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Bio-Hydrogen

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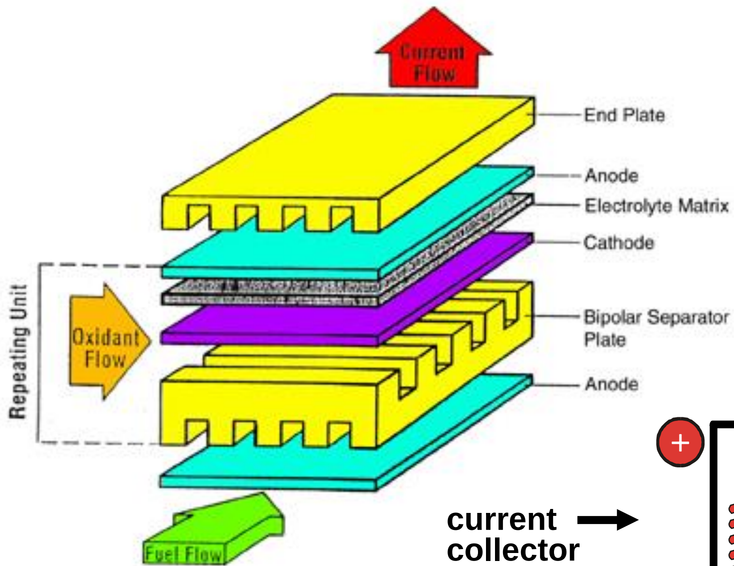
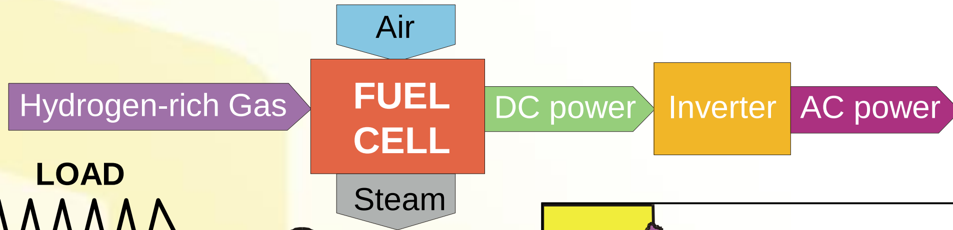
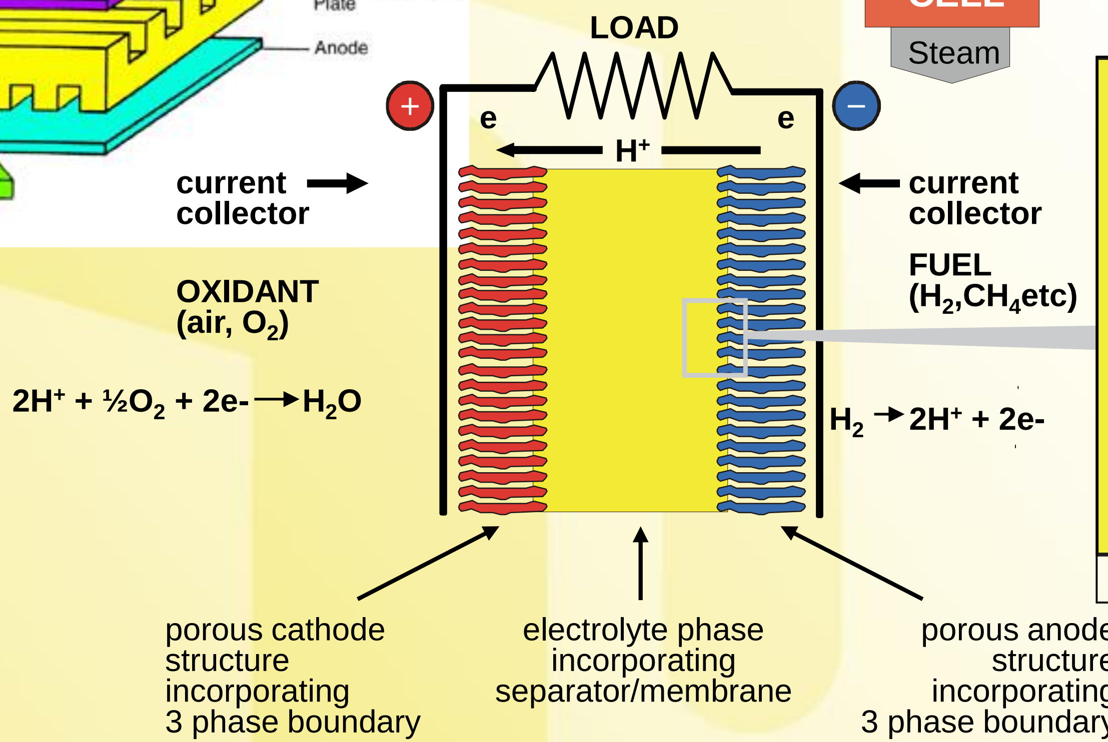
National Metal and Materials Technology Center (MTEC)

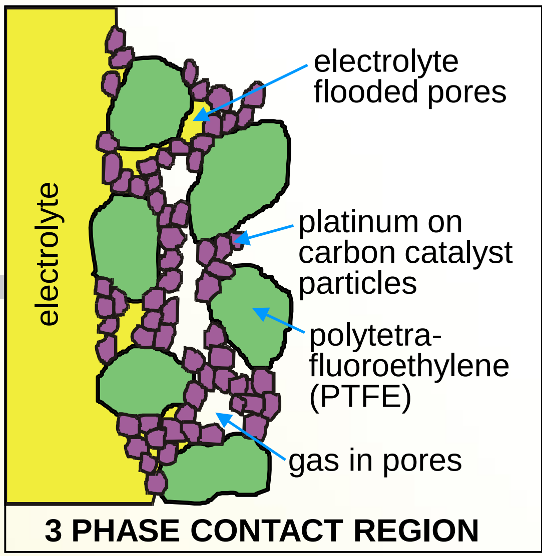
NSTDA

Fuel Cells









B.C.H. Steele

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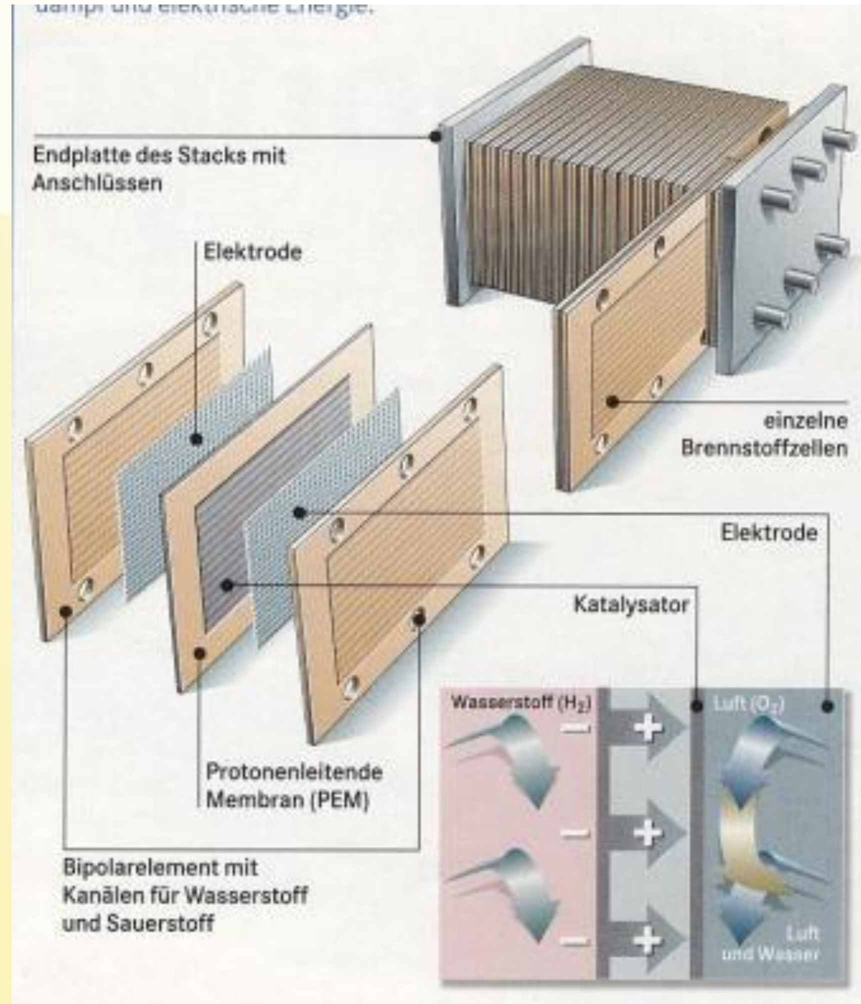
Proton Exchange Membrane Fuel Cell



Ballard fuel cell – 3 generations

www.ballard.com

www.daimler.com

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Toyota Mirai

http://www.toyotaglobal.com/innovation/environmental_technology/fuelcell_vehi

Sources of hydrogen

- Fossil hydrocarbon – natural gas (CH_4), LPG, diesel
- Renewable hydrocarbon – **biogas (CH_4)**
- **Ethanol** – fermentation, lignocellulosic process
- Electrolysis
- Biological process

Catalyst Development

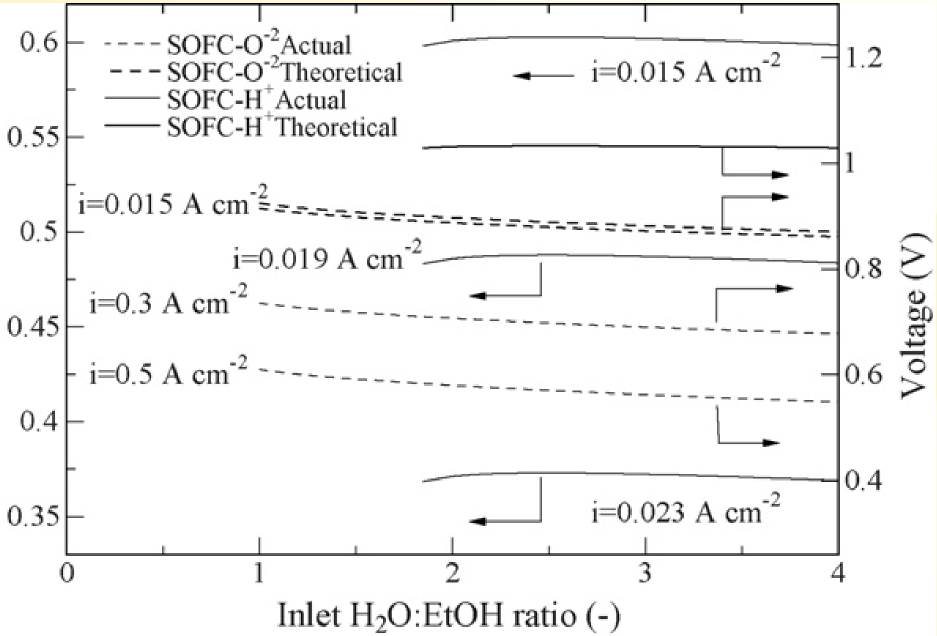
Determination of hydrogen production yield

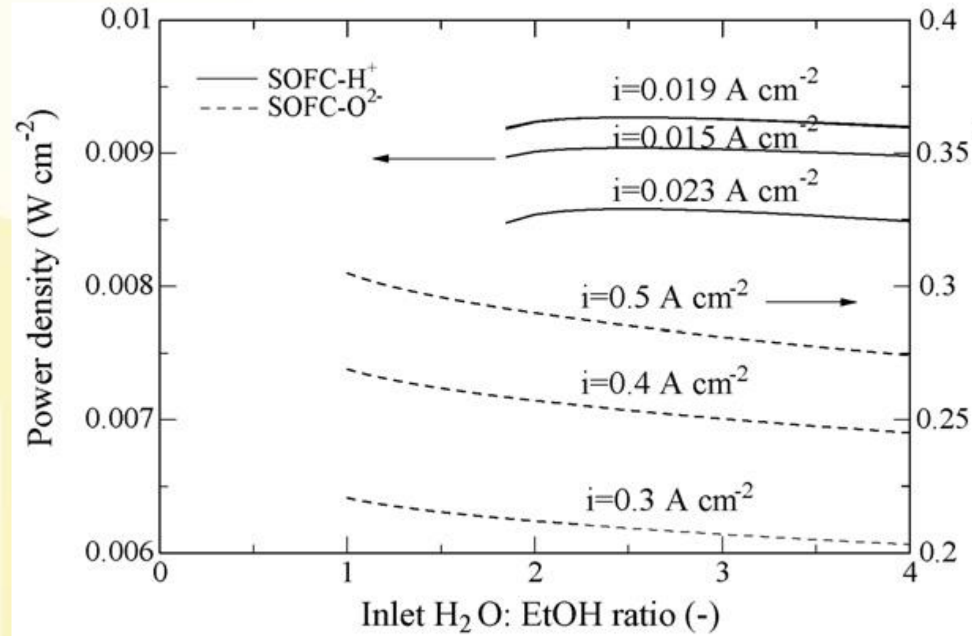
Type of fuels	Yield of H_2 production (%) from the steam reforming at 900◦C over					
	Ni/Al_2O_3	Rh/Al_2O_3	CeO_2	CeO_2 (HSA)	Ni/CeO_2	$Ce\text{-}Ni/Al_2O_3$
Methane	85.9	~100	30.3	**54.8**	85.4	84.0
Natural gas	51.3	88.3	45.4	**78.9**	61.8	59.7
Biogas	53.7	~100	53.3	**81.3**	66.7	67.9
Ethanol	49.5	86.9	41.3	**76.4**	59.0	59.5
Methanol	51.1	84.4	40.1	**72.5**	58.5	54.3
LPG	40.3	81.8	34.9	**70.1**	47.8	42.1

"We reported that CeO_2 (HSA) presents excellent reactivity compared to Ni catalysts but still less than that of noble metal (Rh) catalyst…" *

* N. Laosiripojana and S. Assabumrungrat, "Catalytic steam reforming of ethanol over high surface area CeO_2: The role of CeO_2 as an internal pre-reforming catalyst", *Applied Catalysis B: Environmental*, 66, (2006), 29-39

Influence of steam/ethanol ratio





The theoretical EMF and electrical efficiency of the SOFC-H^+ are superior to those of SOFC-$O^=$, the actual voltage and power density are much lower due to large resistance of the cell.

W. Jamsak et al, Chemical Engineering Journal 133 (2007) 187-194.

Steam reforming of ethanol

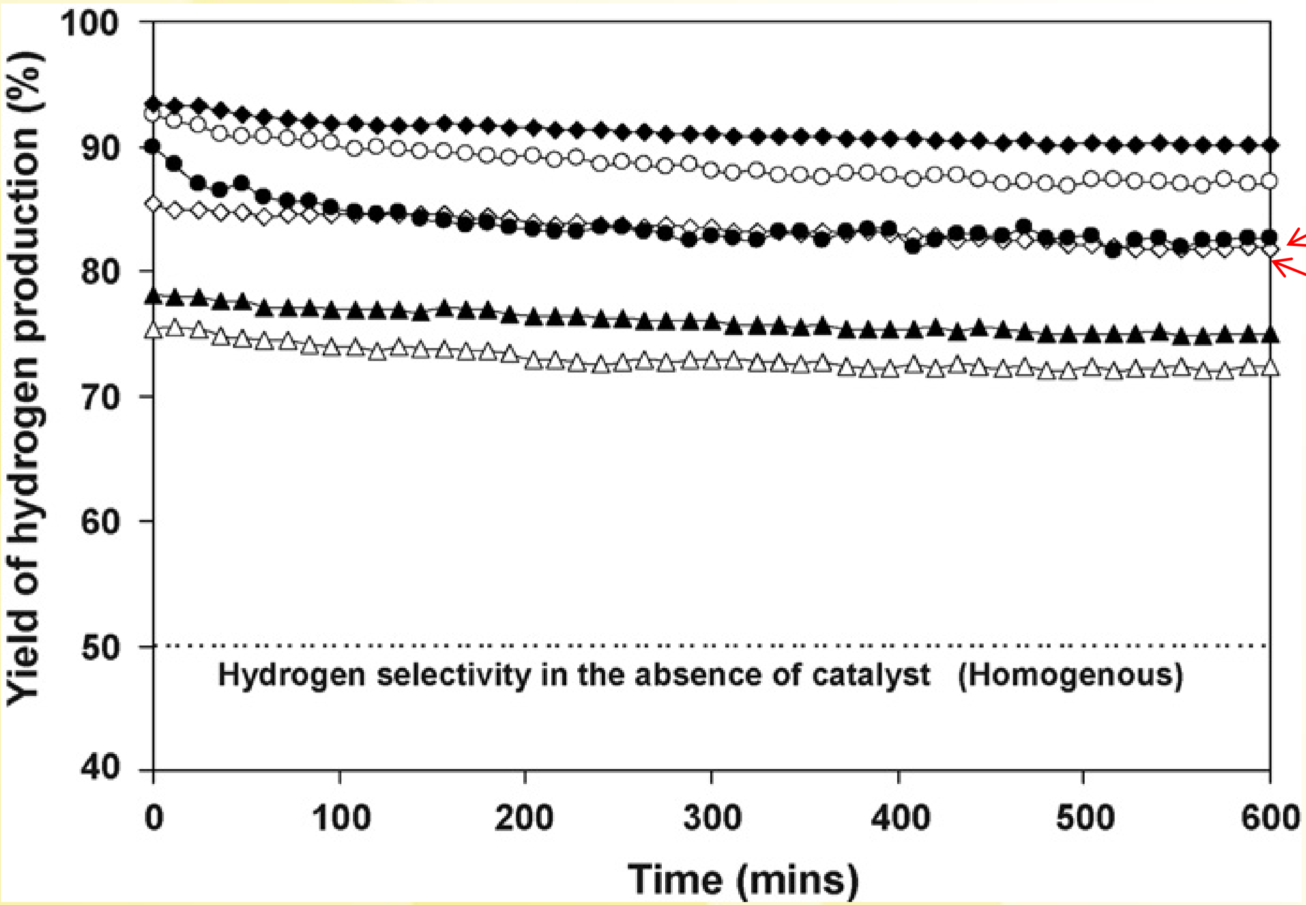
Catalyst	Temperature (°C)	Yield of H_2 production (%)	BET Surface area (m^2/g)	C formation (monolayers)
Ni/CeO_2 (HSA)	700 800 900 1000	67.3 78.3 82.5 86.9	24	1.79 1.35 1.08 0.82
Ni/CeO_2 (LSA)	700 800 900 1000	49.7 55.4 61.1 64.2	8.5	3.02 2.41 2.17 2.09
Ni/Al_2O_3	700 800 900 1000	48.1 51.9 57.2 59.8	40	4.97 4.63 4.52 4.22

Ethanol/steam ratio = 1/3

Significant amount of C_2H_4 and C_2H_6 were observed from Ni/CeO_2(LSA) and Ni/Al_2O_3

N. Laosiripojana et al, Applied Catalysis A: General 327 (2007) 180-188.

Steam reforming of ethanol with co-fed oxygen



Oxygen/ethanol ratio

0.4

0.2

0

0.6

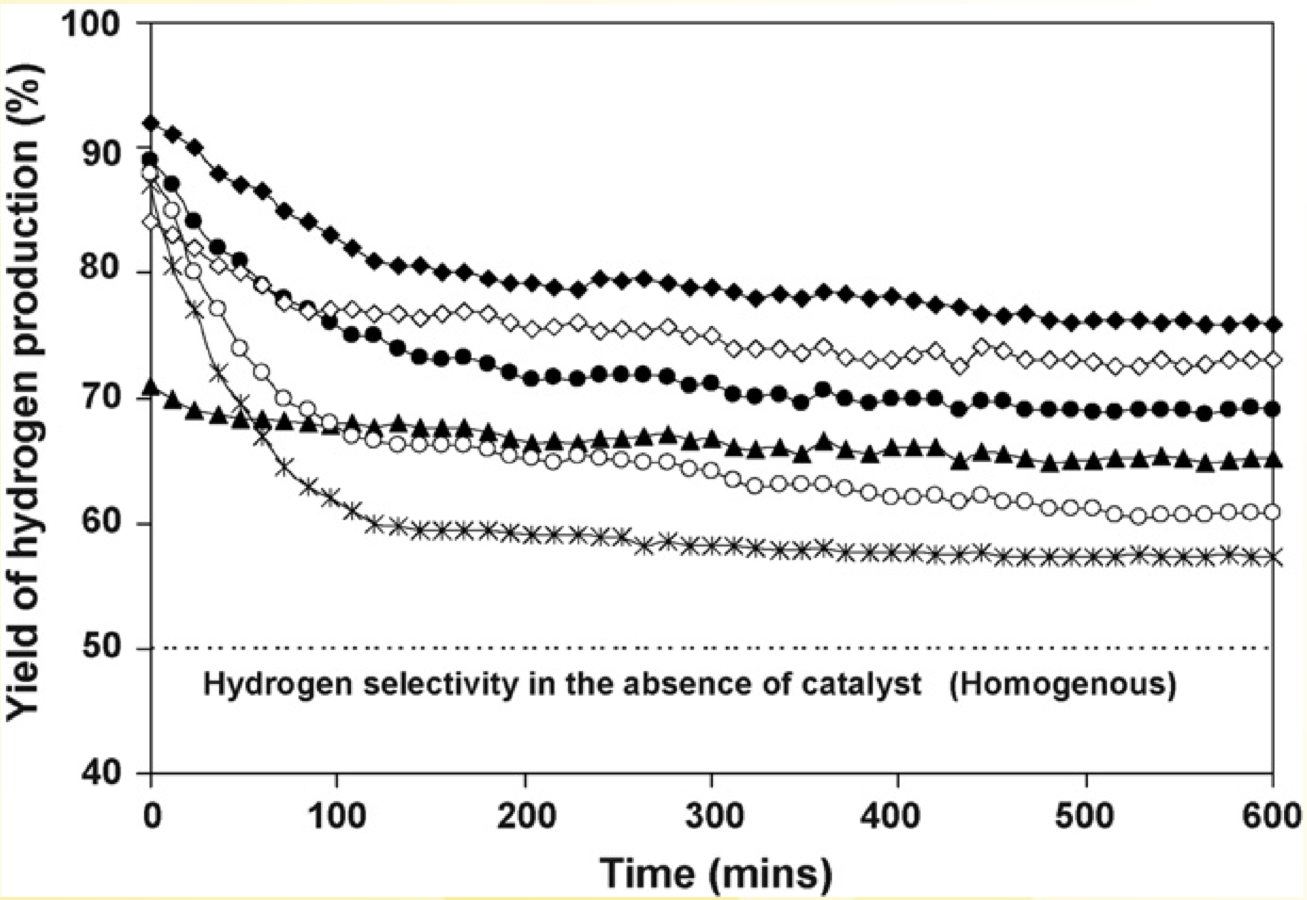
0.8

1.0

Autothermal reforming of ethanol at 900◦C for Ni/CeO_2 (HSA)

N. Laosiripojana et al, Applied Catalysis A: General 327 (2007) 180-188.

Steam reforming of ethanol with co-fed oxygen



Oxygen/ethanol ratio

0.6
0.8
0.4
1.0
0.2
0

Autothermal reforming of ethanol at 900◦C for Ni/Al_2O_3

N. Laosiripojana et al, Applied Catalysis A: General 327 (2007) 180-188.

Steam reforming of ethanol

Ni/CeO_2 (HSA) > Ni/CeO_2 (LSA) > Ni/Al_2O_3

Hydrogen yield increases with reforming temperature

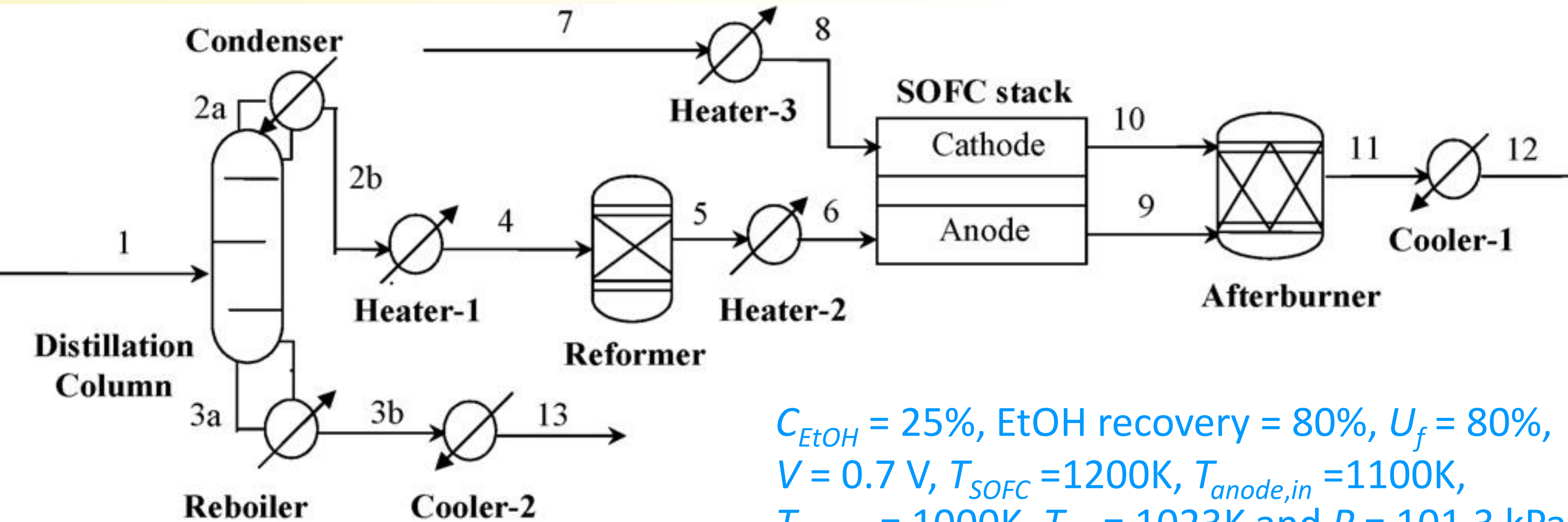
Coke formation is reduced when increasing reforming temperature

Great benefits of Ni/CeO_2 (HSA)
- Stability
- Reactivity towards ethanol reforming
- High resistance towards carbon deposition
- Good product selectivities (high redox property of CeO_2)

N. Laosiripojana et al, Applied Catalysis A: General 327 (2007) 180-188.

Bioethanol-fueled SOFC system

Distillation + SOFC

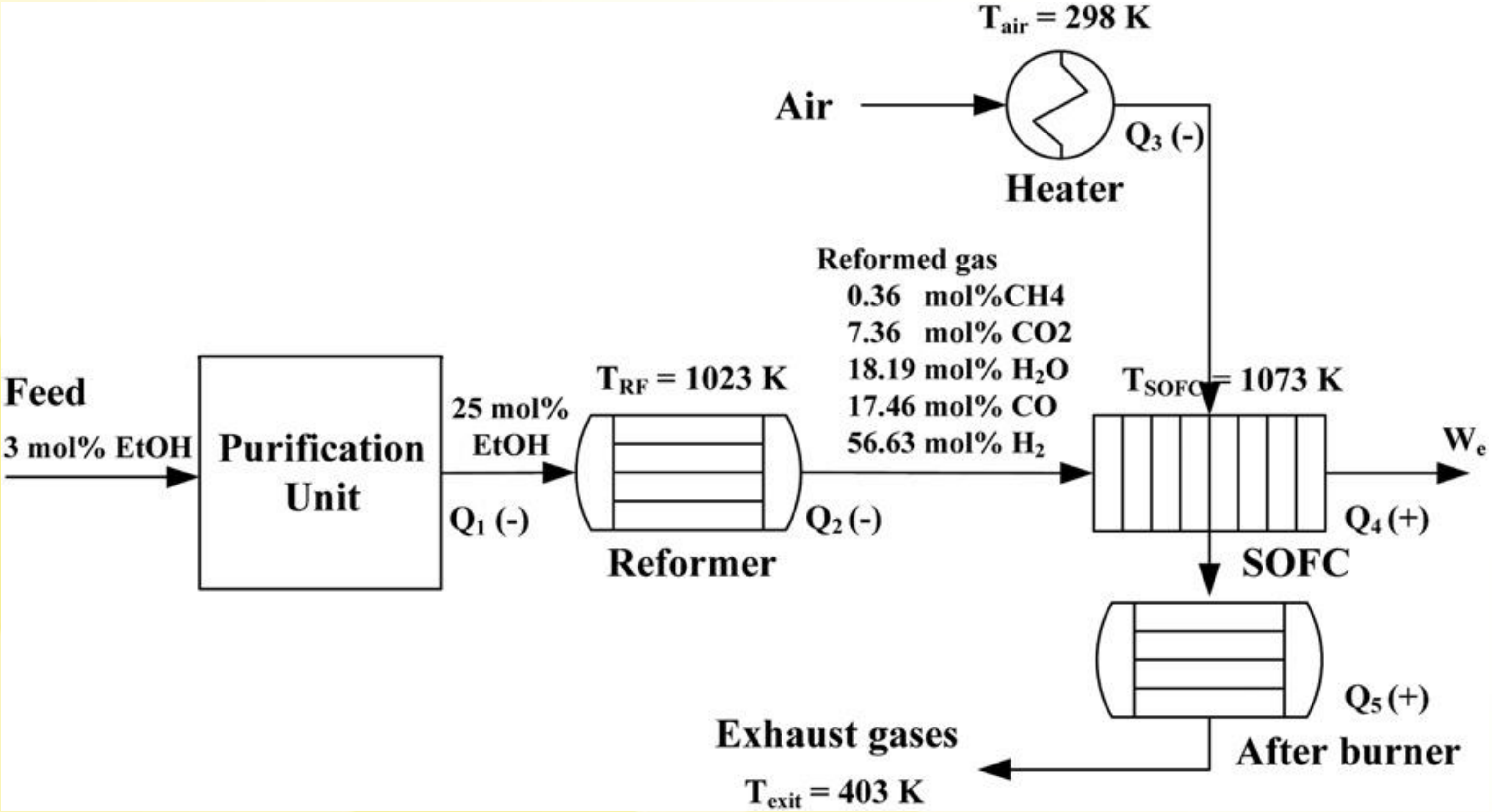


C_{EtOH} = 25%, EtOH recovery = 80%, U_f = 80%, V = 0.7 V, T_{SOFC} =1200K, $T_{anode,in}$ =1100K, $T_{cath,in}$ = 1000K, T_{RF} = 1023K and P = 101.3 kPa

- Utilization of condenser duty to preheat incoming bioethanol and cathode recirculation significantly reduce energy demand for reboiler and air heater
- Higher overall electrical efficiency and lower total cost index

W. Jamsak et al. J.Power Sources 187 (2009) 190-203

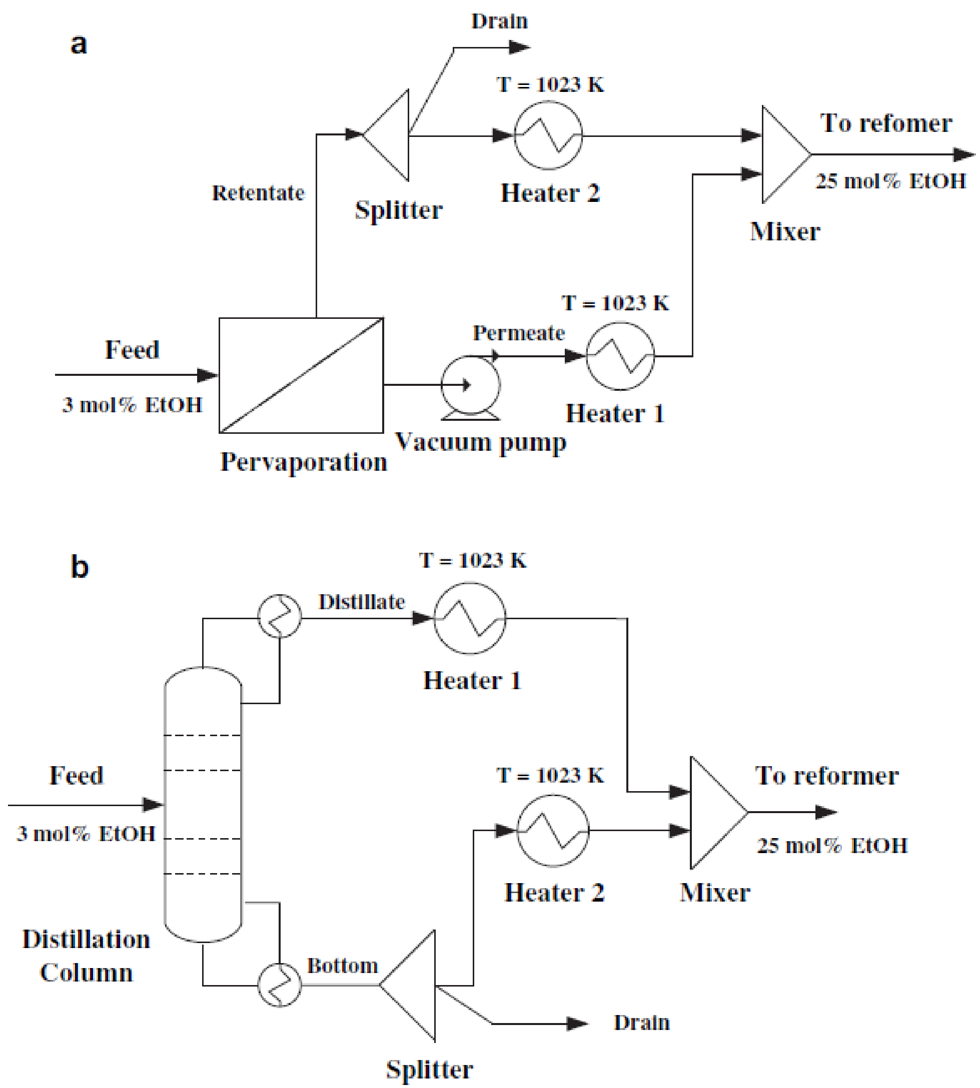
Bioethanol-fueled SOFC system



- Exhaust gases from stack combust in the afterburner.
- Heat released from SOFC (Q4) and afterburner (Q5) supplied to purification process (Q1), reformer (Q2) and air heater (Q3).

J. Choedkiatsakul et al, Inter J Hydrogen Energy 36 (2011) 5067-5075

Bioethanol-fueled SOFC system



- At thermally self-sufficient condition (Qnet = 0), this offers max electrical efficiency.

Distillation+SOFC,   =34%

Pervaporation+SOFC =42%

[low energy requirement due to moderate temperature and pressure operation]*

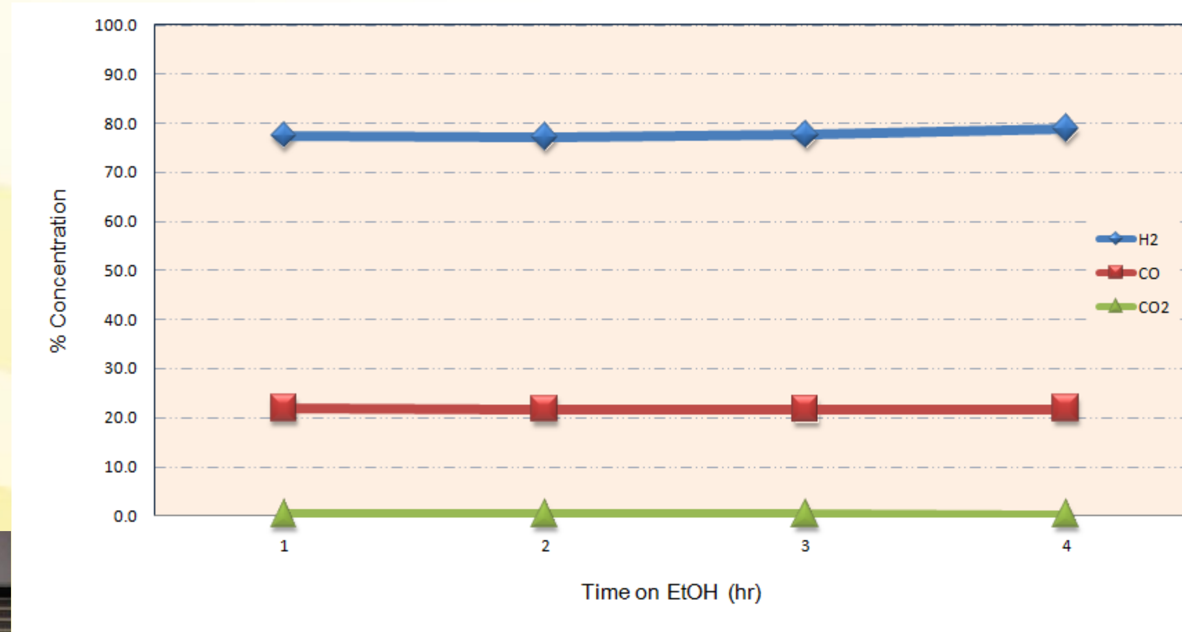
*ES Fernandez et al, Desalination 2010;250:1053-5

*F Lipnizki, Desalination 2010;250:1067-9

Choedkiatsakul et al, Inter J Hydrogen Energy 36 (2011) 5067-5075

Hydrogen production from ethanol

H_2 production reactor

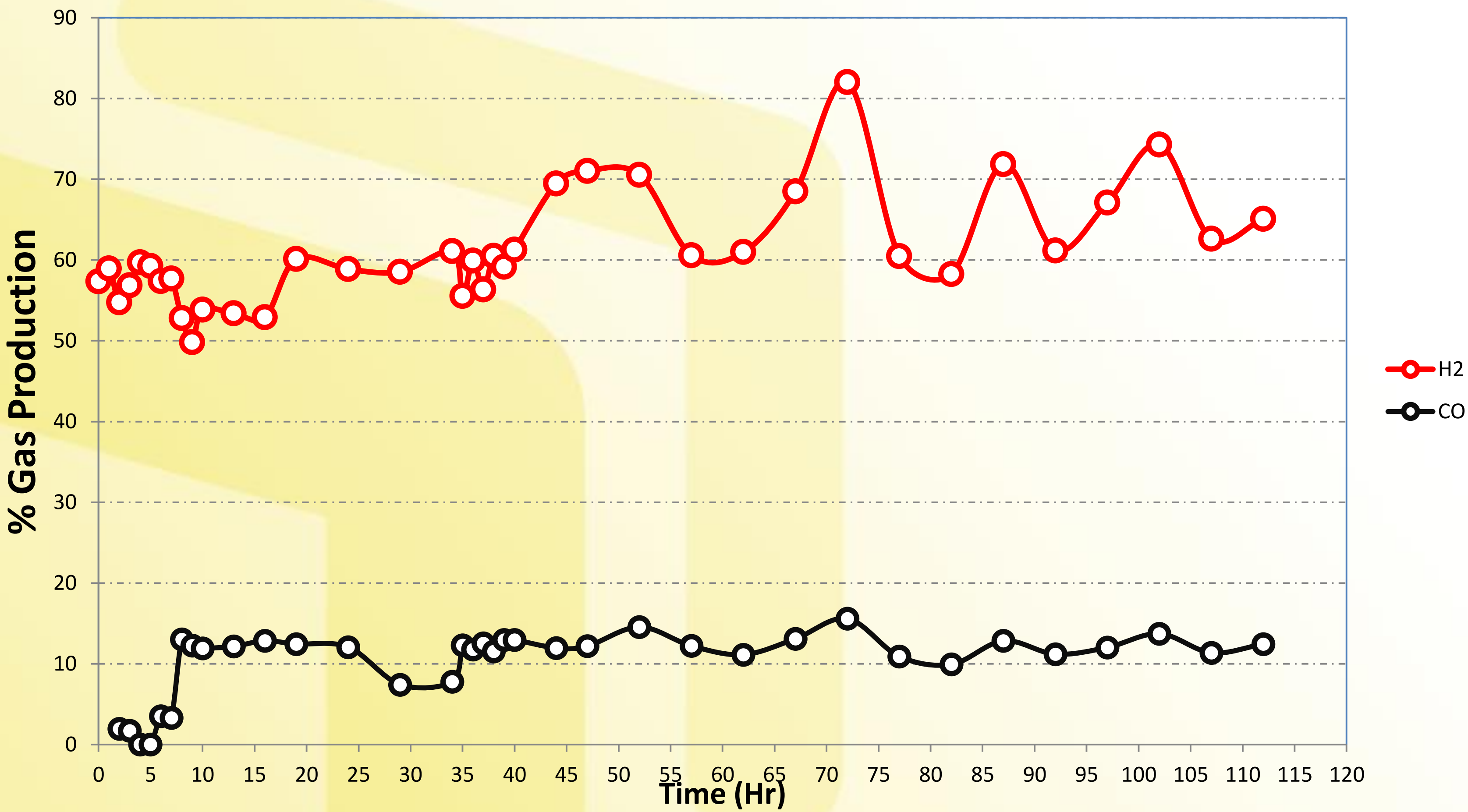


H_2 production at 20 l/min

ratio $H_2/CO_2+CO = 7/3$

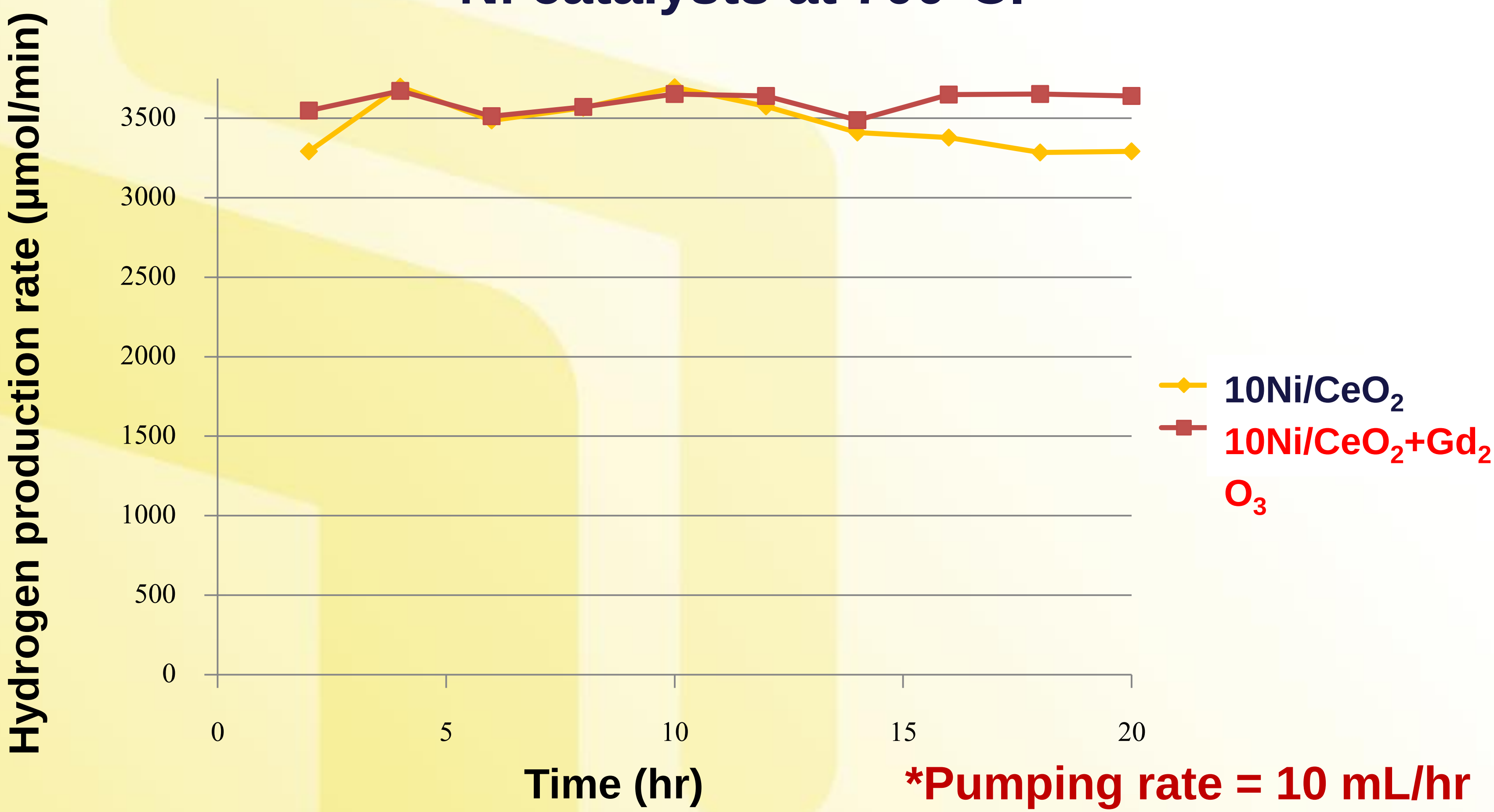
Hydrogen production from ethanol

Hydrogen Production For 1 kW SOFC



Stability of Catalyst

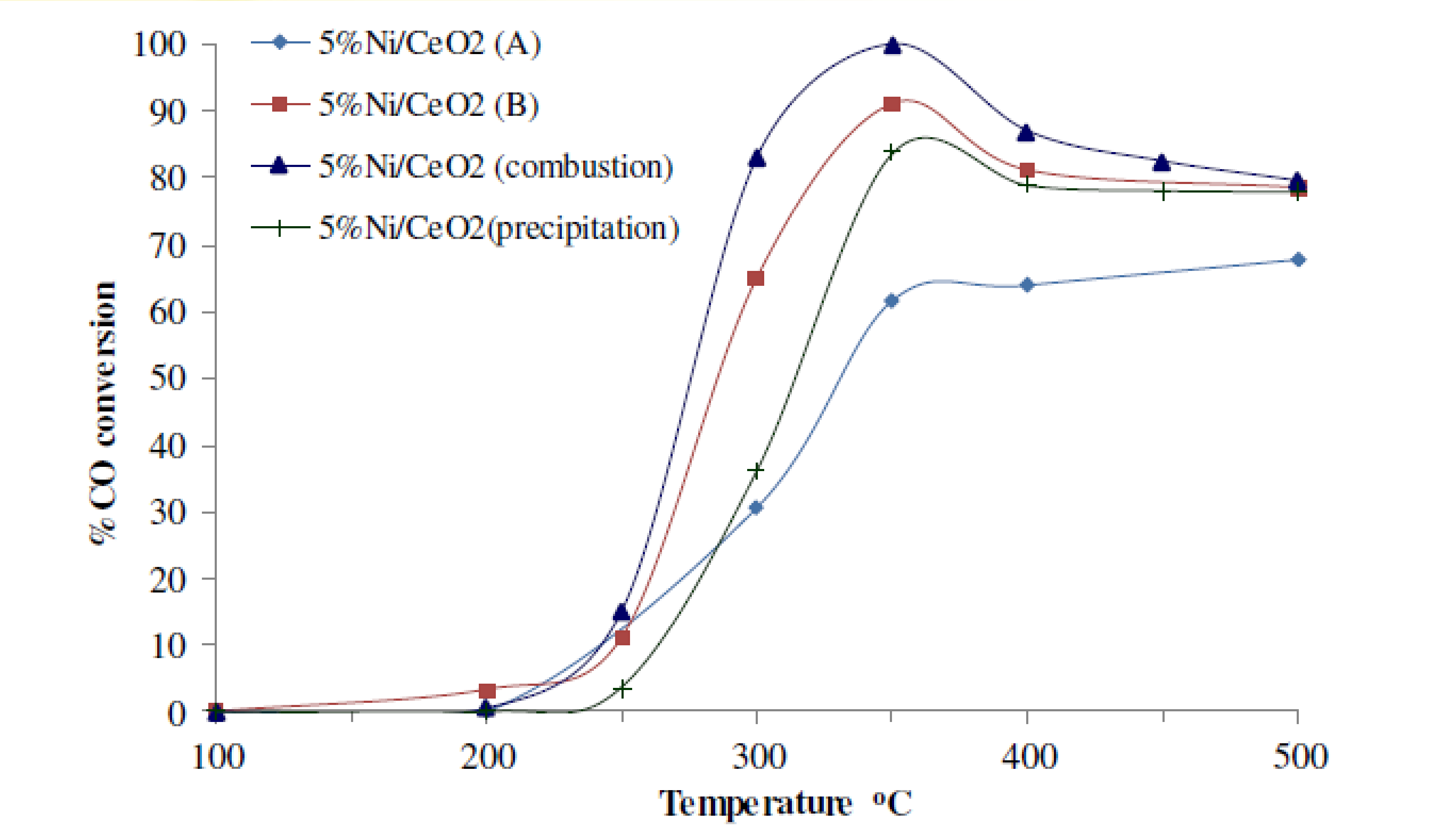
Hydrogen production from ethanol steam reforming over Ni catalysts at 700°C.



***Pumping rate = 10 mL/hr**

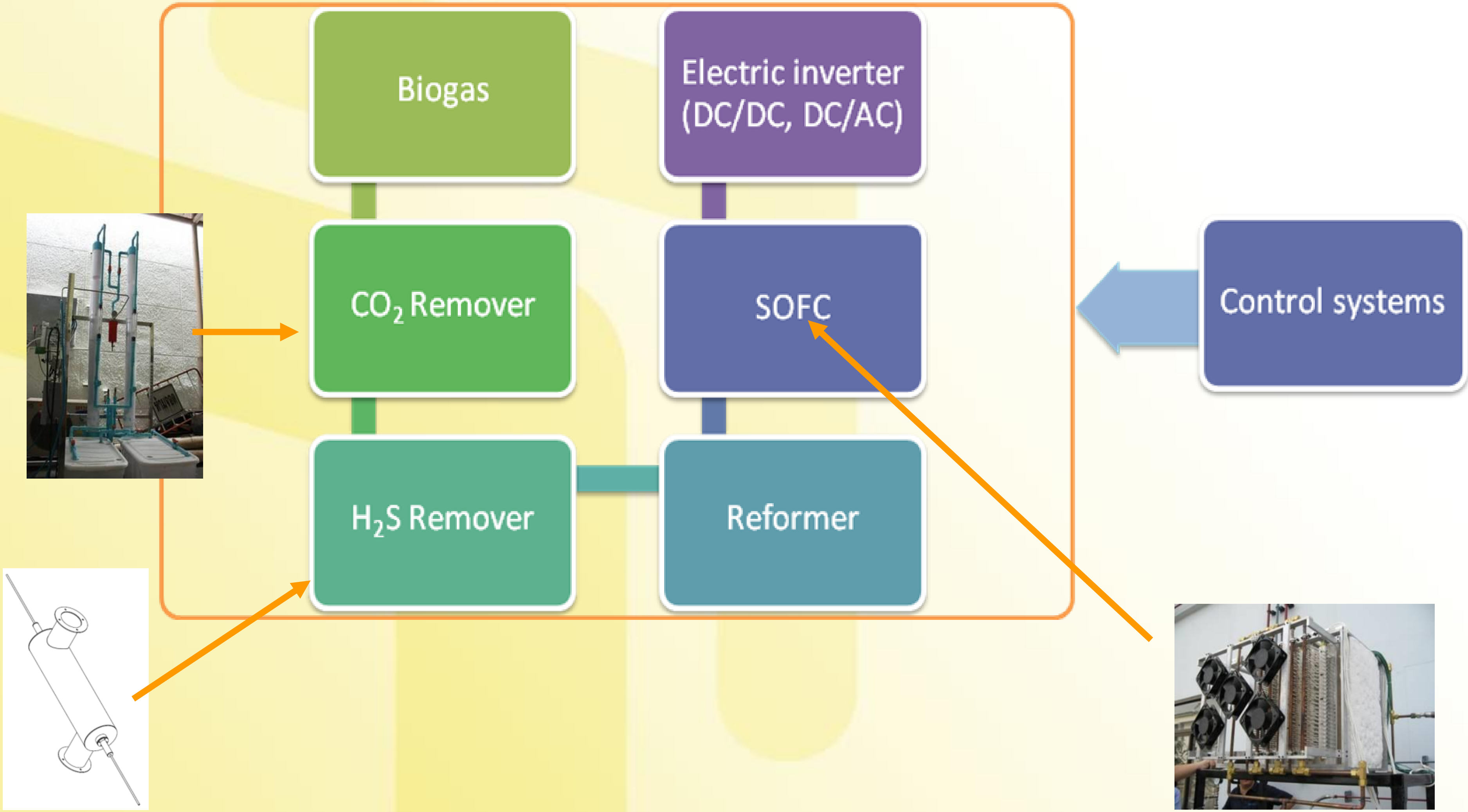
***20 mL/min N_2 carrier gas**

WGS catalytic activities
of Ni catalyst on various supports



P. Tepamatr et al, ECS Transactions, 68(1), 1207-1217, 2015

System Integration 1 kW SOFC using biogas as a fuel



Materials for Hydrogen production

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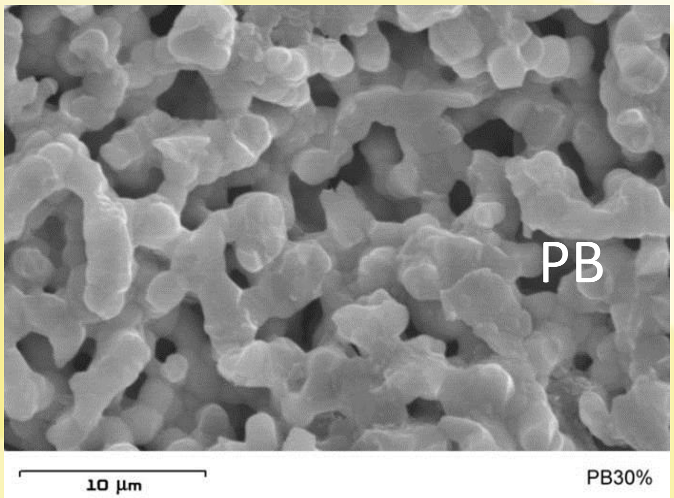
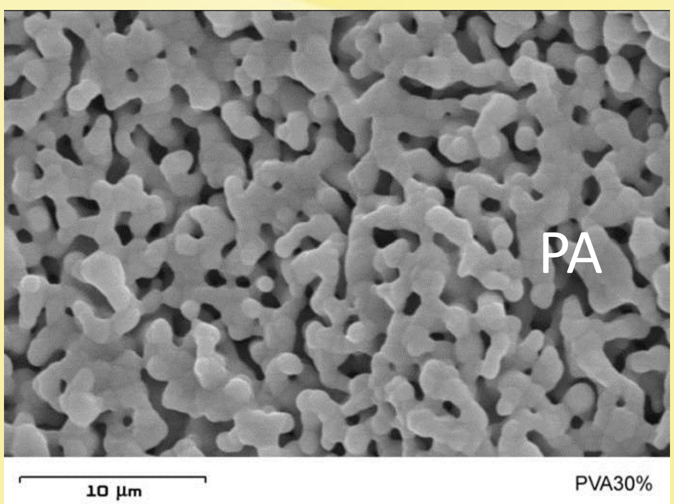
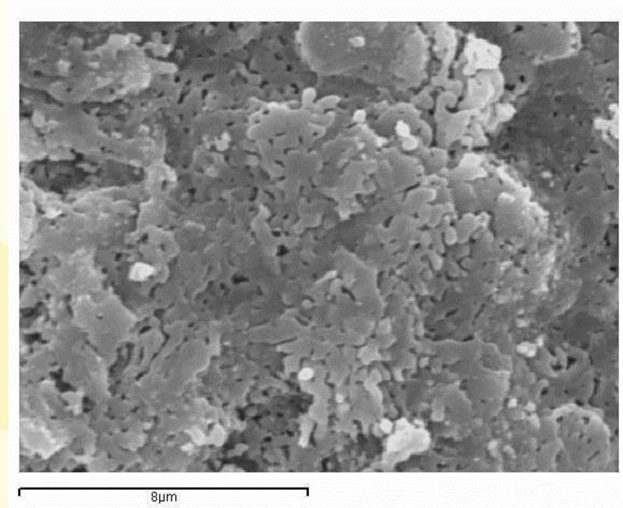
Porous catalyst support for H_2 production

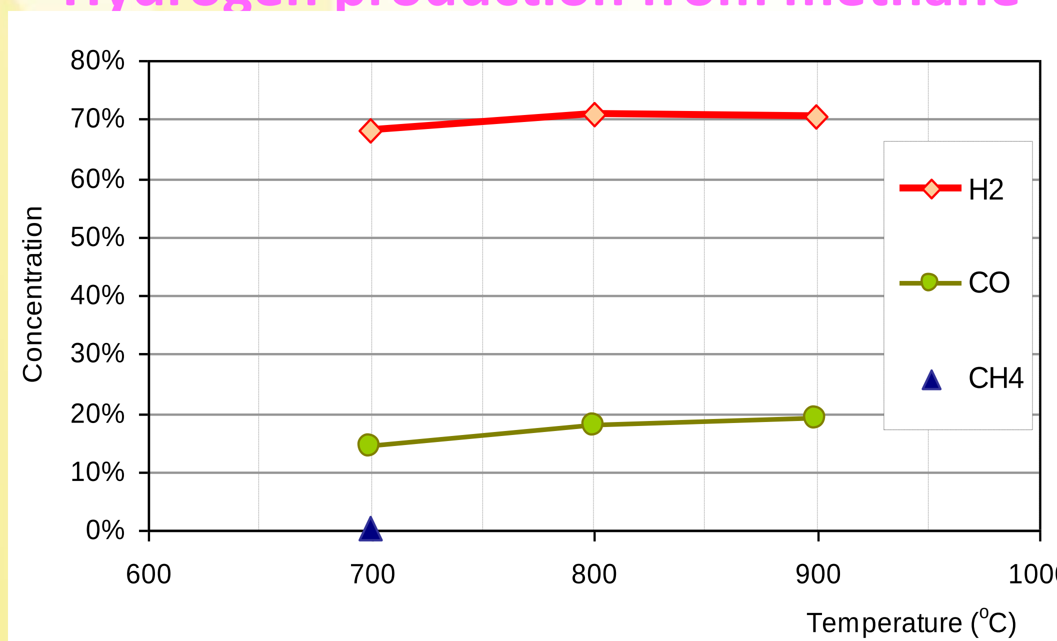




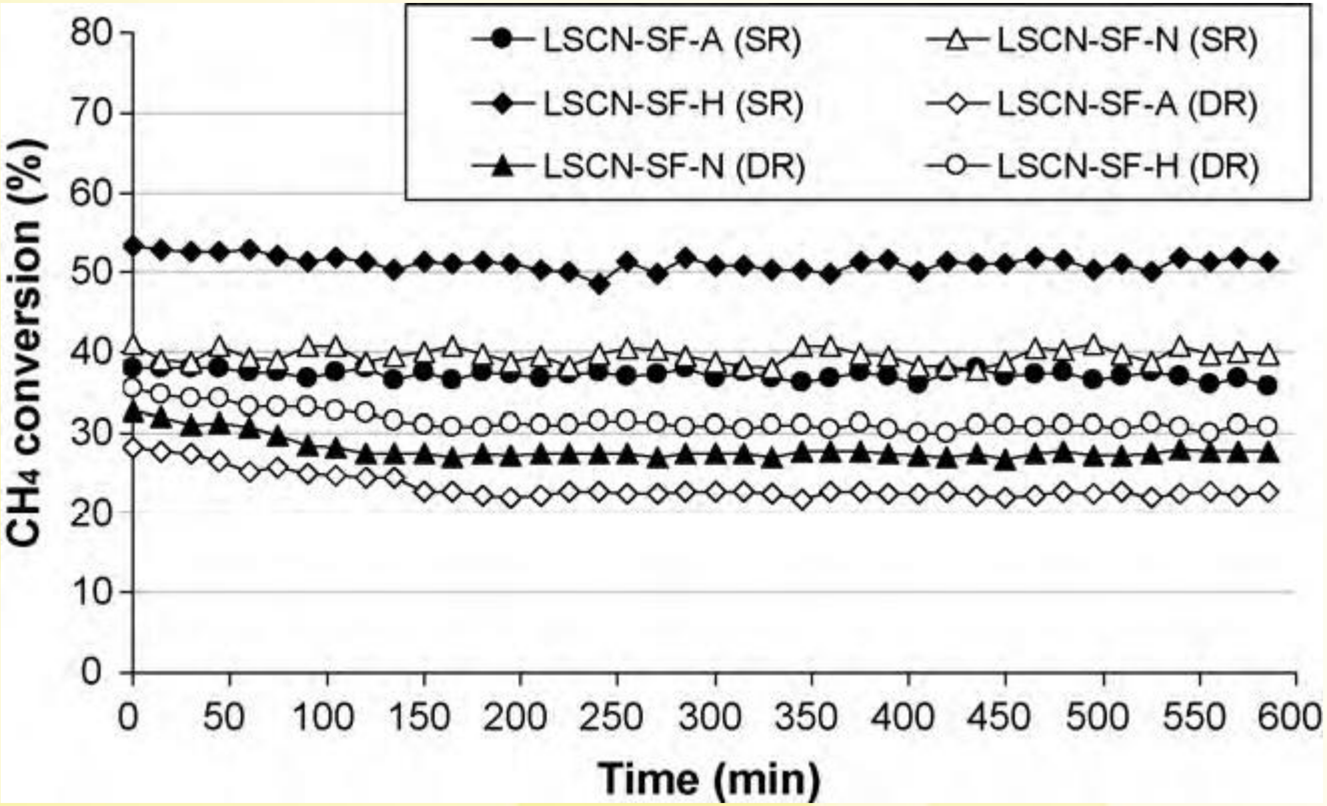


Ni/Al_2O_3 catalyst

Hydrogen production from methane



Reforming of CH_4



$La_{0.8}Sr_{0.2}Cr_{0.9}Ni_{0.1}O$

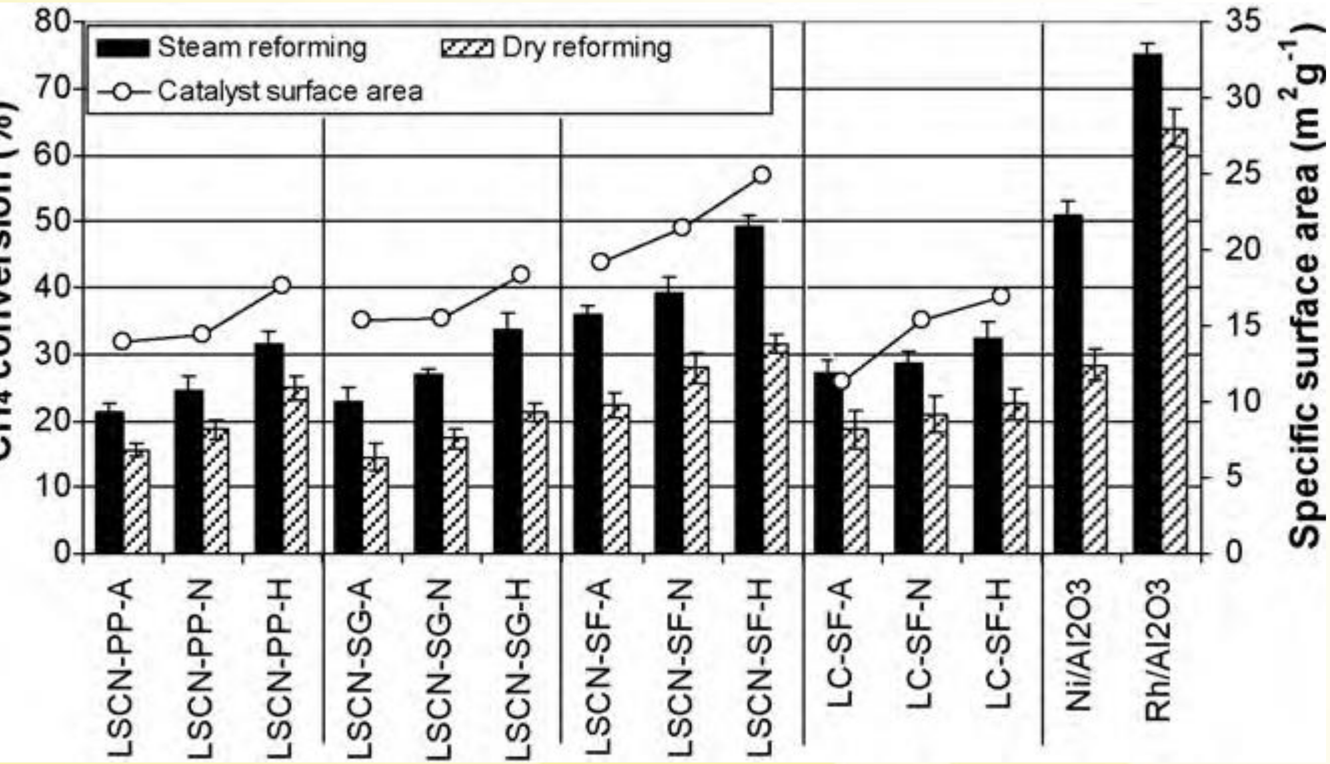
SR = steam reforming
DR = dry reforming
A = air calcination
H = hydrogen calcination
N = nitrogen calcination

At 900◦C
Molar ratio $H_2O/CH_4 = 1$
Molar ratio $CO_2/CH_4 = 1$

Steam reforming > dry reforming
Calcination in H_2 > N_2 > air

C. Chettapongsaphan et al, Applied Catalysis A: General 386 (2010) 194-200

Reforming of CH_4

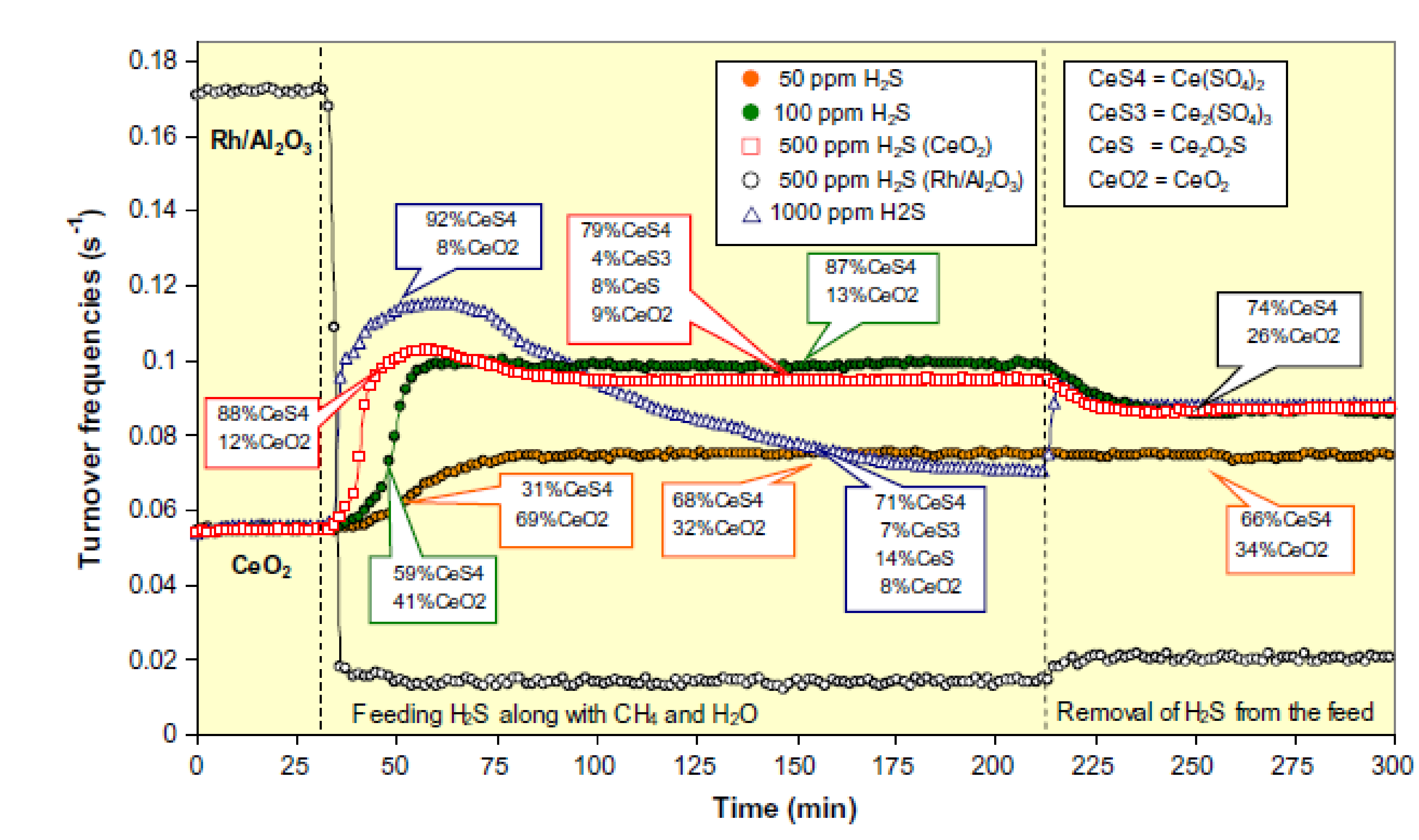


LSCN=$La_{0.8}Sr_{0.2}Cr_{0.9}Ni_{0.1}O_3$
LC = $LaCrO_3$
SR = steam reforming
DR = dry reforming
A = air calcination
H = hydrogen calcination
N = nitrogen calcination
PP=precipitation
SG=sol-gel
SF=surfactant assisted

Steam reforming > dry reforming, Calcination in H_2 > N_2 > air
Surfactant assisted > (sol-gel ~ precipitation)
Steam reforming LSCN-SF-H is comparable with Ni/Al_2O_3

C. Chettapongsaphan et al, Applied Catalysis A: General 386 (2010) 194-200

Advantages of H_2S over CeO_2 based

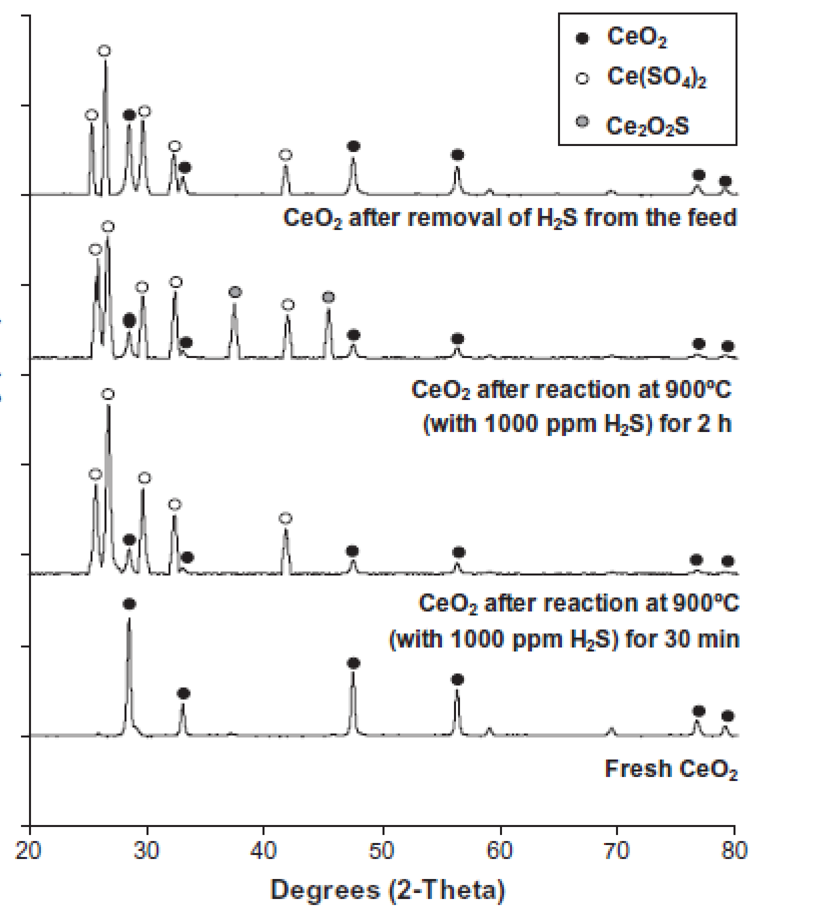


H_2S improves the turnover frequencies with CeO_2

H_2S forms rhodium sulfide which is rarely regenerated.

J. Laosiripojana et al. J. Catalysis 276 (2010) 6-15

Advantages of H_2S over CeO_2 based



$$2CeO_2+8H_2O+3H_2S \leftrightarrow Ce_2(SO_4)_3+11H_2$$

$$Ce_2(SO_4)_3+4H_2O+H_2S \leftrightarrow 2Ce(SO_4)_2+5H_2$$

$$2CeO_2+H_2+H_2S \leftrightarrow Ce_2O_2S+2H_2O$$

Formation of $Ce(SO_4)_2$ promotes the oxygen storage capacity, lattice oxygen mobility and hence reforming activity BUT Ce_2O_2S reduces both properties and lowers the reforming rate.

N. Laosiripojana et al. J. Catalysis 276 (2010) 6-15

Conclusions

- Both ethanol and biogas are feasible to produce hydrogen
- Available resources
- Additional criteria must be considered (supply chain, logistic cost and policy)

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