# Supporting Information for:

# Biomass–formic acid–hydrogen conversion process: Sustainable production of formic acid from biomass using greenhouse gas†

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The supporting information file consists of 30 pages, 7 references, 8 figures and 4 Tables.

Table S1. Results of hydrolysis-oxidation hydrothermal treatment (HOHT) of biomass via various parameters obtained by HPLC with RI detector.

| Entry | Glucose (g/L) | XMG[a] (g/L) | Arabinose (g/L) | Acetic acid (g/L) | Levulinic acid (g/L) | 5-HMF (g/L) | Furfural (g/L) | Formic acid (g/L) |
|---|---|---|---|---|---|---|---|---|
| 1[b] | - | - | - | - | - | - | - | - |
| 2[c] | 0.31 ±0.01 | 0.89 ±0.03 | 0.24 ±0.01 | 2.44 ±0.20 | - | 0.04 ±0.01 | 0.37 ±0.02 | 0.56 ±0.31 |
| 3[d] | 0.21 ±0.01 | 0.17 ±0.02 | 0.26 ±0.02 | 10.61 ±0.42 | 1.03 ±0.01 | 0.56 ±0.07 | 0.07 ±0.01 | 16.32 ±0.29 |
| 4[e] | 1.15 ±0.25 | 2.41 ±0.17 | - | 5.28 ±0.39 | - | 0.61 ±0.02 | 2.85 ±0.16 | 1.73 ±0.08 |
| 5[f] | 3.41 ±0.68 | 0.66 ±0.02 | - | 11.67 ±1.26 | 0.98 ±0.06 | 2.11 ±0.03 | 0.78 ±0.01 | 34.40 ±0.98 |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 6[g] | 4.52 ±0.57 | 2.05 ±0.24 | 0.99 ±0.03 | 12.14 ±1.60 | 4.21 ±0.62 | 1.99 ±0.10 | 0.80 ±0.03 | 39.16 ±1.26 |
| 7[h] | 3.13 ±0.05 | 1.94 ±0.13 | 0.79 ±0.05 | 12.46 ±0.19 | 4.20 ±0.83 | 1.45 ±0.02 | 0.69 ±0.01 | 42.63 ±0.30 |
| 8[i] | 1.30 ±0.53 | 0.45 ±0.09 | 0.47 ±0.07 | 15.00 ±0.93 | 0.82 ±0.01 | 1.64 ±0.17 | 1.02 ±0.35 | 29.25 ±1.13 |
| 9[j] | 1.82 ±0.28 | 0.60 ±0.03 | 0.59 ±0.21 | 15.06 ±1.56 | 0.79 ±0.01 | 2.47 ±0.54 | 1.26 ±0.06 | 31.58 ±0.86 |
| 10[k] | 1.07 ±0.04 | 0.44 ±0.01 | 0.48 ±0.02 | 15.25 ±0.62 | 0.99 ±0.09 | 1.36 ±0.07 | 0.91 ±0.02 | 30.04 ±0.01 |
| 11[l] | 5.15 ±2.01 | 1.05 ±0.08 | 0.79 ±0.03 | 10.95 ±0.57 | 0.74 ±0.01 | 2.86 ±0.29 | 1.07 ±0.34 | 25.03 ±1.08 |
| 12[m] | 1.42 ±0.32 | 0.40 ±0.03 | 0.40 ±0.01 | 10.82 ±1.38 | 0.79 ±0.02 | 1.60 ±0.50 | 0.83 ±0.08 | 18.97 ±0.28 |
| 13[n] | 7.60 ±0.01 | 4.87 ±0.81 | 0.94 ±0.02 | 8.24 ±0.74 | 0.33 ±0.03 | 0.66 ±0.02 | 1.82 ±0.27 | 13.72 ±0.99 |
| 14[o] | - | - | 0.21 ±0.01 | 13.00 ±0.35 | 0.58 ±0.22 | 0.54 ±0.35 | 0.39 ±0.01 | 18.30 ±0.06 |
| 15[p] | 0.31 ±0.03 | 0.89 ±0.17 | - | 2.37 ±0.59 | 0.10 ±0.07 | 0.13 ±0.02 | 0.81 ±0.06 | 1.55 ±0.19 |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 16[q] | - | 0.44 ±0.40 | 0.29 ±0.38 | 6.43 ±0.82 | 0.28 ±0.01 | 0.22 ±0.02 | 0.15 ±0.08 | 6.45 ±0.17 |
| 17[r] | 0.52 ±0.24 | 2.12 ±0.17 | 0.56 ±0.04 | 3.50 ±0.22 | - | 0.24 ±0.06 | 2.18 ±0.28 | 1.89 ±0.38 |
| 18[s] | 2.33 ±0.71 | 1.12 ±0.24 | 0.75 ±0.02 | 9.52 ±0.57 | 0.46 ±0.33 | 0.74 ±0.04 | 1.22 ±0.24 | 14.34 ±0.98 |
| 19[t] | 2.92 ±0.06 | 1.54 ±0.21 | 0.38 ±0.09 | 5.47 ±0.38 | 0.17 ±0.02 | 0.22 ±0.01 | 0.10 ±0.01 | 15.41 ±0.26 |
| 20[u] | 2.97 ±0.39 | 2.23 ±0.10 | 0.73 ±0.07 | 8.46 ±0.08 | 0.38 ±0.03 | 1.10 ±0.10 | 1.56 ±0.82 | 14.23 ±0.37 |
| 21[v] | 0.66 ±0.01 | 2.08 ±0.46 | 1.55 ±0.15 | 2.25 ±0.67 | 0.06 ±0.01 | 0.16 ±0.08 | 0.80 ±0.23 | 0.64 ±0.01 |
| 22[w] | 1.78 ±0.29 | 0.66 ±0.04 | 0.61 ±0.03 | 8.05 ±1.02 | 0.40 ±0.03 | 0.93 ±0.58 | 1.57 ±0.37 | 11.79 ±0.54 |
| 23[x] | 0.62 ±0.07 | 2.39 ±0.39 | 0.47 ±0.03 | 3.79 ±0.07 | - | 0.60 ±0.20 | 4.24 ±0.36 | 2.43 ±0.05 |
| 24[y] | 3.90 ±0.73 | 1.63 ±0.69 | 0.92 ±0.05 | 9.28 ±0.64 | 0.37 ±0.03 | 0.84 ±0.01 | 1.91 ±0.05 | 18.22 ±0.67 |
| 25[z] | 2.91 ±0.17 | 1.15 ±0.20 | - | 4.89 ±0.59 | 2.32 ±1.02 | 0.25 ±0.08 | 0.37 ±0.03 | 18.75 ±0.39 |

[a]: Xylose + Mannose + Galactose

[b]: Reaction condition: carbon dioxide 30 bar, and 78.96 g moisture for 3 h at 170 $^{o}C$

[c]: Reaction condition: 10 g of raw red pine, and 78.96 g moisture for 3 h at 170 $^{o}C$

[d]: Reaction condition: 10 g of raw red pine, and $H_2O_2$ 11 wt% 78.96 g solution for 3 h at 170 $^{o}C$

[e]: Reaction condition: 10 g of raw red pine, carbon dioxide 10 bar, and 78.96 g moisture for 3 h at 170 $^{o}C$

[f]: Reaction condition: 10 g of raw red pine, carbon dioxide 10 bar, and $H_2O_2$ 11 wt% 78.96 g solution for 3 h at 170 $^{o}C$

[g]: Reaction condition: 10 g of raw red pine, carbon dioxide 20 bar, and $H_2O_2$ 11 wt% 78.96 g solution for 3 h at 170 $^{o}C$

[h]: Reaction condition: 10 g of raw red pine, carbon dioxide 30 bar, and $H_2O_2$ 11 wt% 78.96 g solution for 3 h at 170 $^{o}C$

[i]: Reaction condition: 10 g of raw red pine, and carbon dioxide 30 bar, $H_2O_2$ 11 wt% 78.96 g solution for 1 h at 170 $^{o}C$

[j]: Reaction condition: 10 g of raw red pine, carbon dioxide 30 bar, and $H_2O_2$ 11 wt% 78.96 g solution for 2 h at 170 $^{o}$C

[k]: Reaction condition: 10 g of raw red pine, carbon dioxide 30 bar, and $H_2O_2$ 11 wt% 78.96 g solution for 4 h at 170 $^{o}$C

[l]: Reaction condition: 10 g of raw red pine, carbon dioxide 30 bar, and $H_2O_2$ 11 wt% 78.96 g solution for 3 h at 150 $^{o}$C

[m]: Reaction condition: 10 g of raw red pine, carbon dioxide 30 bar, and $H_2O_2$ 11 wt% 78.96 g solution for 3 h at 190 $^{o}$C

[n]: Reaction condition: 10 g of raw red pine, carbon dioxide 30 bar, and $H_2O_2$ 5.6 wt% 78.96 g solution for 3 h at 170 $^{o}$C

[o]: Reaction condition: 10 g of raw red pine, carbon dioxide 30 bar, and $H_2O_2$ 16.8 wt% 78.96 g solution for 3 h at 170 $^{o}$C

[p]: Reaction condition: 10 g of raw corn stover, and 78.96 g moisture for 3 h at 170 $^{o}$C

[q]: Reaction condition: 10 g of raw corn stover, and $H_2O_2$ 11 wt% 78.96 g solution for 3 h at 170 $^{o}$C

[r]: Reaction condition: 10 g of raw corn stover, carbon dioxide 10 bar, and 78.96 g moisture for 3 h at 170 $^{o}$C

[s]: Reaction condition: 10 g of raw corn stover, carbon dioxide 30 bar, and $H_2O_2$ 11 wt% 78.96 g solution for 3 h at 170 $^{o}C$

[t]: Reaction condition: 10 g of raw corn stover, sulfuric acid 2 wt%, and $H_2O_2$ 11 wt% 78.96 g solution for 3 h at 170 $^{o}C$

[u]: Reaction condition: 10 g of ash extracted corn stover, carbon dioxide 30 bar, and $H_2O_2$ 11 wt% 78.96 g solution for 3 h at 170 $^{o}C$

[v]: Reaction condition: 10 g of raw wheat stover, and 78.96 g moisture for 3 h at 170 $^{o}C$

[w]: Reaction condition: 10 g of raw wheat stover, and $H_2O_2$ 11 wt% 78.96 g solution for 3 h at 170 $^{o}C$

[x]: Reaction condition: 10 g of raw wheat stover, carbon dioxide 30 bar, and 78.96 g moisture for 3 h at 170 $^{o}C$

[y]: Reaction condition: 10 g of raw wheat stover, carbon dioxide 30 bar, and $H_2O_2$ 11 wt% 78.96 g solution for 3 h at 170 $^{o}C$

[z]: Reaction condition: 10 g of raw wheat stover, sulfuric acid 2 wt%, and $H_2O_2$ 11 wt% 78.96 g solution for 3 h at 170 $^{o}C$

Table S2. Results of Pd content of Pd catalyst supported on hydroxylated and amine-functionalized mesoporous silica by inductively coupled plasma (ICP)-atomic emission spectroscopy.

| Sample | Pd content (wt%) |
|---|---|
| 9 wt% Pd/ $NH_2$-OH-KIE-6 catalysts | 9.65 |

The elemental composition analysis in Table S2 confirms the successful synthesis of the 9 wt% Pd/$NH_2$-OH-KIE-6 catalyst.

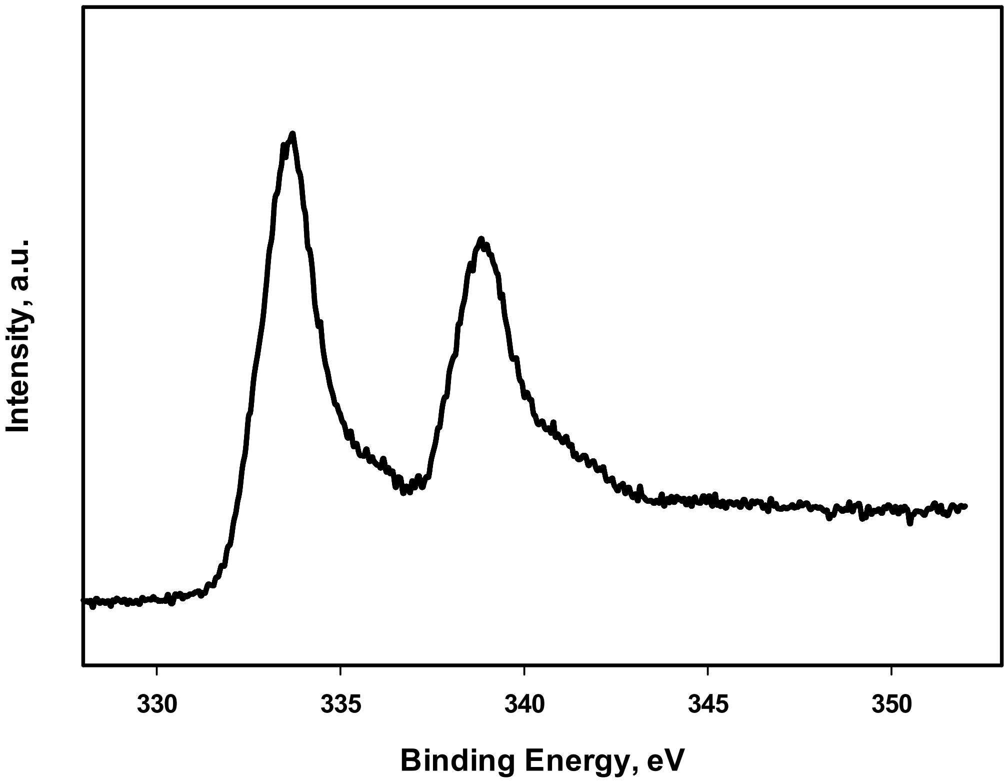



Figure S1. XPS spectra of 9 wt% Pd/$NH_2$-OH-KIE-6 catalysts.

The XPS spectra of Pd 3d exhibit binding energy peaks at ~335.1 eV ($3d_{5/2}$) and ~340.3 eV ($3d_{3/2}$), corresponding to metallic Pd(0), confirming the successful reduction of Pd species. No peaks associated with Pd(II) species are observed, indicating that the catalyst remains unoxidized. Additionally, the N 1s XPS spectrum shows a peak at ~399.8 eV, suggesting strong interactions between Pd nanoparticles and the $NH_2$-functionalized KIE-6 support. This confirms the effective immobilization of Pd on the support material.

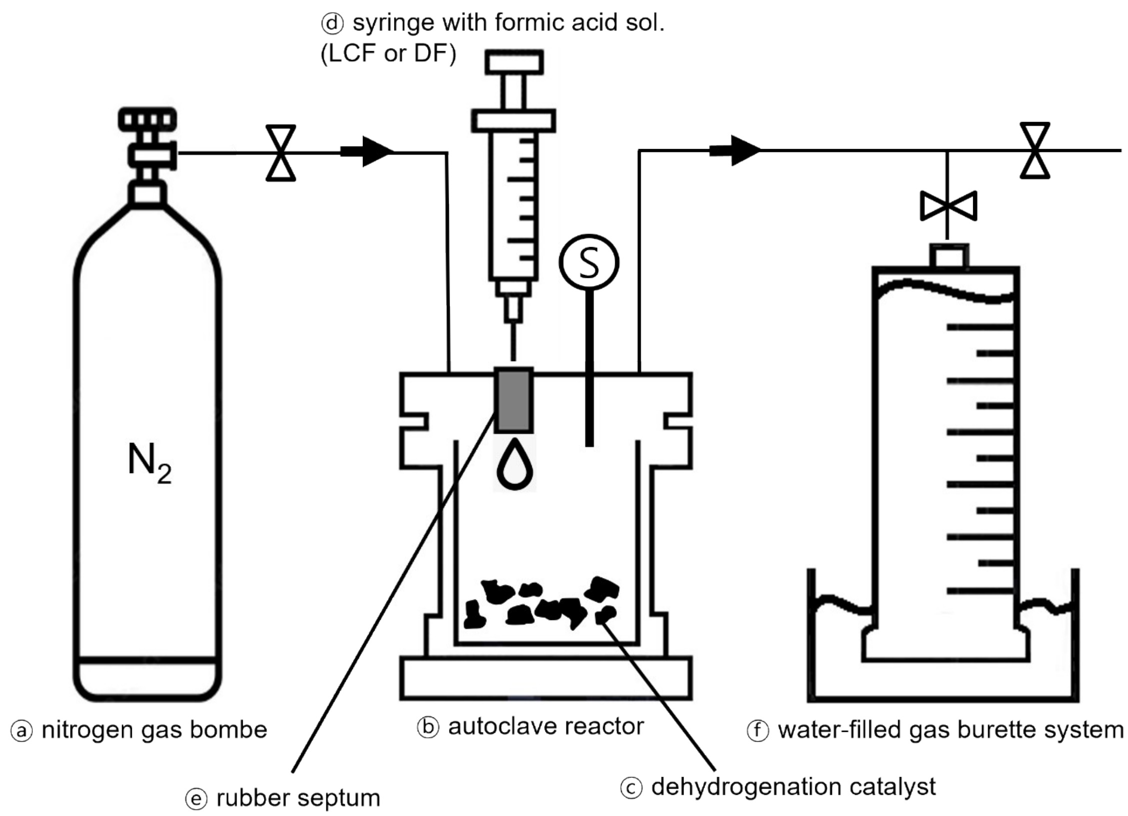



Figure S2. Formic acid dehydrogenation measurement system.

| RetTime [min] | Type | Area [25 uV*s] | Amt/Area | Amount [%mol/mol] | Grp | Name |
|---|---|---|---|---|---|---|
| 2.171 | BB | 1185.37061 | 3.14246e-3 | 3.72498 | | H2 |
| 3.181 | VB | 3101.89307 | 2.72899e-2 | 84.65041 | | N2 |
| 4.765 | | - | - | - | | CO |
| 5.271 | | - | - | - | | CH4 |
| 8.307 | BV | 98.02250 | 3.14704e-2 | 3.08481 | | CO2 |

Figure S3. GC analysis of dehydrogenation gas.

| Solid image |  |  |  |  |  |  |
|---|---|---|---|---|---|---|
| Acid (bar, $CO_2$) | - | - | 10 | 10 | 20 | 30 |
| Oxidant (wt%, $H_2O_2$) | - | 11 | - | 11 | 11 | 11 |
| Temperature (oC) | 170 | 170 | 170 | 170 | 170 | 170 |
| Reaction time (h) | 3 | 3 | 3 | 3 | 3 | 3 |

Figure S4. Recovery solid image.

## Calculation of net $CO_2$ reduction from Biomass-Formic acid-Hydrogen process using $CO_2$

### *1. Mass balance for producing 1 ton hydrogen*

In this study, carbon dioxide emissions were calculated based on using red pine, which had the highest formic acid conversion yield. Red pine requires 67,831 kg, and the chemicals required for the reaction are 476,678 kg of water, 58,915 kg of hydrogen peroxide, and 182,600 kg of carbon dioxide. After the reaction at 170 °C, 22,832 kg of formic acid was produced in the solution. It was assumed that 100 % of formic acid was recovered after distillation. Formic acid was converted into 1,000 kg of hydrogen and 21,832 kg of carbon dioxide by the dehydrogenation catalytic reaction. At this time, the reactions of other organic acids were not considered.

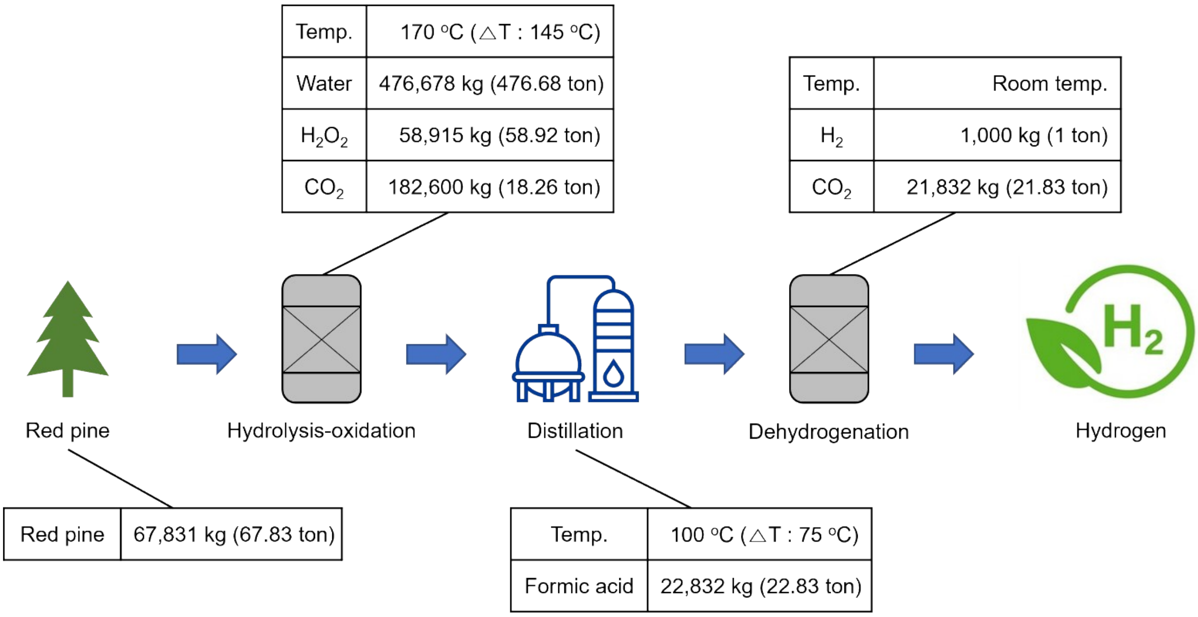



Figure S5. Mass balance of the Biomass-Formic acid-Hydrogen process using $CO_2$.

## *2. Calculation of $CO_2$ emission by hydrolysis-oxidation process*

The amount of energy required for the hydrolysis-oxidation process of biomass was calculated. The amount of energy required for each component to reach 170 $^{o}C$ was calculated.

1) Biomass = 67,831 kg x 0.359 kcal/kg$^{o}$C x 145 $^{o}$C = 3,530,941 kcal

red pine specific heat = 0.359 kcal/kg$^{o}$C [1]

2) water = 476,678 kg x 1 kcal/kg$^{o}$C x 75 $^{o}$C + 476,678 kg x 539.7 kcal/kg = 293,013,975 kcal

water specific heat = 1 kcal/kg$^{o}$C

water latent heat = 539.7 kcal/kg

3) $H_2O_2$ = 58,915 kg x 0.626 kcal/kg°C x 145 °C = 5,347,738 kcal

$H_2O_2$ specific heat = 0.626 kcal/kg°C [2]

4) $H_2O_2$ decomposition heat = 58,915 kg x -689.41 kcal/kg = -40,616,890 kcal

$H_2O_2$ decomposition heat = -689.41 kcal/kg [3]

Since hydrogen peroxide decomposes during the reaction and releases heat, the heat amount for this was taken into consideration.

5) $CO_2$ = 182,600 kg x 0.199 kcal/kg°C x 145 °C = 5,268,931 kcal

$CO_2$ specific heat = 0.199 kcal/kg°C [4]

6) Total 266,544,695 kcal

7) Use LNG for process energy

LNG Gross calorific value = 13,080 kcal/kg

LNG usage = 266,544,695 kcal / 13,080 kcal/kg = 20,378 kg

8) $CO_2$ emission calculation

Total calorific value = 20,378 kg (LNG usage) X 49.4 MJ/kg (net calorific value) = 1,006,673.2 MJ

Carbon emission = Calorific value x Carbon emission factors / 1,000,000 = 1,006,673.2 MJ x 15.281 tC/TJ / 1,000,000 = 15.38297 tC/TJ

$CO_2$ emission = Carbon emission x 44/12 = 15.38297 tC/TJ x 44 / 12 = 56.40 ton$CO_2$

***3. Calculation of $CO_2$ emission by distillation process***

Since the specific heat of 5-HMF is not known, it is not accurate to calculate the amount of heat required to heat each component. Therefore, the total liquid produced was assumed to be water and the amount of heat required for distillation was calculated conservatively. The volume of liquid was calculated as 535,593 kg, which is the sum of water and hydrogen peroxide.

1) water distillation = 535,593 kg x 1 kcal/kg$^{o}$C x 75 $^{o}$C + 535,593 kg x 539.7 kcal/kg = 329,229,186 kcal

2) Use LNG for process energy

LNG Gross calorific value = 13,080 kcal/kg

LNG usage = 329,229,186 kcal / 13,080 kcal/kg = 25,170 kg

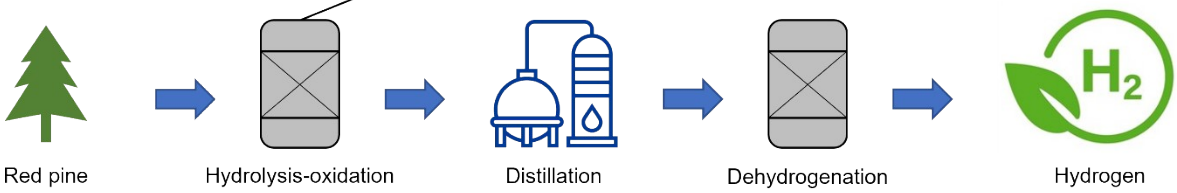
3) $CO_2$ emission calculation

Total calorific value = 25,170 kg (LNG usage) X 49.4 MJ/kg (net calorific value) = 1,243,398 MJ

Carbon emission = Calorific value x Carbon emission factors / 1,000,000 = 1,243,398 MJ x 15.281 tC/TJ / 1,000,000 = 19.00036 tC/TJ

$CO_2$ emission = Carbon emission x 44/12 = 19.00036 tC/TJ x 44 / 12 = 69.67 ton$CO_2$

| Temp. | 170 °C (△T : 145 °C) |
|---|---|
| Red pine | 3,530,941 kcal |
| Water | 293,013,975 kcal |
| $H_2O_2$ | 5,347,738 kcal |
| $H_2O_2$ decomposition | -40,616,890 kcal |
| $CO_2$ | 5,268,931 kcal |
| Hydrolysis-oxidation | 266,544,695 kcal |




| Temp. | 100 °C (△T : 75 °C) |
|---|---|
| Distillation | 329,229,185 kcal |

Figure S6. Calculation of the energy requirement for each unit process.

### ***4. Calculation of $CO_2$ reduction by red pine growing***

Growth rate of red pine = 20 $m^3$/ha [5]

Density of red pine = 510 kg/$m^3$ [6]

Weight red pine per ha = 20 $m^3$ x 150 kg/$m^3$ = 10,200 kgRed pine/ha = 10.2 tonRed pine/ha

$CO_2$ adsorption of red pine = 23 ton $CO_2$/ha [5]

$CO_2$ adsorption per 1 ton red pine = 23 ton $CO_2$ $CO_2$/ha / 10.2 tonRed pine/ha= 2.25 ton$CO_2$/tonRed pine

$CO_2$ adsorption of used red pine for Biomass-Formic acid-Hydrogen process = 67.83 ton x 2.25 ton$CO_2$/tonRed pine = 152.95 ton$CO_2$

## *5. Calculation of $CO_2$ reduction by hydrolysis-oxidation process using $CO_2$*

Solubility of $CO_2$ = 1.45g$CO_2$/L = 0.00000145 ton $CO_2$/L [7]

Dissolution amount of $CO_2$ for Biomass-Formic acid-Hydrogen process = 0.00000145 ton $CO_2$/L x 67.83 ton = 0.78 ton$CO_2$

### *6. Calculation of $CO_2$ reduction from Biomass-Formic acid-Hydrogen process using $CO_2$ process per ton of hydrogen production*

1) $CO_2$ emission

Hydrolysis-oxidation process 56.4 ton$CO_2$

Distillation process 69.67 ton$CO_2$

Dehydrogenation process 21.83 ton$CO_2$

Total 147.90 ton$CO_2$

2) $CO_2$ reduction

Red pine growing 152.95 ton$CO_2$

Hydrolysis-oxidation process 0.78 ton$CO_2$

Total 153.73 ton$CO_2$

3) Net $CO_2$ reduction

$CO_2$ emission - $CO_2$ reduction = -5.83 $tonCO_2/tonH_2$

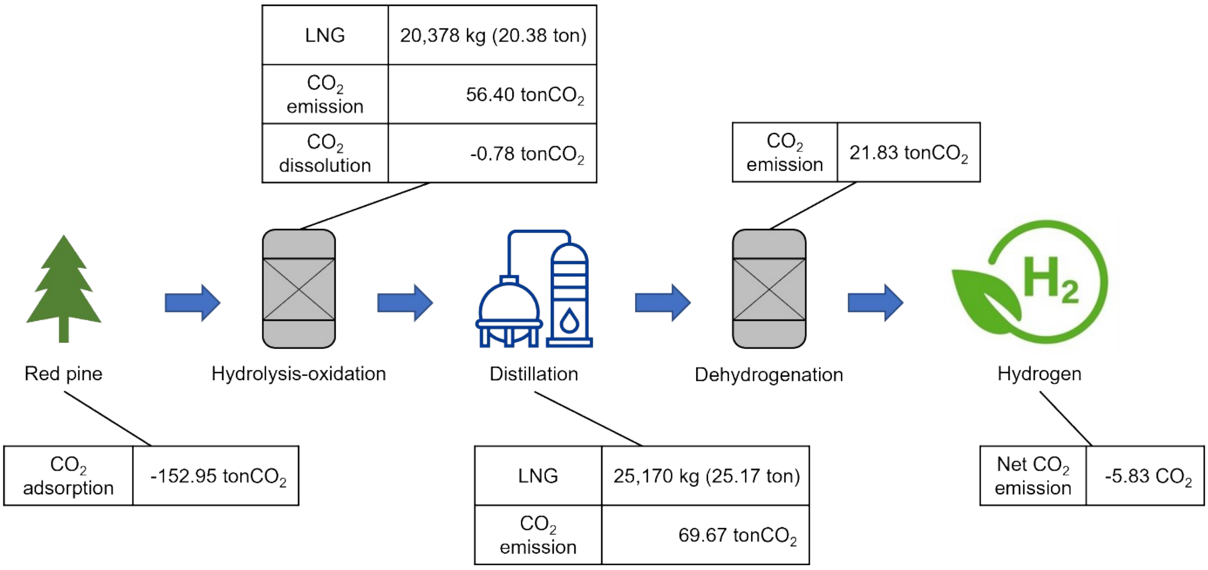



Figure S7. Calculation of carbon dioxide emission per 1 ton of hydrogen production by Biomass-Formic acid-Hydrogen process using $CO_2$.

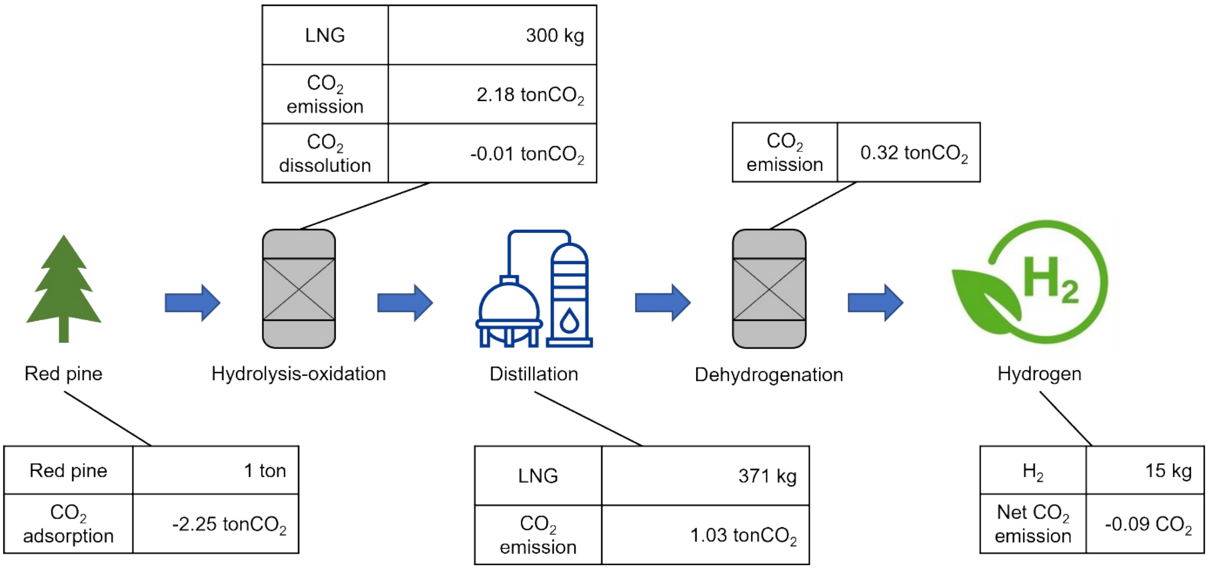



Figure S8. Calculation of carbon dioxide emission per 1 ton of red pine feedstock by Biomass-Formic acid-Hydrogen process using $CO_2$.

## Formic acid empirical correlation

We established the empirical correlation of Equation 3 using ChatGPT 4o version. We input all data related to biomass composition (Table 1), formic acid conversion conditions (carbon dioxide 30 bar, and $H_2O_2$ 11 wt% solution for 3 h at 170 $^oC$ conditions), formic acid concentration (red pine: 42.63 g/L (Table 2 entry 7), corn stover: 14.34 g/L (Table 3 entry 4), wheat stover: 18.22 g/L (Table 4 entry 4), and formic acid production yield (red pine: 36.18 % (Table 2 entry 7), corn stover: 17.43 % (Table 3 entry 4), wheat stover: 20.45 % (Table 4 entry 4). Based on this data, we requested an empirical correlation that predicts formic acid yield according to biomass composition. ChatGPT defined the formic acid yield empirical correlation using linear regression analysis. The initial empirical correlation included a formula with the lignin content variable. However, according to our study, formic acid cannot be produced from lignin, so we requested a revised empirical correlation excluding lignin. Finally, the Equation 3 presented in the manuscript was proposed. We reviewed the formic acid yield calculations for all biomass compositions by applying the respective X values to this formula.

Table S3. Comparison of empirical correlation value with experimental data for formic acid yield

| | Experimental data (FA yield, %) | Empirical correlation value (%) | Relative error (%) |
|---|---|---|---|
| Red pine | 36.18 | 36.36 | 0.50 |
| Corn stover | 17.43 | 17.58 | 0.84 |
| Wheat stover | 20.45 | 20.62 | 0.81 |

# Information of reagents

Table S4. Information of reagents

| Reagents | Brand | Purity |
|---|---|---|
| Sulfuric acid | Sigma Aldrich | 98 % |
| $CO_2$ gas | Jaeil Gas Industry | 99.9% |
| Hydrogen peroxide | SAMCHUN | 34.5 % |
| Tetraethyl orthosilicate (TEOS) | Sigma Aldrich | 98 % |
| Ethanol | EMSURE ACS, ISO, Reag. Ph Eur, | 99.9 % |
| Ammonia | JUNSEI | 28 % |
| Glycerol | DUKSAN | 99 % |
| Hydrochloric acid | Sigma Aldrich | 37 % |
| 3-aminopropyl trimethoxysilane (APTMS) | Sigma Aldrich | 97 % |
| Palladium nitrate hydrate | Sigma Aldrich | - |
| Sodium borohydride | SAMCHUN | 98 % |
| Sodium formate | Sigma Aldrich | 99 % |
| Cellulose | Sigma Aldrich | 95 % |
| Xylan from beechwood | Sigma Aldrich | 90% |

[1] https://www.engineeringtoolbox.com/specific-heat-capacity-d_391.html

[2] https://en.wikipedia.org/wiki/Hydrogen_peroxide

[3] https://en.wikipedia.org/wiki/Hydrogen_peroxide

[4] https://en.wikipedia.org/wiki/Carbon_dioxide_(data_page)

[5] J. Pojola, L. Valsta, K. Mononen: Costs of carbon sequestration in Scots pine stands in Finland. Scandinavian Forest Economics. 2004, 40, 81-90.

[6] https://www.engineeringtoolbox.com/wood-density-d_40.html

[7] https://ko.wikipedia.org/wiki/%EC%9D%B4%EC%82%B0%ED%99%94_%ED%83%84%EC%86%8C