Biomass: liquids

BIOETHANOL

Source

- Solid (wood, straw)
- Wet (waste, manure)
- Sugar/starch
- Oil crops

Process

- Combustion
- Gasification
- Pyrolysis
- Methanation
- Fermentation
- Extraction + esterification

Product

- Heat
- Woodgas
- Woodoil
- Biogas
- Bioethanol
- Biodiesel

Service

- Heat / CHP
- Electricity
- (Transport) Fuels
- Chemicals

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	**32.2**	0.73
Diesel	43	**36.6**	0.85
Ethanol	26.7	**21.1**	0.79
Methanol	20	**15.9**	0.80

Properties

Property	Ethanol	Methanol	Gasoline	Diesel
formula	C_2H_5OH	CH_3OH	C5-C12	C14-C19
molar weight	46.1	32	100	240
C wt% H wt% O wt%	52.2 13.1 34.7	37.5 12.5 50	86 14 0	86 14 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%	
Octane index	**106-111**	**106-115**	**79-98**	
Cetane index	**0-5**	**0-10**	**5-10**	**45-55**

=> *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 /m²

(cf. 1 m² of grapes vineyard yield ca. 1 bottle of wine (0.7 L with 13% ethanol))

Energy balance

- aerobic respiration (O_2 from air):

$$C_6H_{12}O_6(2870kJ/mol) + 6O_2 \rightarrow 6CO_2 + 6H_2O + 38ATP(1160kJ) + heat(37°C)$$

  – 40% storage efficiency

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

$$C_6H_{12}O_6(2870kJ/mol) \rightarrow 2CO_2 + 2C_2H_5OH(2644kJ) + 2ATP(61kJ) + heat$$

  – 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 (→ 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 (→melasse), sterilised and fermented with yeast

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{invertase} 2\,C_6H_{12}O_6 \xrightarrow{zymase} 4\,C_2H_5OH + 4\,CO_2$$

- **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** (⅔ from plant production cost, ⅓ 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** (⅔ plant production, ⅓ 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% to10% 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_2) per L EtOH
  - reduced emissions of CO, HC, SO_X, 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

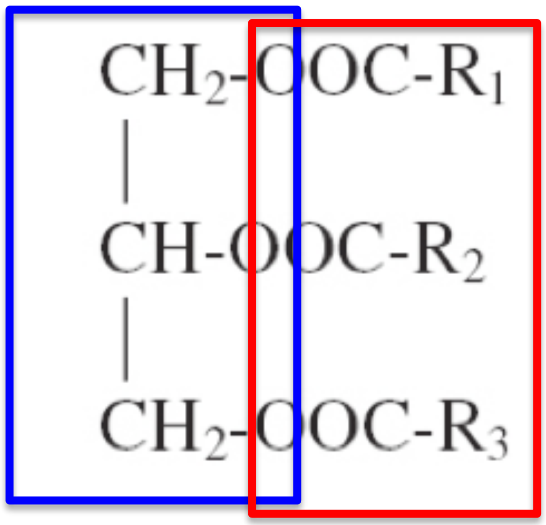
- as hydrated (**96%**, azeotrope) in all-ethanol engines (**Brasil**)
- as ‘dry’ (**99.7%**) blended with gasoline (5-10% in EU, USA; 24% in Brasil)
- its main drawback is the low yield and high land use; its application will thus remain limited (**≈5%** of transport fuel), with notable exceptions like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

BIODIESEL

Source	Process	Product	Service
Solid (wood, straw)	Combustion	Heat	Heat / CHP
Wet (waste, manure)	Gasification	Woodgas	Electricity
Sugar/starch	Pyrolysis	Woodoil	(Transport) Fuels
Oil crops	Methanation	Biogas	Chemicals
	Fermentation	Bioethanol	
	Extraction + esterification	Biodiesel	

Biodiesel

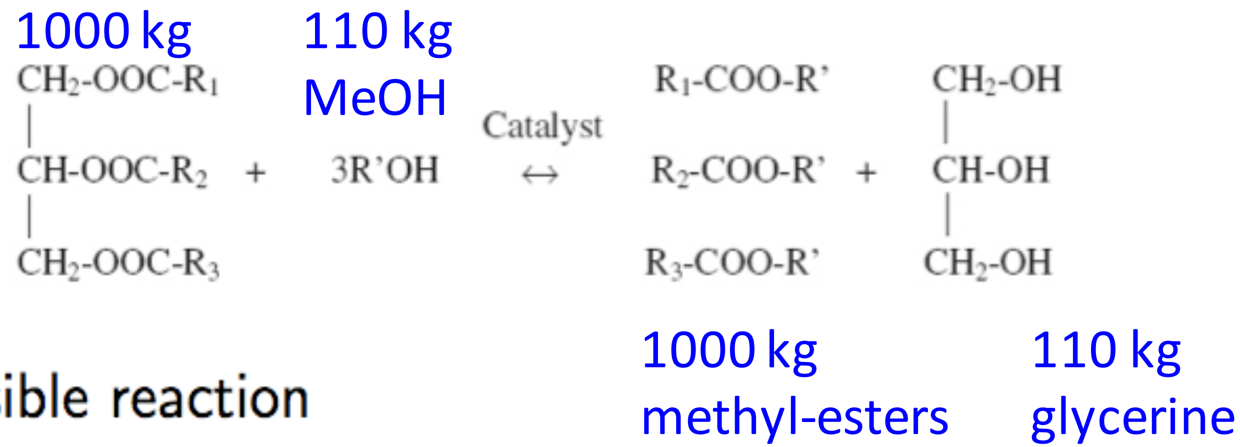
- Source :
  - rapeseed (*colza*), sunflower (*tournesol*), soyabean
    Oil content = 40%
  - animal fats, frying oil
- Triglycerides : 1 mol glycerine + 3 mol fatty acids



Transesterification process

Transesterification (alkoholysis):

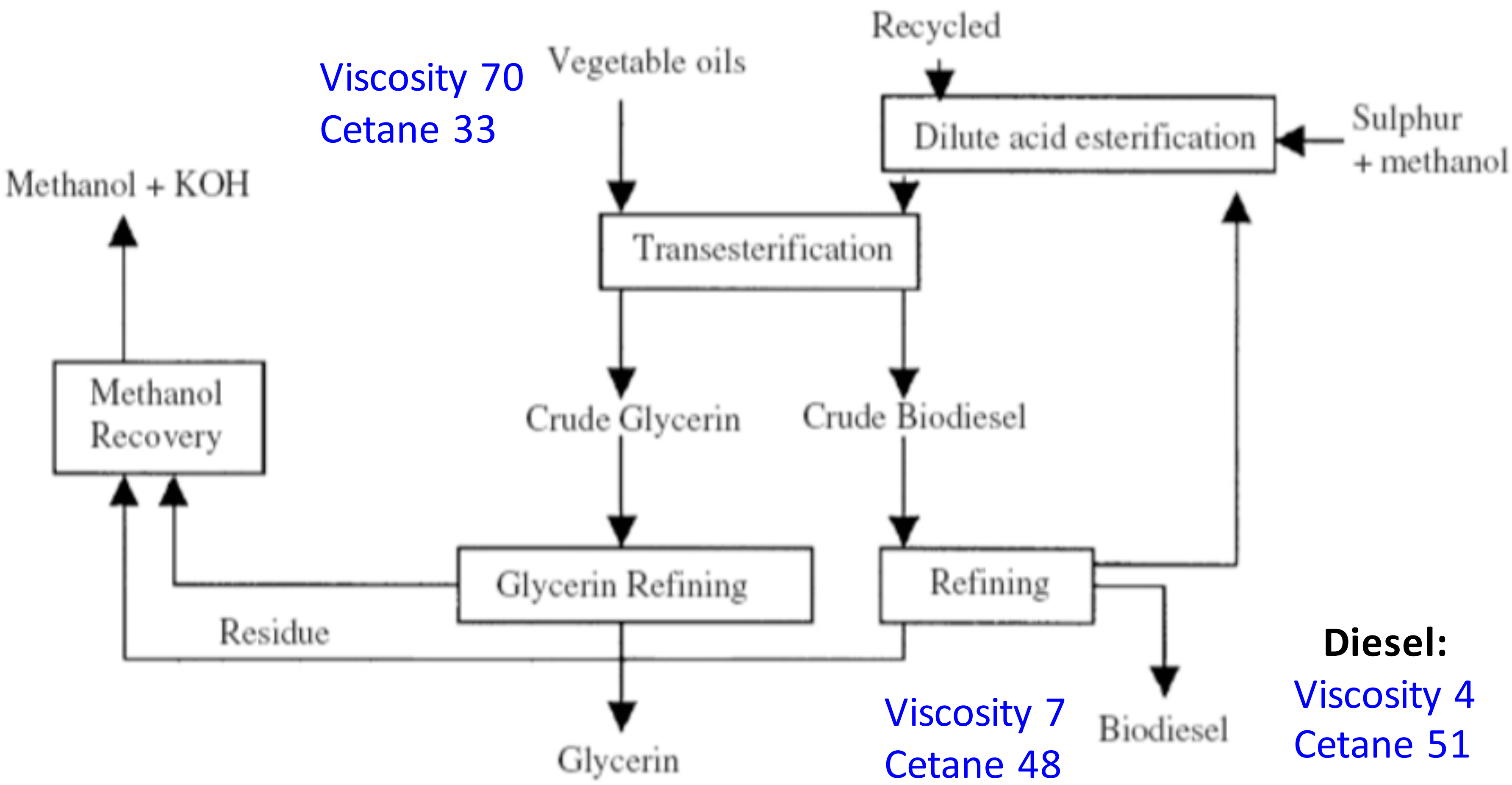
- reaction of triglyceride and alcohol to esters and glycerol:



- 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

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 *ca. ⅓*

Difference = transformation cost *ca. ⅔*

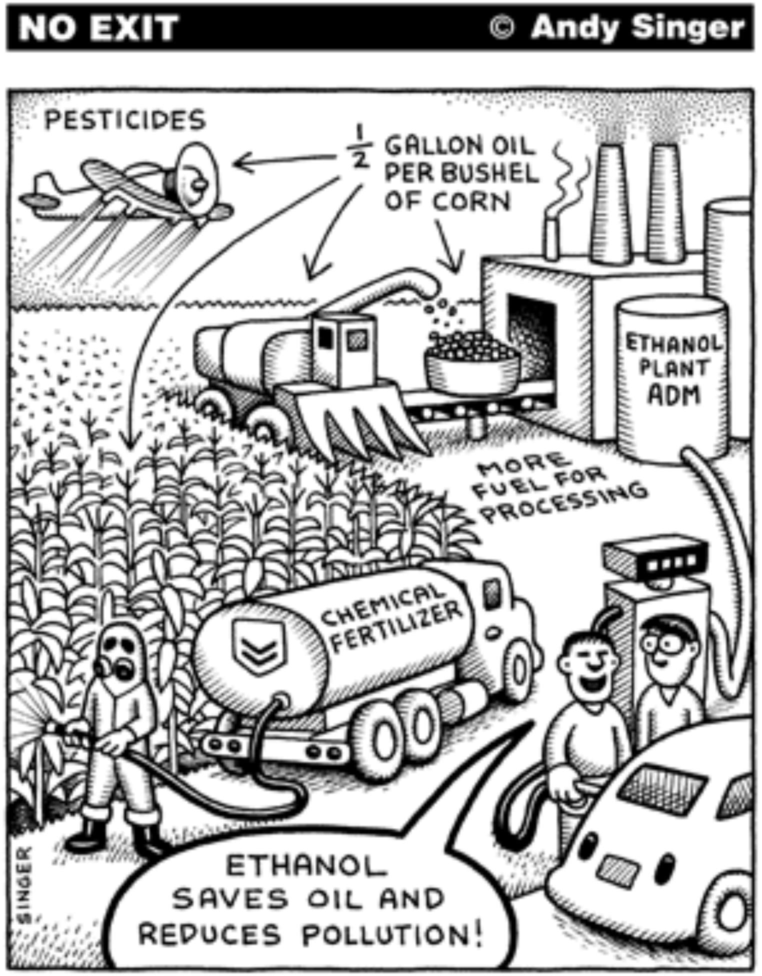
ca. 0.6 € / L

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^2/s 20°C	78	7.5	66	8	4
	Melting point °C	-2	-6	-18		
✔	**Cetane number**	**34**	**48**	**33**	**50**	**51**
✔	Carbon residue%	0.25	0.05	0.42	0.05	0.15
✔	Sulfur %	0.0001	0.24	0.01	0.01	0.29

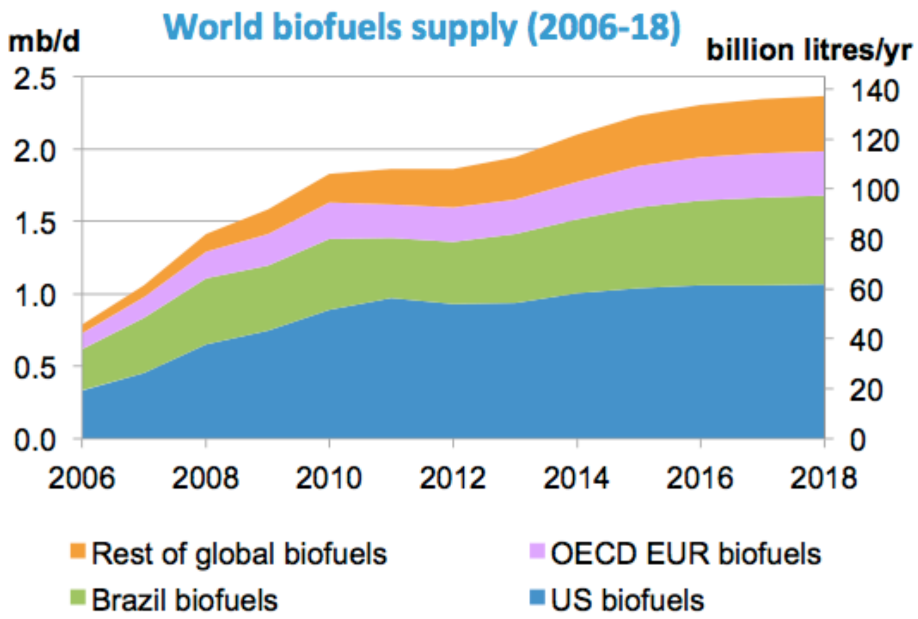
Biodiesel comments

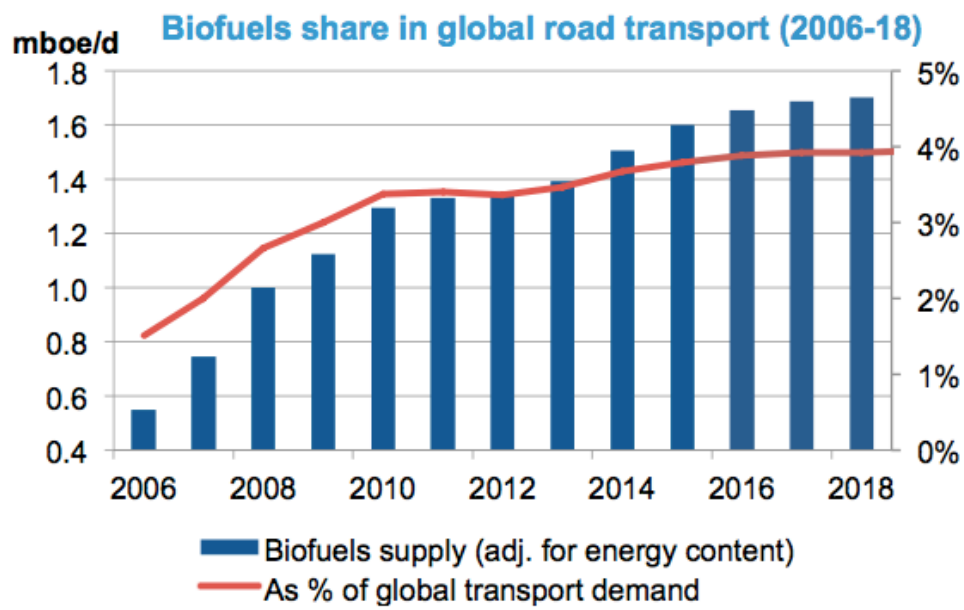
- its low yield and high land use are even (much) worse than for bioethanol
- it has no specific advantages in cost or efficiency over (fossil) diesel
- its use is very controversial and further marginalised



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 (2nd gen)





Mobility fuels from wood: 'secondary' generation biofuels

- **1st generation**
  - Biogas
  - Bioethanol
  - Biodiesel

  - limited conversion
  - slow processes
  - large residues

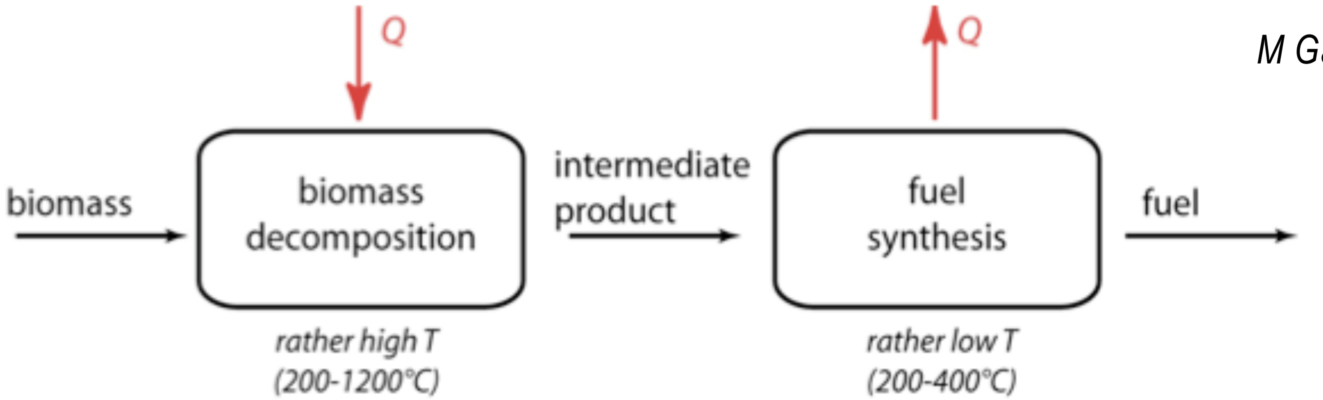
- **2nd generation**
  - **Wood** gas derivatives

  - efficient
  - catalysed (thermochemical)

2nd generation biofuels

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

M Gassner, EPFL



- gasification
- pyrolysis

non-condensable/ condensable substances (H_2, CO, CO_2, H_2O, CH_4, C_xH_y, char, tars)

Fuel synthesis step

- methanation
- FT synthesis
- DME synthesis
- methanol synthesis

Wood → syngas → methane

Gasification with producer gas to methane reforming:

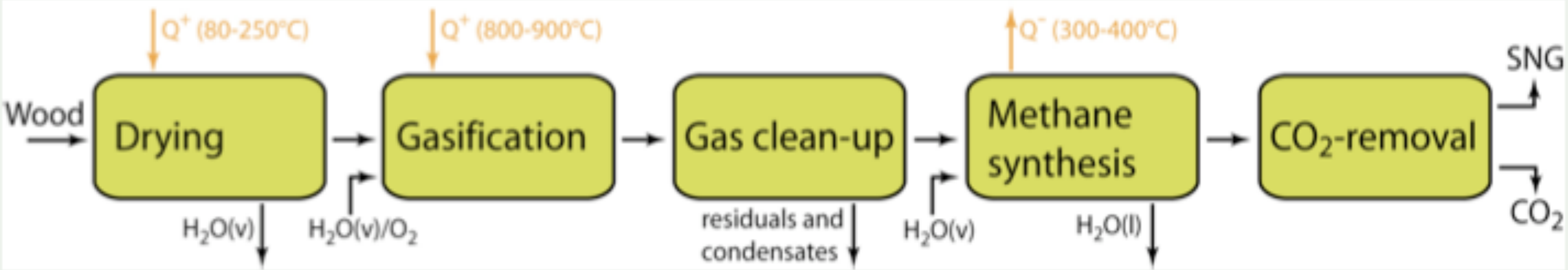
$$CO + 3H_2 \rightleftharpoons CH_4 + H_2O \qquad \Delta h_r^0 = -206 kJ/mol \qquad (1)$$

$$C_2H_4 + 2H_2O \rightleftharpoons 2CO + 4H_2 \qquad \Delta h_r^0 = 210 kJ/mol \qquad (2)$$

$$CO_2 + H_2 \rightleftharpoons CO + H_2O \qquad \Delta h_r^0 = 41 kJ/mol \qquad (3)$$

M Gassner, EPFL

Common wood to SNG route



$$CH_{1.35}O_{0.63} + 0.3475H_2O \xrightarrow{\Delta H^0 = -10.5\ kJ/mol_{wood}} 0.51125CH_4 + 0.48875CO_2$$

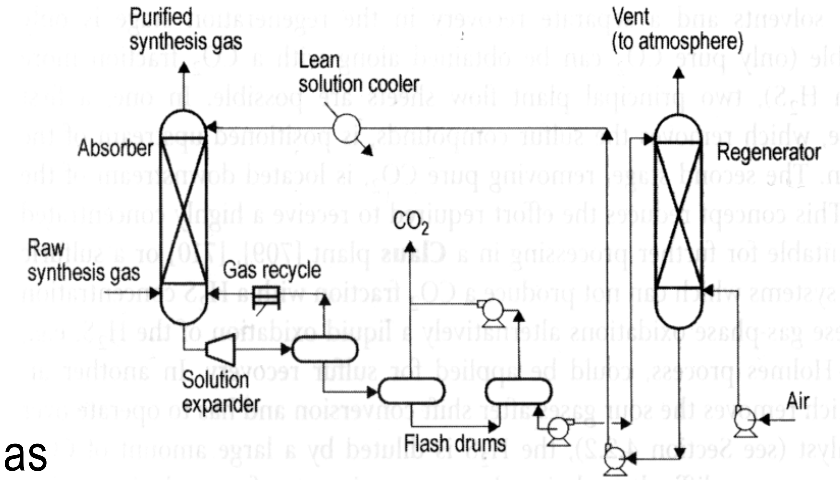
→ *CH_4/CO_2 separation needed*

CH_4 / CO_2 separation

M Gassner, EPFL

Physical absorption

Energy cost:
220 kWh_{el}/kg gas

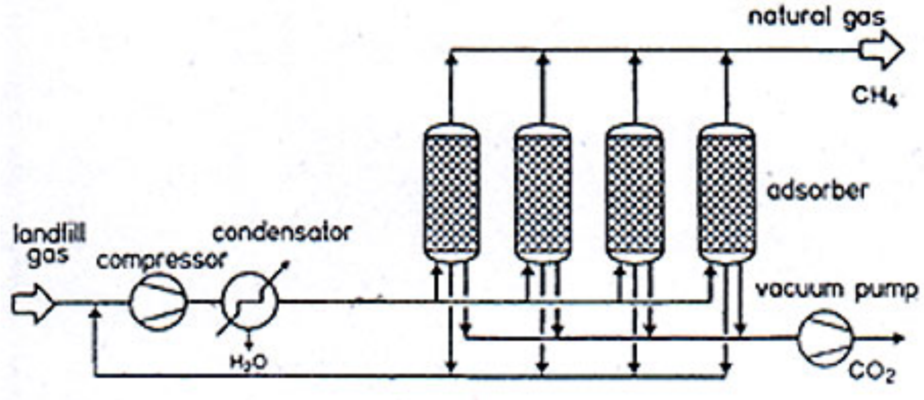


Appl, M.: Ammonia. Principles and Industrial Practice. Wiley, Weinheim, 1999.

P = 50 bar

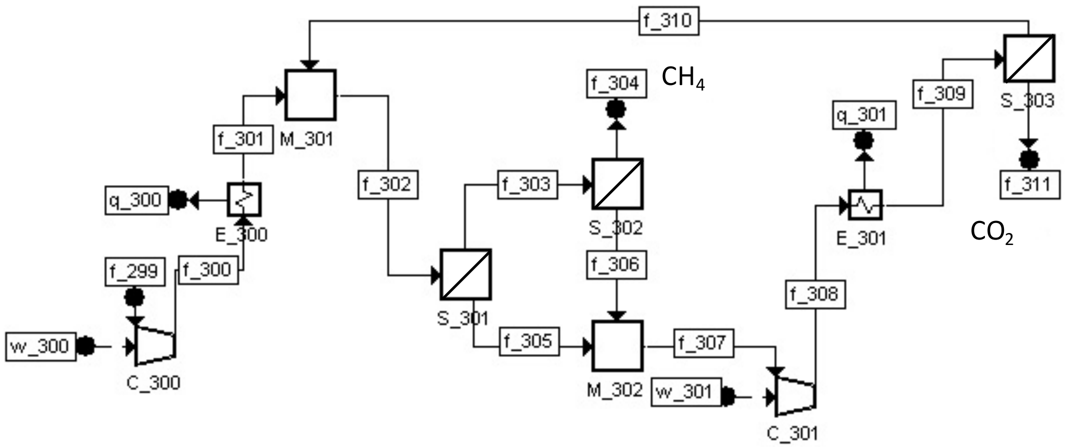
Pressure Swing Absorption

Energy cost:
70 kWh_{el}/kg gas



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

P = 5 – 6 bar



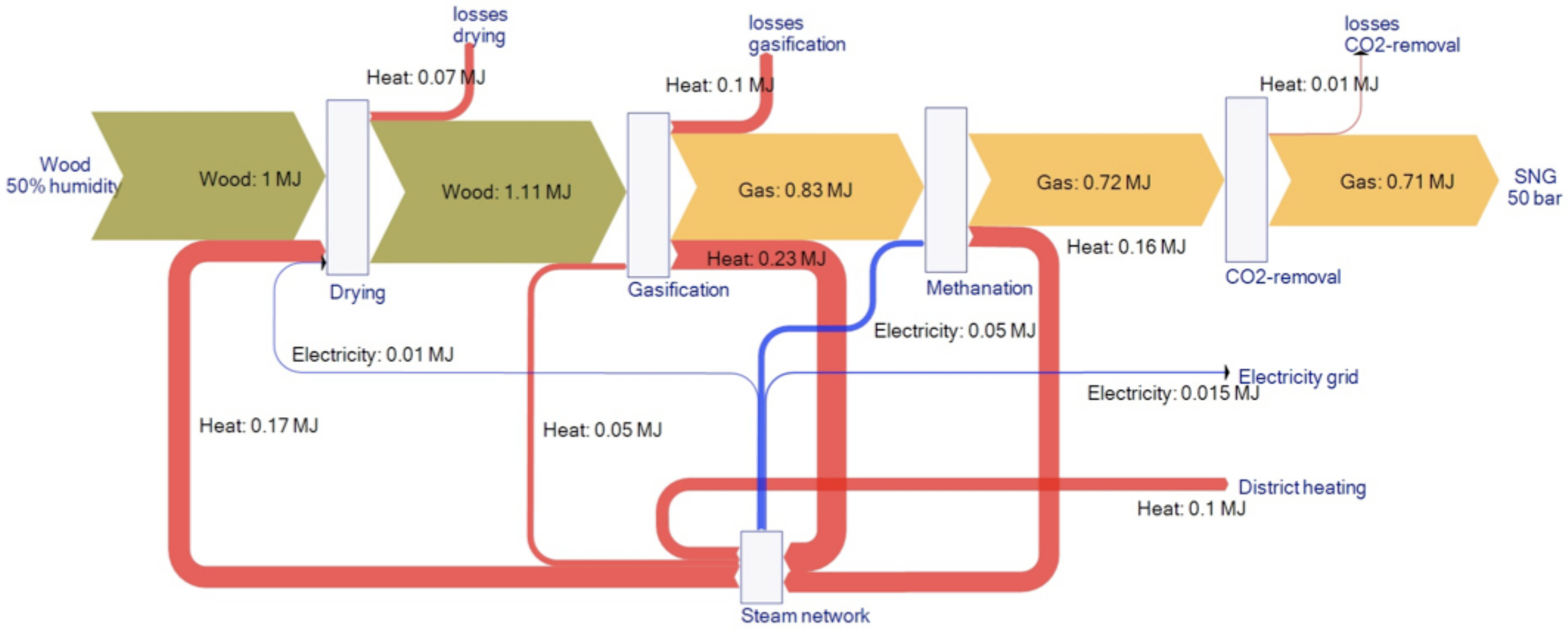
P = 50 bar

Polymer Membranes

Energy cost:
600 kWh_{el}/kg gas

Rem: 1 kg gas (50% CH_4) = 33 moles CH_4 = 3800 kWh

Efficiency for wood-to-CH_4: 70%



M Gassner, EPFL

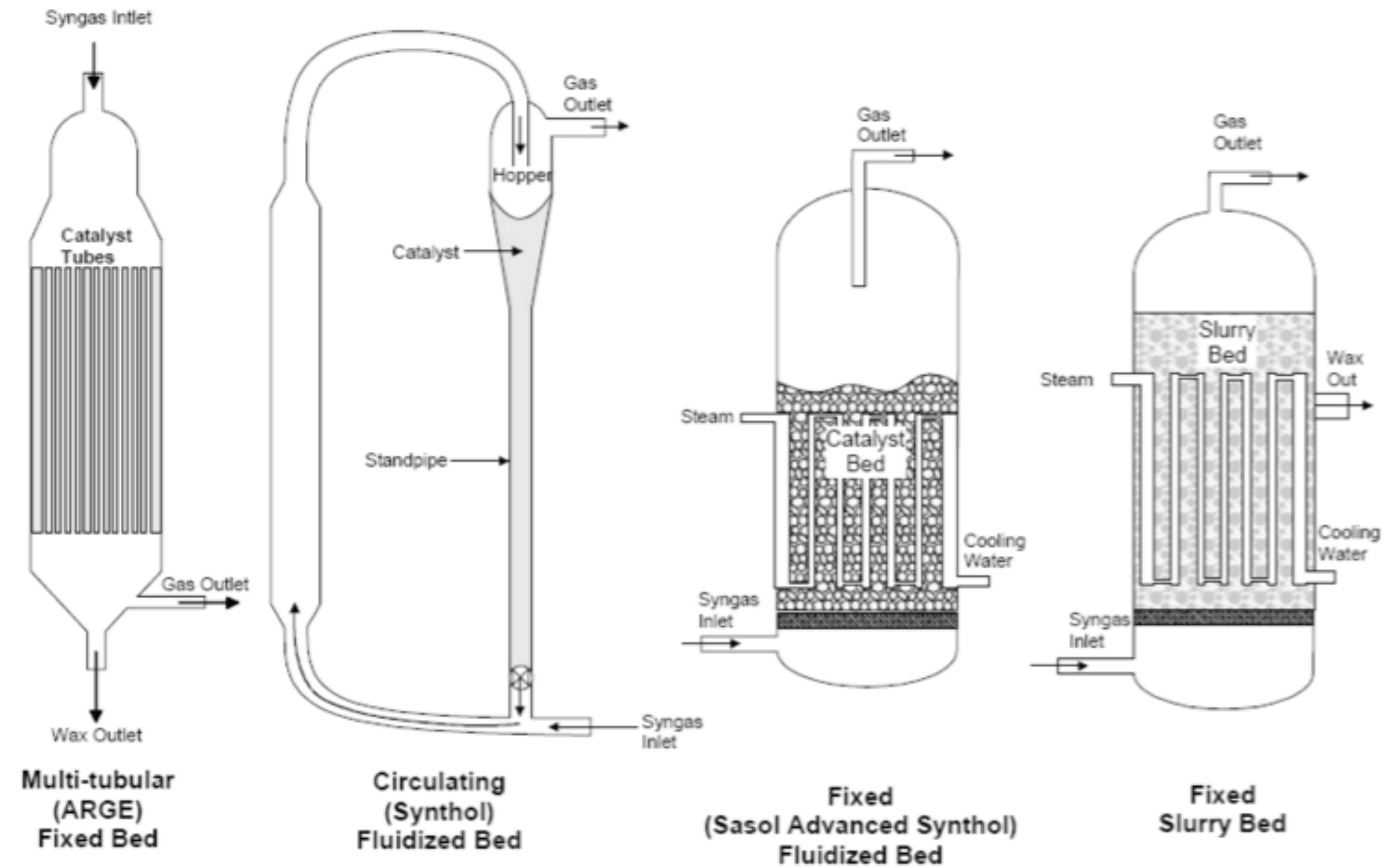
Liquid synfuel fabrication from syngas

Fischer-Tropsch synthesis:

- chain growth reaction (polymerisation) to heavy-weight liquid hydrocarbons:
  $CO + 2H_2 \rightarrow \text{-}CH_2\text{-} + H_2O, \qquad \Delta h_r^0 = \text{-}165\ kJ/mol$
- building blocks: H_2, CO
- CO/H_2-ratio adjustment via upstream water gas shift reaction:
  $CO_2 + H_2 \rightleftharpoons CO + H_2O, \qquad \Delta h_r^0 = 41\ kJ/mol$
- postprocessing
  - hydrocracking with H_2 to remove double bounds
  - wax $\rightarrow$ diesel + kerosene
  - ... petrochemical processing

M Gassner, EPFL

F-T technology is well established



from: Spath, P.L., Dayton, D.C., NREL/TP-510-34929, 2003.

Multi-tubular (ARGE) Fixed Bed	Fixed (Sasol Advanced Synthol) Fluidized Bed	Fixed Slurry Bed
T = 200-260°C	T = 350°C	T = 200-260°C
p = 20-30 bar	p = 25 bar	
Fe-catalyst	Co-catalyst	Fe-catalyst
main product: wax	main products: gasoline, light olefins	mainly products: wax

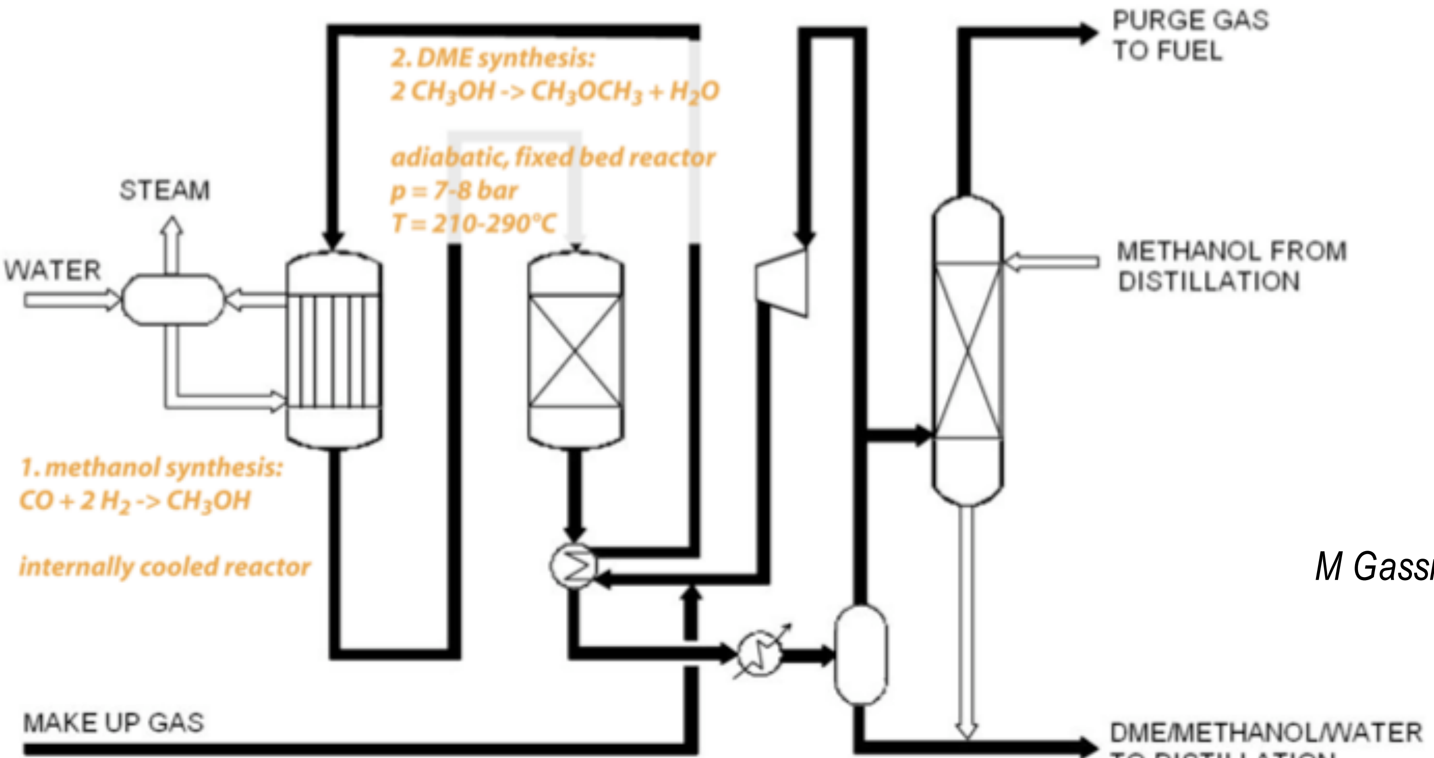
M Gassner, EPFL

DME synthesis

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

two step (via methanol dehydration)

- $CO + 2\,H_2 \rightleftharpoons CH_3OH,\quad \Delta h_r^0 = -90\ kJ/mol$
- $2\,CH_3OH \rightleftharpoons CH_3OCH_3 + H_2O,\quad \Delta h_r^0 = -183\ kJ/mol$

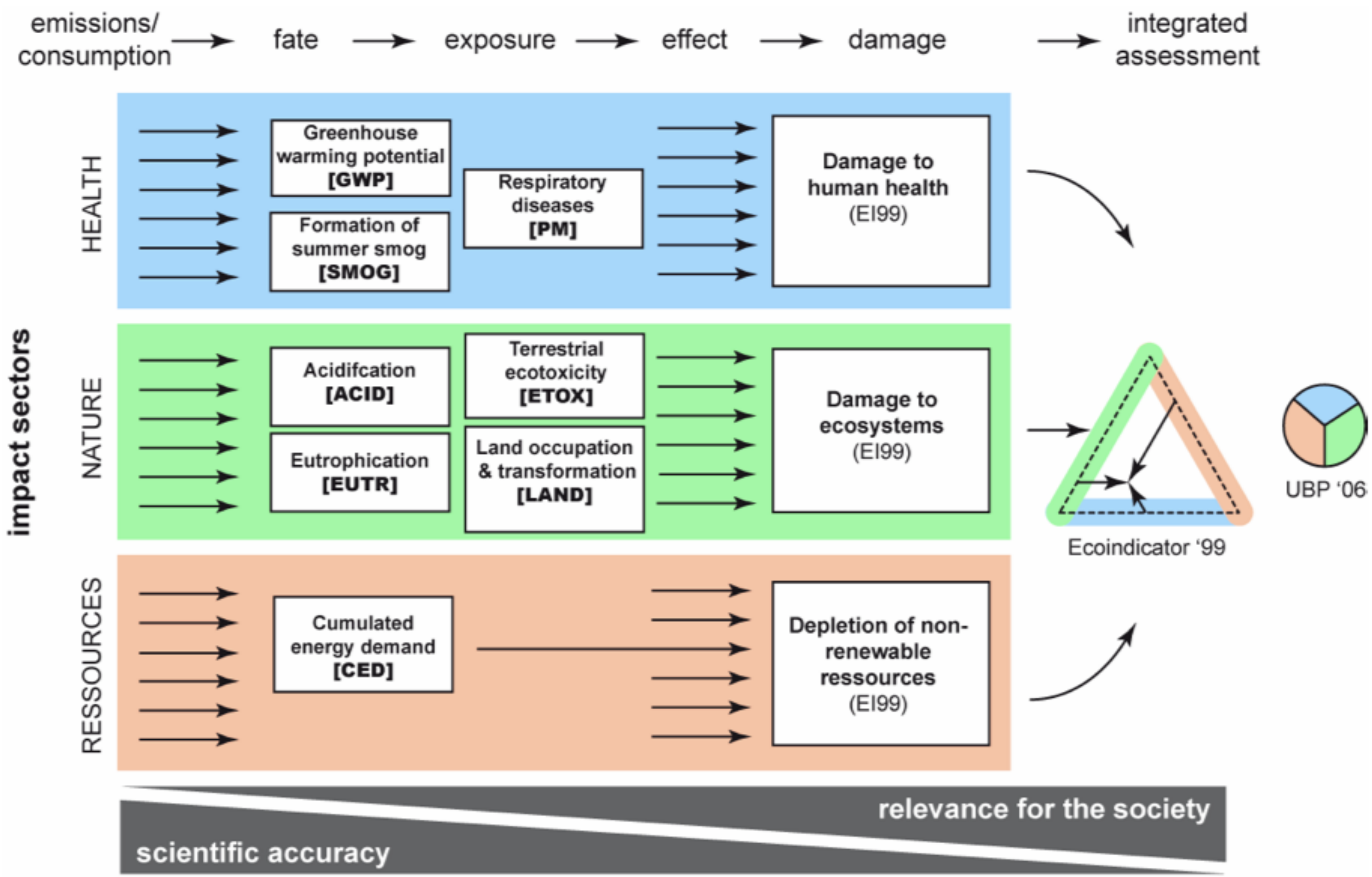


adapted from: Topsoe technology for large-scale production of DME. Topsoe Technologies, Denmark

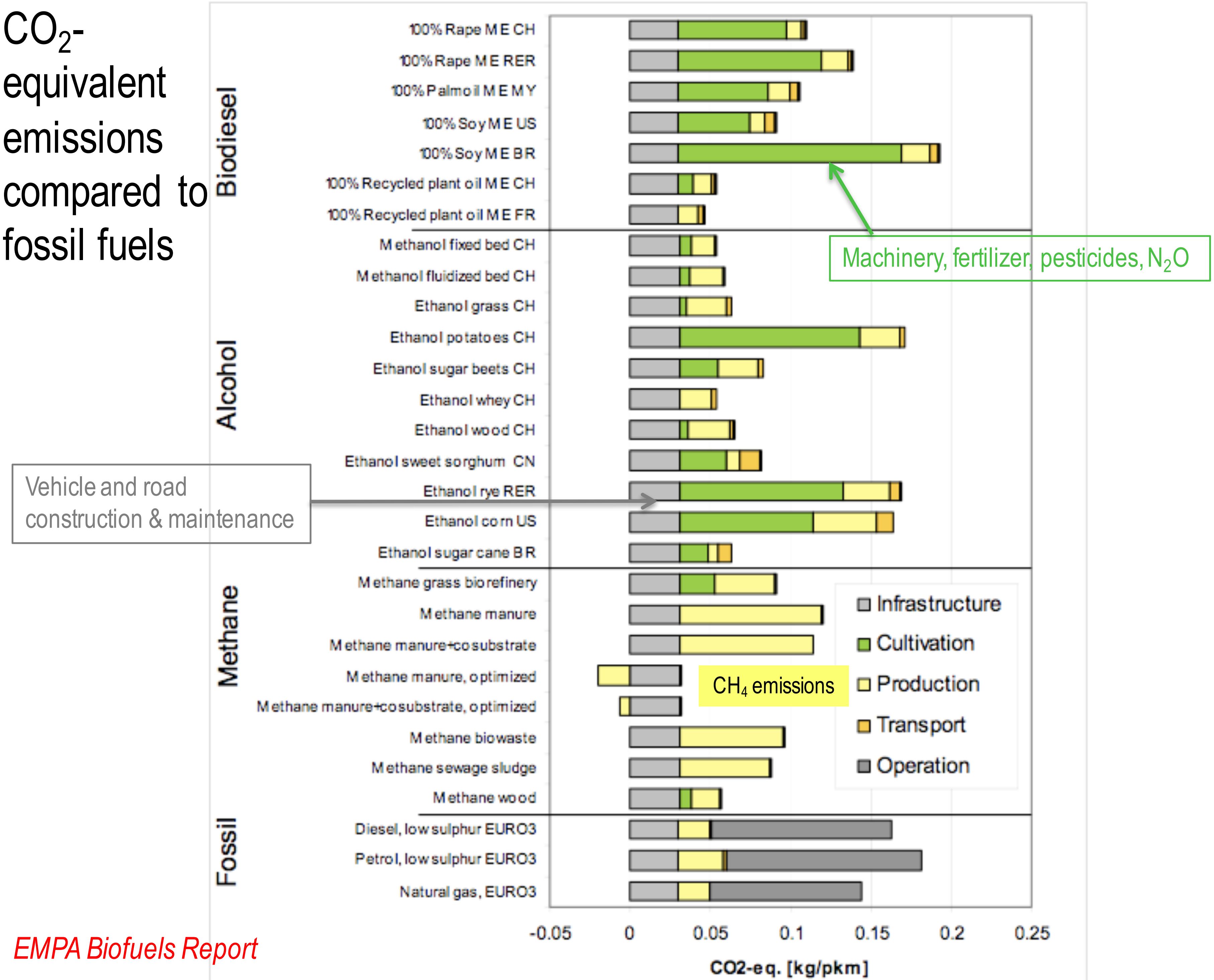
M Gassner, EPFL

EMPA report (2007/2013) on biofuel assessment

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

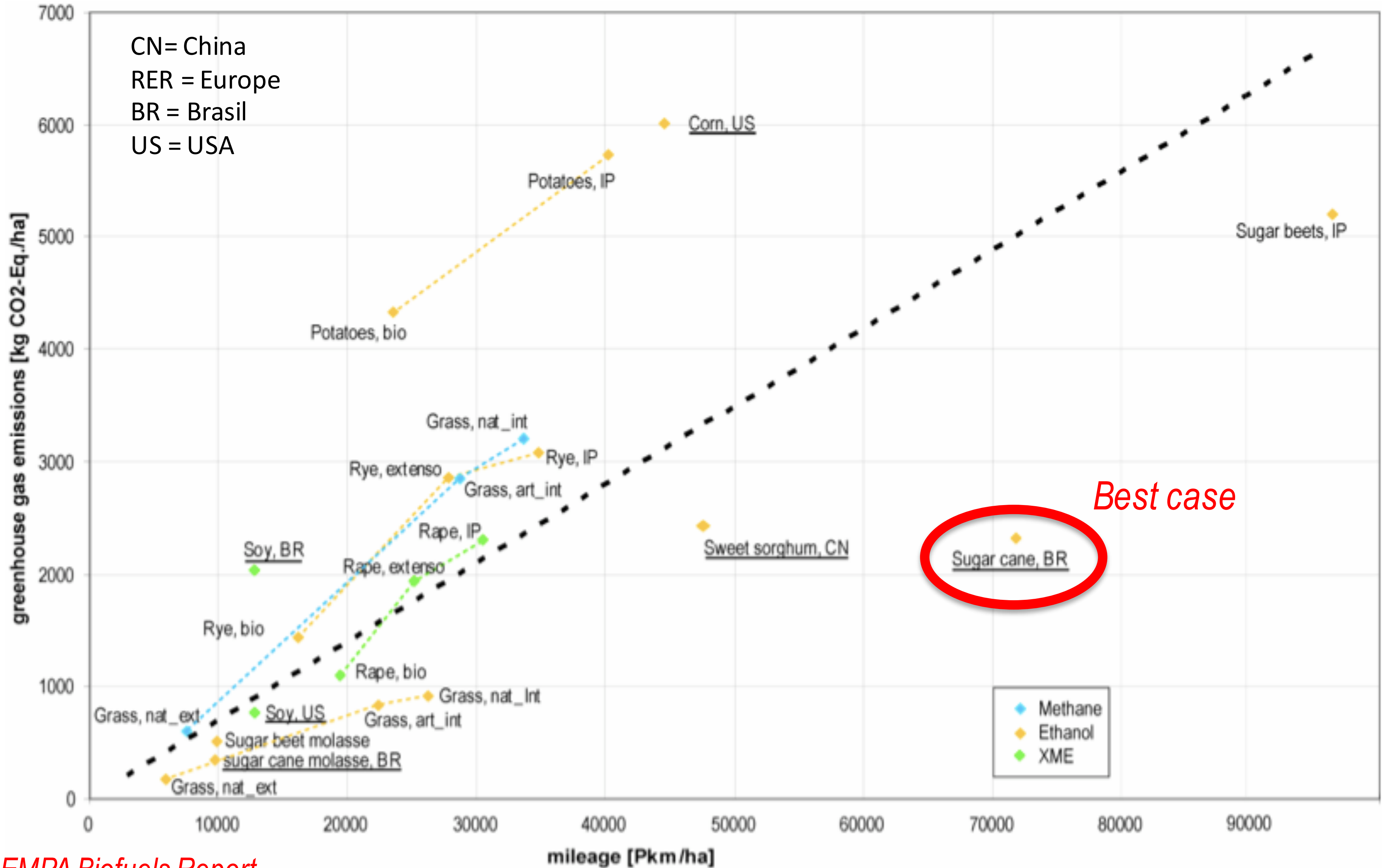


CO_2-equivalent emissions compared to fossil fuels

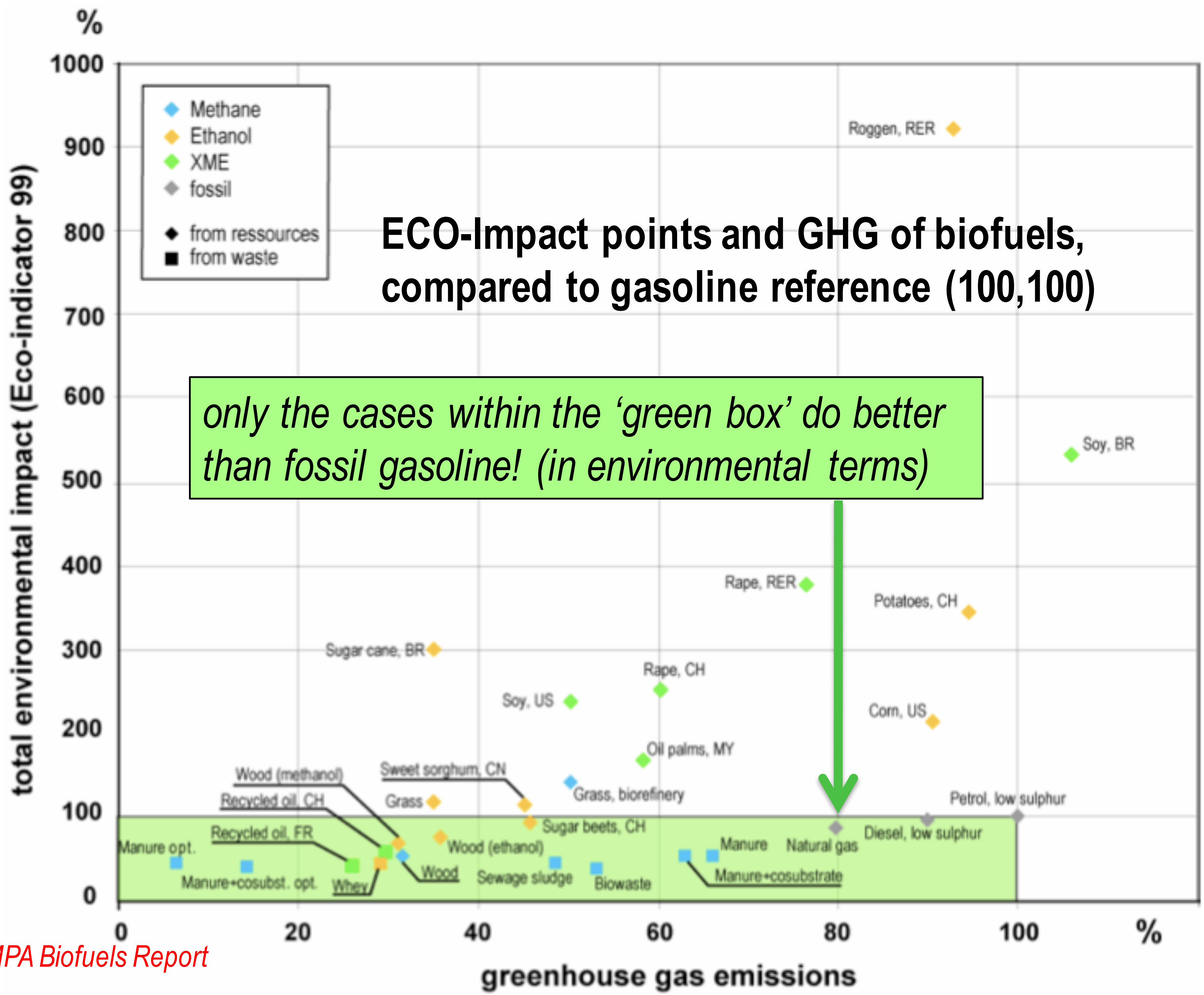


EMPA Biofuels Report

CO_2-equiv. emissions vs. transport-km (per ha land use)



EMPA Biofuels Report

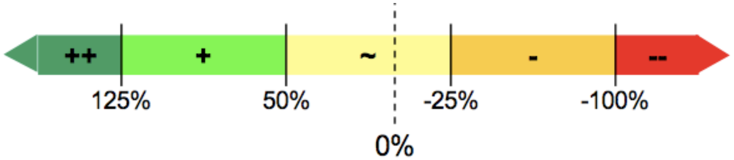


EMPA Biofuels Report

GHG-impact

use path \ energy carrier	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



EMPA Biofuels Report

ECO99’-impact

use path \ energy carrier	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_{el} 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_{el}) or **combined cycles** (multi 10-MW_{el})
- **biogases** are under-used for power generation (esp. from manure, agro-residues and MSW/ISW)
- they are converted in **engines** (0.1-1 MW_{el}) with **30-40%** efficiency, and cogenerated heat

Summary on biomass-to-mobility fuels

- **Bioethanol** may be advantageous in a few cases (sugar-Brasil, 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_4 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 (2nd generation) biomethane and bioethanol