Methanol Steam Reformer – High Temperature PEM Fuel Cell System Analysis

A. Lotrič[1], M. Sekavčnik[2], S. Hočevar[1,3]

[1]Mebius d.o.o., Na jami 3, SI-1000 Ljubljana, Slovenia.

[2]University of Ljubljana, Faculty of Mechanical Engineering, Lab. for Heat & Power, Aškerčeva 6, SI-1000 Ljubljana, Slovenia

[3]National Institute of Chemistry, Lab. Catal. & Chem. React. Eng., Hajdrihova 19, SI-1000 Ljubljana, Slovenia.

[1]andrej.lotric@mebius.si

[2]mihael.sekavcnik@fs.uni-lj.si

[3]stanko.hocevar@ki.si

MEBIUS Ltd.

- Slovenia-based spin-out from the National Institute of Chemistry
- Young SME focused on R&D of core components for LT & HT PEMFC
- Developing products:
  - GDEs
  - LT & HT membranes
  - MEAs
  - LT & HT stacks (up to 250 W_e)

INTRODUCTION

- Why methanol?
  - Sulphur free fuel
  - Far greater energy density per volume than H_2 at SATP
- Why HT PEMFC?
  - Faster kinetics
  - Use of HT heat in cogeneration
  - Simplified water management
  - Greater tolerance to CO poisoning
  - Possibility for integration of methanol steam reformer (MSR)

SYSTEM MODELLING

- Modelling was performed using
  - Mathematica programing language
  - Aspen Plus software
- MSR modelling
  - Directly in Aspen Plus using R-Plug model unit
  - Reactor as a tube 200 mm in length and 10 mm in diameter
  - Kinetic model proposed by Peppley et al is based on Langmuir-Hinshelwood mechanism:

$CH_3OH + H_2O \leftrightarrow CO_2 + 3H_2$	methanol steam reforming
$CH_3OH \leftrightarrow CO + 2H_2$	methanol decomposition
$CO + H_2O \leftrightarrow CO_2 + H_2$	water gas shift reaction

- PEMFC modelling
  - Calculations for HT PEMFC performed in Mathematica
  - Efficiency

$$\eta_{PEMFC} = \frac{P_{out}}{P_{in}} = \frac{2 \cdot F \cdot U(\dot{n}_{H2})}{\Delta H_{HHV}}$$

  - Cell potential (losses)

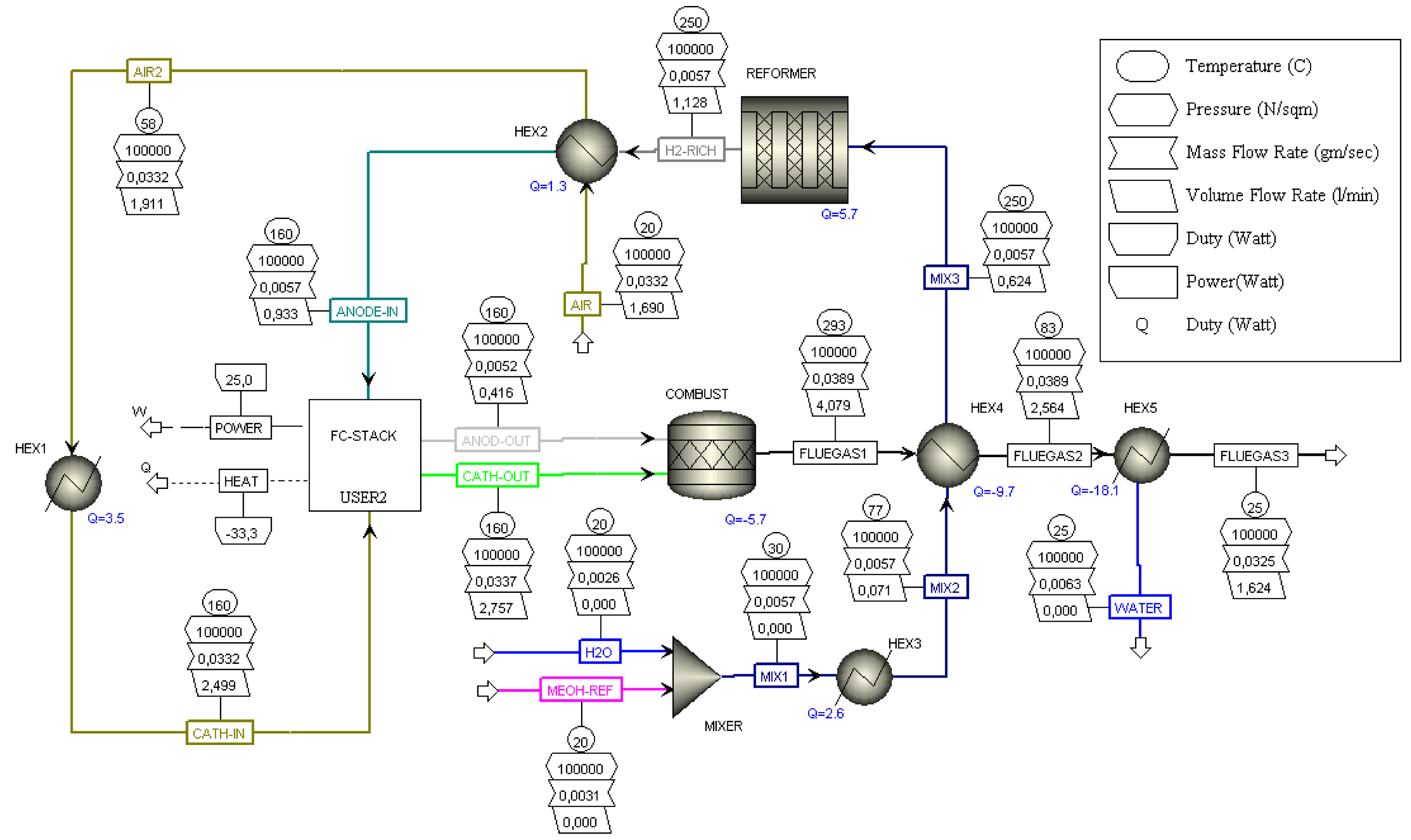
$$E = E_0 + \frac{\Delta s}{z \cdot F}(T - T_0) + \frac{R \cdot T}{z \cdot F} \cdot ln\left(\frac{p_{H2} \cdot p_{O2}^{\frac{1}{2}}}{p_{H2O}}\right) - \eta_{act} - \eta_{con} - \eta_{ohm}$$

$$j = j_0 \cdot \left(e^{\frac{\beta \cdot z \cdot F \cdot \eta_{act}}{R \cdot T}} - e^{\frac{-(1-\beta) \cdot z \cdot F \cdot \eta_{act}}{R \cdot T}}\right) \xrightarrow{\text{numericaly}} \eta_{act}$$

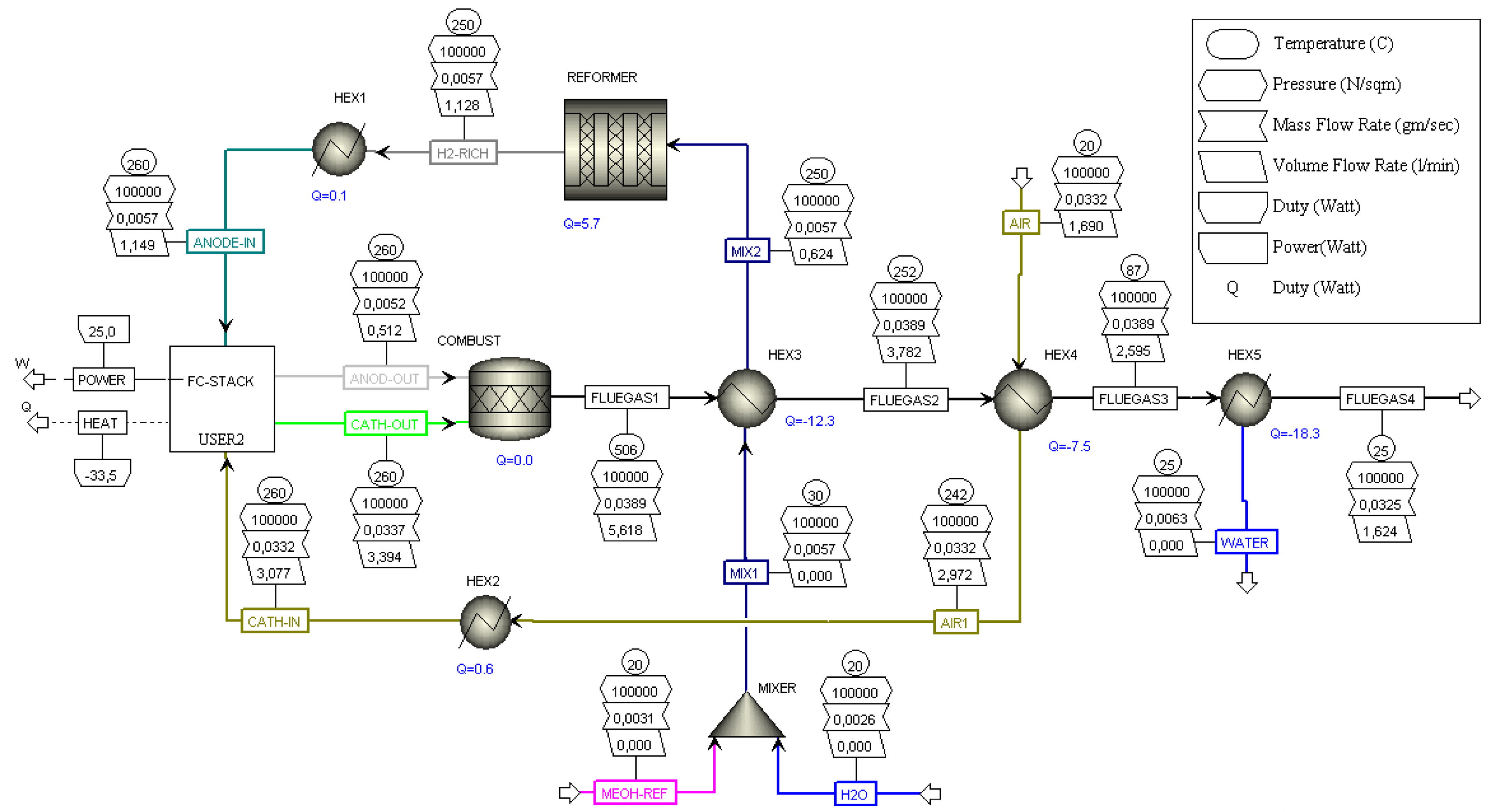
$$\eta_{con} = \frac{R \cdot T}{z \cdot F} \cdot ln\left(\frac{j_L}{j_L - j}\right)$$

$$\eta_{ohm} = j \cdot \frac{d}{A \cdot \sigma}$$

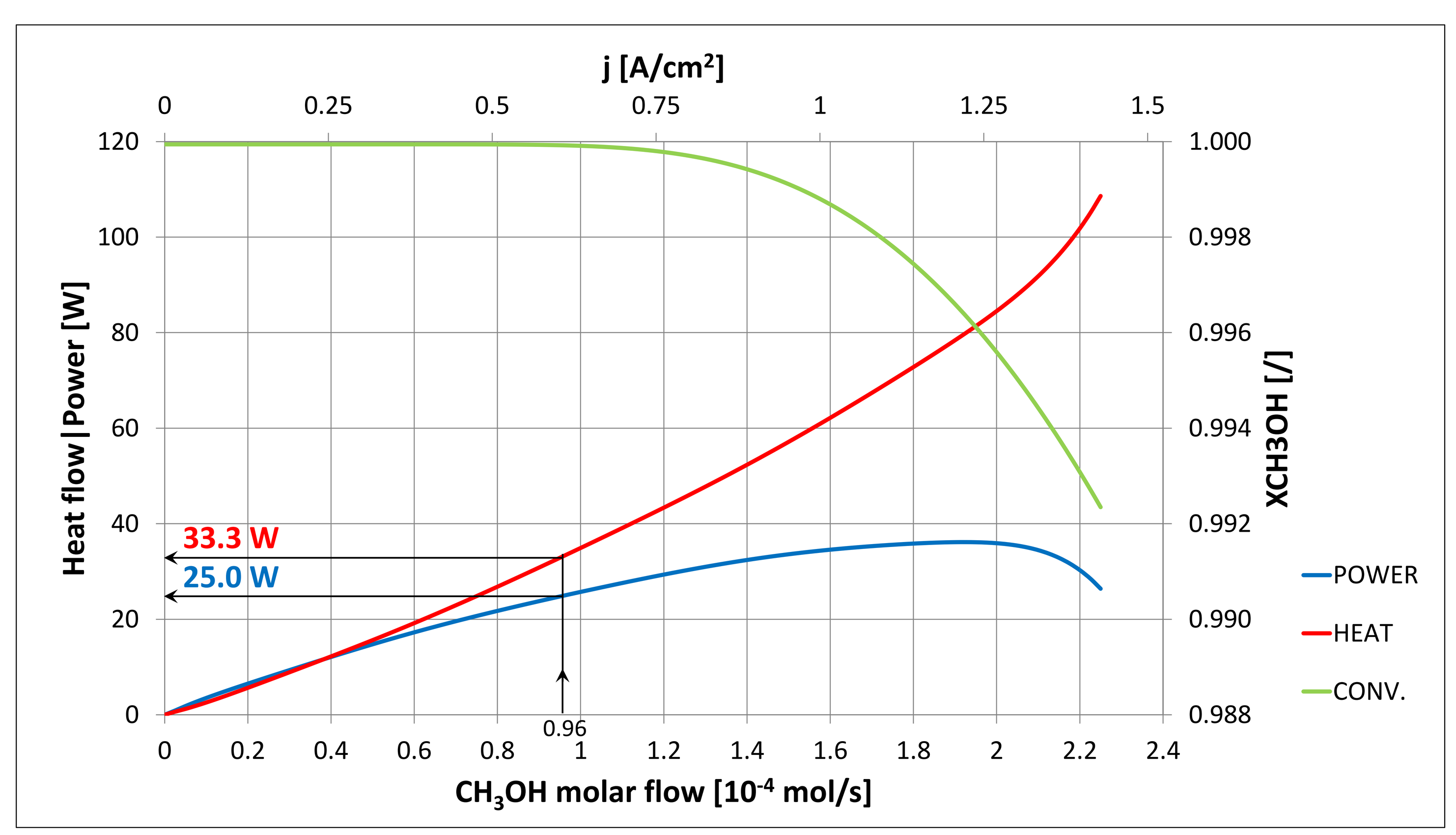
  - HT PEMFC power characteristics vs. H_2 molar flow exported from Mathematica to Aspen Plus User-2 model of HT PEMFC stack



Mass and energy balance analysis of the system with MSR and conventional HT PEMFC stack



Mass and energy balance analysis of the system with MSR and novel HT PEMFC stack



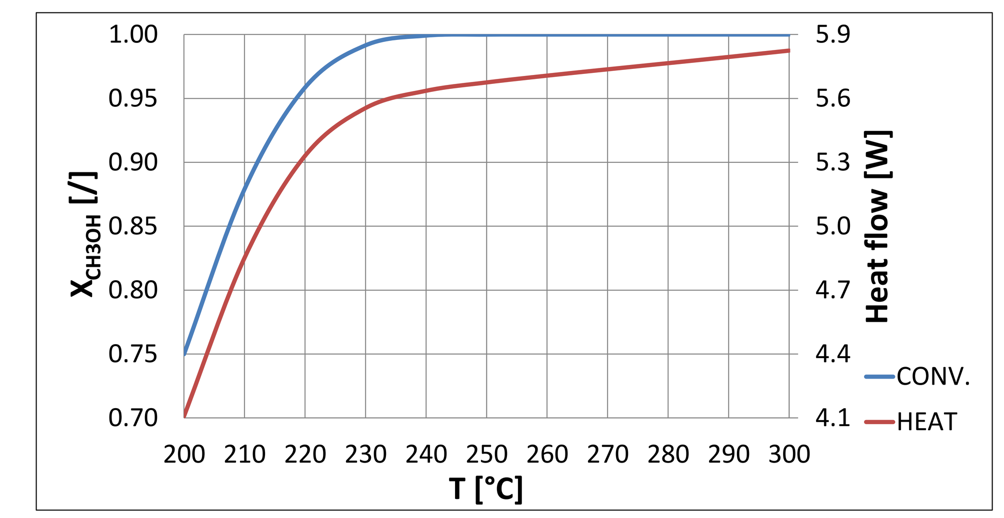
Heat & Power produced in HT PEMFC and CH_3OH conversion at constant temperature

- Combined system
  - Two types of HT PEMFC stack (conventional @ 160°C & novel @ 260 °C)
  - Both types of stacks have the same efficiency characteristics
  - In both cases MSR operates @ 250 °C
  - Steady state conditions
  - Adiabatic insulation
  - Heat regeneration
  - 100% methanol conversion
  - 83.3% H_2 and 50% O_2 utilisation in stack

RESULTS

- MSR
  - Fixed molar flow of methanol @ $9.6 \cdot 10^{-5}$ mol/s
  - Steam-to-methanol ratio 1.5:1
  - 100% conversion @ 250 °C
- Comparison of systems
  - Efficieny of systems (based on HHV)

$$\eta_{sytem} = \frac{P_{out}}{\dot{m} \cdot \Delta H_{HHV}} = 40.6\ \%$$



Methanol conversion and heat consumption as a function of operating temperature of MSR

Stack	Operating temp.	Heat flow produced in stack	Heat flow to MSR	Recycled heat flow	Used heat flow	Unused heat from stack	Heat flow to environment
conventional	160 °C	33.3 W	5.7 W	10.9 W	6.1 W	**27.2 W**	**18.1 W**
novel	260 °C	33.5 W	5.7 W	19.8 W	0.8 W	**27.0 W**	**18.3 W**

- In reality the assumption of adiabatic insulation does not stand. The lower operating point of the system will be defined by the sum of heat losses (dependant on the size, design, insulation and temperature level of the system) and the heat generated in HT PEMFC stack equalling to zero.

CONCLUSIONS

- Two limiting cases presented
  - Because of initial assumptions and idealisations efficiency of 40.6% is equal for both systems. In reality it will be different (different kinetics and proton conduction mechanism).
  - Higher temperature level of produced heat in novel HT PEMFC but also expected higher heat losses (depends on the design of the system)
- Two possibilities for future MSR-HT PEMFC system development:
  - To develop catalyst that allows operation of MSR with 100% conversion below 180 °C; this would enable coupling of conventional PBI/H_3PO_4 and novel MSR
  - To use conventional MSR @ 250 °C and develop novel HT PEMFC that operates at temperatures above 250 °C
- In case of novel HT PEMFC new materials need to be developed (electrodes, membranes, gaskets, etc.)