Autothermal CO_2 hydrogenation reactor for renewable natural gas generation: Experimental proof-of-concept

Yichen Zhuang and David S. A. Simakov*

Department of Chemical Engineering, University of Waterloo, Waterloo ON N2L 3G1, Canada

* *Corresponding author.* Tel.: +1 519 8884567; E-mail addresses: dsimakov@uwaterloo.ca

Supplementary Information

1. Flow system configuration

The flow system used in all reactor tests are shown in Fig. S1. For isothermal experiments, a kinetic reactor (Fig. S2) was placed inside the furnace (Lindberg/Blue M™ Mini-Mite™ Tube Furnaces, Thermo Fisher Scientific). A K type thermocouple (1/8″, Omega Engineering) was inserted through the outlet tube so that the thermocouple tip is in contact with the catalyst bed. For reactor experiments, Reactors 1, 2 and 3 were connected to the flow system using stainless steel tubing. The furnace was used for the feed preheating for Reactors 1 and 2 (Figs S3, S4). For Reactor 3, the feed line was preheated with a heating tape (Fig. S5).

Flow rates were controlled by mass flow controllers (Bronkhorst High-Tech B.V.). Two three-way valves (Swagelok) were used to change the direction of the coolant (for concurrent or countercurrent operation). An electronic back pressure regulator (Bronkhorst High-Tech B.V.) was used to adjust the reactor pressure. Water was removed from the outlet stream using a mist trap (SMC Corporation, AFM40-N02-Z-A) installed before the back pressure regulator, and a silica gel column (Agilent Technologies, 5182-9411, the original adsorbent was replaced with orange silica gel, Fisher Scientific). Concentrations of CO, CO_2 and CH_4 in the outlet stream were measured on a dry basis (after the removal of water and moisture) with an IR analyzer (IR-208, Infrared Industries, Inc., USA). The entire flow system was computer-controlled using a custom-made control panel coded in LabVIEW (National Instruments) and analog-to-digital converters (NI 9215, NI 9263, National Instruments). All flow rates, pressures, temperatures and outlet gas concentrations were continuously monitored and recorded. CO_2 conversion, selectivity to CH_4 formation and carbon balance (see Appendix C) were continuously calculated, displayed and recorded through the duration of the entire experiment.

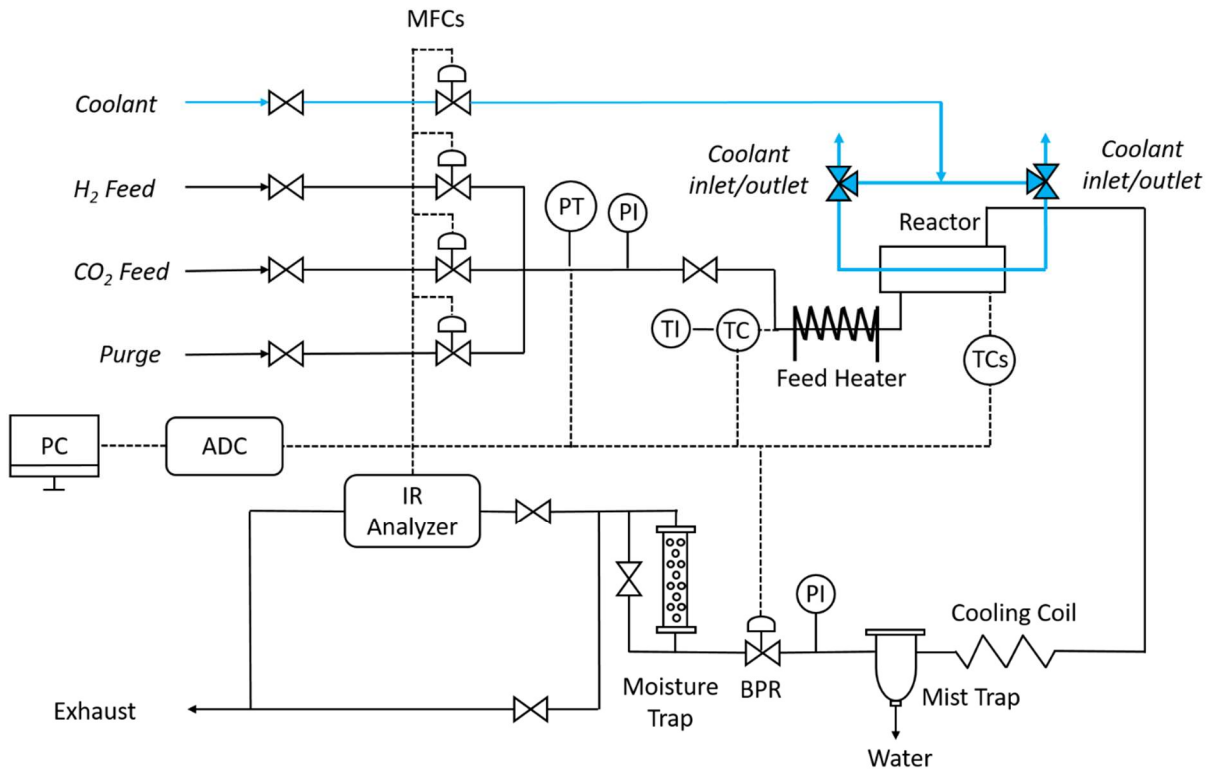

Fig. S1. Flow system setup. Abbreviations: ADC – analog-to-digital converter, BPR – back pressure regulator, IR – infrared, MFC – mass flow controller, PI – pressure indicator, PC – computer, PT – pressure transducer, TC – thermocouple, TI – temperature indicator.

2. Reactor configurations

The kinetic reactor, Fig. S1, was made from a 1/4″ stainless steel union tee (Swagelok) connected to 1/4″ stainless steel tubing on both sides (Swagelok), with a type K type thermocouple (1/8″, Omega Engineering, Inc.) placed in contact with the catalytic bed. Commercial catalytic pellets (12 wt% Ni/Al_2O_3, BASF, supplied by Research Catalysts, Inc. USA) were crushed and sieved to 0.275-0.425 mm pellets. The catalyst (250 mg) was loaded into the union tee, which was sealed at the top with a stainless steel plug (Swagelok). The reactor was placed in a furnace (see Appendix A) to maintain isothermal operation.

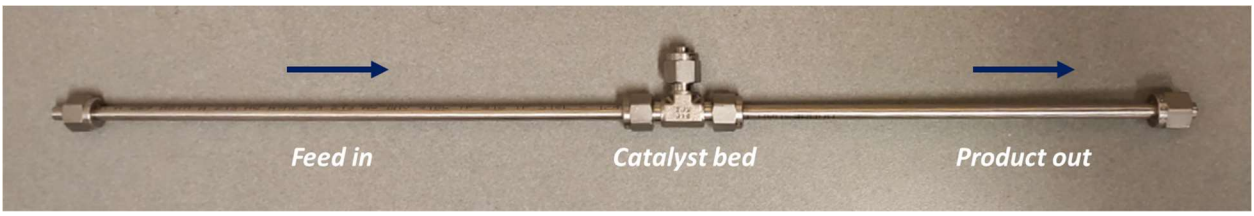

Fig. S2. Kinetic reactor configuration.

Reactor 1 was built from 0.25″ stainless steel tubing and Swagelok connectors, Fig. S3. Commercial catalytic pellets (12 wt% Ni/Al_2O_3, BASF, supplied by Research Catalysts, Inc. USA) were crushed and sieved to 0.275-0.425 mm pellets; 1.4 g of catalyst was used. Two K type thermocouples (1/8″, Omega Engineering) was placed before and after the catalytic bed (being in direct contact with the catalyst) to monitor the reactor inlet (T_{in}) and outlet (T_{out}) temperatures. The reactor was placed next to the furnace, which was used for the feed preheating. Given the small size of the reactor, no active cooling system was installed. The reactor body was warped in quartz wool and covered with aluminum foil for thermal insulation. Feed temperature (T_f) was measured using a thermocouple installed in contact with the feed tube extremal wall close to the furnace exit.

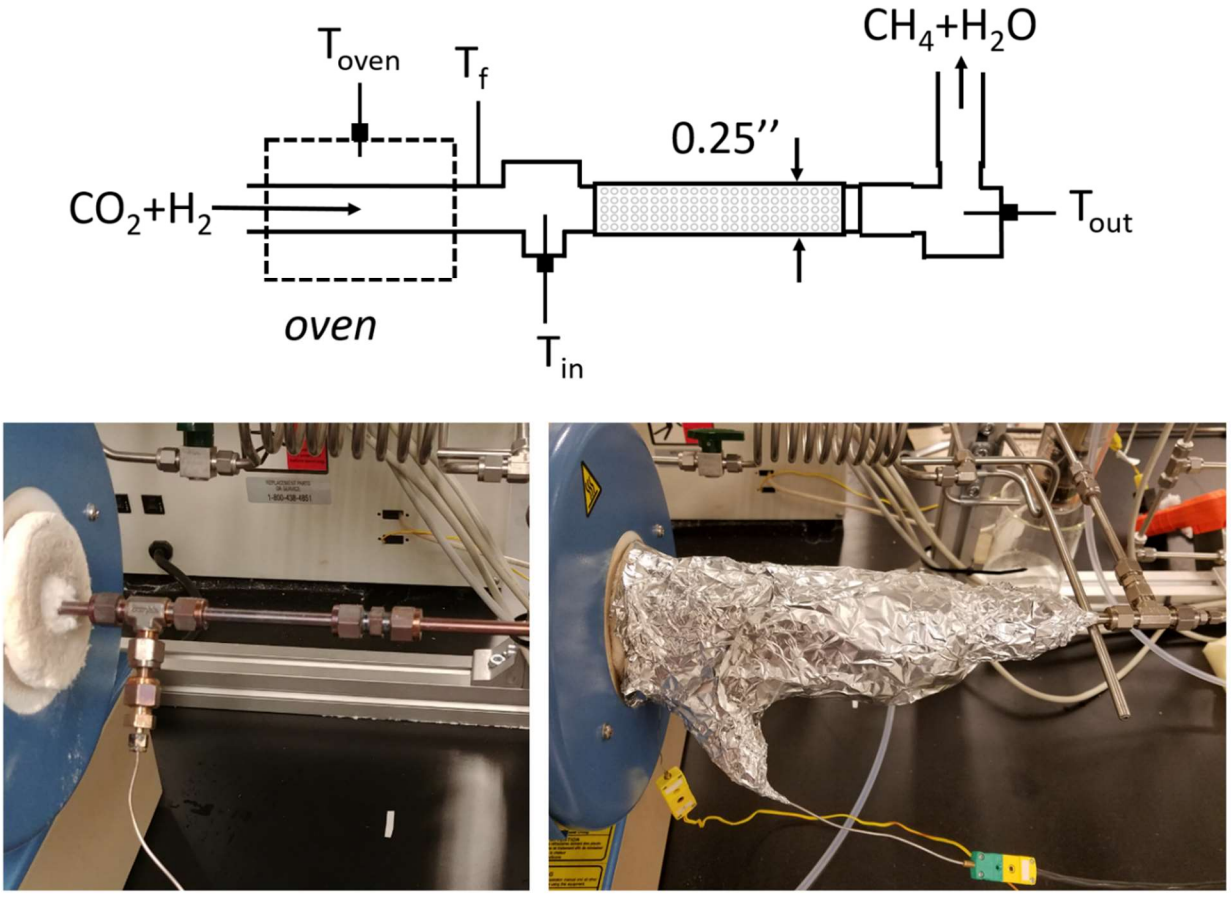

Fig. S3. Reactor 1 scheme and pictures (installed in the flow system, with and without insulation).

Reactor 2 was made from a 5″ long 1/2″ OD stainless steel tube, with a piece of 1/4″ OD tube placed inside (tube-and-shell) for active cooling using compressed air, Fig. S4. Reducing tees (Swagelok) were used to seal the space between the 1/4″ cooling tube and the 1/2″ reactor. K type thermocouples (1/8″, Omega Engineering, Inc.) were placed inside the cooling tube to estimate the reactor inlet (T_{in}) and outlet (T_{out}) temperatures. Another thermocouple (K type, 1/8″, Omega

Engineering, Inc.) was placed before the reactor inlet to measure the feed temperature (T_f). Commercial catalytic pellets (12 wt% Ni/Al_2O_3, BASF, supplied by Research Catalysts, Inc. USA) were crushed and sieved to 0.275-0.425 mm pellets. The resulted pellets (7.2 g) were loaded via the 1/2″ ports of the tee connectors and capped with stainless steel mesh and quartz wool. The oven was used to heat the feed stream. The reactor body assembly was wrapped in 3 cm thick layer of quartz wool and covered with aluminum foil for thermal insulation. The gap between the furnace and the reactor was also filled with quartz wool and covered with aluminum foil to minimize heat losses.

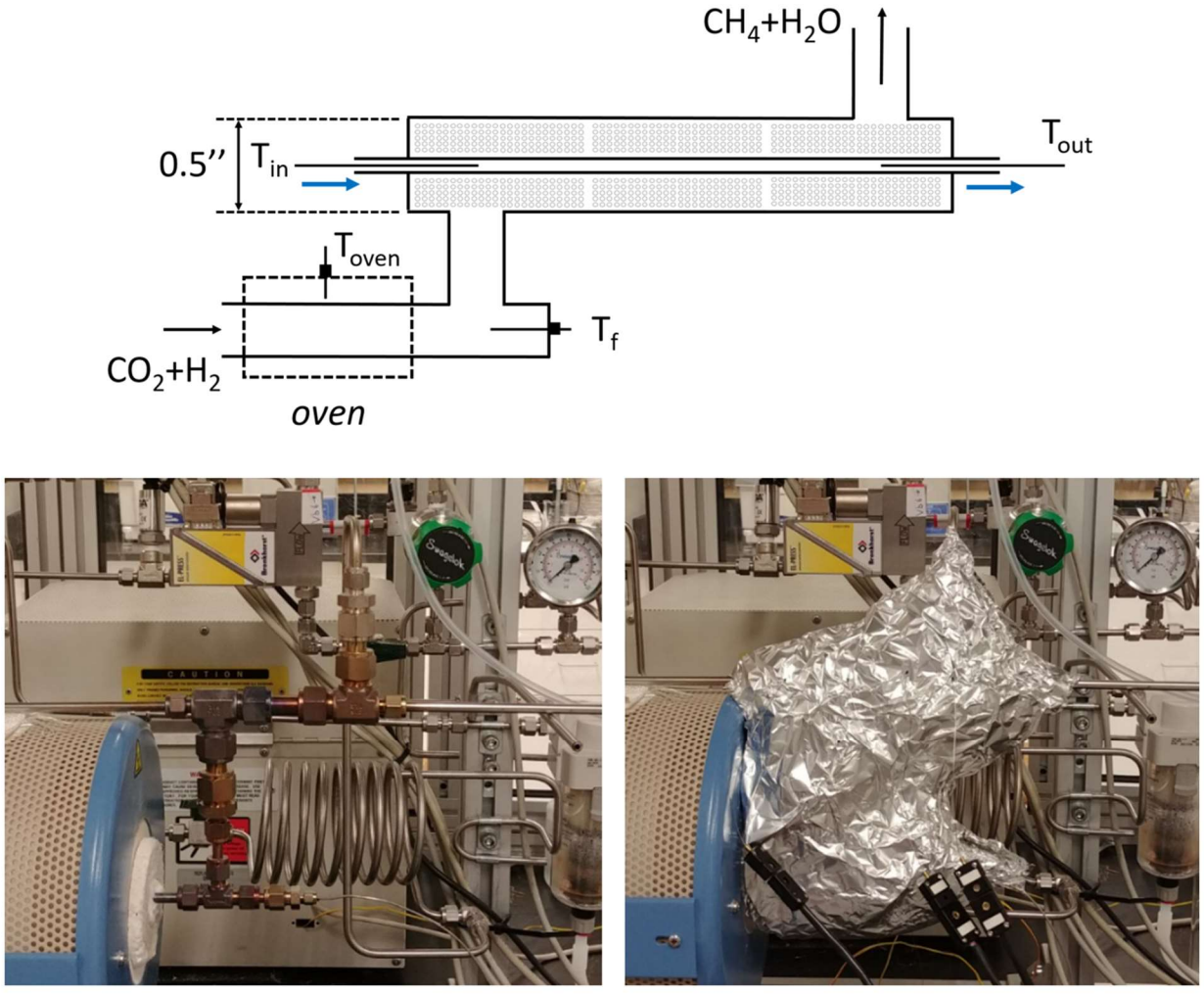

Fig. S4. Reactor 2 scheme and pictures (installed in the flow system, with and without insulation).

The outer diameter of Reactor 3 shell side was increased to 1″. The main reactor body was assembled from a piece of 1″ stainless steel tube and two reducing tees (Swagelok) as shown in Fig. S5. Commercial catalytic pellets (12 wt% Ni/Al_2O_3, BASF, supplied by Research Catalysts, Inc. USA) were crushed and sieved to 0.7-1 mm pellets. The catalyst (63 g) was filled into the

reactor via the 1″ port on the reducing tee and stainless-steel mesh and quartz wool was placed on top of the 1″ port, preventing the catalyst bed from moving. The length of the active bed was 9″. The cooling tube was a 1/4″ OD stainless steel placed inside the 1″ tube (tube-and-shell).

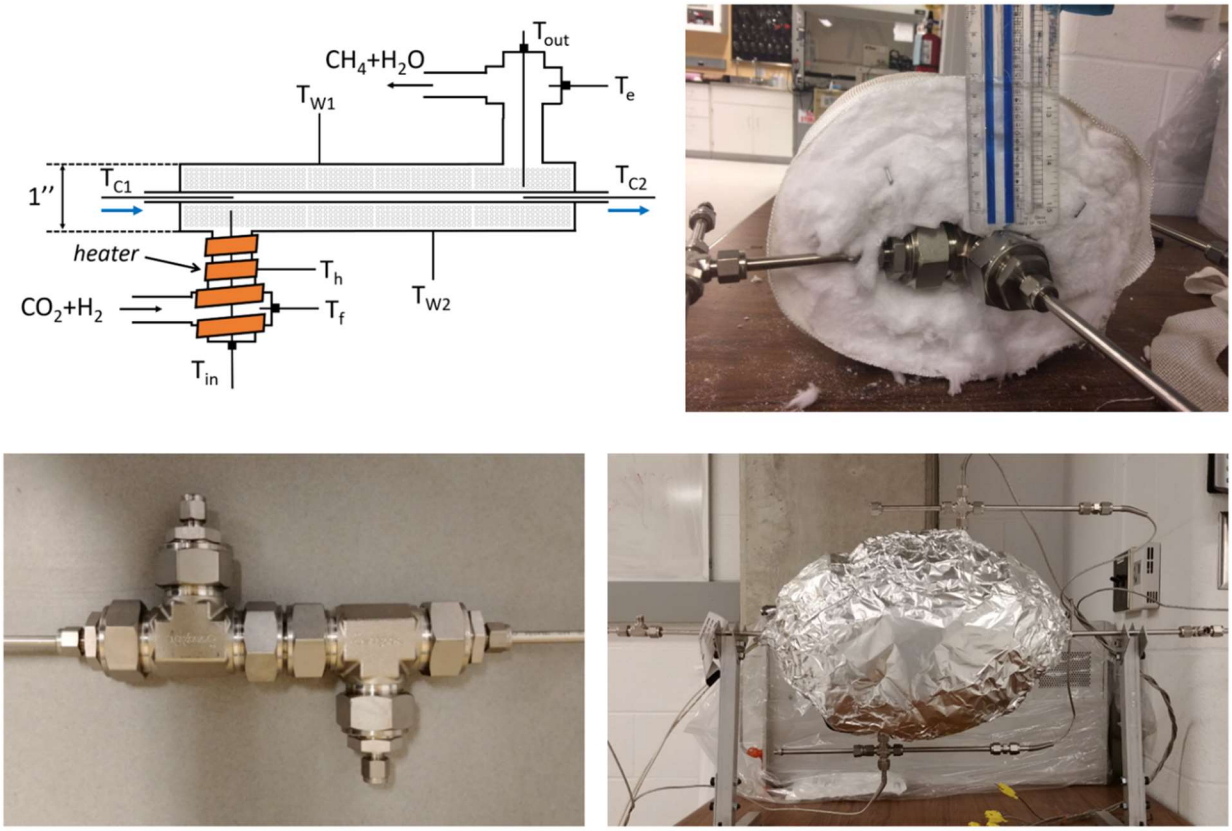

Fig. S5. Reactor 3 scheme and pictures (showing the main reactor body, thickness of the insulation layer and complete reactor with installed thermocouples).

A heating tape (300 W, Omega Engineering) with a temperature controller (CN7200, Omega Engineering) was wrapped around the inlet for feed preheating. A thermocouple (K type, 1/16″, Omega Engineering, Inc.) was placed in contact with the heating tape (T_h in Fig. S5). The reactor body assembly was wrapped with a layer of quartz wool and covered with aluminum foil for thermal insulation. Thermocouples (K type, 1/8″, Omega Engineering, Inc.) were placed inside the catalytic bed at the reactor inlet/outlet (T_{in}, T_{out}), at inlet/outlet ends of the cooling tube (T_{C1}, T_{C2}), and inside the feed/effluent lines (T_{W1}, T_{W2}). Two additional thermocouples (J type, 1/16″, Omega Engineering, Inc.) were placed on the reactor wall (T_{W1}, T_{W2}).

3. Carbon balance derivation

Carbon balance, defined as the total rate of carbon fed to the reactor divided by the rate of carbon exiting the reactor, was computed using the following equation (y_{CO_2}, y_{CO} and y_{CH_4} are mole fractions measured by the IR analyzer):

$$CB = (y_{CO_2} + y_{CO} + y_{CH_4})(1 + \alpha - f_1 - 4f_2) \quad \text{(S1)}$$

In Eq. (S1), α, f_1, and f_2 are the H_2:CO_2 ratio in the feed, conversion to CO, and conversion to CH_4, respectively, as defined in Eqs (S2-S4) below ($F_{C,out}$ is the total outlet molar flow rate of all carbon-containing species):

$$\alpha = \frac{F_{H_2,f}}{F_{CO_2,f}} \quad \text{(S2)}$$

$$f_1 = \frac{y_{CO}}{y_{CO} + y_{CO_2} + y_{CH_4}} \equiv \frac{F_{CO,out}}{F_{C,out}} = \frac{F_{CO,out}}{F_{CO_2,f}} \quad \text{(S3)}$$

$$f_2 = \frac{y_{CH_4}}{y_{CO} + y_{CO_2} + y_{CH_4}} \equiv \frac{F_{CH_4,out}}{F_{C,out}} = \frac{F_{CH_4,out}}{F_{CO_2,f}} \quad \text{(S4)}$$

Eq. (S1) above is obtained from the carbon balance definition, Eq. (S5), using Eq. (S6) to define the total outlet molar flow rate ($F_{CO,out}$ and $F_{CH_4,out}$ correspond to H_2 consumption in RWGS and Sabatier reaction) and Eqs (S2-4):

$$CB = \frac{(y_{CO_2} + y_{CO} + y_{CH_4})F_{t,out}}{F_{CO_2,f}} \quad \text{(S5)}$$

$$F_{t,out} = F_{CO_2,f} + F_{H_2,f} - F_{CO,out} - 4F_{CH_4,out} \quad \text{(S6)}$$