenation might progress in the presence of HCO<sub>2</sub>H. The oil yield was slightly higher than that without HCO<sub>2</sub>H, and the oil yield was not reduced as a function of time by adding HCO<sub>2</sub>H. Figure 5 shows the yields of acetic acid and glycolic acid. The yield of the acids (acetic acid and



Figure 4. Time profile of the yields of  $CO_2$  (mol%), TOC (mol%), and oil (wt%) in the presence of HCO<sub>2</sub>H.



Figure 5. Time profile of the yield of the organic acids in the presence of HCO<sub>2</sub>H.



Figure 6. Effect of  $HCO_2H$  on glucose reaction in hot-compressed water.

glycolic acid) decreased with time in the presence of HCO<sub>2</sub>H. By the analogy of the above discussion, the decrease of the acid yields shows that the reactions between the acids and the oil produced (or the ring compounds), such as polymerization, are still progressing in the presence of HCO<sub>2</sub>H. The rate of oil formation possibly compensates for that of oil polymerization, and thus the yield of oil was constant regardless of the reaction time. The glucose reaction in the presence of HCO<sub>2</sub>H might be considered as shown in Figure 6. Because of the scavenging of active species with hydrogen and the inhibition of polymerization, adding HCO<sub>2</sub>H was slightly effective in making oil from glucose in hot-compressed water. However, the yield of oil was still not high enough, because the oil consumption to form tar or char would still occur.

# 3.3. Effect of $KHCO_3$ and $Co_3O_4$ on the reaction in the absence of $HCO_2H$

We examined the effect of KHCO<sub>3</sub> and Co<sub>3</sub>O<sub>4</sub> on the glucose reaction without HCO<sub>2</sub>H. Figures 7–10 show the yields of gaseous products, of TOC, of some liquid products in the recovered water solution, and of oil, respectively. As shown in Figure 7, the CO<sub>2</sub> yield was enhanced by adding KHCO<sub>3</sub> (composition 5). In the presence of Co<sub>3</sub>O<sub>4</sub>, both CO<sub>2</sub> and H<sub>2</sub> yields were also increased (composition 6, Fig. 7). By adding both, KHCO<sub>3</sub> and Co<sub>3</sub>O<sub>4</sub> (composition 7), a further increase



Figure 7. Yield of gaseous compounds in the absence of  $HCO_2H$ .



Figure 8. Yield of TOC in the absence of  $HCO_2H$ .



Figure 9. Yield of liquid products in the absence of  $HCO_2H$ .



Figure 10. Yield of oil in the absence of  $HCO_2H$ .

of CO<sub>2</sub> and H<sub>2</sub> yields was observed (Fig. 7). The trend of TOC yield depending on the additives (Fig. 8) was similar to that of the CO<sub>2</sub> yield (Fig. 7). From Figure 9, it can be revealed that KHCO<sub>3</sub> promoted the formation of acetic acid, and Co<sub>3</sub>O<sub>4</sub> supported forming both acetic and glycolic acid. By addition of both, KHCO<sub>3</sub> and Co<sub>3</sub>O<sub>4</sub>, the yields of acetic acid and glycolic acid were further enhanced. The effect of additives on the oil formation (Fig. 10) is similar to that on the TOC yield: each addition of KHCO<sub>3</sub> or Co<sub>3</sub>O<sub>4</sub> had a positive impact on the TOC (Fig. 8) and oil (Fig. 10) yields. Both KHCO<sub>3</sub> and Co<sub>3</sub>O<sub>4</sub> addition lead to a further increase of the yield of TOC and oil, as shown in Figures 8 and 10. In this case, the maximum yield of oil was 15.4 g/g% (composition 7).

In the presence of  $KHCO_3$ , the  $CO_2$  and the acid formation improved and the yields of TOC and oil were enhanced. It was proposed that the addition of alkali promotes the formation as well as the decomposition of the small fragment and results in inhibition of tar/ char formation and promotion of oil formation.<sup>3</sup> In the presence of Co<sub>3</sub>O<sub>4</sub>, the formation of acid and oil was increased as well as in the presence of KHCO<sub>3</sub>, and thus Co<sub>3</sub>O<sub>4</sub> was considered to be a basic catalyst in the glucose reaction. In our previous studies,<sup>37-45</sup> we have reported that the acidity and basicity of metal oxides can be roughly estimated from the electronegativity of the metal ion. For example,  $ZrO_2$  is a basic material in some organic reactions, on the other hand, MoO<sub>3</sub> is an acidic material.<sup>43–46</sup> The electronegativities of  $Zr^{4+}$ and  $Mo^{6+}$  are 12.6 and 23.4, respectively.<sup>46</sup> The cobalt ions in  $Co_3O_4$  are  $Co^{2+}$  and  $Co^{3+}$ . The electronegativi-ties of  $Co^{2+}$  and  $Co^{3+}$  are 9 and 12.6, respectively. From the viewpoint of the electronegativity,  $Co_3O_4$  is possibly a solid base material in regard to some organic reactions in hot-compressed water, as well as ZrO2. Thus the results of the present study support the relationship between the electronegativity and the reactivity (aciditybasicity of metal oxides).

# 3.4. Effect of KHCO<sub>3</sub> and $Co_3O_4$ on the reaction in the presence of HCO<sub>2</sub>H

Next, we carried out the experiments to understand the effect of a combination of  $HCO_2H$ ,  $KHCO_3$ , and  $Co_3O_4$  on the glucose reaction under the same conditions. Figures 11–14 show the yields of gaseous products, TOC, and some liquid products in the recovered water solution and in oil, respectively. Figure 11 reveals that the H<sub>2</sub> yield was reduced by adding KHCO<sub>3</sub> (composition



Figure 11. Yield of gaseous compounds in the presence of HCO<sub>2</sub>H.



Figure 12. Yield of TOC in the presence of  $HCO_2H$ .



Figure 13. Yield of liquid products in the presence of  $HCO_2H$ .



Figure 14. Yield of oil in the presence of HCO<sub>2</sub>H.

6). In the presence of  $Co_3O_4$ , both  $CO_2$  and  $H_2$  yields were slightly increased. By adding both, KHCO<sub>3</sub> and  $Co_3O_4$  (composition 8), a further increase of  $CO_2$  and  $H_2$  yields was observed, similar as in the case of the experiments without HCO<sub>2</sub>H (Fig. 7). The trend of the yield of TOC is shown to depend on the additives (Fig. 12): in the presence of HCO<sub>2</sub>H the tendency in TOC yields was similar to that without HCO<sub>2</sub>H (Fig. 8). The effect of KHCO<sub>3</sub> on TOC formation was not so high, and Co<sub>3</sub>O<sub>4</sub> increases the TOC yield; the presence of both KHCO<sub>3</sub> and Co<sub>3</sub>O<sub>4</sub> was shown to further promote TOC formation. From the data in Figure 13, we confirmed that KHCO<sub>3</sub> promoted the formation of acetic acid; Co<sub>3</sub>O<sub>4</sub> supported forming of both acetic and glycolic acid. The yields of acetic acid and glycolic acid were further enhanced by addition of both KHCO<sub>3</sub> and  $Co_3O_4$ . Everything is similar to the results without HCO<sub>2</sub>H (Fig. 9). As shown in Figure 14, the effect of additives on oil formation is similar to that on the TOC yield: KHCO<sub>3</sub> as well as Co<sub>3</sub>O<sub>4</sub> increased the TOC (Fig. 12) and oil (Fig. 14) yields. The oil yield further increased by the addition of both KHCO3 and Co<sub>3</sub>O<sub>4</sub>. The maximum yield of oil was 20.9 wt % (composition 8) under the experimental conditions (nearly 10 wt % of glucose, 300 °C, 60 min, 1 g of KHCO<sub>3</sub>, 1 g of  $Co_3O_4$ , and 2 g of  $HCO_2H$ ).

In comparison of the results with HCO<sub>2</sub>H (Figs. 11-14) to those without  $HCO_2H$  (Figs. 7–10), the yields of TOC and oil were enhanced by adding HCO<sub>2</sub>H; on the other hand, the yield of the organic acids (acetic acid and glycolic acid) were decreased. As explained in Introduction, our new concept of oil formation in hot-compressed water is as follows: glucose is decomposed into small fragments, and the fragments are combined with each other by a FT type reaction and by inhibiting polymerization to char and tar. In the absence of HCO<sub>2</sub>H, the acid and oil formation was improved by KHCO<sub>3</sub> and Co<sub>3</sub>O<sub>4</sub>. As explained just above, these alkali substances promote the reaction to small fragments and inhibit char and tar formation. Further, the FT type reaction and inhibition of polymerization typically demands hydrogen to make C-H bonds.<sup>30</sup> The further increase of oil formation in the presence of HCO<sub>2</sub>H suggests that hydrogenation of the intermediate of the FT type reaction or a precursor of char/tar formation takes place to produce oil as shown in Figure 15.

The composition of the oil corresponds to the chemical composition  $CH_{1,2}O_{0.5}$ . It was the same in every experiment with the relative high experimental error of the determination of the chemical composition. Here an improvement of the analysis procedure is necessary. Compared to the original composition of  $CH_2O$  for



#### 3.5. Dissolution of $Co_3O_4$ in water after the reactions

We measured the amount of cobalt in the recovered water solution in each experiment. Figure 16 shows the loss of Co after reaction, that is, the percentage of Co that was dissolved in the water solution. Under the alkaline conditions (compositions 7 and 10), the dissolution was slightly suppressed; however, over half of the loaded Co<sub>3</sub>O<sub>4</sub> was dissolved in the water under the experimental conditions. Ding et al.<sup>32</sup> stated that oxides of Co are thermally and hydrothermally stable, and these compounds could be tried in hot-compressed water. However, our experimental results show that Co<sub>3</sub>O<sub>4</sub> was not stable under the experimental conditions of this study. Ding et al.<sup>32</sup> also suggested that some additives (such as Bi, Cd, Ga, Ir, K, Mo, Ta, or W) should be effective for increasing of physical strength or stability of metal oxides. In the above results, Co was found to be useful for making oil from glucose in hot-compressed water, and thus a modified Co with an additive would be examined for the further studies on a Co catalyst.

### 3.6. Outlook

Further studies planned for the investigation of a catalyzed liquefaction can be divided in to three parts:

1. Catalyst screening.

In very small autoclaves different catalysts will be tested for activity and stability. In these small autoclaves heating up and cooling down is faster than in the large reactor used here, which is an advantage. As the sample



Figure 15. Effect of additives  $(Co_3O_4, HCO_2H, and KHCO_3)$  on the glucose reaction in hot-compressed water.



Figure 16. Loss of  $Co_3O_4$ .

volumes are necessarily small, the analyses must be restricted to a few parameters.

2. Fundamental understanding.

After a catalyst is selected, experiments with glucose will be performed in a tubular reactor with a fixed bed of catalyst. This reactor shows very short heating up and cooling down times and therefore gives very precise results. Additionally the volumes of the different samples are, in principle, unlimited; therefore, sampling problems can be minimized. The disadvantage of this type of reactor is that the residence time range is rather small. Therefore, the reactor must be designed for a special purpose, which means, in this case, for a special catalyst. Therefore, these studies can only be done after the catalyst screening studies.

3. Experiments with real biomass.

Experiments in a fixed bed tubular reactor are difficult to perform because of the risk of plugging. So first experiments will be carried out in the large autoclave described here. The disadvantage of this reactor is the high heating and cooling time. One the other hand, because of the large sample volume natural inhomogenities in a piece of biomass can be neglected. The sample volumes of the products are also relatively large, large enough to perform a number of analytical measurements.

### 4. Conclusions

It is found that  $HCO_2H$  and  $Co_3O_4$  show a positive effect on oil formation from glucose in hot-compressed water. The role of  $HCO_2H$  is probably that of a hydrogenating agent that inhibits further polymerization of the produced oil. The catalytic activity of  $Co_3O_4$  was sometimes similar to alkali (KHCO<sub>3</sub>), and thus  $Co_3O_4$ worked as a solid base material under these conditions. In the presence of  $HCO_2H$ , oil formation was further increased by  $Co_3O_4$ . We assume the process is that of an FT-type reaction in the presence of  $HCO_2H$  and  $Co_3O_4$ . However, the stability of  $Co_3O_4$  was low.

The research for the best conditions for producing oil from cellulosic material is still lacking, and further experimental studies will be conducted. A bimetallic catalyst including Co with a stabilization metal will be studied. In that case, the activity of the mixed catalyst is sensitive for a method of preparation, and thus we must examine the catalyst by taking the preparation into account.

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