PG&E GAS R&D AND INNOVATION

Methanation Technical Analysis

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1 What is Methanation

Methanation is a chemical reaction converting carbon monoxide and/or carbon dioxide into methane. The "Sabatier" reaction (1) converts CO2 to CH4. It is thermodynamically favored at low temperatures and high pressures. The reverse Steam Reforming reaction (2) (aka CO-methanation) converts CO to CH4. Both reaction (1) and (2) can be considered the methanation reactions. The reverse WGS (Water Gas Shift reaction) (3) produces CO from CO2 and H2. Summing reactions (2) and (3) together yields the first Sabatier reaction (Helmeth Project, n.d.).

$CO_2 + 4H_2 \leftrightarrow CH_4 + 2H_2O$	$\Delta rH298 = -165$ kJ/mol	(1)
$CO + 3H_2 \leftrightarrow CH_4 + H_2O$	$\Delta rH298 = -206$ kJ/mol	(2)
$CO_2 + H_2 \leftrightarrow CO + H_2O$	$\Delta rH298 = +41$ kJ/mol	(3)
$CO + H_2O \leftrightarrow CO_2 + H_2$	$\Delta rH298 = -41$ kJ/mol	(4)
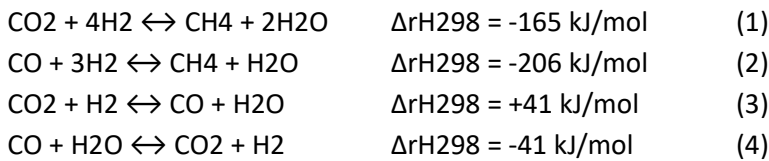
The WGS reaction is used to shift the H_2:CO ratio in favor of H_2 production. When biomass is used as the feedstock for producing syngas, there is more carbon-based products (e.g. CO) relative to H_2. According to reaction (2), 3 moles of H_2 are needed for every 1 mole of CO to produce 1 mole of CH_4. Similarly, according to reaction (1), 4 moles of H_2 are needed for every 1 mole of CO_2 to produce 1 mole of CH_4 (Helmeth Project, n.d.).

The Gibbs free energy, ΔG, could be used to approximate the products from the methanation process, which form at certain temperatures. The figure below shows the relationship between the Gibbs enthalpy and temperature for the various reactions.
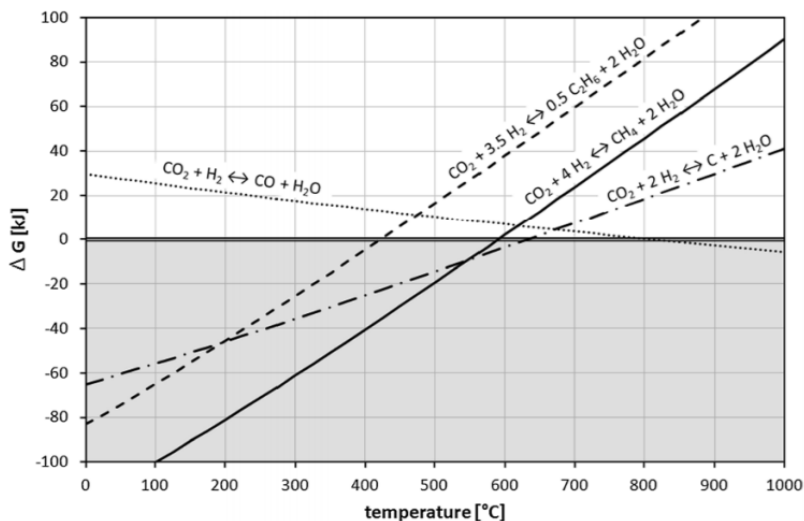

Figure 1 Gibbs Free Energy as a function of temperature. CO2/H2 = ¼ (Schaaf, Grunig, Schuster, Rothenfluh, & Orth, 2014)

If ΔG=0, a reaction is in equilibrium. If ΔG > 0 (grey area in figure above), the reaction is shifted to the products. If ΔG < 0 (white area in figure above), the reaction is shifted to the reactants. For example, methane formation from CO_2 and H_2 is favored up to 600°C (Schaaf, Grunig, Schuster, Rothenfluh, & Orth, 2014).

Pressure also affects the production of methane. For example, the conversion of CO_2 increases with increasing pressure and decreasing temperature. At 1 bar and 450°C, CO_2 has a conversion of 78%. If using a single stage process, 93% conversion can be achieved at 20 barg and 450°C (Schaaf, Grunig, Schuster, Rothenfluh, & Orth, 2014).

Aside from the thermodynamics of a process, the catalyst influences the methanation process. Typical commercial catalysts are based on nickel, due to the high activity and low prices. Catalysts need to be able to withstand fast (few seconds) temperature changes between 50-100°C from the operating conditions. For nickel-based catalysts, poisonous nickel carbonyl forms from CO at temperatures below 200°C (Schaaf, Grunig, Schuster, Rothenfluh, & Orth, 2014). To avoid catalyst poisoning by other chemicals (e.g. sulfur or siloxane), syngas cleaning is required prior to the methanation process. In addition, temperatures above 550°C would deactivate the catalyst through sintering or carbon formation (Schaaf, Grunig, Schuster, Rothenfluh, & Orth, 2014). The figure below shows CO_2 conversion at different pressures and temperatures, as well as the catalyst's operating range (grey area).
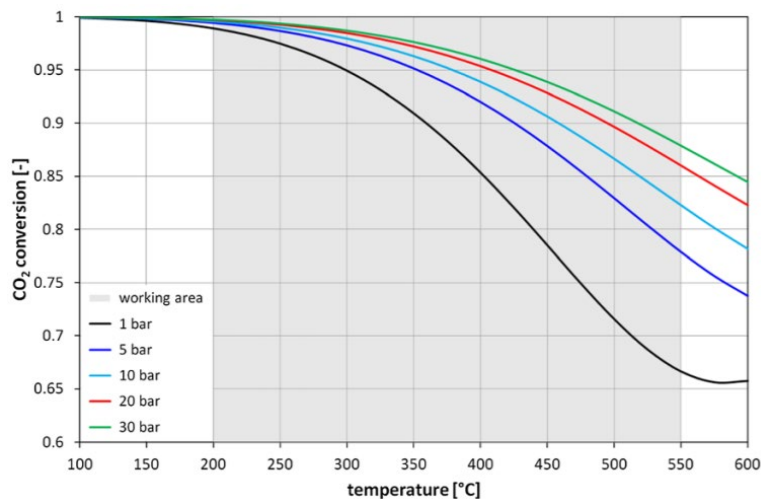

Figure 2 CO2 conversion as a function of temperature and pressure. CO2/H2 = 1/4 (Schaaf, Grunig, Schuster, Rothenfluh, & Orth, 2014)

A challenge in methanation is temperature control of the exothermic reactions, which requires continuous and efficient removal of excess heat and is linked to reactor design. For example, for the methanation of CO_2, an increase in methane's molar gas fraction of ~1% causes a temperature rise of ~60K (Schaaf, Grunig, Schuster, Rothenfluh, & Orth, 2014). There are two state-of-the-art reactor types that can be used: (1) Two-phase fixed bed reactors and (2) Fluidized bed reactors.

Temperature reduction can be achieved by reducing the reactive feed by a controlled dilution of the reactor inlet gas stream. This can be done by cooling and recirculating a portion of the reactor's outlet gas stream. However, cooling results in energy losses. Alternatively, isothermal operation of the reactor could be used. A cooled reactor would be used to transfer reaction heat to the cooling medium. For fixed bed reactors, there are radial and axial heat transfer limitations, meaning at least two adiabatic reactors are needed in series. Recirculation of the reactor outlet gas streams and by intermediate gas cooling steps can be done.

In fluidized bed reactors, methanation reactions occur within the fluidized bed of catalyst particles. Fluidized beds allow for good mixing of gas and solid catalyst particles, resulting in high mass and heat transfer and near isothermal conditions. Fluidized beds allow for good process control. But, abrasion and entrainment of catalyst particles in the gas flow are a challenge.
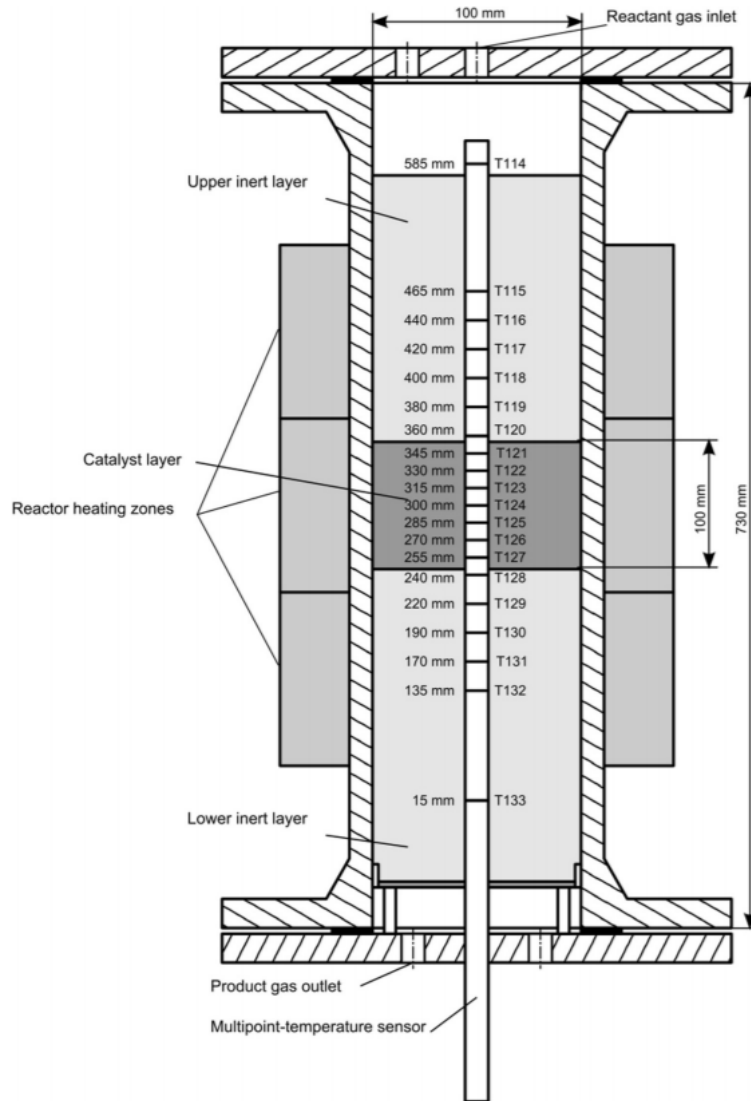
Figure 3 Cross section of the methanation reactor (Schaaf, Grunig, Schuster, Rothenfluh, & Orth, 2014)

2 Methanation Technologies

The table below lists key state-of-the-art methanation technologies.

Additional information about the technologies (Schaaf, Grunig, Schuster, Rothenfluh, & Orth, 2014):

(a), (b), (d), (g)	Partial product gas recirculation with intermediate cooling steps allow for temperature control within the reactor
(c)	A 'one through' process with 4-6 fixed bed reactors in series. Gas recirculation isn't necessary, since the cold feed gas is split and fed to the first 4 reactor stages in different ratios
(g)	A commercial methanation plant commission in 1984 in North Dakota. It was originally designed for synthetic natural gas (SNG) production of 3.54 Mio m^3/day. Production was increased in the nineties to 4.81 Mio m^3/day and is still in operation.
(h)	A high temperature methanation process with 3 adiabatic reactors in series and gas cooling in between
(i)	Two reactors. First reactor is an isothermal fixed bed with indirect heat exchanger. Second reactor is an adiabatic fixed bed reactor to increase total CH_4 yield
(j)	Two fluidized bed reactors. Both with two feed inlets and two in-tube heat exchanger bundles. The reactors have a diameter of 0.4 m and was operated for several hundred hours between 1977 – 1981. In 1982, a 1 m diameter reactor was built to demonstrate a production rate of 2,000 m^3/h of synthetic natural gas (SNG).
(k)	Two fluidized bed reactors. The first reactor has an inner diameter of 19 mm with only one gas inlet. The second reactor has an inner diameter of 25.4 mm with 3 gas inlets at the bottom.

Other concepts like catalytic tube wall reactors, adiabatic parallel-plate or hybrid reactors were brought to commercialization.

Table 1 Already developed processes for fixed bed and fluidized methanation (as of 2014) (Schaaf, Grunig, Schuster, Rothenfluh, & Orth, 2014)

Process number	Process/company	Reactor type	Process stages	Operation range p (bar)	Operation range T (°C)	Feed
(a)	TREMP/Haldor Topsøe	Fixed bed	3	30	300…700	Coal, petrol coke, biomass
(b)	Hicom/British Gas Corp.	Fixed bed	4	25…70	230…640	Coal
(c)	RMP/Ralph M. Parson Co.	Fixed bed	4…6	1…70	315…780	Coal, heavy fuel
(d)	SuperMeth, ConoMeth/Conoco	Fixed bed	4/4	Approximately 80	n. s.	Coal
(e)	CRG/British Gas Corp.	Fixed bed	2	Approximately 25	300	Naphtha (refinery residue)
(f)	Hygas/Institute of Gas Technology	Fixed bed	2	70	280…480	Coal
(g)	Lurgi, Sasol/Lurgi GmbH	Fixed bed	2	18	Approximately 450	Coal
(h)	ICI, Koppers/Imperial Chemical Industries	Fixed bed	3		400…700	Coal
(i)	Linde/Linde AG	Fixed bed	2	n. s.	n. s.	Coal
(j)	Bi-Gas/Bituminous Coal Res. Inc	Fluidized bed	1	86	n. s.	Coal
(k)	Bureau of Mines/US department of the Interior	Fluidized bed		20	200…400	
(l)	Comflux/Thysengas GmbH	Fluidized bed	1	20…60	400…500	Coal (biomass)

3 R&D Opportunities

- Catalysts are easily poisoned by H2S, siloxanes, formation of poisonous substances at certain operating temperatures (depends on catalyst material). Need catalysts that are highly active, low cost, but also more resistant to poisoning / degradation.
- Methanation reactions are very exothermic, need an effective and efficient way to control temperature and heat removal

References

Helmeth Project. (n.d.). *Methanation Process*. Retrieved from Helmeth Project: http://www.helmeth.eu/index.php/technologies/methanation-process

Schaaf, T., Grunig, J., Schuster, M. R., Rothenfluh, T., & Orth, A. (2014). Methanation of CO2 - storage of renewable. *Springer*, 14. Retrieved from https://energsustainsoc.biomedcentral.com/track/pdf/10.1186/s13705-014-0029-1