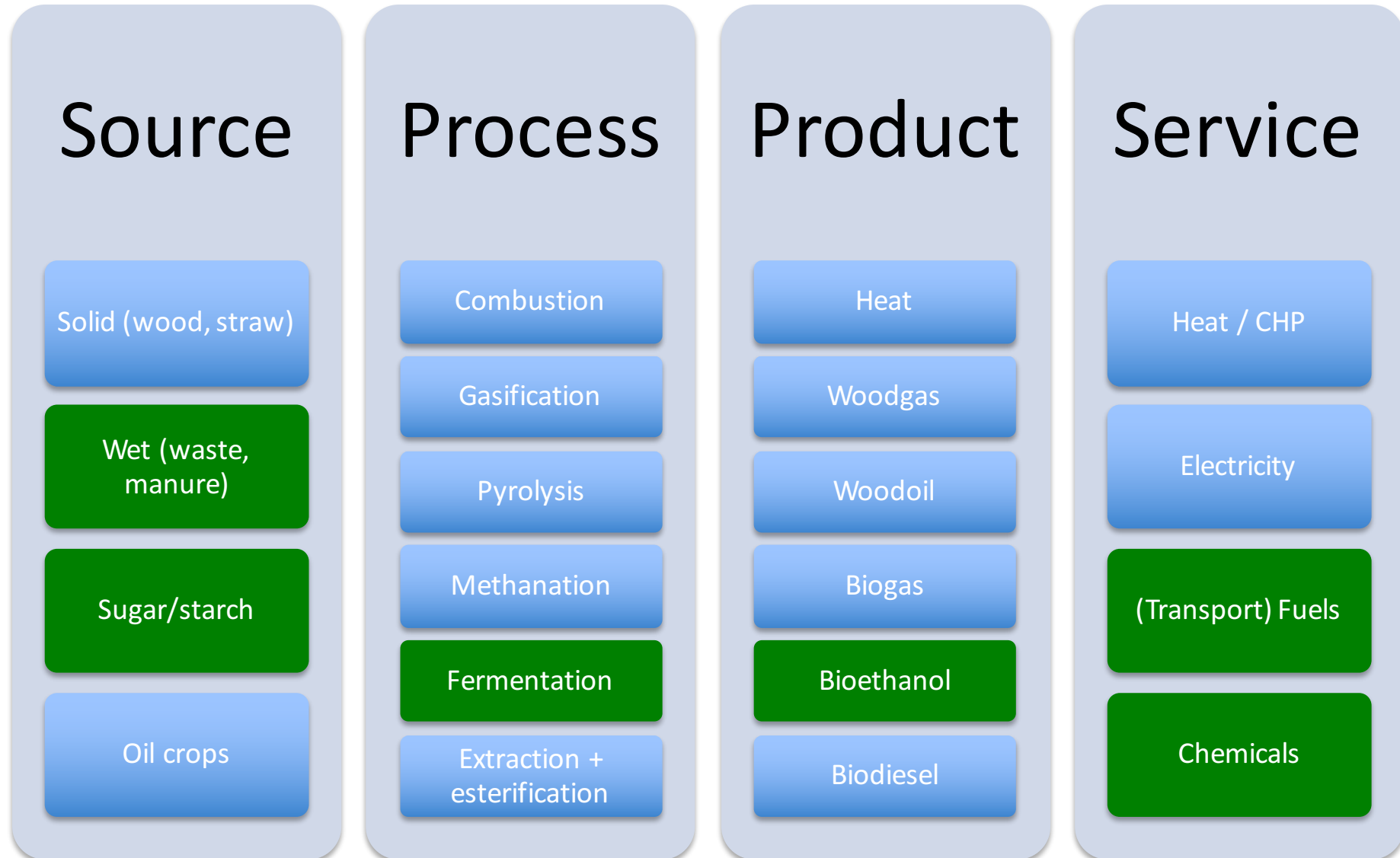


# **Biomass: liquids**

# BIOETHANOL



# General characteristics

- **Advantages:**
  - (indigenous) natural resource; reduces oil import
  - known and simple technology; labour-intensive
  - large application domain; small plants
- **Limitations:**
  - production and substitution (for oil) are limited
  - requires important infrastructure and land
  - requires adaptations (engines)
- *Rem: only **ethanol** is of interest;  
**methanol** is more difficult to synthesize (wood pyrolysis), toxic and best made from natural gas*

# Engine fuels

FUEL	MJ / kg	MJ / L	kg / L
Gasoline	43.9	<b>32.2</b>	0.73
Diesel	43	<b>36.6</b>	0.85
Ethanol	26.7	<b>21.1</b>	0.79
Methanol	20	<b>15.9</b>	0.80

# Properties

Property	Ethanol	Methanol	Gasoline	Diesel
formula	$\text{C}_2\text{H}_5\text{OH}$	$\text{CH}_3\text{OH}$	C5-C12	C14-C19
molar weight	46.1	32	100	240
C wt%	52.2	37.5	86	86
H wt%	13.1	12.5	14	14
O wt%	34.7	50	0	0
Boiling point	78	65	30-220	240-360°C
Autoignition	423	470	257°C	
Explosion limits	4-19 vol%		1.4-7.6 vol%	
<b>Octane index</b>	<b>106-111</b>	<b>106-115</b>	<b>79-98</b>	
<b>Cetane index</b>	<b>0-5</b>	<b>0-10</b>	<b>5-10</b>	<b>45-55</b>

=> *Ethanol is a **gasoline substitute**, not one for diesel*

# Biomass sources for bioethanol

1. **Sugars**: sugar cane, melasse (=sirupy residue after sugar extraction), sweet sorghum, beet
  - direct fermentation
  - the plant *residues* (=bagasse) deliver the energy to operate the site
2. Amylaceous plants (**starch**, inulin): manioc, corn, potatoes, cereals, artichoke (*topinambour*)
  - requires a prior so-called **saccharification** step
  - no self-sufficiency like with sugar-only plants
3. **Cellulosic**: wood, agro-residues, energy crops
  - requires aggressive **hydrolysis** (dilute acid at high temperature or concentrated acid at low temperature)
  - examples: american aloe, ficus indica, cat-tail plant



# Bioethanol **yield** (land-use)

Source	t biomass / ha.yr	EtOH L / t biomass	EtOH L / ha.yr
sugar cane	50	70	3500
melasse		280	
sweet sorghum	35	86	3000
manioc	12-20	180	2200-3600
potato	15	125	1875
corn	6	370	2200
wood	5-20	160	800-3200

*100 g glucose yield in practice 47 g ethanol (59 ml anhydrous)*

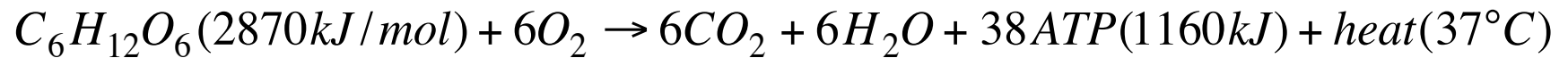
**LOW !**

**0.35 L / m<sup>2</sup>**

*(cf. 1 m<sup>2</sup> of grapes vineyard yield ca. 1 bottle of wine (0.7 L with 13% ethanol))*

# Energy balance

- aerobic respiration ( $O_2$  from air):



- 40% storage efficiency

- **fermentation** (the yeast uses  $O_2$  from glucose, not from air)



- 90% theoretical efficiency to transform sugars into ethanol

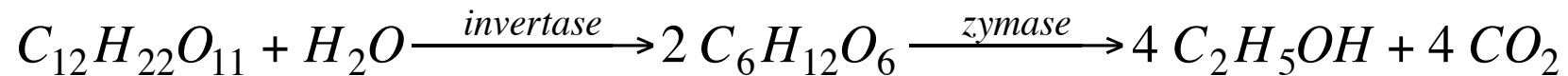
- the glucose energy stays in the ethanol and is not stored in the bacteria (only 2 ATP); above 13% ethanolic solution, the yeast bacteria do not survive ( $\rightarrow$  wine!)

- **practical** yield: 0.5 L ethanol from 1 kg glucose = **70% efficiency**

# Sugar cane



- cellulosic fibres (bagasse) containing sugars
- milling, washing and filtration separates the bagasse (=fuel for the site) from the sugar juice
- the juice is concentrated ( $\rightarrow$  melasse), sterilised and fermented with yeast



- **1-3 days fermenting** yields a 8-10% alcohol solution (**slow process**)
- a 'stripping' filtration is then done to separate EtOH from solids and water
- distillation until the **96% EtOH-4% $H_2O$**  azeotrope
- benzene addition + final distillation until anhydrous ethanol (**99.7%**)
- the distillation effluent (=animal food and fertilizer) is **10-13 times** the produced ethanol volume (**large volume process**)
- for **starches** (manioc), the process is similar with one prior step: sugars are extracted from the milled/washed manioc by amylase and gluco-amylase enzymes (=saccharification step)

# ‘Jerusalem artichoke’



- american & mediterranean, ‘sunflower’-like
- 3 m high, inuline tubers (fructose), 1 to 3 kg per plant
- very resistant plant; survives even down to -15°C
- 70-80 t/ha fresh, 10 t/ha dry matter, 20 wt% of tubers
- the tubers are hydrolysed to a juice (80% fructose, 20% glucose)
- 1 L ethanol (0.8 kg) per 12 kg fresh tubers (2.4 kg dry) = 33% yield by mass: **6000 L / ha**
- cost ca. **0.5 €/L** ( $\frac{2}{3}$  from plant production cost,  $\frac{1}{3}$  from the transformation cost tubers→ethanol)

# Sweet sorghum



- up to **30 tonnes dry matter / ha**; warm wet areas
- 10-14 t sugars (sucrose, in the stalks) / ha
- **4000 L / ha**
- bagasse used for site self-sufficiency
- cost ca. **0.66 €/L** ( $\frac{2}{3}$  plant production,  $\frac{1}{3}$  transformation)
- crop cycle is from May to October; very short harvest time

# Ethanol efficiency effects in engines

- Overall transport efficiency loss due to larger tank volume & weight:  
-1% loss
- Volume of combustion products is higher with ethanol
- Gain with **higher octane** number of ethanol  
+6% -10% compared to gasoline
- In total, the overall **transport efficiency for ethanol** is  
**more efficient than gasoline** in light duty vehicles (LDV)
- Benefits :
  - saving of 0.7-1 L gasoline (2.3-3 kg CO<sub>2</sub>) per L EtOH
  - reduced emissions of CO, HC, SO<sub>x</sub>, benzene (**cleaner combustion**)

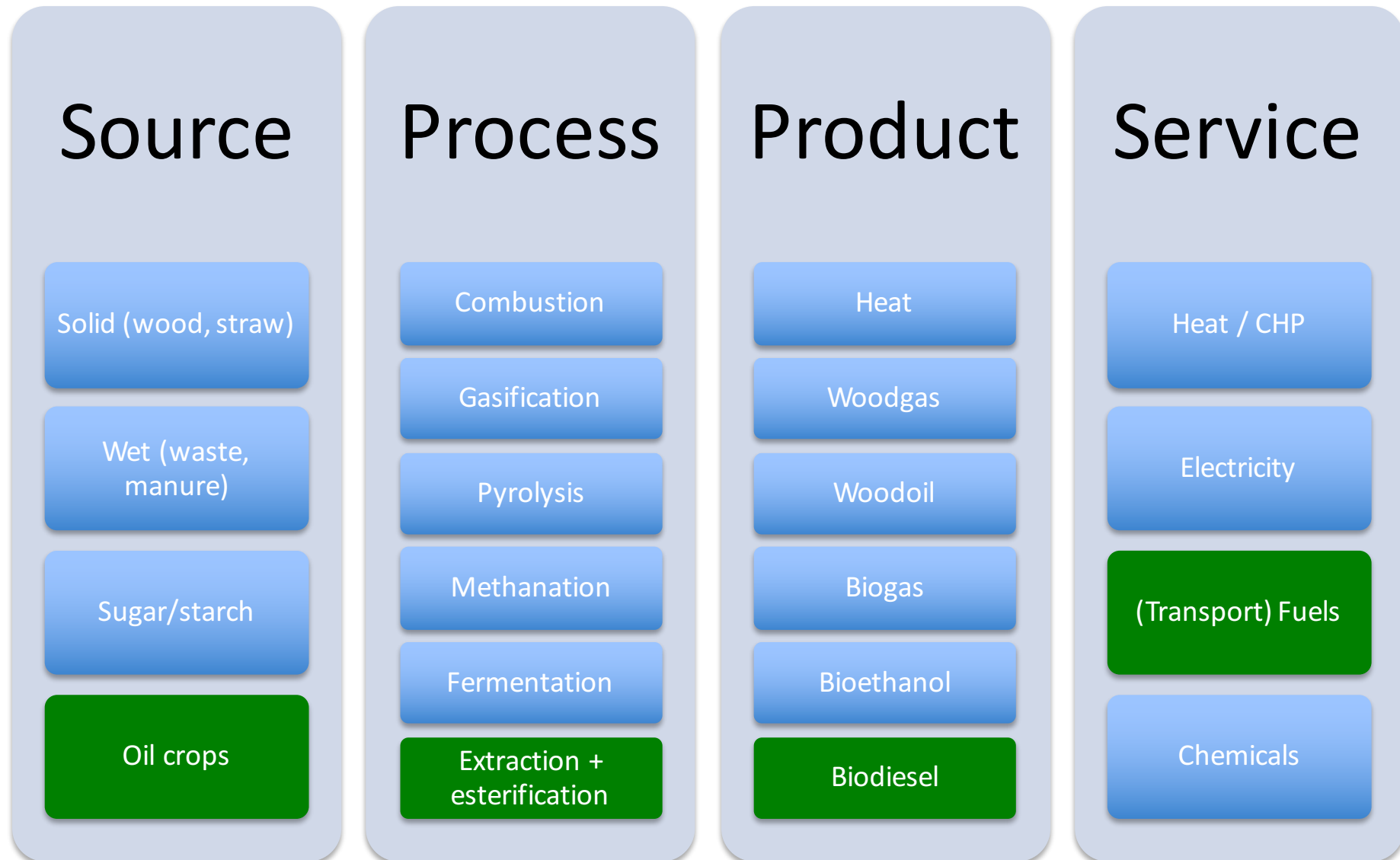
Source:

1) Wyman, Charles E. Handbook on Bioethanol: Production and Utilization. Tylor and Francis 1996. ISBN 1-56032-553-4

# Bioethanol use

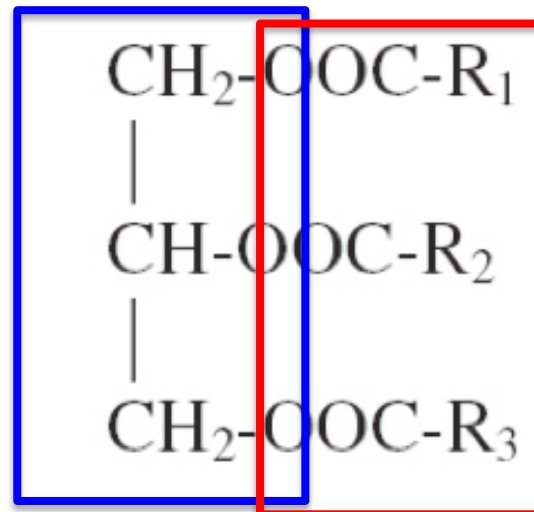
- as hydrated (**96%**, azeotrope) in all-ethanol engines (**Brasil**)
- as 'dry' (**99.7%**) blended with gasoline (5-10% in EU, USA; 24% in Brasil)
- its main drawback is the **low yield and high land use**; its application will thus remain limited (**≈5%** of transport fuel), with notable exceptions like Brazil (which has huge land reserves and the appropriate climate for sugar cane and high yield (**8000 L/ha.yr**))

# BIODIESEL



# Biodiesel

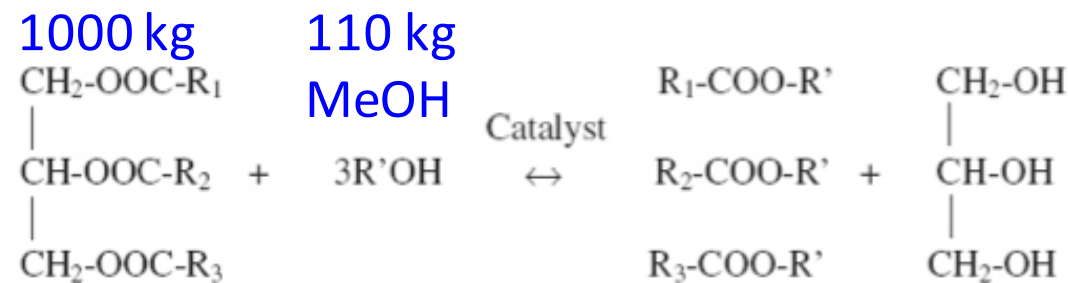
- Source :
  - rapeseed (*colza*), sunflower (*tournesol*), soyabean
  - Oil content = 40%
  - animal fats, frying oil
- Triglycerides : 1 mol glycerine + 3 mol fatty acids



# Transesterification process

## Transesterification (alkoholysis):

- reaction of triglyceride and alcohol to esters and glycerol:

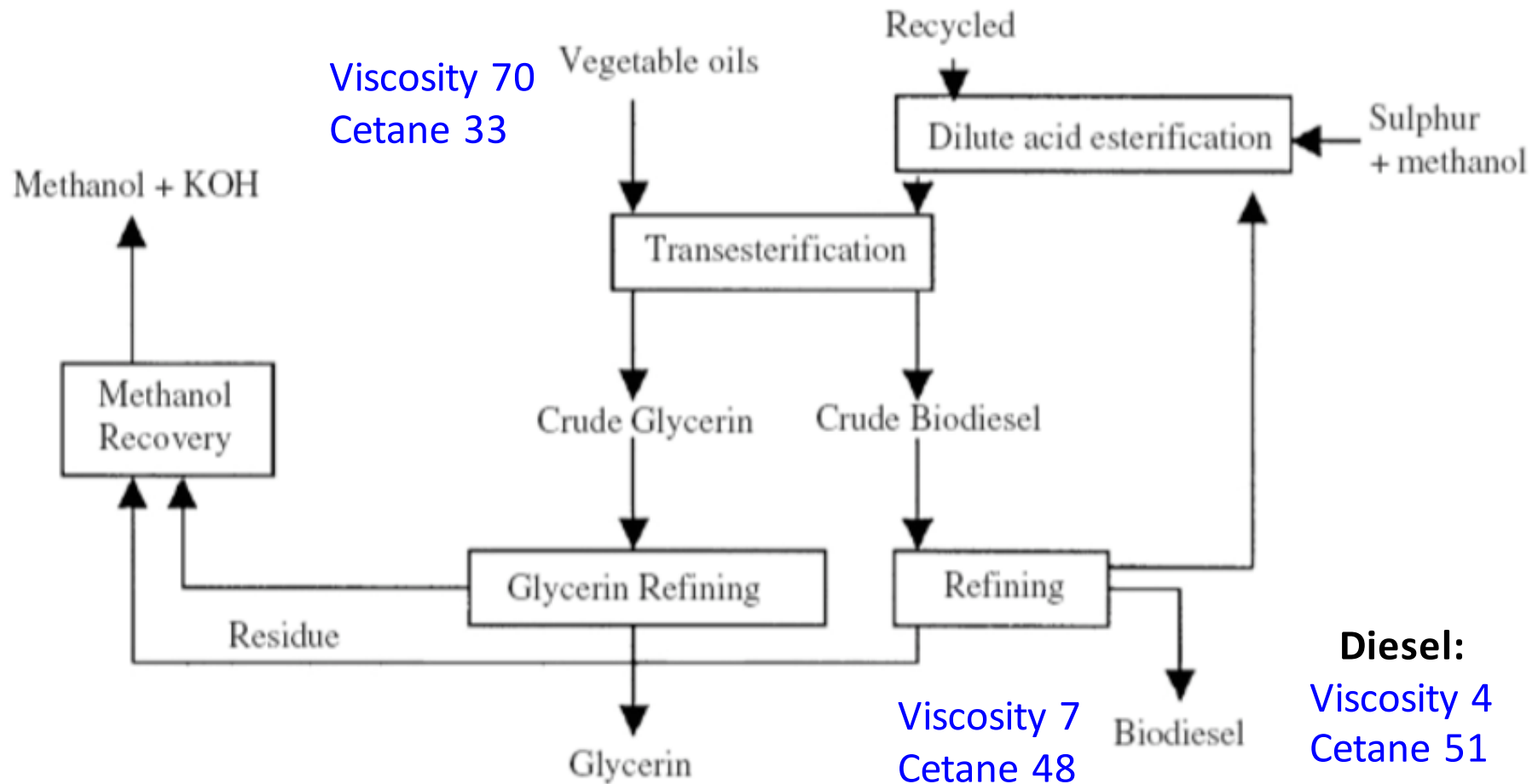


- reversible reaction
  - use of excess alcohol to shift equilibrium towards products
- usable alcohols: methanol, ethanol, propanol, butanol, ...
- most frequently used: methanol
  - cheap
  - polar
  - fast reaction

1000 kg                  110 kg  
 methyl-esters        glycerine

# Process goal: oil **viscosity** reduction ÷ 10

## Transesterification: Process scheme



from: Marchetti, J.M. et al., Renewable and sustainable energy reviews 11, pp. 1300-1311, 2007.

# Cost of biodiesel

*very low yield! => land use!*

*1 order of magnitude still further below ethanol yields*

Crop	Seeds yield (t / ha)	Seeds oil content (%)	Seeds prod. cost (€ / t)	Oil cost (€/t)	Yield L / ha
Sunflower w.o. irrig.	0.76	44	302	687	380
Sunflower (irrigated)	2.214	44	267	606	1100
Rapeseed (colza)	1.49	40	264	661	680
Saf-flower (safran)	0.856	35	268	766	340
Cynara (cardon)	2.0	25	118	472	570

*Biomass production cost = 25-44% of oil cost*  
*Difference = transformation cost*

*ca. 1/3*  
*ca. 2/3*

**ca. 0.6 € / L**

# Biodiesel vs. diesel

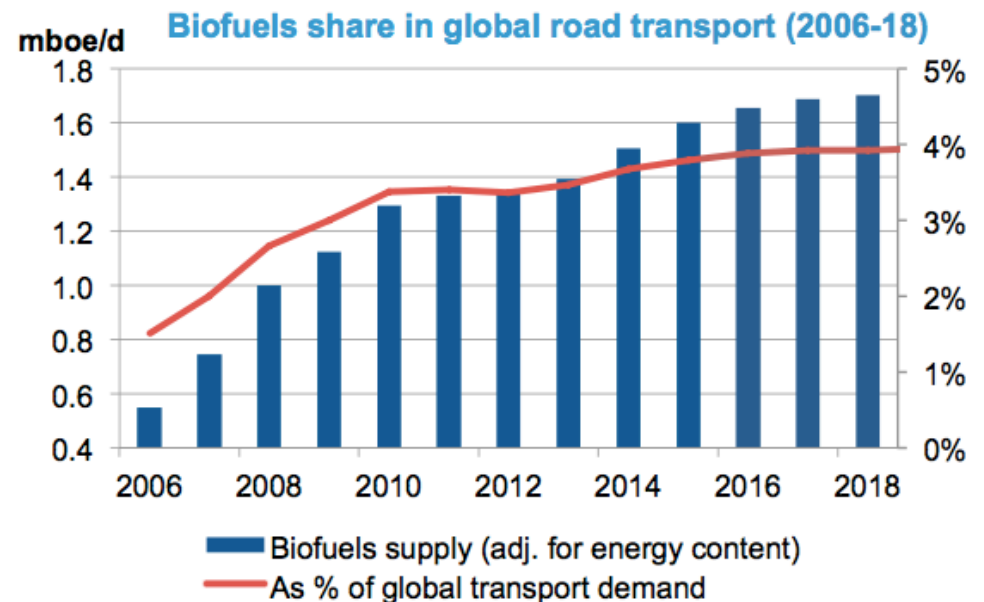
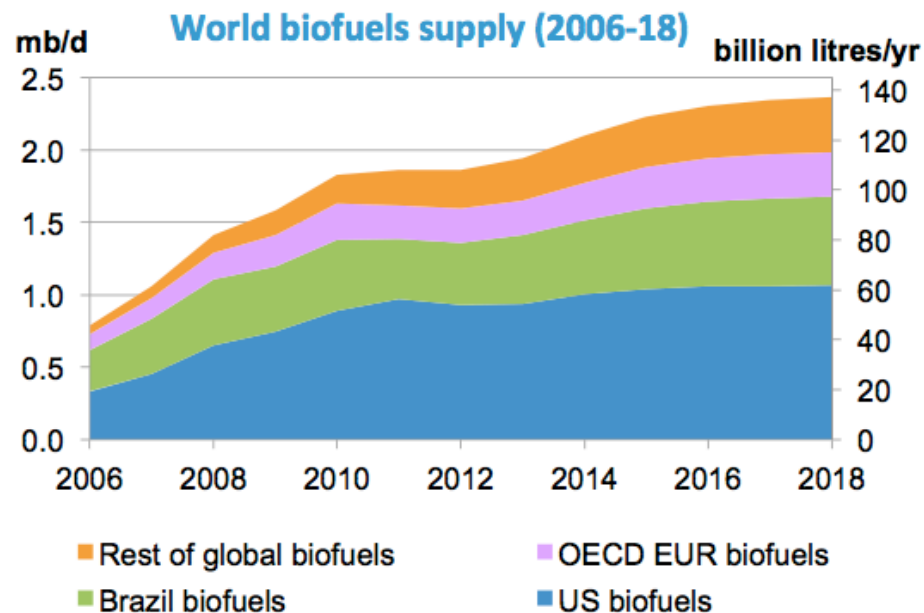
Property	Rapeseed oil	Methyl-ester	Sunflower oil	Methyl-ester	Diesel
Density kg/L	0.92	0.88	0.92	0.88	0.84
✓ LHV MJ/L	34.3	33.1	34.1	33.0	35
Viscosity mm <sup>2</sup> /s 20°C	78	7.5	66	8	4
Melting point °C	-2	-6	-18		
✓ <b>Cetane number</b>	<b>34</b>	<b>48</b>	<b>33</b>	<b>50</b>	<b>51</b>
✓ Carbon residue%	0.25	0.05	0.42	0.05	0.15
✓ Sulfur %	0.0001	0.24	0.01	0.01	0.29

# Biodiesel comments

- its **low yield and high land use** are even (much) worse than for bioethanol
- it has no specific advantages in cost or efficiency over (fossil) diesel
- its use is very controversial and further marginalised

# IEA Facts on biofuels

- Biofuels world output (**90%=ethanol**) grows from 20 Mtoe (2005) to 92 Mtoe (2030), to meet **4%** of road transport
- Current land use for biofuel production: 14 mio ha = 1% of arable land. By 2030 this would rise to 2.5% (i.e. the size of France+Spain).
- Cost of bioethanol production: 0.2 \$/L (Brasil), 0.3 \$/L (USA), 0.55 \$/L (EU); shipping costs are v. small
- Biofuels are expected to play a bigger role in future from **wood**-gasification (2<sup>nd</sup> gen)



# Mobility fuels from wood: 'secondary' generation biofuels

- **1<sup>st</sup> generation**

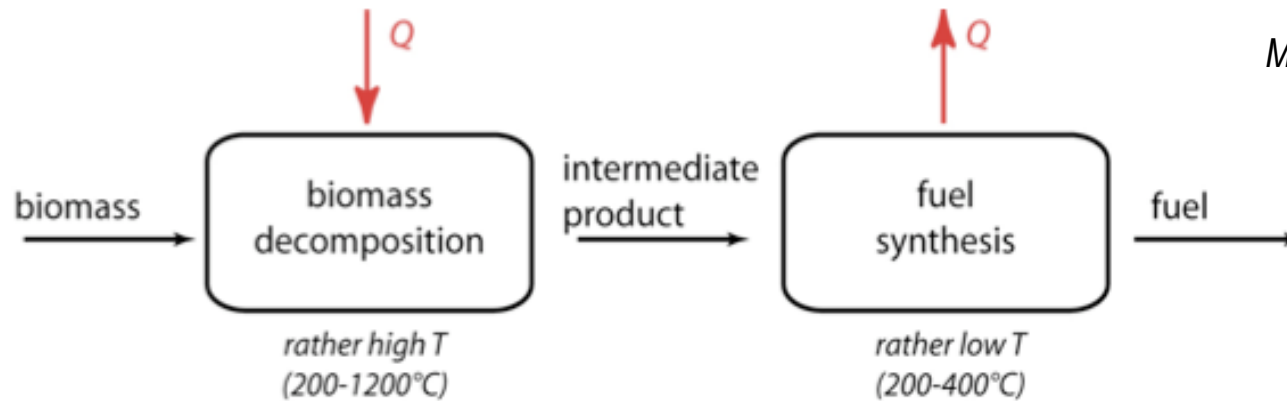
- Biogas
- Bioethanol
- Biodiesel
- limited conversion
- slow processes
- large residues

- **2<sup>nd</sup> generation**

- **Wood** gas derivatives
- efficient
- catalysed (thermochemical)

# 2<sup>nd</sup> generation biofuels

Thermochemical biomass to fuel reforming proceeds typically in two (or more) reaction steps:



*M Gassner, EPFL-LENI*

- gasification
- pyrolysis

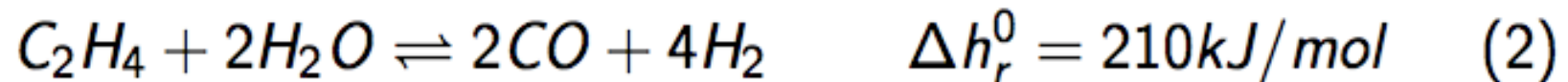
non-condensable/  
condensable  
substances  
(H<sub>2</sub>, CO, CO<sub>2</sub>, H<sub>2</sub>O,  
CH<sub>4</sub>, C<sub>x</sub>H<sub>y</sub>,  
char, tars)

Fuel synthesis step

- methanation
- FT synthesis
- DME synthesis
- methanol synthesis

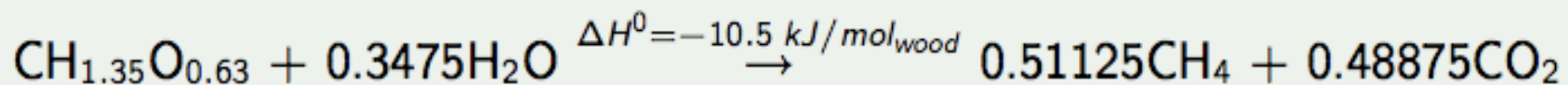
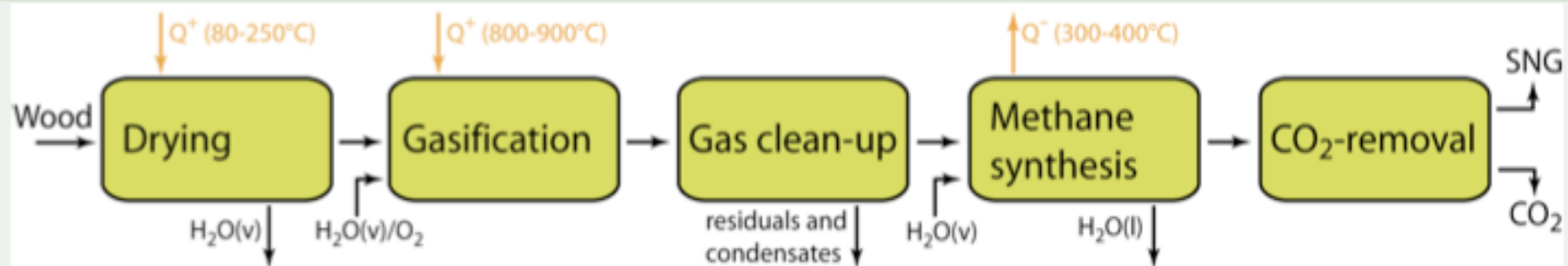
# Wood → syngas → methane

**Gasification with producer gas to methane reforming:**



*M Gassner, EPFL-LENI*

## Common wood to SNG route



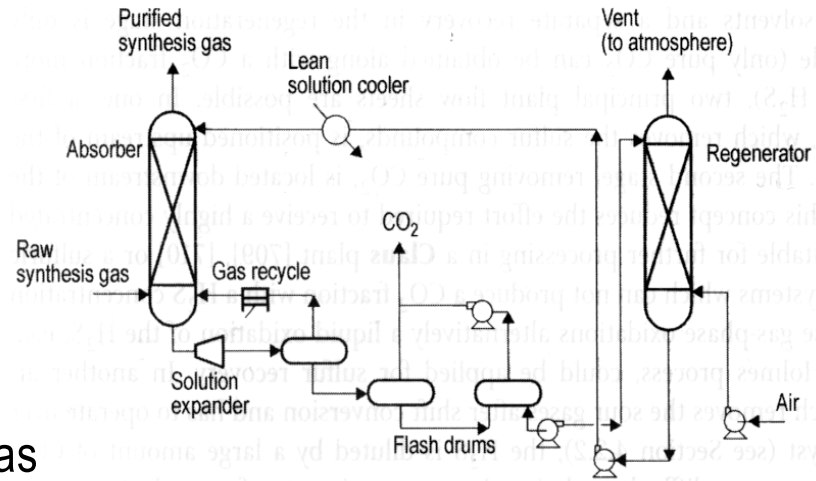
→  $CH_4/CO_2$  separation needed

# CH<sub>4</sub> / CO<sub>2</sub> separation

M Gassner, EPFL-LENI

## Physical absorption

Energy cost:  
220 kWh<sub>el</sub>/kg gas

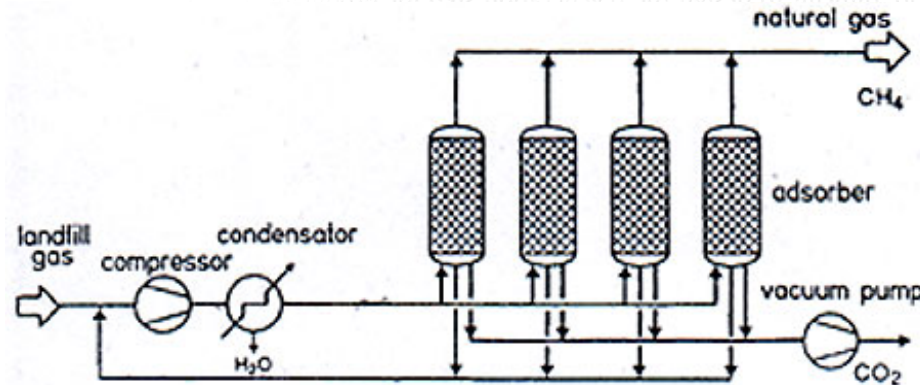


Appl, M.: Ammonia. Principles and Industrial Practice. Wiley, Weinheim, 1999.

**P = 50 bar**

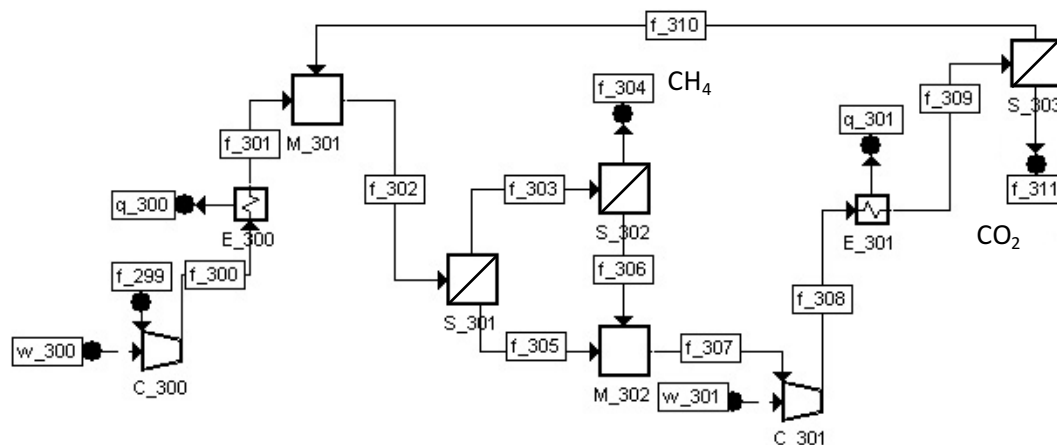
## Pressure Swing Adsorption

Energy cost:  
70 kWh<sub>el</sub>/kg gas



Pilarczyk et al.: Natural Gas from Landfill Gases. Resources and Conservation 14 (1987).

**P = 5 – 6 bar**



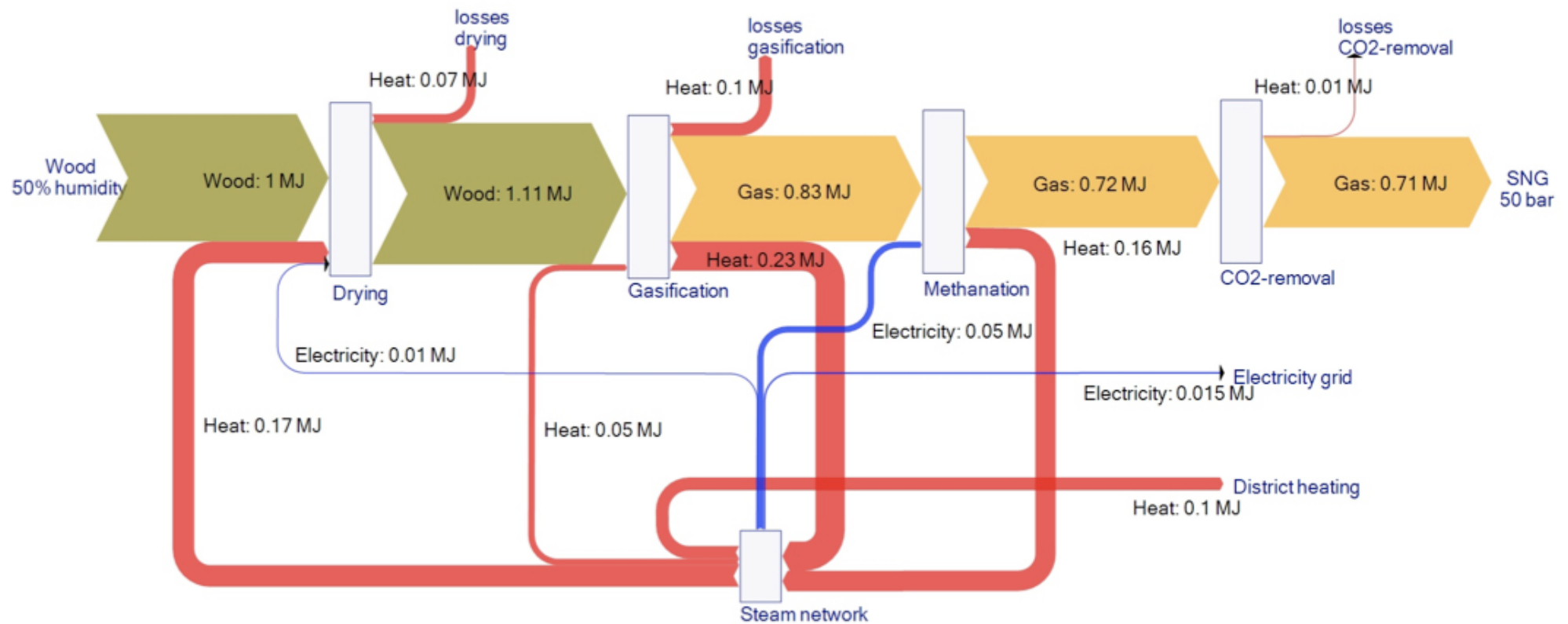
**P = 50 bar**

## Polymer Membranes

Energy cost:  
600 kWh<sub>el</sub>/kg gas

Rem: 1 kg gas  
(50% CH<sub>4</sub>)  
= 33 moles CH<sub>4</sub>  
= 3800 kWh

# Efficiency for wood-to-CH<sub>4</sub>: 70%

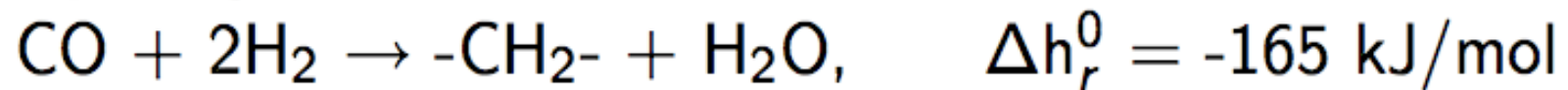


M Gassner, EPFL-LENI

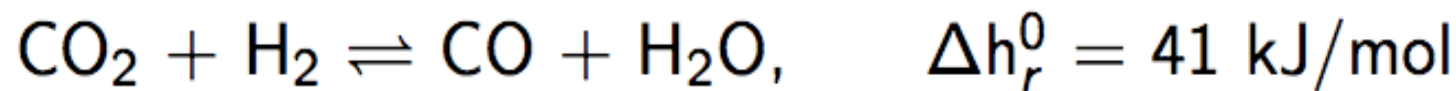
# Liquid synfuel fabrication from syngas

## **Fischer-Tropsch** synthesis:

- chain growth reaction (polymerisation) to heavy-weight liquid hydrocarbons:



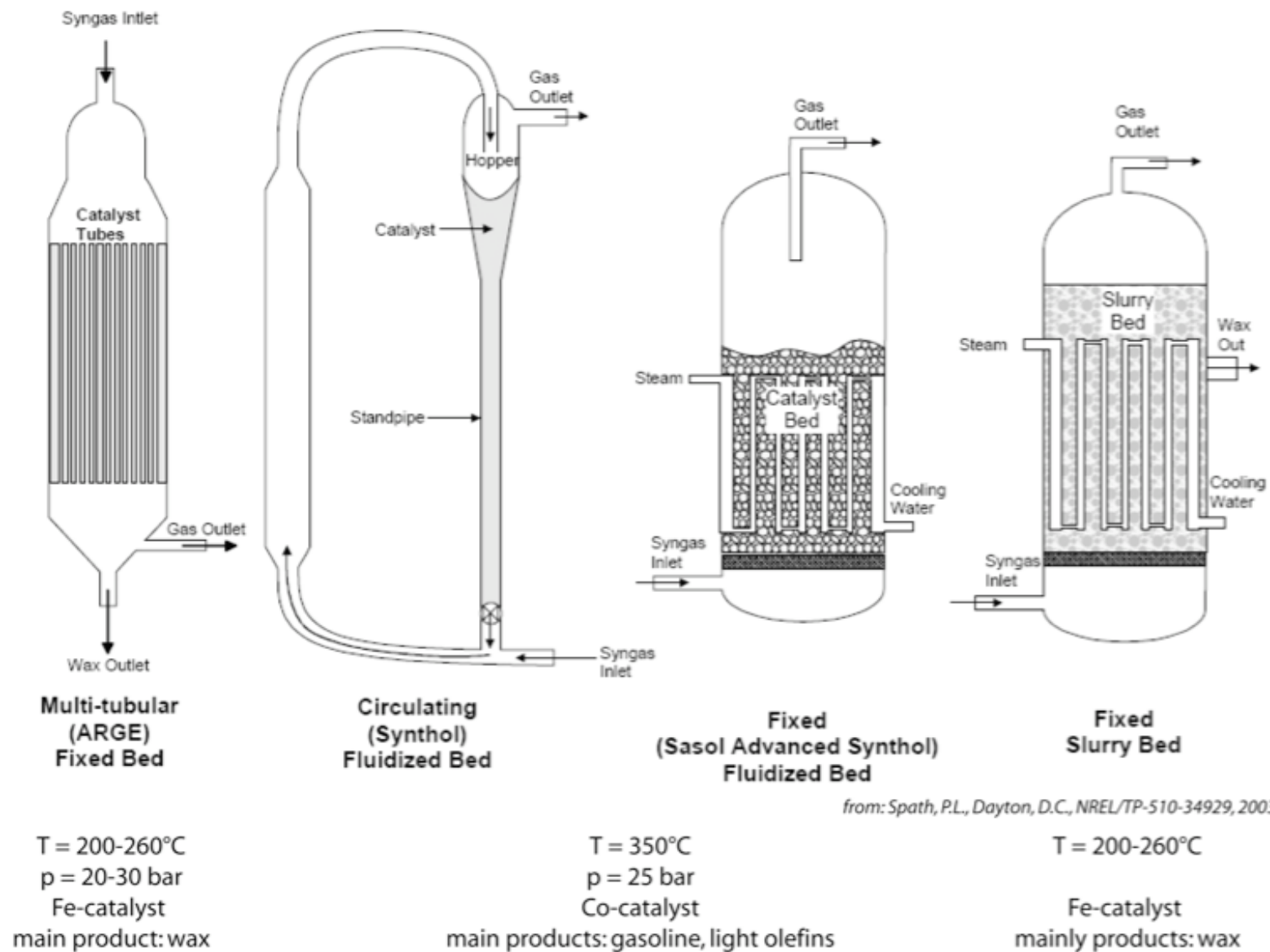
- building blocks:  $\text{H}_2$ ,  $\text{CO}$
- $\text{CO}/\text{H}_2$ -ratio adjustment via upstream water gas shift reaction:



- postprocessing
  - hydrocracking with  $\text{H}_2$  to remove double bounds
  - wax  $\rightarrow$  diesel + kerosene
  - ... petrochemical processing

*M Gassner, EPFL-LENI*

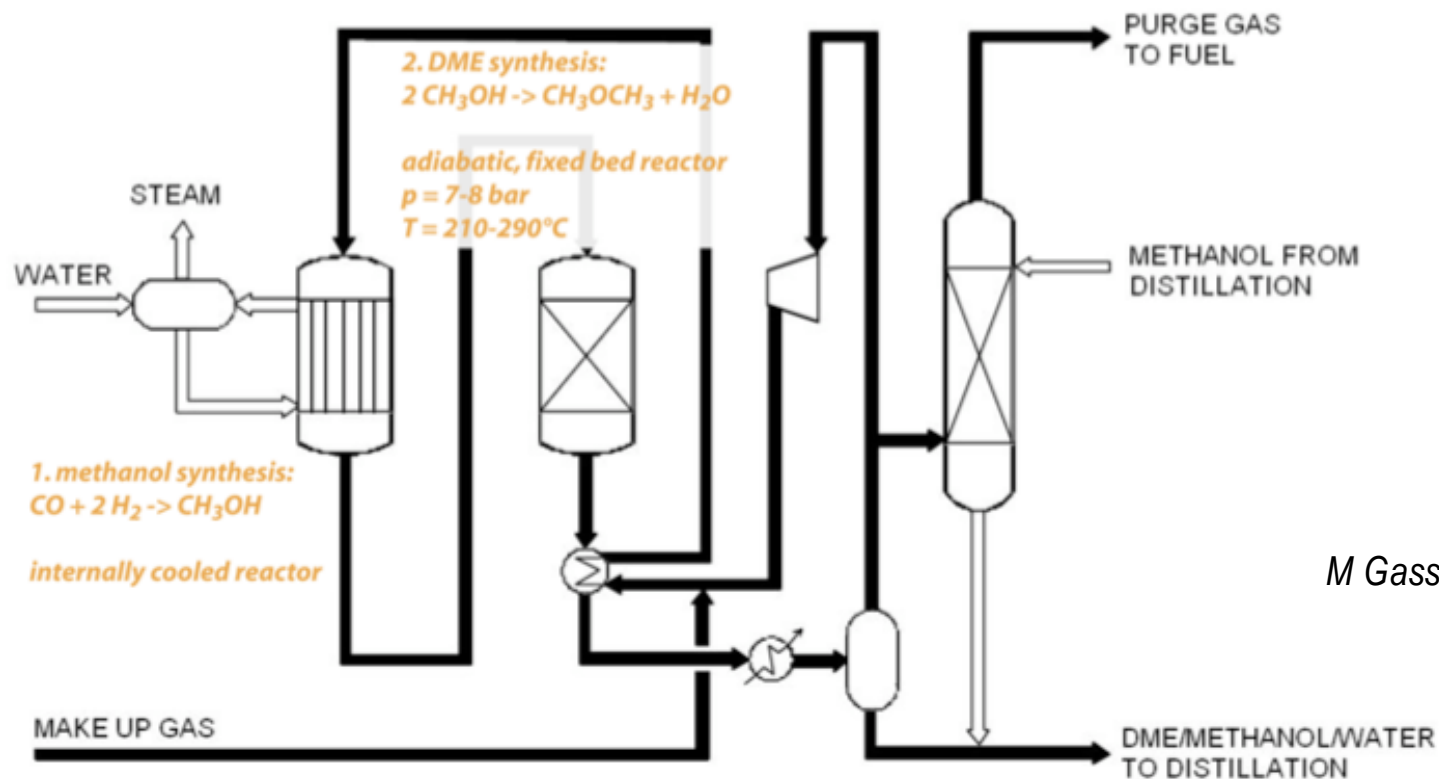
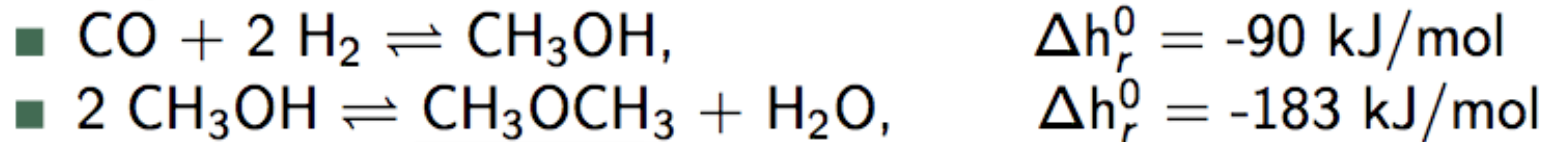
# F-T technology is well established



# DME synthesis

*clean alternative fuel for diesel or LPG; also a gas turbine fuel*

two step (via methanol dehydration)

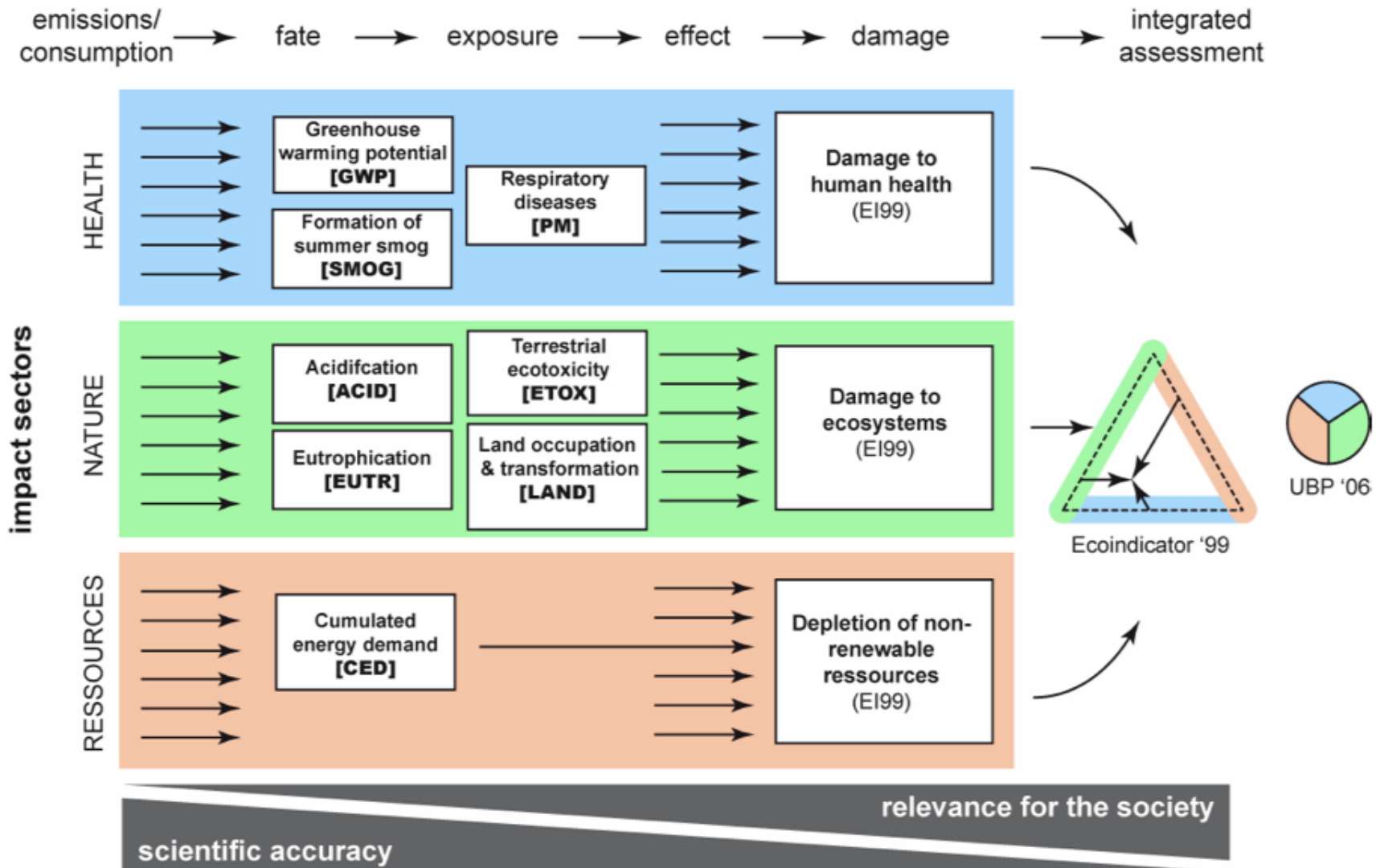


*adapted from: Topsoe technology for large-scale production of DME. Topsoe Technologies, Denmark*

*M Gassner, EPFL-LENI*

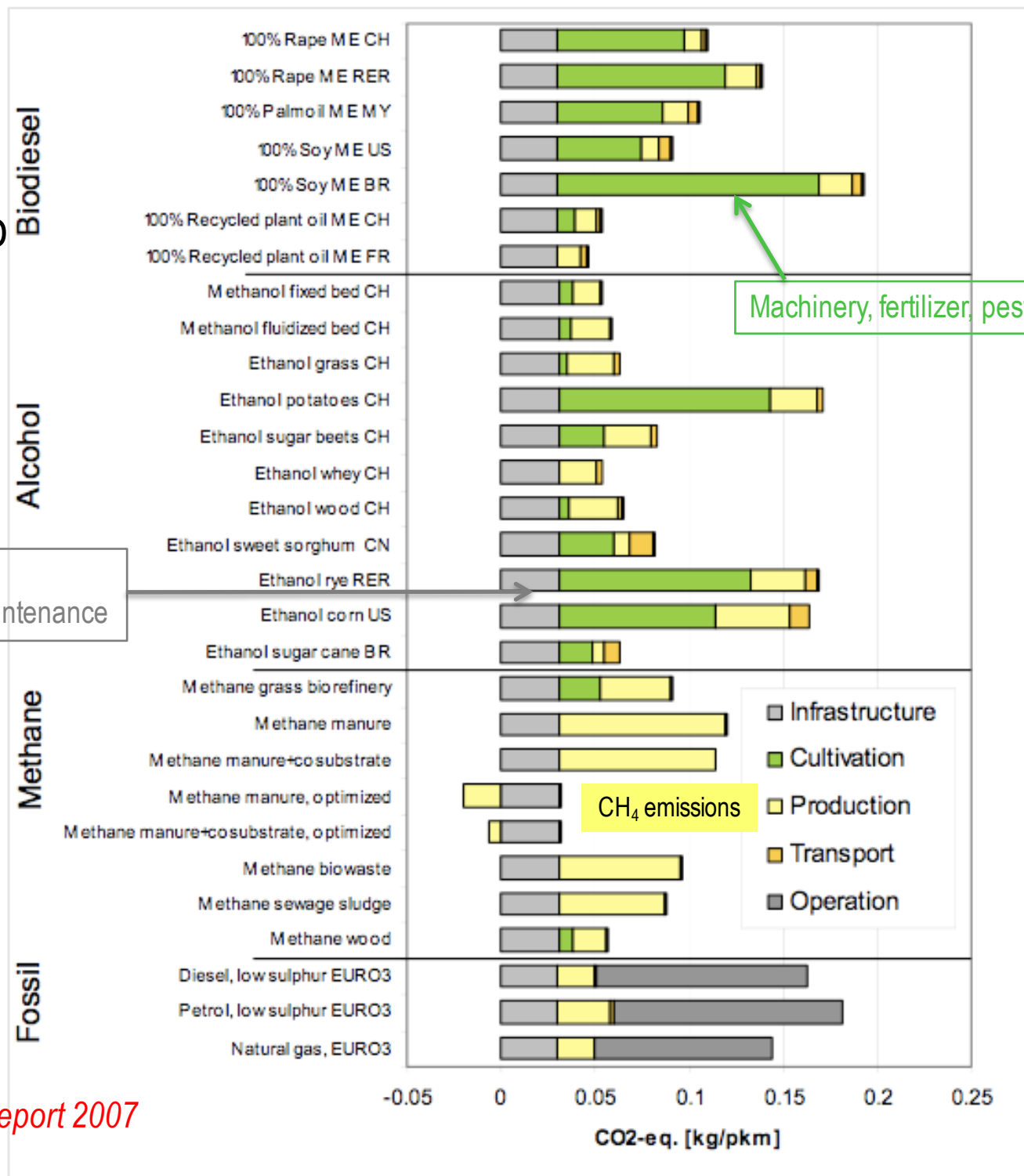
# EMPA report (2007/2013) on biofuel assessment

- LCA study (Life Cycle Analysis), biofuels use in CH only



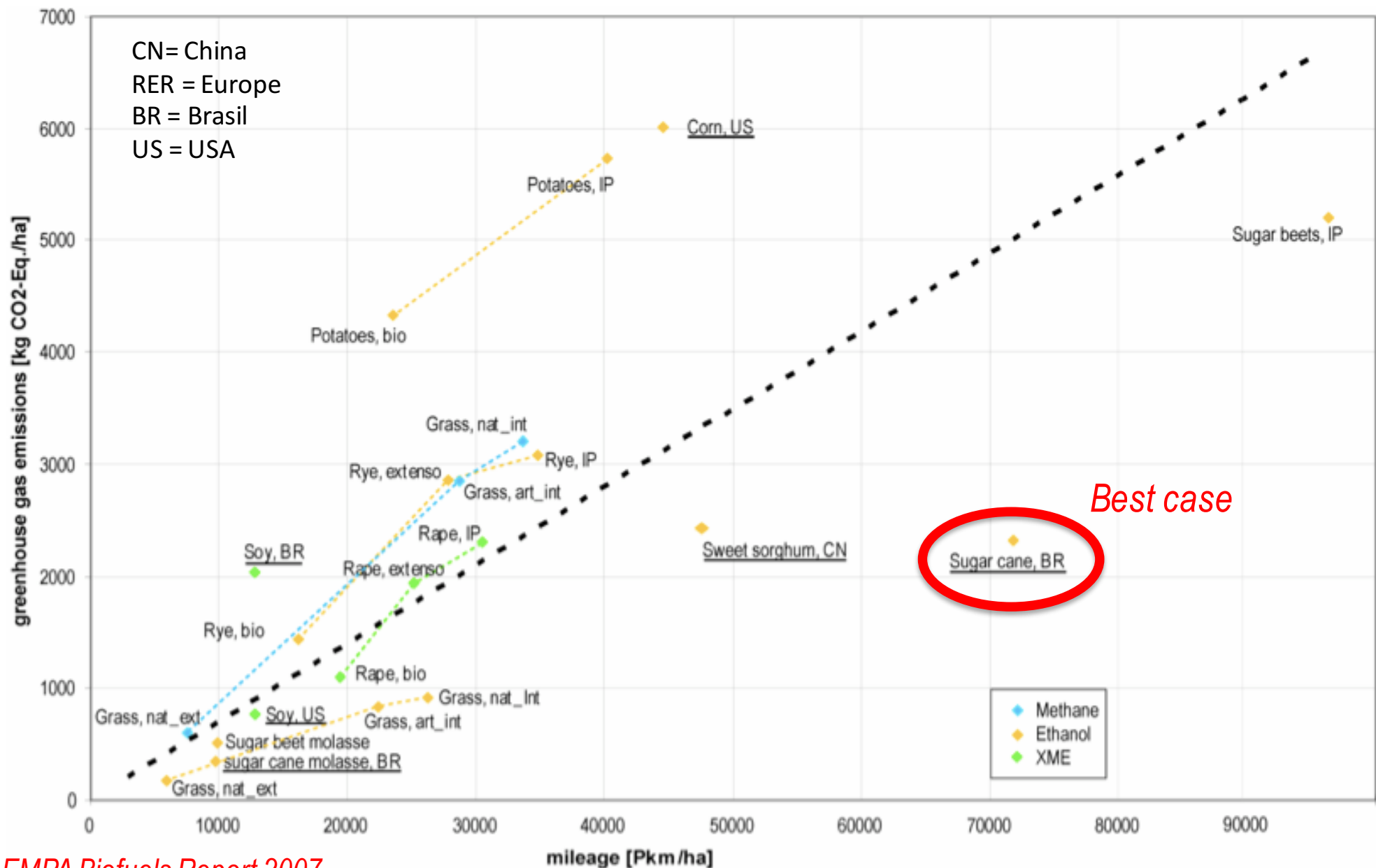
# CO<sub>2</sub>-equivalent emissions compared to fossil fuels

Vehicle and road construction & maintenance

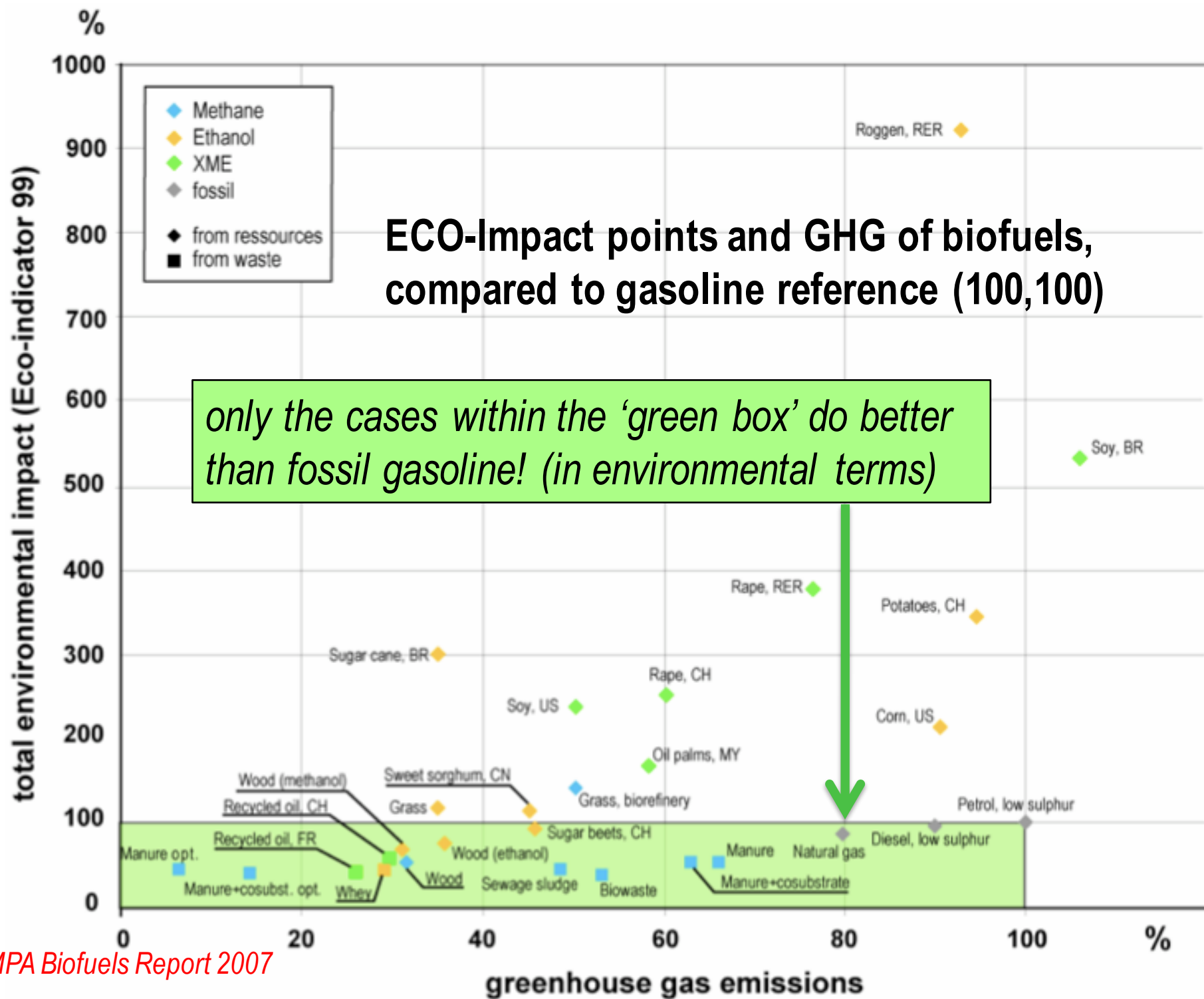


EMPA Biofuels Report 2007

# CO<sub>2</sub>-equiv. emissions vs. transport-km (per ha land use)



EMPA Biofuels Report 2007

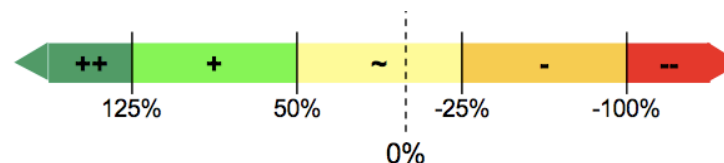


# GHG- impact

energy carrier \ use path	Wood		Grass		Manure		Waste wood		Whey		Biowaste		Sewage sludge	
	min	max	min	max	min	max	min	max	min	max	min	max	min	max
Heating	++	++												
Cogeneration (CHP)	++	++	+	++	++	++			++	++	~	+	++	++
Car (methane)	++	++	+	+	++	++	++	++	+	+	~	~	+	+
Car (ethanol)	++	++	++	++					+	+				
Municipal solid waste incineration "average technology"							++	++			~	~	--	--
Municipal solid waste incineration "latest technology"											++	++		
Cement kiln							++	++					~	~

**‘Best use’ practice of the biofuels**

SCALE:



EMPA  
Biofuels  
Report 2007

# ECO99'- impact

energy carrier \ use path	Wood		Grass		Manure		Waste wood		Whey		Biowaste		Sewage sludge	
	min	max	min	max	min	max	min	max	min	max	min	max	min	max
Heating	~	++												
Cogeneration (CHP)	~	++	~	~	+	++			+	++	-	-	+	++
Car (methane)	+	+	~	~	++	++	+	+	+	+	~	~	++	++
Car (ethanol)	~	~	+	+					++	++				
Municipal solid waste incineration "average technology"							~	+			-	-	--	--
Municipal solid waste incineration "latest technology"											+	++		
Cement kiln							+	+					-	-

# Summary on biomass in general

What you are expected to know:

- the composition of 'biomass'
- the essential numbers (potential, energy density,...)
- how to distinguish bio-mass,-gas,-ethanol,-diesel
- the conversion roadmap

# Summary on biomass-to-electricity

- **wood** is under-used for power generation
- in direct **combustion** (alone, or with wastes, 1-10 MW<sub>el</sub> plants), it reaches **≈20%** efficiency with **steam cycles** (exception: co-combustion in coal plants), and usually additional cogenerated heat (30%)
- efficiency is improved with prior **gasification** and use in gas **engines** (< 5 MW<sub>el</sub>) or **combined cycles** (multi 10-MW<sub>el</sub>)
- **biogases** are under-used for power generation (esp. from manure, agro-residues and MSW/ISW)
- they are converted in **engines** (0.1-1 MW<sub>el</sub>) with **30-40%** efficiency, and cogenerated heat

# Summary on biomass-to-mobility fuels

- **Bioethanol** may be advantageous in a few cases (sugar-Brazil, corn-USA) as a gasoline additive or replacement but can only supply a few% of world mobility fuel
- **Biodiesel** may remain marginal
- **Biogas** (as CH<sub>4</sub> in gas cars) is very valuable from manure, agro-residues, MSW as a natural gas substitute and still a largely untapped resource
- **Wood**-reserves could be used via gasification for upgrading to (2<sup>nd</sup> generation) biomethane and bioethanol