Multi-criteria approach to optimal mixed reforming of biogas

F. De Rosa[a]*, **A. Goguet**[a]*, **D. Rooney**[a], **B. Smith**[b], **G. McCullough**[b]

[a] *School of Chemistry and Chemical Engineering, Queen's University Belfast, BT9 5AG, UK*

[b] *School of Mechanical and Aerospace Engineering, Queen's University Belfast BT9 5AH UK*

**Corresponding author: a.goguet@qub.ac.uk; f.derosa@qub.ac.uk*

1. Introduction

Because of the concern related to greenhouse gas emissions, hydrogen is considered by many as the fuel of the future. It is usually obtained through steam reforming of methane/natural gas, but biogas represents a valid alternative. The latter is a renewable source of energy obtained from the anaerobic digestion of organic waste, mainly made of CH_4 and CO_2 with different ratios according to the source. This paper aims to develop a methodology for identifying the optimal operating conditions during mixed reforming of biogas from a thermodynamic point of view. Air and steam can be added to the original reacting mixture, while all the contaminants present in real biogas have been neglected (i.e. H_2S).

2. Materials and methods

The mixed reforming of biogas involves a series of reactions, namely steam reforming, dry reforming, partial oxidation, cracking, and disproportionation. As a consequence the optimization of the reaction as a whole is not trivial, because all the reactions are bound to each other and the relationships are not always clear. Therefore a trade-off between conflicting parameters is required (i.e. costs versus benefits).

ASPEN Plus v7.3 was used to simulate the mixed reforming of biogas using RGibbs blocks, based on the minimization of the Gibbs free energy. The biogas comprised a fixed CH_4/CO_2 ratio and all the processes were held at 1 bar, with the temperature changing from 573.15 to 1473.15 K. The results arising from the thermodynamic modelling of the mixed reforming of biogas in ASPEN Plus were subjected to two multi criteria decision making techniques (MCDM) in series, namely the Entropy [1] and the Technique for Order Preference by Similarity to the Ideal Solution [2] (TOPSIS) (Figure 1). The Entropy method can be used to determine objective weights or relative importance for the criteria within MCDM problems. This method helps to avoid deviation of the weights due to subjective factors, making results more in accordance with facts. The TOPSIS method is a goal-based decision-making technique. It needs information about the weights for the criteria and is able to find which alternative is as close as possible to the positive-ideal solution (PIS), where all the benefit criteria are maximized and all the cost are minimized at the same time. The distance between an alternative and the PIS is called closeness to the positive-ideal solution (C^*). The overall method consists of a Matlab code written in-house.

3. Results and discussion

The methodology was first developed in a relatively simpler environment, considering steam reforming of methane with a fixed steam-to-carbon ratio equal to 3. Several combinations of criteria were examined, considering as a reference that this reaction is usually run between 700 and 1100°C. The method is able to find the operating conditions at which methane conversion, hydrogen yield, and LHV-based efficiency are maximized (x_{CH4}, Y_{H2}, η), while the yield of coke and carbon monoxide, together with heat requirements, are minimized (Y_{COKE}, Y_{CO}, $SRM_{(kW)}$, $Hx1_{(kW)}$, $Hx2_{(kW)}$, $Hx3_{(kW)}$).

The same criteria were used in a bigger scenario, where H_2O/CH_4, O_2/CH_4 and CO_2/CH_4 ratios in the feed can be changed together with the operating temperature (Figure 2).

When pure methane is employed, optimal conditions are at 780°C and S/C=1.5 (Table 1). If air is allowed in the feed, the steam-to-carbon ratio can be decreased, while the optimum temperature increases up to 1180°C. When biogas made of 20% CO_2 is considered, the best results are obtained at T=785°C, O_2/CH_4=0.3, H_2O/CH_4=0.5. Values at CO_2/CH_4=0.43 are reported in Table 1.

These results were validated through experiments by using simulated biogas and different catalyst, whose performances were reasonably close to the equilibrium data. They show how biogas can be exploited to produce hydrogen as efficiently as methane/natural gas over an effective range of operating conditions.

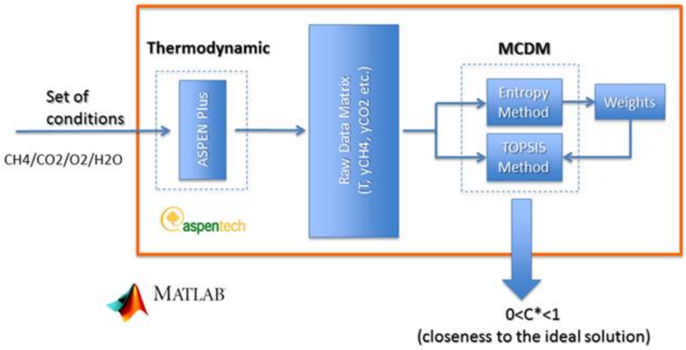

Figure 1. Graphical representation of the method

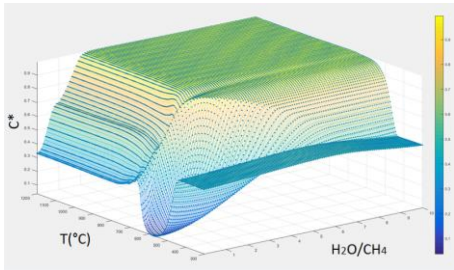

Figure 2. C* in two dimensions

Table 1. Highlights of the results from the MCDM technique

$CH_4/CO_2/O_2/H_2O$	T_{opt}(°C)	x_{CH4}(%)	Y_{H2}(%)	η	Y_{COKE}(%)	Y_{CO}(%)
1/0/0/1.5	780	97.05	86.88	1.38	0	84.11
1/0/0.3/1.1	1180	99.99	80.41	1.21	0	90.73
1/0.25/0.3/0.5	785	98.09	89.04	1.18	0	109.76
1/0.43/0.2/0.5	800	98.10	89.88	1.25	0	127.68

4. Significance

The method hereby developed is comprehensive, rational and understandable. It is novel because employs well-known MCDM techniques that have never been used before as an optimization tool for chemical reactions. It is based on thermodynamics and requires less computational workload compared to other optimization techniques.

It can be virtually transferred into different scenarios, where the multi-criteria optimization of complicated networks of reactions is involved.

References

[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.