# *Supporting information*

*Chemical looping reforming of glycerol for continuous $H_2$ production by moving-bed reactors: Simulation and experiment*

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**Supplementary text**

Definitions of Ni/G, S/G, conversion, $H_2$ yield, and selectivity in experiments and simulations were shown as follows.

$$Ni/G = \frac{Ni\ mole\ flow\ in\ feedstock}{Glycerol\ mole\ flow\ in\ feedstock} \tag{S1}$$

$$S/G = \frac{Steam\ mole\ flow\ in\ feedstock}{Glycerol\ mole\ flow\ in\ feedstock} \tag{S2}$$

$$X_{gly} = \frac{F_{gly,in} - F_{gly,out}}{F_{gly,in}} \times 100\% \tag{S3}$$

where $F_{gly,in}$ and $F_{gly,out}$ represent the glycerol mole flow of inlet and outlet, respectively.

$$H_2\ yield = \frac{mole\ flow\ rate\ of\ H_2\ produced}{3 \times mole\ flow\ rate\ of\ glycerol\ feed} \tag{S4}$$

$$S_j = \frac{F_{out} \times c_j}{3 \times F_{gly,in}} \times 100\% \tag{S5}$$

where $F_{out}$ is the total mole flow of the outlet and $c_j$ represents the concentrations of $CO_2$, CO, and $CH_4$. C selectivity is calculated on the basis of C balance.

$$S_C = \left(1 - \sum S_j\right) \times 100\% \tag{S6}$$

$$S_{H_2} = \frac{3}{7} \times \frac{mole\ flow\ rate\ of\ H_2\ produced}{mole\ flow\ rate\ of\ glycerol\ feed \times X_{gly}} \times 100\% \tag{S7}$$

## Carbon balance

The effluents were analyzed online by a gas chromatograph (GC, Agilent 7890B) with two detectors. One is a flame ionization detector with a Porapak-A column using $N_2$ as a carrier gas to analyze the organic species including $C_2H_4$, $C_2H_6$, $CH_3OH$, $CH_3CHO$, $C_2H_5OH$, $CH_3COOH$, and $C_3H_8O_3$. The other one is a thermal conductivity detector with a TDX-01 column using He as a carrier gas to detect incondensable gas species including $H_2$, CO, $CH_4$ and $CO_2$. The carbon balance for all runs was greater than 95%. Table S1shows a typical carbon balance calculation (S/G = 3, T= 650℃ and Ni/G = 0.9 for the NiW-Al). We calculated the C balance according to the following equation:

$$Carbon\ balance = \frac{C\ mole\ flow\ rates\ in\ the\ products}{3 \times glycerol\ mole\ flow\ rates \times X_{gly}} \times 100\% \tag{S8}$$

**Table S1** Carbon balance in moving-bed reactors

| CO | $CO_2$ | $CH_4$ | Other | C balance |
| --- | --- | --- | --- | --- |
| 44.0% | 51.1% | 4.5% | 0.2% | 99.8% |

In the simulation, the FR and AR were set at isothermal conditions. The solids and fuels entering the reactors were preheated to the reactor temperatures, and the pressure of the system was set to 1 atm.

Key simulation parameters are listed in Table S2. The reaction conditions corresponds to our experimental ones. The property method is based on the guidelines for choosing a property method in Aspen plus user guide.

**Table S2** Description of the Aspen Plus Model

| | |
|---|---|
| Reactor model | RGibbs (all possible products) |
| Stream class | MIXCISLD、CISOLID |
| Property method | NRTL and STEAM-TA for free water |
| Calculation method | Sequential Modular |
| Databank | PURE28, AQUEOUS, SOLIDS, INOGANIC |
| Product | $C_2H_4$, $C_2H_6$, $CH_3OH$, $CH_3CHO$, $C_2H_5OH$, $CH_3COOH$, $C_3H_8O_3$, $CH_4$, CO, $CO_2$, $H_2$, $H_2O$, C, $NiWO_4$, Ni, W |

**Table S3** Input Conditions for Aspen Simulation

| | |
|---|---|
| Glycerol flow rate | 100 kmol/hr |
| $NiWO_4$ flow rate | 10 kmol/hr-150 kmol/hr |
| Steam flow rate | 150 kmol/hr-600 kmol/hr |
| Block temperature | 600℃-700℃ |
| Input stream temperature | 650℃ |

Table S4 shows the the fuelout flow rates of 5-stage and 10-stage systems. The results indicate that our 5-stage model converges.

**Table S4** Flow rates of the last fuel reactor outlets of 5-stage and 10-stage systems (S/G = 1, Ni/G = 0.9, FR temperature = 650°C, and AR temperature = 650°C).

| | 5-stage (kmol/h) | 10-stage (kmol/h) |
|---|---|---|
| $C_3H_8O_3$ | 6.9083E-26 | 6.9083E-26 |
| $H_2$ | 317.9918 | 317.9918 |
| $H_2O$ | 145.4745 | 145.4745 |
| CO | 119.1185 | 119.1185 |
| $CO_2$ | 112.7035 | 112.7035 |
| $C_2H_4$ | 1.80499E-05 | 1.80499E-05 |
| $C_2H_6$ | 9.12719E-05 | 9.12719E-05 |
| $CH_3CHO$ | 2.26272E-07 | 2.26272E-07 |
| $CH_3OH$ | 2.01221E-06 | 2.01221E-06 |
| $CH_3COOH$ | 2.07871E-08 | 2.07871E-08 |
| $CH_4$ | 18.26666 | 18.26666 |

**Table S5** Material and energy stream table for different Ni/G ratios (FR = 650℃, AR = 650℃, and S/G = 4.5).

| $NiWO_4$ | $H_2$ | CO | $CO_2$ | $CH_4$ | C | AR1 | AR2 | AR3 | AR4 | AR5 | FR1 | FR2 | FR3 | FR4 | FR5 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| KMOL/HR | KMOL/HR | KMOL/HR | KMOL/HR | KMOL/HR | KMOL/HR | MJ/HR | MJ/HR | MJ/HR | MJ/HR | MJ/HR | MJ/HR | MJ/HR | MJ/HR | MJ/HR | MJ/HR |
| 10.00 | 505.41 | 124.59 | 161.11 | 14.30 | 0.00 | 3540.31 | 0.00 | 0.00 | 0.00 | 0.00 | 529.13 | 0.00 | 0.00 | 17533.48 | 17533.48 |
| 20.00 | 499.38 | 122.42 | 164.43 | 13.15 | 0.00 | 7080.62 | 0.00 | 0.00 | 0.00 | 0.00 | 1042.85 | 0.00 | 0.00 | 17533.48 | 17533.48 |
| 30.00 | 493.12 | 120.19 | 167.73 | 12.07 | 0.00 | 10620.93 | 0.00 | 0.00 | 0.00 | 0.00 | 1541.71 | 0.00 | 0.00 | 17533.48 | 17533.48 |
| 40.00 | 486.64 | 117.92 | 171.02 | 11.06 | 0.00 | 14161.25 | 0.00 | 0.00 | 0.00 | 0.00 | 2026.29 | 0.00 | 0.00 | 17533.48 | 17533.48 |
| 50.00 | 479.95 | 115.61 | 174.28 | 10.11 | 0.00 | 17701.56 | 0.00 | 0.00 | 0.00 | 0.00 | 2497.17 | 0.00 | 0.00 | 17533.48 | 17533.48 |
| 60.00 | 473.04 | 113.26 | 177.52 | 9.23 | 0.00 | 21241.87 | 0.00 | 0.00 | 0.00 | 0.00 | 2954.93 | 0.00 | 0.00 | 17533.48 | 17533.48 |
| 70.00 | 465.94 | 110.87 | 180.73 | 8.40 | 0.00 | 24782.18 | 0.00 | 0.00 | 0.00 | 0.00 | 3400.15 | 0.00 | 0.00 | 17533.48 | 17533.48 |
| 80.00 | 458.63 | 108.44 | 183.92 | 7.63 | 0.00 | 28322.49 | 0.00 | 0.00 | 0.00 | 0.00 | 3833.43 | 0.00 | 0.00 | 17533.48 | 17533.48 |
| 90.00 | 451.14 | 105.99 | 187.09 | 6.92 | 0.00 | 31862.80 | 0.00 | 0.00 | 0.00 | 0.00 | 4255.36 | 0.00 | 0.00 | 17533.48 | 17533.48 |
| 100.00 | 443.46 | 103.52 | 190.23 | 6.26 | 0.00 | 35403.12 | 0.00 | 0.00 | 0.00 | 0.00 | 4666.54 | 0.00 | 0.00 | 17533.48 | 17533.48 |
| 110.00 | 435.61 | 101.02 | 193.34 | 5.64 | 0.00 | 38943.43 | 0.00 | 0.00 | 0.00 | 0.00 | 5067.55 | 0.00 | 0.00 | 17533.48 | 17533.48 |
| 120.00 | 427.58 | 98.50 | 196.42 | 5.08 | 0.00 | 42483.74 | 0.00 | 0.00 | 0.00 | 0.00 | 5458.97 | 0.00 | 0.00 | 17533.48 | 17533.48 |
| 130.00 | 419.40 | 95.97 | 199.47 | 4.56 | 0.00 | 46024.05 | 0.00 | 0.00 | 0.00 | 0.00 | 5841.39 | 0.00 | 0.00 | 17533.48 | 17533.48 |
| 140.00 | 411.05 | 93.42 | 202.49 | 4.08 | 0.00 | 49564.36 | 0.00 | 0.00 | 0.00 | 0.00 | 6215.36 | 0.00 | 0.00 | 17533.48 | 17533.48 |
| 150.00 | 402.56 | 90.87 | 205.49 | 3.64 | 0.00 | 53104.67 | 0.00 | 0.00 | 0.00 | 0.00 | 6581.45 | 0.00 | 0.00 | 17533.48 | 17533.48 |

**Table S6** Material and energy stream table for different S/G ratios (FR = 650℃, AR = 650℃, and Ni/G = 0.9).

| Steam | $H_2$ | CO | $CO_2$ | $CH_4$ | C | AR1 | AR2 | AR3 | AR4 | AR5 | FR1 | FR2 | FR3 | FR4 | FR5 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| KMOL/HR | KMOL/HR | KMOL/HR | KMOL/HR | KMOL/HR | KMOL/HR | MJ/HR | MJ/HR | MJ/HR | MJ/HR | MJ/HR | MJ/HR | MJ/HR | MJ/HR | MJ/HR | MJ/HR |
| 150.00 | 345.06 | 130.36 | 132.58 | 17.63 | 19.44 | -39561.27 | 0.00 | 0.00 | 0.00 | 0.00 | 6649.78 | 0.00 | 0.00 | 0.00 | 12068.78 |
| 200.00 | 374.52 | 137.83 | 144.05 | 18.11 | 0.00 | -31862.80 | 0.00 | 0.00 | 0.00 | 0.00 | 6434.63 | 0.00 | 0.00 | 0.00 | 14375.98 |
| 250.00 | 394.70 | 130.68 | 154.47 | 14.86 | 0.00 | -31862.80 | 0.00 | 0.00 | 0.00 | 0.00 | 5837.64 | 0.00 | 0.00 | 0.00 | 15332.43 |
| 300.00 | 412.06 | 123.91 | 163.89 | 12.21 | 0.00 | -31862.80 | 0.00 | 0.00 | 0.00 | 0.00 | 5330.85 | 0.00 | 0.00 | 0.00 | 16097.39 |
| 350.00 | 427.01 | 117.53 | 172.40 | 10.06 | 0.00 | -31862.80 | 0.00 | 0.00 | 0.00 | 0.00 | 4904.51 | 0.00 | 0.00 | 0.00 | 16701.60 |
| 400.00 | 439.93 | 111.56 | 180.11 | 8.33 | 0.00 | -31862.80 | 0.00 | 0.00 | 0.00 | 0.00 | 4549.10 | 0.00 | 0.00 | 0.00 | 17172.34 |
| 450.00 | 451.14 | 105.99 | 187.09 | 6.92 | 0.00 | -31862.80 | 0.00 | 0.00 | 0.00 | 0.00 | 4255.36 | 0.00 | 0.00 | 0.00 | 17533.48 |
| 500.00 | 460.89 | 100.81 | 193.42 | 5.77 | 0.00 | -31862.80 | 0.00 | 0.00 | 0.00 | 0.00 | 4014.44 | 0.00 | 0.00 | 0.00 | 17805.60 |
| 550.00 | 469.43 | 96.00 | 199.16 | 4.84 | 0.00 | -31862.80 | 0.00 | 0.00 | 0.00 | 0.00 | 3818.15 | 0.00 | 0.00 | 0.00 | 18006.15 |
| 600.00 | 476.93 | 91.54 | 204.38 | 4.08 | 0.00 | -31862.80 | 0.00 | 0.00 | 0.00 | 0.00 | 3659.14 | 0.00 | 0.00 | 0.00 | 18149.68 |

**Table S7** Material stream table for different FR temperatures (Ni/G = 0.9 and S/G =4.5).

| T | H2 | CO | $CO_2$ | $CH_4$ | C | Ni | AR1 | AR2 | AR3 | AR4 | AR5 | FR1 | FR2 | FR3 | FR4 | FR5 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| ℃ | KMOL/HR | KMOL/HR | KMOL/HR | KMOL/HR | KMOL/HR | KMOL/HR | MJ/HR | MJ/HR | MJ/HR | MJ/HR | MJ/HR | MJ/HR | MJ/HR | MJ/HR | MJ/HR | MJ/HR |
| 600.00 | 416.26 | 78.75 | 198.80 | 22.45 | 0.00 | 90.00 | 31904.94 | 0.00 | 0.00 | 0.00 | 0.00 | 5761.36 | 0.00 | 0.00 | 9347.98 | 9347.98 |
| 650.00 | 451.14 | 105.99 | 187.09 | 6.92 | 0.00 | 90.00 | 31862.80 | 0.00 | 0.00 | 0.00 | 0.00 | 4255.36 | 0.00 | 0.00 | 17533.48 | 17533.48 |
| 700.00 | 454.04 | 123.70 | 174.53 | 1.76 | 0.00 | 90.00 | 31830.56 | 0.00 | 0.00 | 0.00 | 0.00 | 3634.77 | 0.00 | 0.00 | 22581.06 | 22581.06 |

The XRD results show that only Ni, W, and $Al_2O_3$ phases existed in the samples, indicating that the glycerol feedstock is capable of completely reducing the $NiWO_4$ to its metallic states. This result is consistent with the analysis from the Ellingham diagram.

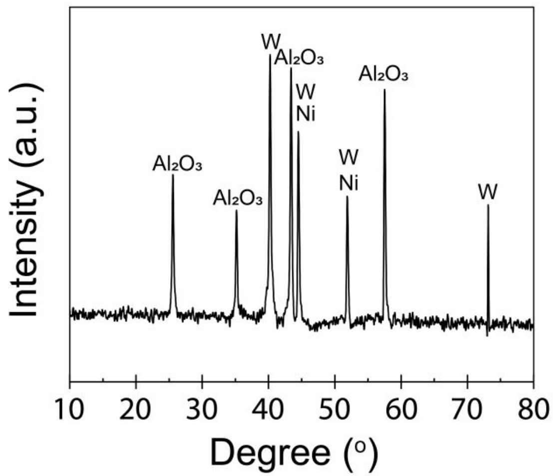


**Fig. S1.** XRD profiles of the OCs from the FR outlet (NiW-Al, S/G = 4.5, Ni/G = 0.9, FR temperature = 650°C, and AR temperature = 650°C).