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Multi-criteria approach to optimal mixed reforming of biogas

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Intro - Mixed reforming of CH_4

$CH_4 + H_2O = CO + 3H_2$	ΔH^0_{298}=208.813 kJ mol^{-1}
$CH_4 + 0.5O_2 = CO + 2H_2$	ΔH^0_{298}=-36 kJ mol^{-1}
$CH_4 + CO_2 = 2CO + 2H_2$	ΔH^0_{298}=246.979 kJ mol^{-1}
$CO + H_2O = CO_2 + H_2$	ΔH^0_{298}=-41.166 kJ mol^{-1}
$CH_4 = C + 2H_2$	ΔH^0_{298}=74.52 kJ mol^{-1}
$2CO = CO_2 + C$	ΔH^0_{298}=-172.459 kJ mol^{-1}
$CO + 0.5O_2 = CO_2$	ΔH^0_{298}=-282.984 kJ mol^{-1}
$H_2 + 0.5O_2 = H_2O$	ΔH^0_{298}=-241.818 kJ mol^{-1}

Hydrogen is regarded as the fuel of the future. It can be produced via catalytic SR, POx, DR of methane, or a combination of the latter.
The main issues associated are the carbon deposition on the surface of the catalyst, exergy losses and high energy input.

Two thirds of the cost for H_2 production are for feed, fuel and utilities, and they can be lowered by using **optimal process conditions** and low-cost feedstock (e.g. renewable biogas).

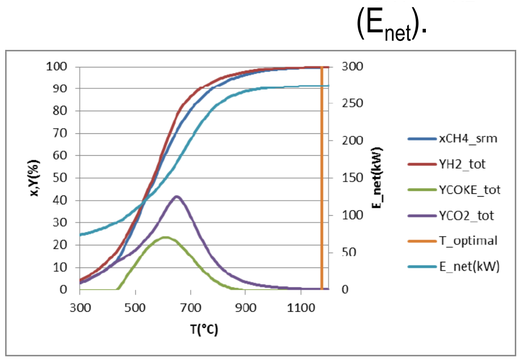
Calculations

Criteria

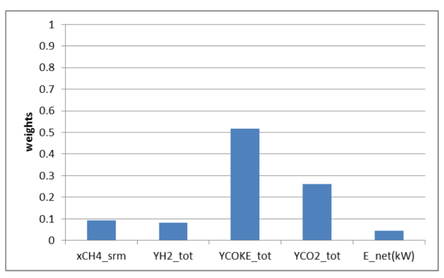
$x_{CH_4} = 100\frac{(CH_{4(5)} - CH_{4(6)})}{CH_{4(5)}}$	MAX
$Y_{H_2} = 100\frac{2(H_{2(12)})}{4(CH_{4(5)}) + 2(H_2O_{(5)})}$	MAX
$Y_{COKE} = 100\frac{(COKE_{(8)} + COKE_{(12)})}{CH_{4(5)}}$	min
$Y_{CO_2} = 100\frac{(CO_{2(8)} + CO_{2(12)} - CO_{2(5)})}{CH_{4(5)}}$	min
$E_{net}(kW) = SRM(kW) + HTS(kW) + LTS(kW) + Hx1(kW) + Hx2(kW) + Hx3(kW)$	min

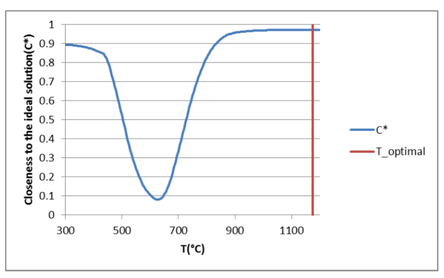
	Range	Step size
CH_4 in the biogas (%)	50-100	10
T(°C)	300-1200	5
H_2O/CH_4	0-5	0.05
O_2/CH_4	0-0.5	0.05

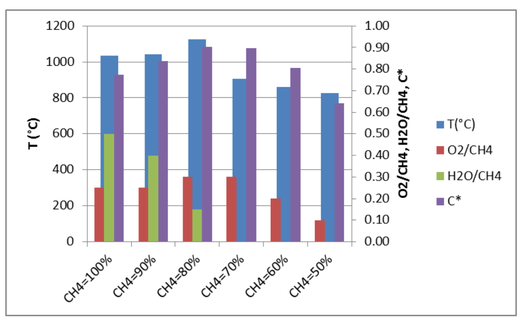
The composition of CH_4 in the biogas was changed from 50 to 100%, with the temperature ranging from 300 to 1200°C, while the criteria of interest were x_{CH4}, Y_{H2}, Y_{COKE}, Y_{CO2}, and the net energy input (E_{net}).



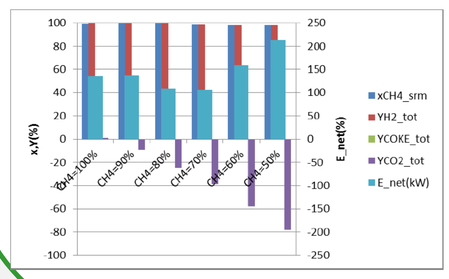
The method was run in 2 dimensions with $CH_4/CO_2/O_2$ fixed at 1/0/0, resulting in H_2O/CH_4=1 and T=1175°C. It is indeed reported how H_2O/CH_4<2.5 would reduce the formation of CO_2 during the WGS stage and the energy to vapourize water [4] [5] [6] .

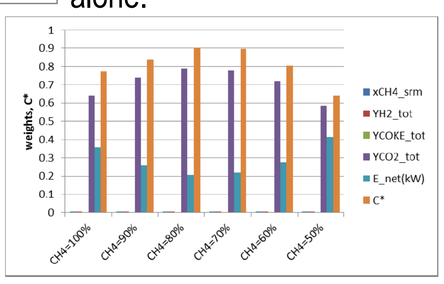






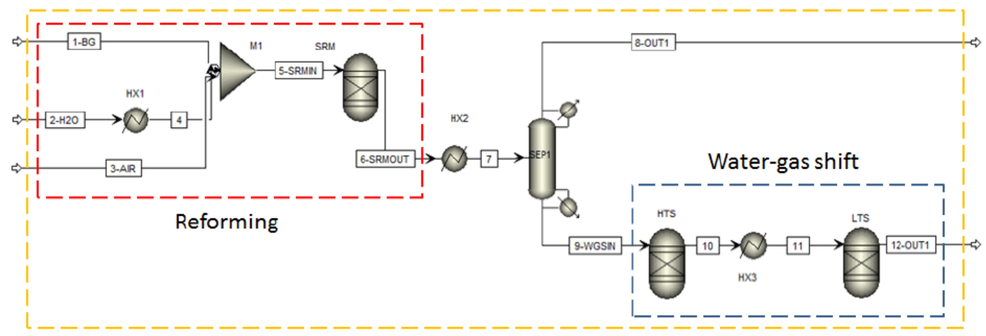
The method was run in 3 dimensions (T(°C), O_2/CH_4 and H_2O/CH_4 free to change), at different values of CH_4 concentration in the biogas.
As a result, a combination with partial oxidation and/or steam reforming is always preferred over dry reforming alone.





Methodology - MCDM methods

In this work a **novel methodology to find the optimal operating conditions** during the mixed-reforming of simulated biogas to H_2, based on thermodynamic data , was developed.

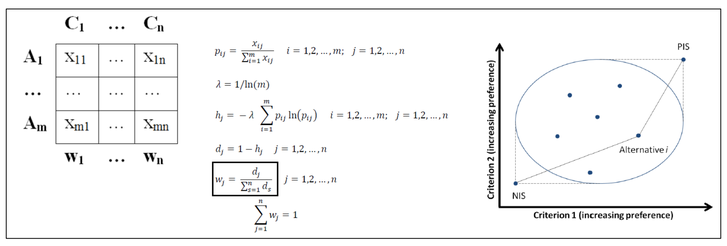


The mixed-reforming of biogas, together with the water-gas shift stages, were simulated in ASPEN Plus v7.3, in order to gather the equilibrium data used in the rest of this work.

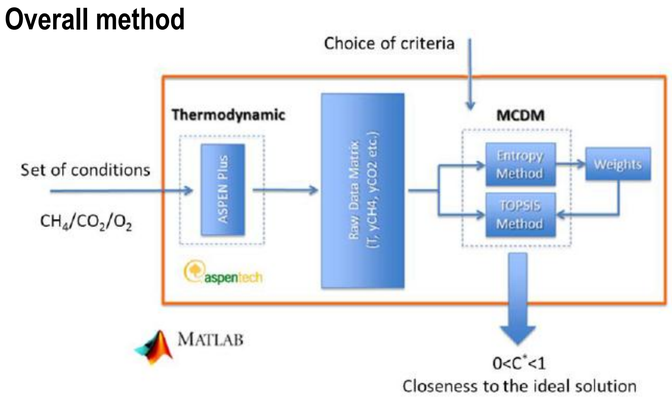
The data were subjected to two multi-criteria decision making (MCDM) techniques in series: the entropy [1] and the TOPSIS [2] methods (Technique for Order Preference by Similarity to the Ideal Solution).
The first is able to measure the **objective weights for the criteria** in a MCDM problem by evaluating the data distributions, while the second is able to find the operative condition which **maximizes all the benefits and minimizes all the cost** simultaneously.

The overall method consists of a Matlab script, which connects to ASPEN Plus to generate the thermodynamic data over a range of temperature, using a specific value of $CH_4/CO_2/O_2$ for the feed.
The thermodynamic data are stored in a matrix and then manipulated to generate the weights for the criteria of interest. These are then used in the TOPSIS to evaluate the closeness to the ideal solution values (C*) associated with the inlet feed.
The method is repeated over a range of O_2/CH_4 ratios, while the different operative conditions are ranked according to the C* value.

Entropy method **TOPSIS**

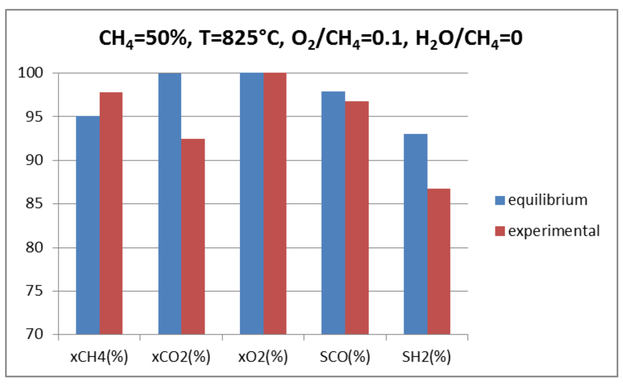


Overall method



Results - equilibrium vs. experiments

Real catalytic tests were run by using the optimal operating conditions suggested by the method, and a commercial catalyst (HiFuel by Johnson Matthey) at GHSV~20,000 mL h^{-1} g$_{cat}^{-1}$.



Final outcome of the MCDM method

	T(°C)	O_2/CH_4	H_2O/CH_4	C*
CH_4=100%	1035	0.25	0.5	0.775
CH_4=90%	1040	0.25	0.4	0.835
CH_4=80%	1125	0.3	0.15	0.903
CH_4=70%	905	0.3	0	0.896
CH_4=60%	860	0.2	0	0.806
CH_4=50%	825	0.1	0	0.642

		xCH_4(%)	xCO_2(%)	xO_2(%)	SCO(%)	SH_2(%)
CH_4=50%	equilibrium	95.12	99.98	100.00	97.92	93.07
	experimental	97.76	92.45	100.00	96.74	86.75
CH_4=60%	equilibrium	96.54	99.99	100.00	96.25	95.47
	experimental	97.74	97.04	100.00	84.75	83.51
CH_4=70%	equilibrium	97.96	100.00	100.00	99.72	98.30
	experimental	97.82	98.35	100.00	73.21	76.36

Conclusions

- A novel methodology for identifying the optimal operating conditions during mixed reforming of biogas from a thermodynamic point of view has been developed;
- The methodology is able to find the trade-off between multiple criteria (x_{CH4}, Y_{H2}, Y_{COKE}, Y_{CO2}, E_{net}) to be maximized/minimized simultaneously;
- When the percentage of methane in the biogas is higher than 70%, it is suggested to have SR+POx+DR at temperature higher than 1000°C; at lower concentration a combination of partial oxidation and dry-reforming at lower temperature is preferred;
- A commercial catalyst has showed reasonable activity, but lower selectivity to CO and H_2 than that provided by the MCDM method. The latter can be improved by using a kinetic model in ASPEN Plus, with Rplug blocks replacing the RGibbs.

[1] C.E. Shannon, A Mathematical Theory of Communication, The Bell System Technical Journal, 27 (1948).
[2] K.Y. C. L. Hwang, Multiple Attribute Decision Making, 1981
[3] N.R. Udengaard, Hydrogen production by steam reforming of hydrocarbons, 2004
[4] V.P. M. C. Annesini, L. Turchetti, Carbon Formation in the Steam Reforming Process: a Thermodynamic Analysis Based on the Elemental Composition, Chemical Engineering Transaction, 11 (2007).
[5] T.R.-N. J. R. Rostrup-Nielsen, Large-scale Hydrogen Production 2002