

Fuels for SOFC systems

From feedstock to power using High-temperature fuel cells – part I

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2nd Joint European Summer School for Fuel Cell and Hydrogen Technology



Today

- Fuels and sustainable development
- Renewables and distributed generation
- The pathway from fuel to SOFC power
- Landfill and anaerobic digestion
- Gasification
- Gas clean-up
- Reforming basics
- Liquid fuels
- SOFC performance on alternative fuels

Sustainable development

"Sustainable development is development that meets the needs of the present without compromising the ability of future generations to meet their own needs".

> Brundtland Report, World Commission on Environment and Development (WCED) -1987

A global mission



A global mission

World population, 1950-2050





MBDOE: Millions of Barrels per Day; 1 MBDOE = 50 Million ton/year

Source: Exxon Mobil, IEA

A global mission

Fossil fuel Reserves (readily recoverable) vs Resources (recoverable in future?), 2008

Fuel type	Reserves in Gtoe	R/P ratio in years	Resources in Gtoe
Crude oil	184	46	91
Natural gas	166	63	216
Total conventional hydrocarbons	350)	307
Oil sands and extra heavy oil	39		190
Oil shale	-		119
Non-conventional natural gas	4		2469
Total non-conv. hydrocarbons	43		2778
Anthracite & bituminous coal	356		9225
Sub-bituminous coal & lignite	218		1175
Total coal	574	119	10 400
Uranium ^a	17		139
Thorium ^a	22		24
Total Nuclear	39	I	163
Fossil fuels total	~1000		~13 500

^a Assuming 1 t of Uranium (or Thorium) to yield $0.5 \text{ PJ} \approx 12 \text{ Mtoe}$ (not considering nuclear breeder technology)

Gtoe: Billions of tons of oil equivalent = $41.9 \times 10^{18} \text{ J} = 42 \text{ EJ}$

Sources: various, averaged

A global mission





A global mission



High-temperature fuel cells (SOFC & MCFC) maximize utilization of hydrocarbons

Sustainable consumption of fossil fuels:

Rate of production = Rate of consumption

Rate of production: Reserves/accumulation time

accumulation time: 70 My (Carboniferous period: 360-290 Mya)

Sustainable rate of consumption per head of population: ...?

Current rate of consumption: ca. 1.5 toe/head.y

From squandering reserves to earning your deserves



From squandering reserves to earning your deserves



From squandering reserves to earning your deserves

Realistically... It is a question of CONCENTRATION Renewable energy sources are DILUTE: average incoming solar radiation: 0.355 kW/m² Suzuki Swift (0.57m² drag area): 60 kW... ≈ 100 kW/m²



From squandering reserves to earning your deserves



From squandering reserves to earning your deserves



Source: IEA Bioenergy 2009

From squandering reserves to earning your deserves

World Biomass potential 2050

Biomass category	Technical potential in 2050 (EJ/yr)
Energy crop production on surplus agricultural land	0 - 700
Energy crop production on marginal land	<60 - 100
Agricultural residues	15 - 70
residues	30 - 150
Dung	5 - 55
Organic wastes	5 - 50 +
Total	<50 - >1,100

Note that bioenergy from macro- and micro-algae is not included owing to its early stage of development

From squandering reserves to earning your deserves



Fuel vs. food?

- Increased CO₂ levels will increase yields
- Temperature rise will change areas of production



- Maximize production per unit land
 - Multi-use crops, biorefinery
 - Increase biomass yield/quality
- Exploit marginal lands (contaminated, poor soils)



Fuel vs. food?

kg/person/vear	1969/71	1979/1981	1989/91	1999/01	2030	2050
Cereals (food)a	148.7	160.1	171	165.4	165	162
Roots and tubers	83.7	73.4	64.5	69.4	75	75
Sugar (raw sugar equiv)	22.4	23.4	23.3	23.6	26	27
Pulses, dry	7.6	6.5	6.2	5.9	6	6
Vegetable oils (oil Equiv)	6.8	8.3	10.3	12	16	17
Meat	26.1	29.5	33	37.4	47	52
Milk and diary	75.3	76.5	76.9	78.3	92	100
Otherb	216	224	241	289	325	340
Total ^b	2411	2549	2704	2789	3040	3130

World food consumption

Food footprint

	Food group	Food	CO2-
		roou	Emissions
			(g/kg food)
		Beef	13'300
		Raw sausages	8'000
	Meat and sausages	Ham (pork)	4'800
		Poeltry	3'500
		Pork	3'250
		Butter	23'800
		Hard cheese	8'500
		Cream	7'600
	Milk- and dairy	Eggs	1'950
		Quark (curd)	1'950
	products	Farmer cheese	1'950
		Margarine	1'350
		Yogurt	1'250
		Milk	950
	Fruits	Apples	550
		Strawberries	300
	Baked	Brown bread	750
	goods	White bread	650

b kcal/person/day

a includes grain equivalent of beer and corn sweeteners

From squandering reserves to earning your deserves



Primary energy & electricity production from municipal solid waste (MSW)

Italy (2009):

- 180 Mtoe primary energy
- 18 Mtoe renewables (inc. hydro)
- 0.9 Mtoe from MSW
- 22 Mtoe biogas potential from residues

6,144: Primary energy production from renewable municipal solid waste in the EU, 2007 (ktoe). 13,962: Gross electricity production from renewable municipal solid waste in the EU, 2007 (GWh).

Source: EurObserv'ER 2009



WASTE

Chemical and refinery refuse flows

Medical and farmaceutical waste

Industrial waste & by-products

Municipa Solid Waste (MSW)

Sewage sludge and wastewater

Animal oils, fat and manure

Agricultural and forestry residues

Dedicated energy crops

Again: these energy sources are DILUTE...

 \rightarrow How to maximize their yield?

BIOMASS

Spread the risk, spread the profit



Centralized System

- Large quantities, large losses
- One-directional flow
- Precarious equilibrium

Spread the risk, spread the profit



Distributed system



Spread the risk, spread the profit

- Local sources and productivity
- Small quantities, high efficiencies
- Webbed flow
- Diffused equilibrium

Distributed system



Spread the risk, spread the profit



Spread the risk, spread the profit

To make the most of a dilute source, capillarity of the channels of exchange is required

Biforcating, fractal systems: Local resources & distributed generation

Spread the risk, spread the profit





Gaseous fuels



Gaseous fuels



Landfill Anaerobic digestion Gasification Breakdown of organic Anaerobic fermentation Thermal breakdown of of organic fraction of compounds with selected (lignocellul.) compounds dumped waste and volatilisation bacteria T: 20-30℃ T: 30-70℃ T: 700-1200℃ Yield: 0,2-0,5 m³/kgVS Yield: 2-6 m³/kg Yield: variable Product gas: Product gas: Product gas: Medium: Air Steam CH_4 CH₄ CH_{4} 50-70% 40-45% 1-5% 1-10% CO_2 35-40% CO_2 30-40% CO_2 10-20% 10-20% N_2 H_2 H_2 10-20% 0-1% 10-20% 30-50% N_2 10-20% 25-45% 0-10% CO

N₂ 50-60% ~0

Landfill

Anaerobic digestion

Gasification



Landfill

Landfill or storage of MSW is still the predominant treatment method in Europe (41% in 2008, from 62% in 1995), followed by recycling and composting (40%) and incineration (19%).

(New) landfill sites are prohibited in EU since 2007.



In 2006 the landfill gas production in the EU was 3.1 Gtoe

Anaerobic digestion

Breakdown of organic compounds by selected bacteria


Breakdown of organic compounds by selected bacteria

3. Acetogenesis: VFA are converted to acetic acid CH₃COOH.

 $\begin{array}{l} \mathsf{CH}_3\mathsf{CH}_2\mathsf{COOH}+2\:\mathsf{H}_2\mathsf{O}\to\mathsf{CH}_3\mathsf{COOH}+\\ \mathsf{CO}_2+3\:\mathsf{H}_2\\ \mathsf{CH}_3\mathsf{CH}_2\mathsf{CH}_2\mathsf{COOH}+2\:\mathsf{H}_2\mathsf{O}\to 2\\ \mathsf{CH}_3\mathsf{COOH}+2\:\mathsf{H}_2\\ \mathsf{CH}_3\mathsf{COOH}+2\:\mathsf{H}_2\\ \mathsf{CH}_3\mathsf{CH}_2\mathsf{OH}+\mathsf{H}_2\mathsf{O}\to\mathsf{CH}_3\mathsf{COOH}+2\:\mathsf{H}_2 \end{array}$

4. Methanogenesis: acetic acid and hydrogen are converted to methane

POLYMERS Proteins, polysaccharides, lipids (i) Hydrolysis а MONOMERS & OLIGOMERS amino acids, sugars, fatty acids (ii) Fermentation а INTERMEDIATES Propionate, butyrate, alcohols b (iii) Acetogenesis ACETATE H2 + CO2 (iv) Methanogenesis CH₄ + CO₂ TRENDS in Biotechnology

 $\begin{array}{l} \textbf{4} \ \textbf{H_2} + \textbf{CO}_2 \rightarrow \textbf{CH}_4 + 2 \ \textbf{H}_2\textbf{O} \\ \textbf{CH}_3\textbf{COOH} \rightarrow \textbf{CH}_4 + \textbf{CO}_2 \end{array}$



Breakdown of organic compounds by selected bacteria



In Europe

- Over 4000 biogas plants on manure: Germany (over 3500), Austria, Denmark, Italy, Switzerland, Sweden
- Circa 1600 plants for waste water treatment
- Circa 450 landfill gas exploitation plants
- Over 400 plants on industrial waste flows
- Circa 130 plants on organic fraction of MSW



Manure-fed biogas plants in EU



In Europe

Co-digestion of different substrates is recommendable:

- stabilizes seasonal variability of feedstocк
- dilutes inhibiting compounds which can predominate in a certain substrate
- improves plant flexibility and pay-back time
- but increases plant complexity
- Circa 130 plants on organic fraction of MSW



Manure-fed biogas plants in EU



Thermal breakdown of lignine compounds and volatilisation



Thermal breakdown of lignine compounds and volatilisation



Gasification: maximization of chemical energy in an easy-to-handle carrier

Thermal breakdown of lignine compounds and volatilisation



Reactor types

Fluidized bed reactor types



	Fixed bed	Fluid bed
Scale (MWe)	0.1 – 10	1 — 50
Granulometry (mm)	10 - 100	0 - 20
Temperature (ºC)	800 - 1400	750 - 900
Start-up time	Minutes	Hours

In the world

Country	Capacity (MWth)	Technology	Location	Note
Austria	8	TUV FICFB CHP demonstration	Güssing	2.0 MWe + 4.5 Wth Heat, 50 t/day of wood chips from forestry
	2	Down-draft CHP at demonstration	Wr. Neustadt	0.5 MWe + 0.7 MWth Heat, 12 tons/day of wood chips from forestry
Denmark	5	VØlund up-draft CHP demonstration	HarbØre	1.5 MWe + 2 MWth Heating
	0.7	Viking 2-stage gasification and power generation	Lyngby	Electrical efficiency could exceed 35%
	3.125 and 0.833 (Japan)	TKEnergi 3-stage, gasification process demonstration	Gjøl	Two gasifiers were designed at a cost of € 3.1 million (Denmark) and € 1 million (Japan) and the thermal efficiencies are 56% and 60 while the electrical efficiencies are estimated to be 32 and 24%, respectively
	30	Carbona Renugas fluidized bed CHP demonstration	Skive	5.5 MWe, and 11.5 MWth district heat
Finland	4–5	Bioneer up-draft gasifiers	8 in Finland and one in Sweden	In operation for over 20 years
	60 (50-86)	Foster Wheeler Energy CFB co-firing plant	Lahti (Ruien, Belgium)	The Foster Wheeler Energy Oy has developed CFBG process that was successfully
	40	Foster Wheeler Energy fluidized bed metal recovery gasifier	Varkaus	deployed at a paper mill in Pietersaari and for co-firing at Lahti and a BFB gasifier for aluminium and energy recovery in Varkaus. A completely new, 160 MWth CFB BMG plant is now in the design phase
	7	NOVEL Updraft demonstration	Kokemäki	This CHP facility employs low-temperature waste heat from the plant to dry wood fuels to about 20% moisture. The design power output is 1.8 MWe and the district heat output is 4.3 MWth (3.1 MWth without boiler). The overall investment cost is € 4.5–5 million

In the world

Country	Capacity (MWth)	Technology	Location	Note
Germany	130	Commercial waste to methanol plant (Fixed bed + Pressurized entrained flow)	Schwarze Pumpe	The largest renewable waste gasification plant in the world has been built and operated for nearly 20 years. Feed materials is waste mix brown coal
	100	Lurgi CFB gasifier firing cement kiln	Rüdersdorf	The successful Lurgi CFBGs are the 100 MWth waste gasification plant to fire cement kilns
	0.5	Fraunhofer Umsicht CFB pilot plant	Oberhausen	Based on tests conducted at feed rates of 70–120 kg/h of wood and for over 1,600 h, developments are underway to build a 1–5 MWth CHP and a 5 MWth demonstration BMG plant
	1	CHOREN Carbo-V 2-stage entrained pilot plant	Freiberg	The resulting tar-free synthesis gas from the 1 MWth capacity pilot plant tests has been converted to fuels by F-T and methanol synthesis
	3–5	Future Energy pyrolysis/ entrained flow GSP gasifier	Freiberg	It produces a tar- and CH ₄ -free raw gas, with C-conversion > 99%, at very short residence times (seconds) and at high throughput rates
Italy	15	TPS CFB RDF plant	Greve in Chianti	TPS Termiska Processer of Sweden has built the first large scale TPS CFB plants in Greve, in the Chianti district. The plant has operated intermittently with RDF pellets and it is currently shutdown with an indefinite future.
	0.5;1.2	ENEA CFBG pilot plant	Trisaia	Described in Chap. 4

(continued)

In the world

Country	Capacity (MWth)	Technology	Location	Note
Netherlands	85	AMER/Essent/Lurgi CFB gasification co-firing plant	Geertruidenberg	Feedstock for this plant is demolition wood and the resulting fuel gas is co-fired in a 600 MWe pulverised coal boiler
	250 (35 MWe from biomass)	Biomass co-gasification Shell entrained coal gasification plat	Willem-Alexander Centrale	The biomass materials included sewage sludge, chicken manure, wood
	3	CFBG Plan	Tzum	The leading small-scale gasification system supplier in Netherlands, HoST also has built a 3 MWth chicken litter gasifier in Tzum NL, which is currently being commissioned
		Several pilot plants at ECN	Petten	Torrefaction, a 5 kg/h allothermal gasifier, testing and evaluation of the TREC granular bed filter, development of lab- scale integrated BMG system for SNG production, and the OLGA gas clean-up process which has recently completed 700 h of operation during a long-duration test at 0.5 MWth scale
New Zealand	2	Page Macrae updraft BMG plant	Tauranga	Page MaCrae Engineering Ltd is operating a 2 MWth commercial, updraft co-firing BMG plant, using the wood residues generated in a plywood mill to supply heat for manufacturing plywood. Based on the same technology, Page MaCrae is planning to manufacture an 8 MWth BMG plant

(continued)

In the world

Country	Capacity (MWth)	Technology	Location	Note
Sweden	30 20	Bioneer up-draft BMG plant Foster Wheeler Energy CFBG Foster Wheeler Energy CFBG	Karlsborg paper mill Norrsundet paper mill	Some of the early biomass gasification plants were built in Sweden. The 20 MWth FWE/Ahlstrom CFB plant at Norrsundet and the 30 MWth plant at Karlsborg are still in operation
	30	Gotaverken CFBG	Södracell paper mill	Fuelled by bark and wood wastes
	18	Bioflow/Sydkraft/Foster Wheeler Energy CHP demonstration at	Värnamo	The most significant technical accomplishment in biomass gasification is the successful demonstration of the pressurized, CFB Bioflow BMG in Värnamo, supplied by Ahlstrom/FWE and Sydkraft. The 18 MWth capacity plant was operated at 18 bar pressure. The raw gases were cleaned without condensation employing candle filters and successfully combusted in a closely integrated Typhoon gas turbine to generate 6 MWe and 9 MWth heat for district heating
Switzerland	0.2	Pyroforce down draft BMG system	Spiez (scale-up to 1 MWe plant in Austria)	The plant employs a Pyroforce gasifier, based on the KHD (Kloeckner Humbolt Deutz) high temperature gasification process and a dry gas cleaning system
UK	100 KWe	Rural Generation downdraft BMG system	Northern Ireland	The 100 kWe Brook hall plant has exceeded 15,000 h of operation
	Up to 250 KWe	Biomass Engineering Ltd., down draft BMG CHP systems	Northern Ireland	Biomass Engineering continues progress with manufacturing six small (250 kWe) commercial CHP units while three other units are in operation or commissioning

(continued)

In the world

Source: E4Tech (2009)

Country	Capacity (MWth)	Technology	Location	Note
	Up to 300 KWe	Exus Energy down draft BMG CHP systems	Northern Ireland	BEDZED a 100 kWe CHP installation has completed 5000 h of operation in total, but problems have been reported recently. A 300 kWe CHP plant is to be installed in a limekiln operation. The Blackwater Valley plant will be a redesigned for a 200 kWe CHP plant. The company is reportedly restructuring and the status of these projects is unclear at this time
	7 MWe	Charlton Energy rotary kiln waste gasification	Gloucestershire	A 7 MWe, rotary kiln gasifier CHP plant is operating in Gloucestershire. The plant will include Eco-tran equipment, reciprocating engines and it will use agricultural and forestry biomass as feed materials. Support comes from Capital Grant plus Renewable Obligation. Revenues will be derived from heat sale to nearby sawmill for drying wood
	2 MWe	Compact Power two-stage waste gasification plant	Bristol	This plant has completed three years of commercial operation on wastes with excellent emissions performance
USA	Up to 120	Primenergy gasification/ combustion systems	6 in USA and 1 in Italy	1 plant at Tulsa (Oklahoma), feed material: various, 3 plants at Stuttgart (Arkansas) feed material: ricehusks, a at Rossano,
	Up to 22 KWe	Community Power Corporation small modular down-draft gasification systems		22 kWe gasification gas engine system has been demonstrated at Aliminos in the Philippines with coconut shells. 15 Similar units were also tested and being demonstrated in the USA for a variety of heating applications
		FERCo SilvaGas dual CFBG Process RENUGAS fluidized bed BMG Process FERCo SilvaGas dual CFBG Process		The notable biomass gasification processes that have been scaled up to near commercial scale and operated with varying degrees of success are the Battelle/FERCO dual CFB SilvaGas process and the Renugas [®] Process,

The pathway from fuel to SOFC power

Landfill

Easy gas extraction and operation

Anaerobic digestion

Established process Improved fertilizer yield Efficient at any scale

Gasification

Large source flexibility High product gas yield @ high temperature

Negative visual and odorous impact Large potential for GHG emissions Low gas yield

Careful monitoring of conditions (esp. in co-digestion) Low-temperature/-HV product gas

Difficult to operate Convenient at medium-large scale

The pathway from fuel to SOFC power

Multifuel possibilities

Clean power

SOFC fuel requirements

Contaminant	FC Tolerance	Effects	Cleaning method	
Sulphides:		Electrode deactivation	Methanol washing (T < -50°C)	
H_2S , COS, CS ₂	0.1-10 ppm	Reaction w electrolyte	Carbon beds (T < 0° C)	
			Scrubber (T < 100°C)	
			ZnO/CuO adsorption (T < 300°C)	
			High-T CeO ads. (T > 700°C)	
Halides:	0.1-1 ppm	Corrosion	Alumina or bicarbonate	
HCI, HF		Reaction w electrolyte	Activated carbon	
Siloxanes:	10-100 ppm	Silicate deposits	Ice absorption (T = -30° C)	
HDMS, D5			Graphite sieves	
NH ₃	1%	Reaction w electrolyte to	Catalytic cracking	
		form NO _x	Bag filter as NH ₄ Cl	
		(Fuel at low conc.)		
Particulates	10-100 ppm	Deposition, plugging	Cyclone + bag/ceramic filter	
			Electrostatic precipitator	
Tars	2000 ppm	C deposition	Catalytic cracking T > 1000°C	
Heavy metals:	1-20 ppm	Deposition	Bag/ceramic filter	
As, Pb, Zn, Cd, Hg		Reaction w electrolyte	Electrostatic precipitator	

 \hookrightarrow Exact limit ? ... f(operating conditions)

SOFC fuel requirements

H₂S effects compared with other CHP technologies:

Conversion Tech.	Tolorance	Effects	Operational implications
SOFC	0.1-10 ppm	Electrode deactivation	Interruption for electrode regeneration
		Reaction w electrolyte to	Stack replacement
		form SO ₂	
Internal Combustion	100-1000	Lubricant contamination	Frequent oil changes
Engine	ppm	Catalyst deactivation	Moving parts overhaul
		Acid gas formation	Exhaust catalyst replacement
Turbine	10 000 ppm	Acid gas formation	Moving parts overhaul
		Corrosion	

→ Extensive clean-up required *before* power generator device.. BUT...

Emission directives

	24 h	Yearly basis	Average over 8 h
SO ₂	$125-185 \ \mu g/m^3$	-	
NO ₂	-	$40-50 \ \mu g/m^3$	
PM_{10}	-	$20-50 \ \mu g/m^3$	
Pb	-	$0.5-1 \ \mu g/m^3$	
Benzene	-	$5 \ \mu g/m^3$	
СО	-	-	$7.5-10 \text{ mg/m}^3$

Before or after power generation...

There is no way around purification!

Interlude...

WHAT IS A CATALYST?

"a substance that is chemically unaltered by a reaction, but which it accelerates by allowing it to proceed along a pathway of lower activation resistance; it does not modify equilibrium ".

Interlude...

WHAT IS AN ADSORBENT?

"Adsorption is the adhesion of atoms, ions, or molecules from a gas, liquid, or dissolved solid to a <u>surface</u>. It is a surface phenomenon: creates a film of the <u>adsorbate</u> on the surface of the <u>adsorbent</u>. Desorption is the reverse of adsorption"

Absorption

Reaction

Film lato liquido

bu k liquido

Liquido

Gas

Processes

Often a material acts both as adsorbent and as catalyst

Adsorbents

Zeolites

EACH sphere is microstructured:

Adsorbents

Activated carbon

□ Nickel \rightarrow Ni (10-20 %) deposited on commercial refractory supports: Al₂O₃, MgAl₂O₄, CeO₂-Al₂O₃ in pellets o SiC foams, or custom-developed

Supports

Noble metals such as Rh, Ir, Pt and Pd have excellent catalytic properties, but Ni is very good at <u>high temperature</u> and <u>costs a lot less</u>

Requirements for catalyst supports: good bonding affinity with catalyst particles promoting uniform dispersion and controlled sintering

Catalyst poisoning:

Coke formation Reacts with sulphur, arsenic, phosphorus, lead Deposition of inert compounds (siloxanes)

Catalyst deactivation:

Sintering leading to reduced active area

A catalysts needs to be exchanged on average after one year, max. 5

Fuels for SOFC systems

From feedstock to power using High-temperature fuel cells – part II

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SULPHUROUS COMPOUNDS

Sulphurous compounds

- Defined by an –SH group or an S atom
- Generated through biological degradation or added for odorization
 <u>(Odorants</u> do not harm piping or burners and do not influence energetic yield)

- ➢ React easily and IRREVERSIBLY to stable compounds (SO₂)
- Contribute to acid rain
- Present in Natural Gas, Biogas and Oil
- Can corrode system materials and components
- Deactivate catalysts based on Ni and react with electrolytes.

Sulphurous compounds: Mercaptans

- Organic compounds similar to alcohols with S atoms
- Malodorous and react with many metal species

Mercaptans are pollutant to water and soil, and carry toxins which are transferreed to living organisms and through the entire food chain.

Sulphurous compounds: Hydrogen sulphide

- Derived from break-down of aminoacids in biomass
- Particularly corrosive, toxic, reactive and harmful

H₂S is pollutant to water and soil, and carries toxins which are transferreed to living organisms and through the entire food chain.

Sulphurous compounds: Hydrogen sulphide

INTERACTIONS H₂S – NICKEL (in SOFC):

• Physical-chemical adsorbtion:

 $Ni+H_2S \rightarrow Ni-H_2S_{(ads)}$

•Sulphide formation by bulk chemical reaction:

 $xNi+yH_2S \rightarrow Ni_xS_y+yH_2$

•Sulphide formation by electrochemical reactions:

 $xNi+yS^{-} \rightarrow Ni_xS_y+2xe^{-}$

INTERACTIONS H_2S -ELECTROLYTE:INTERACTIONS H_2S -Steel•Chemical reaction:current collectors: $O^=+H_2S \rightarrow S^=+H_2O$ •ACC: $O^=+H_2S+3H_2O \rightarrow SO_4^=+4H_2$ $Fe+H_2S \rightarrow FeS+H_2$ •Electrochemical reaction:•CCC: $SO^=+4H_2+H_2S \rightarrow S^=+5H_2O+8e^ 7Fe + 3SO_2 \rightarrow 2Fe_2O_3 + 3FeS$ $SO^=+H_2S \rightarrow SO_4^=+H_2O+8e^ 7Fe + 3SO_2 \rightarrow 2Fe_2O_3 + 3FeS$

Desulphurizing material

- Aluminosilicates (macroporous): limited activity and selectivity;
- Zeolites: good activity at T>300°C, but limited selectivity and sensitive to humidity;
- Metal oxides (V₂O₅, TiO₂, Fe₂O₃, CuO, ZnO) good activity towards oxidation reactions, at high temperatures. Good capacity for regeneration;
- Impregnated activated carbon, high activity and selectivity

 $NaOH>Na_2CO_3>KOH>K_2CO_3$

Regeneration is problematic due to break-down of carbon structure.
Desulphurizing processes

- Adsorption
- Dry removal by molecular sieves
- Dry removal by activated carbon

 $H_2S + Sub \rightarrow H_2S-Sub$

Active towards: H₂S, SO₂, NH₃, COS, mercaptans

(in case of impregnated AC adsorption is accompanied by reaction)

Desulphurizing processes

• Adsorption \rightarrow Regeneration processes

Regeneration Process	Description
Temperature Swing Adsorption (TSA)	Regeneration takes place primarily through heating. The differences between the equilibrium loadings at the two temperatures represent net removal capacity. Considerable energy and time are required to heat and cool the bed. TSA is often achieved by preheating a purge gas.
Pressure Swing Adsorption (PSA)	Regeneration is achieved by lowering the pressure of the bed and allowing the adsorbate to desorb. Typically adsorption takes place at elevated pressures to allow for regeneration at atmospheric pressure or under slight vacuum. PSA is relatively fast compared to TSA
Inert Purge	A non-adsorbing gas containing very little of the impurity is passed through the bed, reducing the partial pressure of adsorbate in the gas-phase so that desorption occurs.
Displacement Purge	A purge gas that is more strongly adsorbed than the impurity is used to desorb the original contaminant. Steam regeneration, while mostly a thermal process, also regenerates through displacing some of the original adsorbate.

Desulphurizing processes

• Absorption

SulFerox[®], LO-CAT[®] processes

 $2Fe(III)L + H_2S \rightarrow 2Fe(II)L + S + 2H^+$

 $2Fe(II)L + 1/2O_2 + 2H^+ \rightarrow 2Fe(III)L + H_2O$

Active towards: H₂S and light mercaptans

Desulphurizing processes

Reaction

Precipitation as iron-sulphide in solution FeCl₂ + H₂S → FeS_↓ + 2 HCl;
Dry removal by iron oxides Fe₃O₄ + H₂S → FeS_↓ + Fe₂O_{3↓} + H₂O 2Fe₂O₃ + H₂S + 2H₂ → FeS_↓ + Fe₃O_{4↓} + 2H₂O 2Fe₂O₃ + H₂S + 2CO → FeS_↓ + Fe₃O_{4↓} + 2CO₂
Dry removal by zinc oxides ZnO + H₂S → ZnS_↓ + H₂O
Dry removal by alkaline solutions AOH + HB → AB_↓ + H₂O
Biological oxidation to elemental sulphur or sulphates 2n(H₂S) + n(CO₂) + light → 2nS + n(CH₂O) + n(H₂O)



SILOXANES

$$\begin{array}{cccc} R & R & R \\ I & I & I \\ -Si - O - Si - O - Si - O - \\ I & I & I \\ R & R & R \end{array}$$

volatile Si compounds in traces (< 10 ppm) in landfill and biogas deriving from cosmetics, detergents and processing

At high temperatures these form solid SiO₂ causing:

- I. Accumulation on mechanical (moving) parts
- II. Erosion in conditions of large flows
- III. Deactivation of various catalysts

Name	Formula	MW
Hexamethylcyclotrisiloxane	$\mathbf{C}_{12}\mathbf{H}_{18}\mathbf{O}_{3}\mathbf{S}\mathbf{i}_{3}$	222
Octamethylcyclotetrasiloxane	$C_{_{B}}H_{_{24}}O_{_{4}}Si_{_{4}}$	297
Decamethylcyclopentasiloxane	$C_{10}H_{30}O_{5}Si_{5}$	371
Dodecamethylcyclohexasiloxane	C ₁₂ H ₃₆ O6Si ₆	445
Hexamethyldisiloxane	$C_6H_{18}Si_2O$	162
Octamethyltrisiloxane	$C_{B}H_{24}Si_{3}O_{2}$	236
Decamethyltetrasiloxane	$C_{\scriptscriptstyle 10}H_{\scriptscriptstyle 30}Si_{\scriptscriptstyle 4}O_{\scriptscriptstyle 3}$	310
Dodecamethylpentasiloxane	$C_{_{12}}H_{_{36}}Si_{_5}O_{_4}$	384

Gas Clean-up Siloxanes

> Adsorption on Activated Carbon

> Adsorption on Silica Gel

Cooling/freezing

Absorption

Siloxanes

Adsorption on Activated Carbon

- Commercial process
- Competition for adsorbent sites with humidity, VOCs, sulphurous compounds...



Siloxanes

Adsorption on Silica Gel

Higher adsorbing capacity compared to activated Carbon

(up to 1 - 1.5 % by weight)

- Higher selectivity for Hexamethildisiloxane (C₆H₁₈Si₂O)
- No competition with H₂S
- Competition with H₂O

Siloxanes

Cooling/freezing

- Gas is cooled to circa 4°C at 24 atm
- Long-term removal capacity circa 32%
- Highest selectivity towards Octamethilciclotetrasiloxane C₈H₂₄O₄Si₄



Siloxanes

Absorption

Gas is washed in a column in counterflow with a liquid phase (Selexol)

Selexol: mixture of dimethilether and poliethilenglycol





Removal potential of 99 % but very costly due to the need for regeneration of the liquid phase



HALOGENATED COMPOUNDS

Halogenated compounds

Compounds generated by combustion or decomposition of compounds as

 CCI_4 , chlorobenzene (C_6H_5CI), chloroform ($CHCI_3$), trifluoromethane (CHF_3)

Acid gas products: HCl and HF, in presence of humidity

Or: Dioxins and Furans, in presence of hydrocarbons

- Cause metals corrosion
- Lubricant degradation
- Harmful to humans and environment



Halogenated compounds

> Adsorption on Activated Carbon

- Halogenated hydrocarbons (CHX) can be removed through AC beds
- Regeneration required at 200°C (flammable compounds are formed)

Hydro-dehalogenation

• Halogenated compounds are transformed into their respective HX acids and made to react with alkaline absorbents

Biological scrubbing

- Gas passes through a bed of woody material where a population of bacteria degrades all volatile organic compunds (VOCs)
- Removal capacities achievable of 90 %



TARS & PARTICULATES

Tars & particulates



Typical gasification-induced contaminants and their problems

Contaminant	Examples	Problems	Solution
Tars	Refractive aromatics	Clogs filters Difficult to burn Deposits internally	Tar cracking thermally or catalytically, or tar removal by scrubbing
Particulates	Ash, char, fluidised bed material	Erosion	Filtration, scrubbing
Alkali metals	Sodium, potassium compounds	Hot corrosion	Cooling, condensation, filtration, adsorption
Fuel-bound nitrogen	Mainly ammonia and HCN	NOx formation	Scrubbing, Selective catalytic removal (SCR)
Sulfur, chlorine	HCI, H ₂ S	Corrosion emissions	Lime or dolomite, scrubbing,
Review: Biomass for energy. T	Cony Bridgwater. J Sci Food Agric 86:175	5–1768 (2006)	absorption

Tars & particulates

Source: P. Hasler et al.. Biomass and Bioenergy 16 (1999) 385-395

		Fixed bed DownDraft	Fixed bed UpDraft	CFB gasifier
Fuel moisture	% mf	6 25	nd ^a	13 20
Particles	mg/Nm ³	100-8000	100-3000	8000-100,000
Tars	mg/Nm ³	10-6000	10,000-150,000	2000-30,000
LHV	MJ/Nm ³	4.0-5.6	3.7-5.1	3.6-5.9
H_2	Vol.%	15-21	10-14	15-22
CO	Vol.%	10-22	15-20	13-15
CO_2	Vol.%	11-13	8-10	13-15
CH_4	Vol.%	1-5	2–3	2-4
C_nH_m	Vol.%	0.5-2	n.d. ^a	0.1-1.2
N_2	Vol.%	rest	rest	rest

^a n.d. = not determined.











Tars & particulates







Tars & particulates

Table 3

Reduction of particles and tars in various producer gas cleaning systems (with various definitions of "tar")

	Temperature (°C)	Particle reduction (%)	Tar reduction (%)
Sand bed filter ^a	10–20°C	70–99	50-97
Wash tower ^a	50-60	60–98	10-25
Venturi scrubber			50-90
Rotational atomizer	< 100	95–99	
Wet electrostatic precipitator	40-50	>99	0-60
Fabric filter ^a	130	70–95	0-50
Rotational particle separator ^a	130	85-90	30-70
Fixed bed tar adsorber ^a	80		50
Catalytic tar cracker	900		>95

^a Data based on own results from cocurrent gasifier test runs with identical sampling method (see [8] and [12]; other data from literature according to [11]. Source: P. Hasler et al.. Biomass and Bioenergy 16 (1999) 385-395

High- or low-temperature clean-up?



Promising high-temperature desulphurization:

 $H_2S + CeO \rightarrow CeS + H_2O$

Catalyst regeneration:

 $CeS + H_2O \rightarrow CeO + H_2S$ $CeS + 2O_2 \rightarrow CeO + SO_2 + \frac{1}{2}O_2$

SOFC inlet conditions: Gas temperature T > 600°C Steam-to-carbon ratio S:C > 2







What is reforming?

Reforming is a hydrocarbon synthesis reaction, generally:

$$\square C_m H_{2m+2} + C_n H_{2n+2} \rightarrow C_{m+n} H_{2(m+n)+2} + H_2$$

Thermochemical process to obtain hydrogen-rich fuels from heavy hydrocarbons

Hydrogen production





Currently H₂ is produced mainly by reforming of Natural Gas

Reforming processes

□Steam Reforming (SR)

Steam Methane Reforming (SMR)

Partial Oxidation (POx)

Autothermal Reforming (ATR)



Thermal and catalytic Cracking



Steam reforming

$C_nH_{2n+2} + nH_2O \rightarrow nCO + (2n+1)H_2$

Steam reforming is the catalytic conversion of **light hydrocarbons** and **steam** in hydrogen and carbon monoxide. Light hydrocarbons have low C-content (e.g. methane, CH_4 , and benzenes, $C_{5-10}H_{12-22}$).

Hydrocarbon conversion and product (*syngas*) composition depend on:

- 1. Type of feedstock
- 2. Pressure
- 3. Temperature
- 4. H_2O /fuel ratio
- 5. Catalyst activity

Steam methane reforming (SMR)

 $CH_4 + H_2O \rightarrow CO + 3H_2$



Heat reqired can be supplied by a fraction (1/3 ca.) of inlet methane which is burned

Operating at less extreme conditions less methane is converted – unless a catalyst is used

Steam methane reforming (SMR)







- <u>Increasing H₂O/Fuel</u> = Coke formation zone shifts from A to B
 - $CO + H_2 \rightarrow C + H_2O$
- <u>Alkaline catalyzers</u> = promote CO formation and reduce Coke deposition zone.

Partial oxidation (POx)

$C_nH_m + (n/2)O_2 \rightarrow nCO + (m/2)H_2$

Partial oxidation is the non-catalytic conversion of **heavy hydrocarbons** (e.g. oil residues in refinery processes) and **substoichiometric oxygen** in hydrogen and carbon monoxide.



Autothermal reforming

Combination of steam reforming and partial oxidation.



Heat from the exothermal POx reaction is supplied to the SR reaction inside the reactor.

Partial Oxidation: $C_nH_m + (n/2)O_2 \rightarrow nCO + (m/2)H_2 + heat$

Steam Reforming: $C_nH_m + nH_2O \rightarrow nCO + (n+m/2)H_2$

Hydrocarbons react with air and steam

Energy efficiency: SR > AR > POx Reactor volume: POx < AR < SR

Carbon coking

Carbon forming reactions:

 $\begin{array}{l} \mathsf{CH}_4 \rightarrow \mathsf{C} + 2\mathsf{H}_2 \\ \mathsf{2CO} \rightarrow \mathsf{C} + \mathsf{CO}_2 \\ \mathsf{CO} + \mathsf{H}_2 \leftrightarrow \mathsf{C} + \mathsf{H}_2 \mathsf{O} \end{array}$





Whisker carbon formation by irreversible decomposition of hydrocarbons on catalyst surface

Polymer film formation through conversion of accumulated deposited hydrocarbon species

Pyrolytic carbon from olefins in the gas phase encapsulating catalyst pellet

Syngas treatment – increasing H₂ purity



• Chemical adsorption or Pressure Swing Adsorption (PSA)

 Preferential or selective oxidation (PROx o SOx)

Water-gas shift reaction






Reforming basics

Chemical adsorption

Solvent scrubbing in adsorption column to remove carbon dioxide (NB: carbon separation and sequestration!)

<u>Most used solvents</u>: amines \rightarrow costly in terms of expenditure and disposal

Biomethane CH, Pressure swing adsorption N₂/O₂ H,O / H,S • CO, •The higher gas pressure, the more it is adsorbed on solid surfaces Exploit selectivity of different materials towards different species Carbon molecular sieve Pressurization (adsorbtion) 1. Depressurization (desorption of adsorbed species) 2. Flushing of adsorbed species 3. **Biogas** off-gas Repressurization CH, / CO, / N, / O, / H,O / H,S CO, / N, / O, / H,O / H,S 4.

Reforming basics

Pressure swing adsorption





Purity achievable ~ 99.999%

Reforming basics

External

Reforming for HTFC

<u>Internal</u>

Heat from combustion of anode off-gas + heat exchange with stack



Simplicity inside cellsSystem complexitySeparation of tasksLarge coolant flow required

Heat directly from cell reactions



Optimum cooling of stack Extra catalists required Simplicity inside system Increased malfunction risks





Liquid fuels are useful alternatives for SOFC:

- They are easy to store, transport and handle;
- Steam reforming of oxygenated HCs (like ____ (m)ethanol) is less endothermic than methane SR;
- They can be obtained from biomass;
- Their production process dictates sulfur-free ____ conditions;

Biofuels



EU Goal:		IPCC 450 ppm scenario:		
5.75%	in 2010	9%	in 2030	
10%	in 2020	26%	in 2050 (30 EJ, 90% 2 nd gen. biofuels)	

Biofuels – 2nd generation: biofuel from waste



Heating

Biofuels – direct liquefaction

Thermochemical treatment for converting biomass into solubilized and/or liquid products

- Medium temperatures (120 400 °C)
- High pressures (up to 90 MPa)
- Reagents / Solvents (phenol, glycols, water)
- Catalysts (acid or base)

Mechanism

- 1. Solubilization + depolymerization
- 2. Reactions among products
- 3. Long term re-condensation reaction



Biofuels – direct liquefaction









Biofuels – pyrolysis

Thermal degradation of biomass in the absence of an oxidizing agent Pyrolysis always produces:



- The liquid (bio-oil, pyro-oil) is an homogenous mixture of compounds (sometimes even > 500!) and water in a single phase.
- 2)The gas has a medium heating value and can be used internally to provide process heat, re-circulated as reactive gas or exported.
- 3) The solid (char) is similar to coal and it may be sold as sorbent or used to

provide heat (e.g. internally for the process)

Ash consists of inorganic compounds (alkali and heavy metal salts ...) is the waste product of pyrolysis (can be used as nutrients).

pyrolysis technology	residence time	heating rate	temperature (°C)	products
carbonization	days	very low	400	charcoal
conventional	5-30 min	low	600	oil, gas, char
fast	0.5 - 5 s	very high	650	bio-oil
flash-liquid ^b	<1 s	high	<650	bio-oil
flash-gas ^c	<1 s	high	<650	chemicals, gas
ultrad	< 0.5	very high	1000	chemicals, gas
vacuum	2-30 s	medium	400	bio-oil
hydro-pyrolysis ^e	<10 s	high	<500	bio-oil
methano-pyrolysis ^r	<10 s	high	>700	chemicals



Biofuels – synthesis





High P (50-100 bar)

Modified Diesel vehicle

Heavy Vehicle



Fuel	Storage T [°C]	Storage P [bar]	Density [kg m ⁻³]	H2 gravimet. density [kg _{H2} kg ⁻¹]	H2 volumet. density [kg _{H2} m ⁻³]	HHV [kWh kg ⁻¹]	Energy density [kWh m ⁻³]	Energy cost [€ kWh ⁻¹]
Ammonia (NH ₃)	20	10	629.6	18%	0.111	5.1	3261.1	0.05
Gaseous hydrogen (H ₂)	20	250	20.5	100%	0.021	33.3	685.0	0.12
Liquid hydrogen (H ₂)	253	1	76.3	100%	0.070	33.3	2547.7	0.07
Metal hydride (Mg ₂ NiH ₄)	20	1	25.0	4%	0.001	39.44	986.11	0.10
Methanol (CH ₃ OH)	20	1	800	13%	0.100	4.2	3377.7	0.06
Natural gas (CH ₄)	20	250	164.1	25%	0.041	13.8	2279.8	0.07
Gasoline (C ₈ H ₁₈)	20	1	736	16%	0.116	12.9	9547.5	0.18



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Ethanol – fermentation of corn stover/sugar cane



Country	Туре	Energy balance		
United States	Corn ethanol	1.3		
Brazil	Sugarcane ethanol	8		
Germany	Biodiesel	2.5		

	Annual F Top (Mill	uel Ethanc (2007–20 10 countr ions of U.S. I	el Productio (11) ^{[2][64][65} (ies/regiona iquid gallons	on by Coun][66] al blocks s per year)	try	
Vorld rank	Country/Region	2011	2010	2009	2008	2007
1	United States	13,900	13,231	10,938	9,235	6,485
2	📀 Brazil	5,573.24	6,921.54	6,577.89	6,472.2	5,019.2
3	European Union	1,199.31	1,176.88	1,039.52	733.60	570.30
4	China China	554.76	541.55	541.55	501.90	486.00
5	Thailand			435.20	89.80	79.20
6	Canada	462.3	356.63	290.59	237.70	211.30
7	💶 India			91.67	66.00	52.80
8	📥 Colombia			83.21	79.30	74.90
9	👬 Australia	87.2	66.04	56.80	26.40	26.40
10	Other			247.27		
	World Total	22,356.09	22,946.87	19,534.993	17,335.20	13,101.7

Ethanol can be produced from waste to improve E balance...

Ethanol – distillation of digestate



Physical and hazard properties compared

	Methane	Methanol	Ethanol
	CH_4	CH ₃ OH	C ₂ H ₅ OH
Density, g/cm ³	$0.72 \ 10^{-3}$	0.787	0.789
Combustion heat, Kcal/g	13.3	5.416	7.120
Viscosity, cP	0.0109 _(g)	$0.541_{(l)}/\ 0.00968_{(v)}$	0.12 ₍₁₎
Specific heat, cal/h K	0.53 _(g)	$0.6054_{(l)}$	$0.577_{(l)}$
Flammability (air), vol. %	$5.0_{Low}\text{-}75.0_{Up}$	6.3_{Low} -39.2 _{Up}	3.5_{Low} - 15.0_{Up}
Autoignition T, K	811	843	698
Flash point, °C	- 188	15.6_{open} - 12.2_{closed}	13_{closed}
Toxic acute (ingestion, inhal., skin abs.)	0, 1, 0	3, 2, 2	1, 0, 0
Toxic chronic (ingestion, inhal., skin abs.)	0, 1, 0	2, 2, 2	1, 1, 1
Fire (flame, spontaneous, explosive)	3, 0, 2	3, 0, 2	3, 0, 2
Storage and handling	gaseous fuel	liquid fuel - toxic	liquid fuel

(*) 0 =None; 1 =Slight; 2 =Moderate; 3 =High