Research on the reforming of ethanol

LAMNET Workshop, Brasilia, Dec. 2 - 4, 2002

Fraunhofer Institut Solare Energiesysteme

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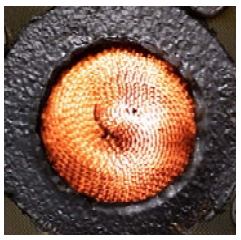
CH_3CH_2OH

H_2O



H_2-rich gas

Introduction

- regenerative energy sources for hydrogen fuel cells
- motivation for ethanol as fuel

Reforming of fossil fuels

- allothermal reforming
- partial oxidation
- autothermal reforming

European Project: bioethanol reforming

- reformer and shift conversion device
- burner development
- catalyst screening

Summary, Outlook

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Introduction

regenerative energy sources for hydrogen fuel cells

regenerative power sources:

until now neglegible market penetration

1. Electrolysis of water with electricity from regenerative sources like
- windenergy
- hydropower
- solar energy

bio-ethanol
- can be reformed most „easily“
- is economically attractive (see following slides)

⇒motivation for ethanol

2. Reforming of biogenic (CO_2-neutral) fuels
- solid biomass (wood, wood pellets)
- biogas
- pyrolysis oil
- biogenic ethanol

Introduction:

motivation for ethanol as fuel - economic potential

potential contribution of ethanol to energy supply is significant

Preliminary estimation of worldwide market penetration:

550 million tons per year in the transport sector (20 % of present consumption)

500 million tons per year for co-generation capacity (10 % of present capacity)

several hundred million tons per year in the domestic market

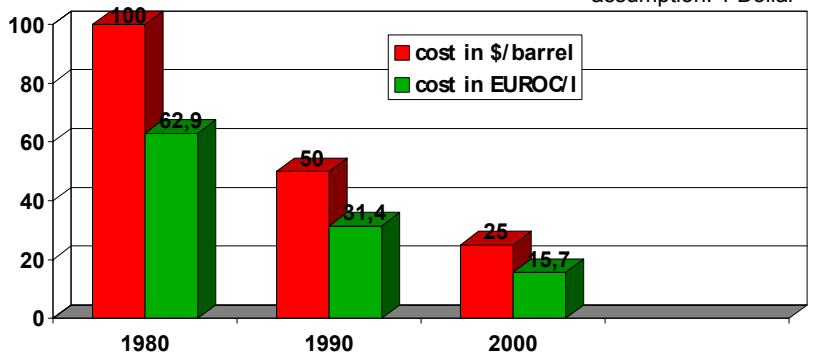
200 million tons per year for the chemicals market

Source: Guiliano Grassi, “Bioethanol - Industrial world perspectives” in Renewable Energy World, May-June 2000, p. 86 - 97

Introduction: Motivation for ethanol as fuel

1 Barrel = 159 liter
assumption: 1 Dollar = 1 Euro

Cost reduction potential: the Brazilian example



Source: José Goldberg in "Tagungsband zur Veranstaltung Biotreibstoffe", 22. Juni 1999, Rüschlikon, Switzerland

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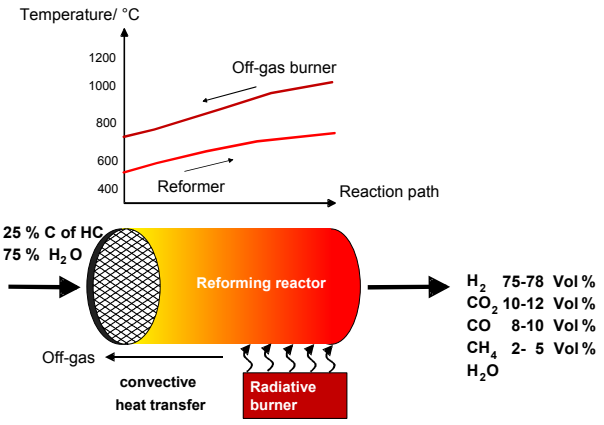
Reforming of fossil fuels

allothermal reforming

heat is transferred via a burner, special burner design required

high hydrogen content of the reformate



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Reforming of fossil fuels

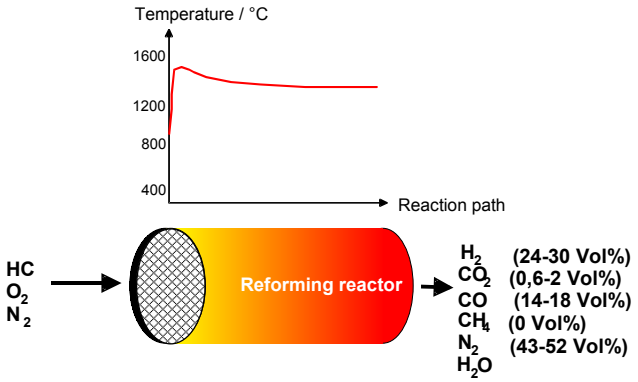
partial oxidation

without catalyst
at 1300 °C - 1400 °C

good dynamic behaviour

simple construction

lowest hydrogen content



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Reforming of Ethanol, LAMNET-Workshop, Brasilia

Reforming of fossil fuels

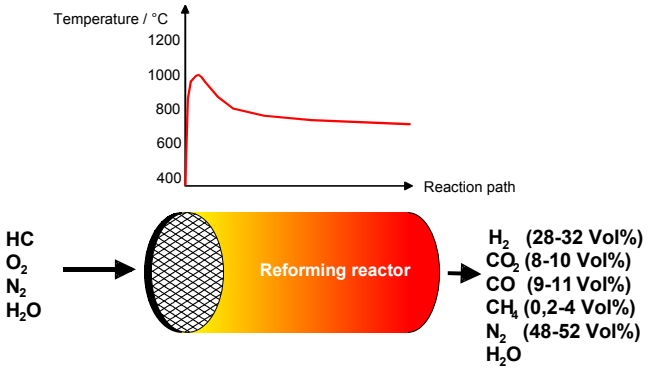
autothermal reforming

heat is released in the
catalyst bed

quick start-up

good dynamic behaviour

temperature peak at
the reactor inlet



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Reforming of fossil fuels

steam reforming of alcohols, general equation	$C_nH_{2n+1}OH + (2n-1)\,H_2O \Leftrightarrow 3n\,H_2 + n\,CO_2$	
steam reforming of ethanol	$C_2H_5OH + 3H_2O \Leftrightarrow 6\,H_2 + 2\,CO_2$	Δ_RH = 173,5 kJ/mol
endothermal cracking of ethanol	$C_2H_5OH + H_2O \Leftrightarrow 4\,H_2 + 2\,CO$	Δ_RH = 255,9 kJ/mol
exothermal CO-conversion	$CO + H_2O \Leftrightarrow H_2 + CO_2$	Δ_RH = -41,2 kJ/mol

Bioethanol as fuel for fuel cell vehicles and small scale stationary applications JOR3-CT97-0174

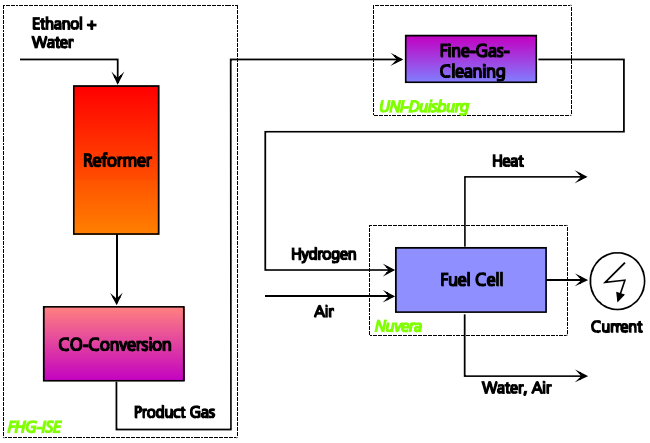
Partnership:

Fraunhofer ISE	Reforming of bioethanol, CO-conversion Co-ordination
Universtity of Duisburg	Fine purification by PSA
Nuvera	Fuel cell requirements, implementation and dissemination of the results

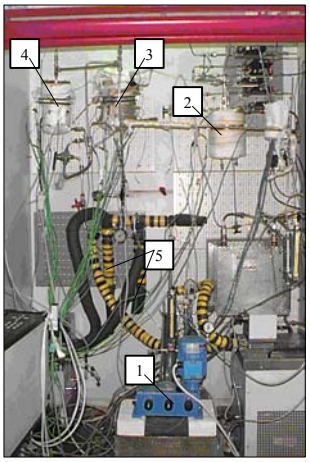
Summary of results: May, 2001

European project: bioethanol reforming

Reformer- PEM fuel cell system with ethanol as fuel

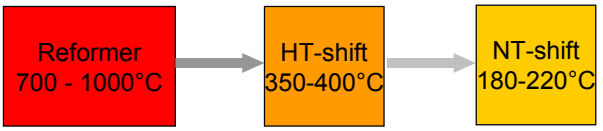


European project: bioethanol reforming



Reformer und CO-conversion device at Fraunhofer ISE

1. Water/ethanol pump
2. Reformer
3. HT-shift reactor
4. NT-shift reactor
5. Gas cooling heat exchanger



European project: bioethanol reforming

Experimental set-up:

Reformer:

Height: 150 mm

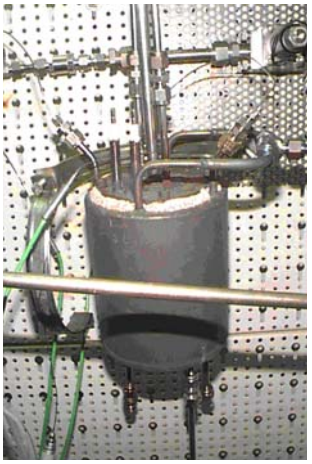
Diameter: 121 mm

Catalyst Volume: 600 cm^3

Burner:

Height: 150 mm

Diameter: 81 mm



European project: bioethanol reforming

advantages of the porous burner

high effective heat conduction of the pore material
(60 - 100 higher then the effective heat conduction of gas)

⇒ large combustion reaction zone
(flame burner reaction zone thickness 1 mm)
⇒ lower temperature in the reaction zone
⇒ homogeneous temperature profile
⇒ lower NO_x- and CO-emission

high flame velocity in the pore medium without flame instability
(8 - 10 higher then a flame burner)

⇒ large performance modulation range 1:20 (flame combustion 1:3)

European project: bioethanol reforming

catalyst screening

name	composition	sign.	operation range
nickel-cat.	nickel on Al_2O_3	Ni	$t_{reaction} < 800$
ruthenium-cat.	ruthenium on Al_2O_3	Ru	$t_{reaction} < 800$
platinum –cat.	platinum on Al_2O_3	Pt	$t_{reaction} < 800$
palladium –cat.	palladium on Al_2O_3	Pd	$t_{reaction} < 800$
Perovskite-cat.	lanthanum, manganese, cobalt, strontium	Pe	$t_{reaction} < 800$
nickel-platinum-cat.	nickel; platinum on Al_2O_3	PtNi	$t_{reaction} < 800$
nickel-palladium-cat.	nickel; palladium on Al_2O_3	NiPd	$t_{reaktion} < 800$

investigation parameters

Temperature: 600; 700; 800 °C

steam to carbon ratio: 2; 3; 4

pressure: 2; 5; 9 bar

gas hourly space velocity: 2000 - 6500 $sl_{educts}/(l_{cat}$ h)

European project: bioethanol reforming

operation parameters of the Fraunhofer ISE-Reformer

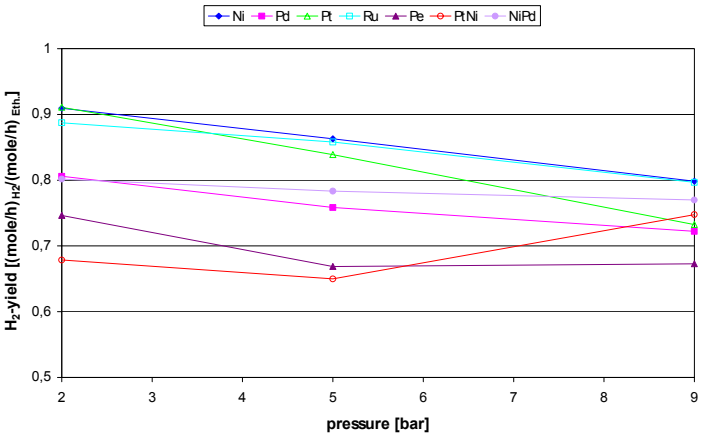
Operation load	**38**	**115**	**[%]**
Porous burner temperature	910	1100	[°C]
Temperature of the fixed catalyst bed	720 - 800	390 - 880	[°C]
Pressure	7,3	7,3	[bar]
S/C ratio	4	4	$[mole_{H2O}/atom_C]$
Reformer ethanol inlet stream	3,45	10,36	[mole/h]
Enthalpy stream of the ethanol	1,19	3,57	[kW]
Product gas stream	42,89	128,9	[mole/h]
Hydrogen stream of the product gas	14,90	44,63	[mole/h]
Enthalpy stream hydrogen reformer	1,00	3,00	[kW]
Burner hydrogen stream	7,5	22	$[l_N/min]$
Enthalpy stream hydrogen burner	1,35	3,96	[kW]
Burner exhaust stream	23,7	64,3	$[l_N/min]$

European project: bioethanol reforming

catalyst screening

T = 700 °C
S/C = 4

⇒ selection of Ni-catalyst



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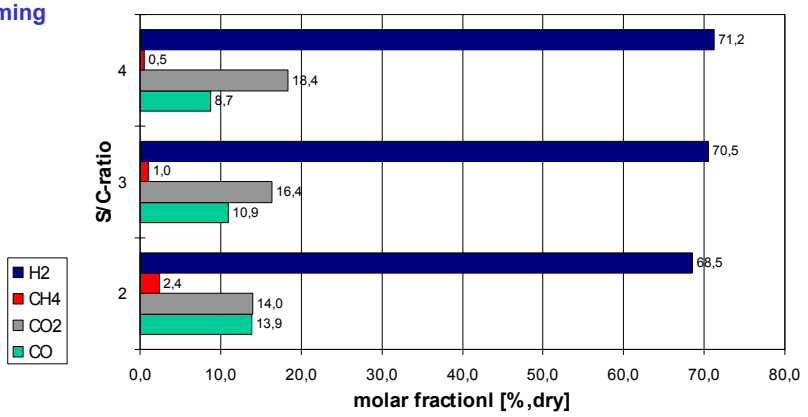
European project: bioethanol reforming

Ni catalyst

T = 700 °C
p = 2 bar

influence of S/C



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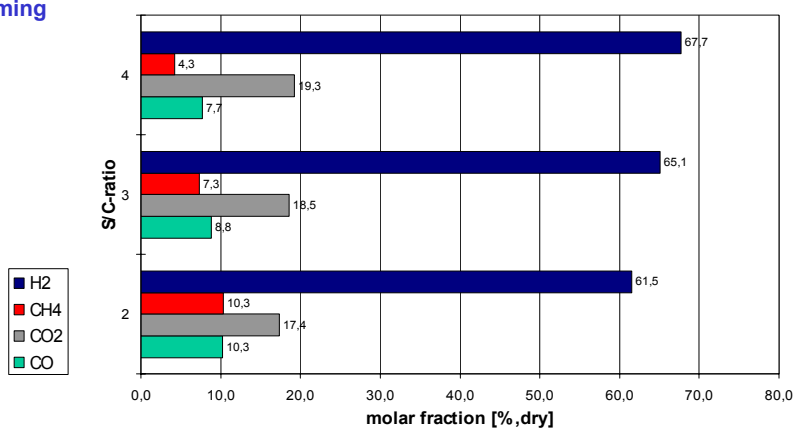
European project:
bioethanol reforming

Ni catalyst

T = 700 °C
p = 9 bar

influence of S/C

higher pressure
due to PSA



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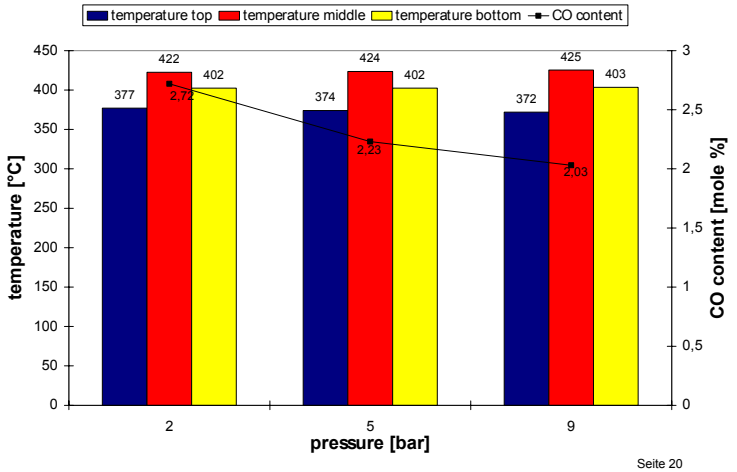
Reforming of Ethanol, LAMNET-Workshop, Brasilia

European project:
bioethanol reforming

HTS

Fe-oxide-catalyst
GHSV = 4000/h
S/C = 4



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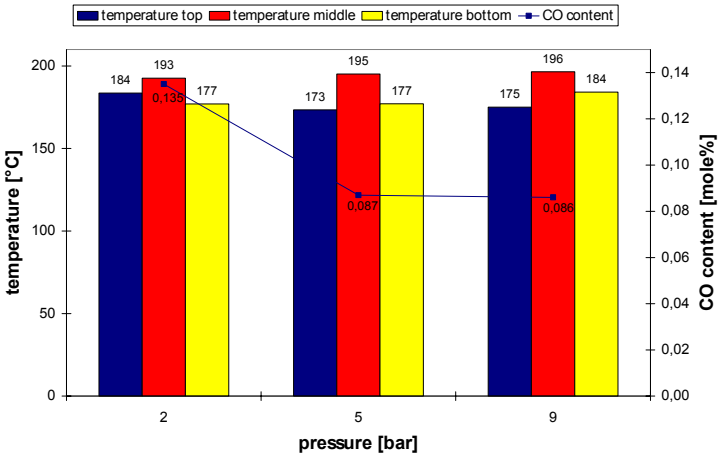
European project:
bioethanol reforming

LTS

Cu/Zn-catalyst
GHSV = 4000/h
S/C = 4



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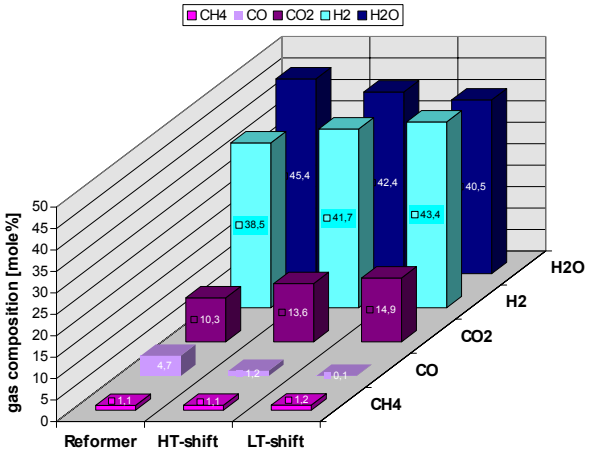
European project:
bioethanol reforming

Results of reformer and CO-shift device

S/C = 4
p = 9 bar

With CO fine purification:
Reformate suitable for PEM- fuel cell



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Summary

Hydrogen generation from biogenic ethanol is attractive due to
- good availability,
- competitive costs,
- „easy“ realisation of reforming process

European project: bioethanol reforming Summary

Research of bioethanol reforming at Fraunhofer ISE:

- development of a compact steam reformer with preheating of liquid reformer feedstream (with burner exhaust gas) and of the air for the burner (with the reformer product gas)

- development of a porous burner with stable combustion for offgas, methane, or ethanol

- optimisation of heat losses and performance

Outlook:

- reduction of volume and weight of the reforming unit
- reduction of start-up time
- further improvement of performance
- cost reduction
- longtime-operation to show catalyst stability

Outlook

5 kW Fuel processor unit for stationary electricity generation

Source: Nuvera Fuel Cells Europe, Milan, methanol reformer

Thank you very much for your attention!

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