Characterization of a Methanation Catalyst for Power to Gas Application

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Abstract

The production of renewable natural gas (RNG) from biogenic resources requires a methanation catalyst to convert CO and CO_2 with H_2 generated from electrical power, i.e. power to gas. Both CO and CO_2 are present in producer gas (Table 1) from the steam gasification of biomass, but at a low H_2/C ratio of ~0.83. In this study a new methanation catalyst+ (Ni-Ru-MgO) is evaluated for the production of RNG from producer gas with additional hydrogen. Methanation experiments were conducted in a temperature-controlled flow reactor (Fig. 1) with the catalyst on a high surface area (~100 m^2/g) alumina spherical support. Measurements of CO and CO_2 conversion and the production of CH_4 were made with a microGC (Agilent 3000) to determine methanation yield and selectivity with increasing levels of additional hydrogen over a temperature range from 250°C to 450°C.

Materials and Methods

Catalyst Preparation: Wet impregnation of $Ni(NO_3)_2 \cdot 6H_2O$, $RuCl_3 \cdot xH_2O$ and $Mg(NO_3)_2 \cdot 6H_2O$ salts.

Catalyst Support: Alumina (Sasol Puralox 300/200 – BET surface area – 106 (m^2/g))

Catalyst Composition: Ni, Ru and MgO weight proportions of 2.5% MgO and 25% Ni:Ru with a ratio of 95:5.

Reaction Procedure & Conditions

Catalyst:Quartz Wt. Ratio = 1:20 , Reaction temperatures: 250°C to 450°C,

Gas flow rate:400 sccm, WHSV - 96000 cc g^{-1} h^{-1}

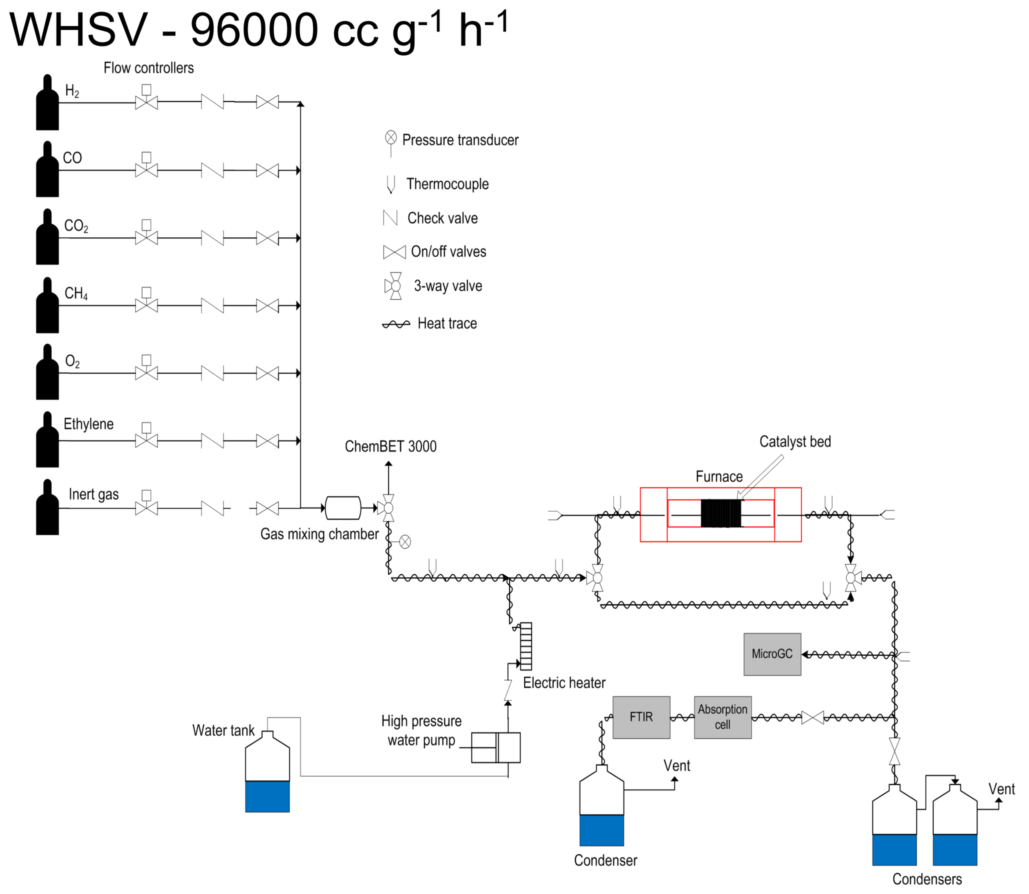


Figure 1: Schematic of the experimental setup for methanation-catalyst development in a fixed-bed reactor

Stoichiometric methanation reactions for CO and CO_2

$$CO + 3 H_2 = CH_4 + H_2O$$

$$CO_2 + 4 H_2 = CH_4 + 2 H_2O$$

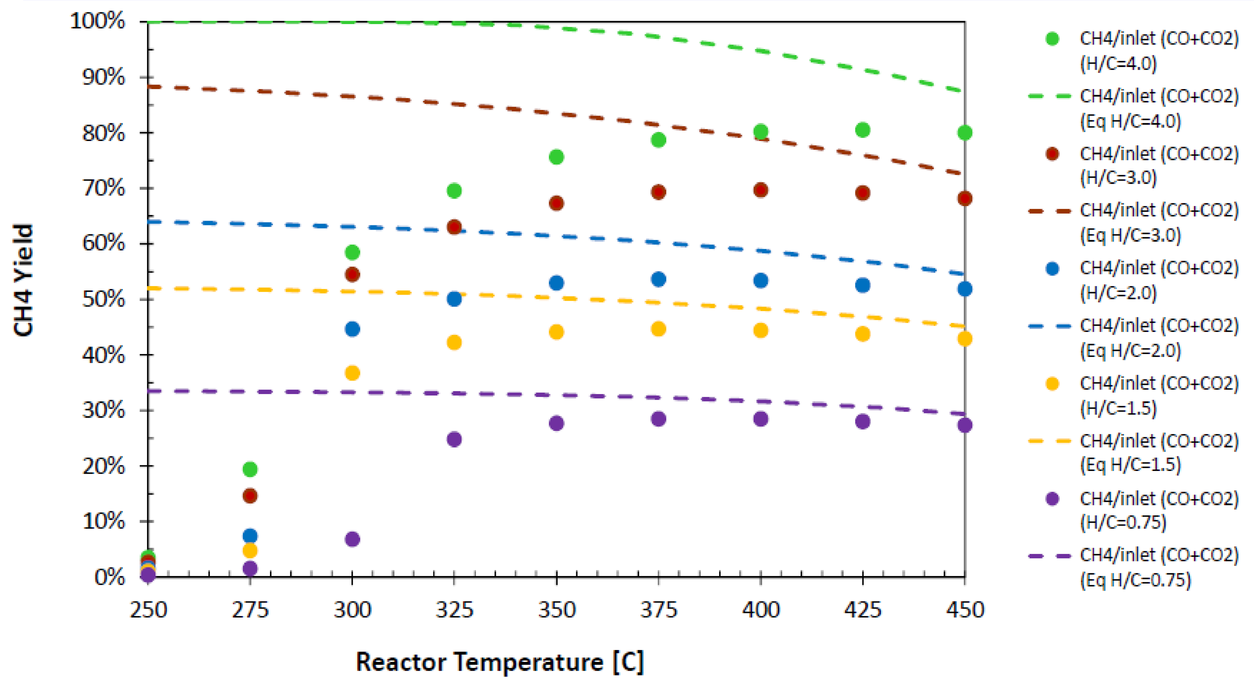
Research gas compositions, increasing $H_2/(CO+CO_2)$ ratio from 0.75 to 4.0

	H2/(CO+CO2)	H2	CO	CO2	CH4	C2H4	N2
Producer Gas	0.813	39.0%	29.0%	19.0%	8.0%	2.0%	3.00%
Research Gas	0.75	34.38%	26.91%	18.70%	-	-	20.0%
	1.50	48.06%	18.85%	13.10%	-	-	20.0%
	2.00	53.36%	15.72%	10.92%	-	-	20.0%
	3.00	60.01%	11.79%	8.20%	-	-	20.0%
	4.00	64.00%	9.43%	6.56%	-	-	20.0%

Table 1: Producer gas composition (molar) from the steam gasification of biomass and research gas compositions for the study of enhanced methanation of CO and CO_2 with the addition of hydrogen.

+ "Catalyst for the Methanation of Syngas and Producer Gas," Robert Cattolica, Reinhard Seiser, and Tinku Baidya, The Regents of the University of California, United States Patent, US11,224,865 B2 Jan. 18,2022.

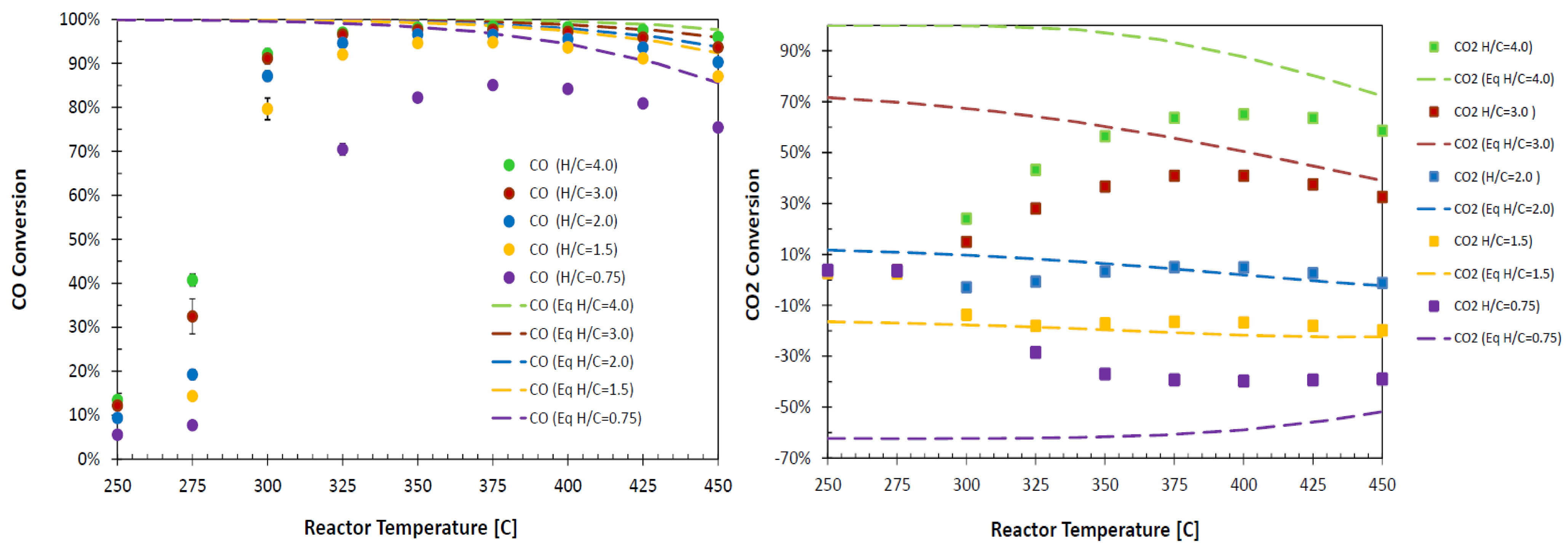
Methane yield $[CH_4]_{out}/[CO+CO_2]_{in}$ with increasing H/C=[H2]/[C] ratio



- Methane yield increases with H/C ratio
- Methane yield approaches chemical equilibrium at higher temperature
- Methane yield is ~ constant T > 375 °C
- Equilibrium not reached at higher H/C ratios
- Reduced WHSV could improve approach to equilibrium at higher H/C ratios and low temperature performance

Figure 2: Comparison of methanation experiments with chemical equilibrium model for methane yield

CO and CO_2 conversion during methanation with increasing H/C ratio



(a) (b)

Figure 3: CO conversion (a) and CO2 conversion (b) and comparison with chemical equilibrium model

- CO conversion is very high for T > 375°C, except for lowest H/C = 0.75
- CO conversion produces CO_2 for H/C < 2.0
- CO_2 conversion is negative (no net methanation) until H/C >2.0

Maximum methane yield at 400°C with increasing H/C ratio

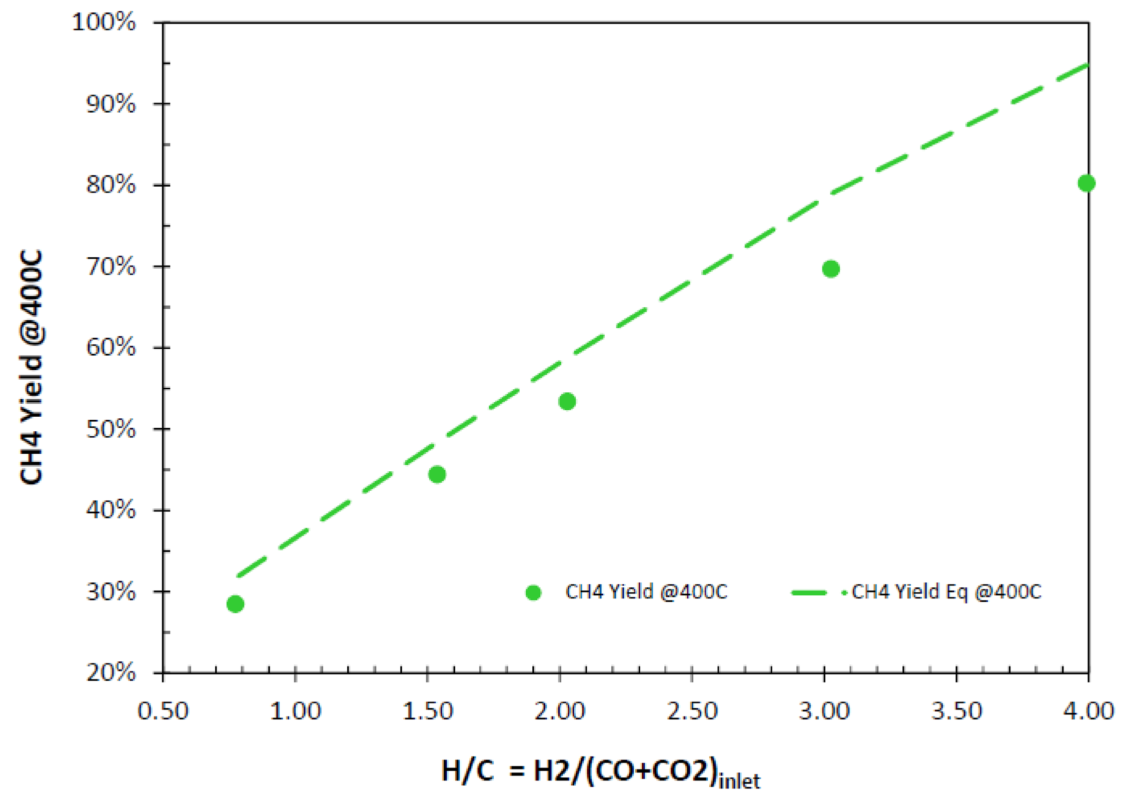


Figure 4: Maximum methane yield at 400°C and comparison with chemical equilibrium model

- Maximum methane yield is lower than equilibrium and the difference increases with increasing temperature
- With addition of hydrogen at H/C = 4.0, ~80% of the carbon (CO+CO_2) can be converted to produce CH_4
- Using producer gas with H/C = 0.813 and no H_2 addition, ~35% CH_4 can be produced primarily from CO

Acknowledgements

Support for this project was provided by the California Energy Commission (2021 CalTestBed Project – West Biofuels, LLC) and the University of California San Diego, Center for Energy Research.

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