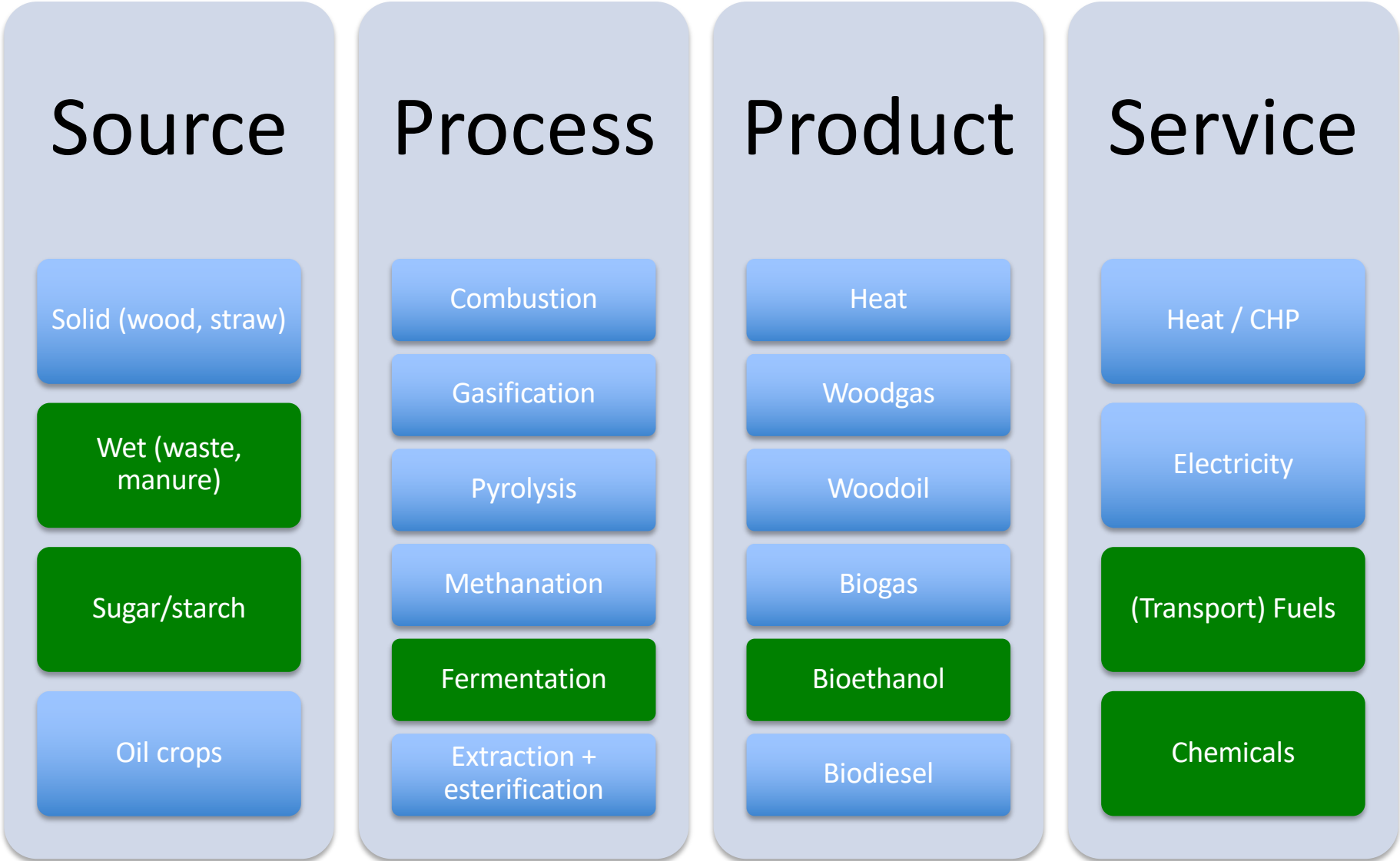


# **Biomass: liquids**

# BIOETHANOL



# General characteristics

- **Advantages:**
  - (indigenous) natural resource; reduces oil import
  - known and simple technology; labour-intensive
  - large application domain; usually 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	C <sub>2</sub> H <sub>5</sub> OH	CH <sub>3</sub> 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)*

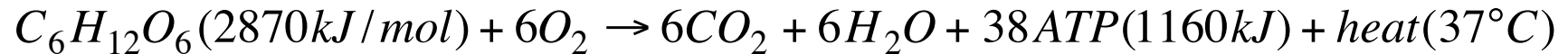
**LOW !** 

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

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

# Energy balance

- aerobic respiration (O<sub>2</sub> from air):



- 40% storage efficiency

- **fermentation** (the yeast uses O<sub>2</sub> 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 (→ wine!)

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

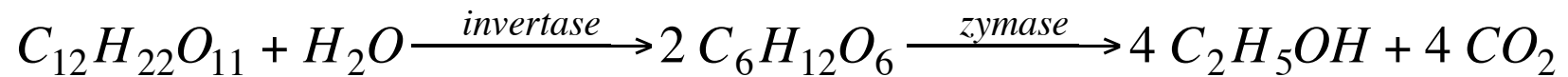
Yields a pure CO<sub>2</sub> output stream : perfect for CO<sub>2</sub> capture! => C-negative process



# 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)

# Ethanol efficiency effects in engines

- 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% to 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**)

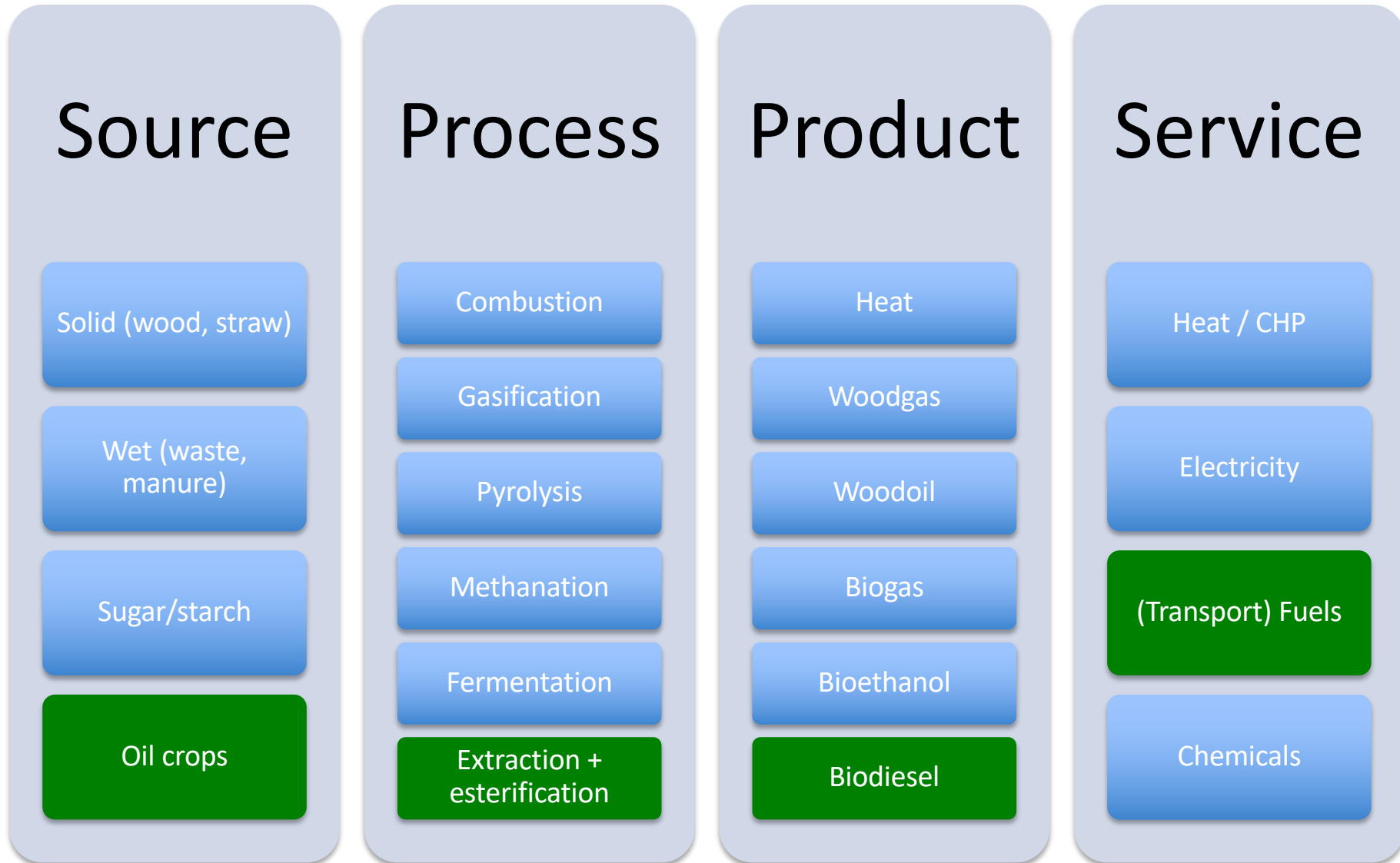
Source:

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

# Bioethanol use

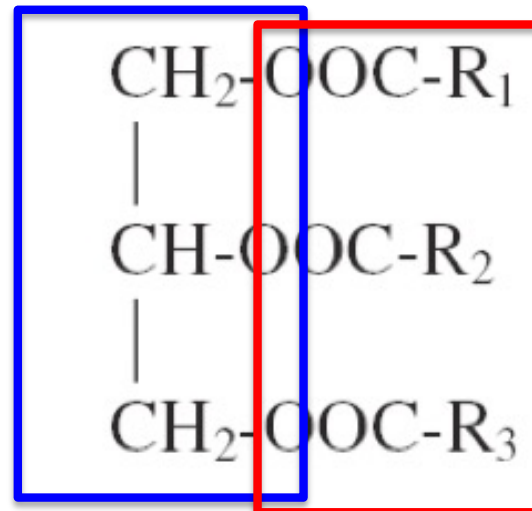
- as hydrated (**96%**, azeotrope) in all-ethanol engines (**Brasil**)
- as 'dry' (**99.7%**) blended with gasoline (5-10% in EU, USA; 24% in Brasil)
- its main drawback is the **low yield and high land use**; its application is expected to remain limited (**≈5%** of transport fuel), with notable exceptions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

# BIODIESEL



# Biodiesel

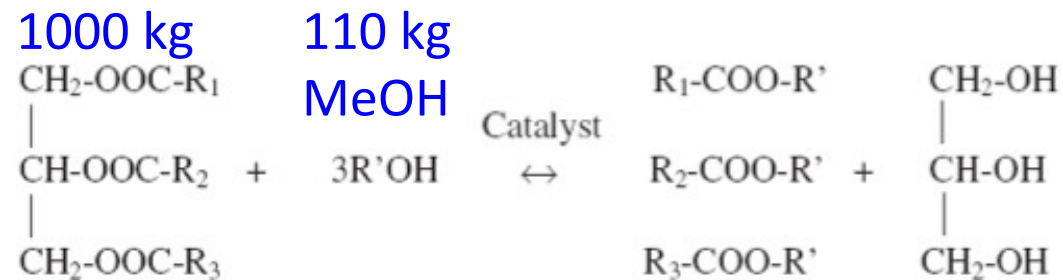
- Source : oil-rich plants
  - rapeseed (*colza*), sunflower (*tournesol*), soyabean,...
  - Oil content = 40%
  - animal fats, frying oil
- Triglycerides : 1 mol glycerine + 3 mol fatty acids



# 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, ...

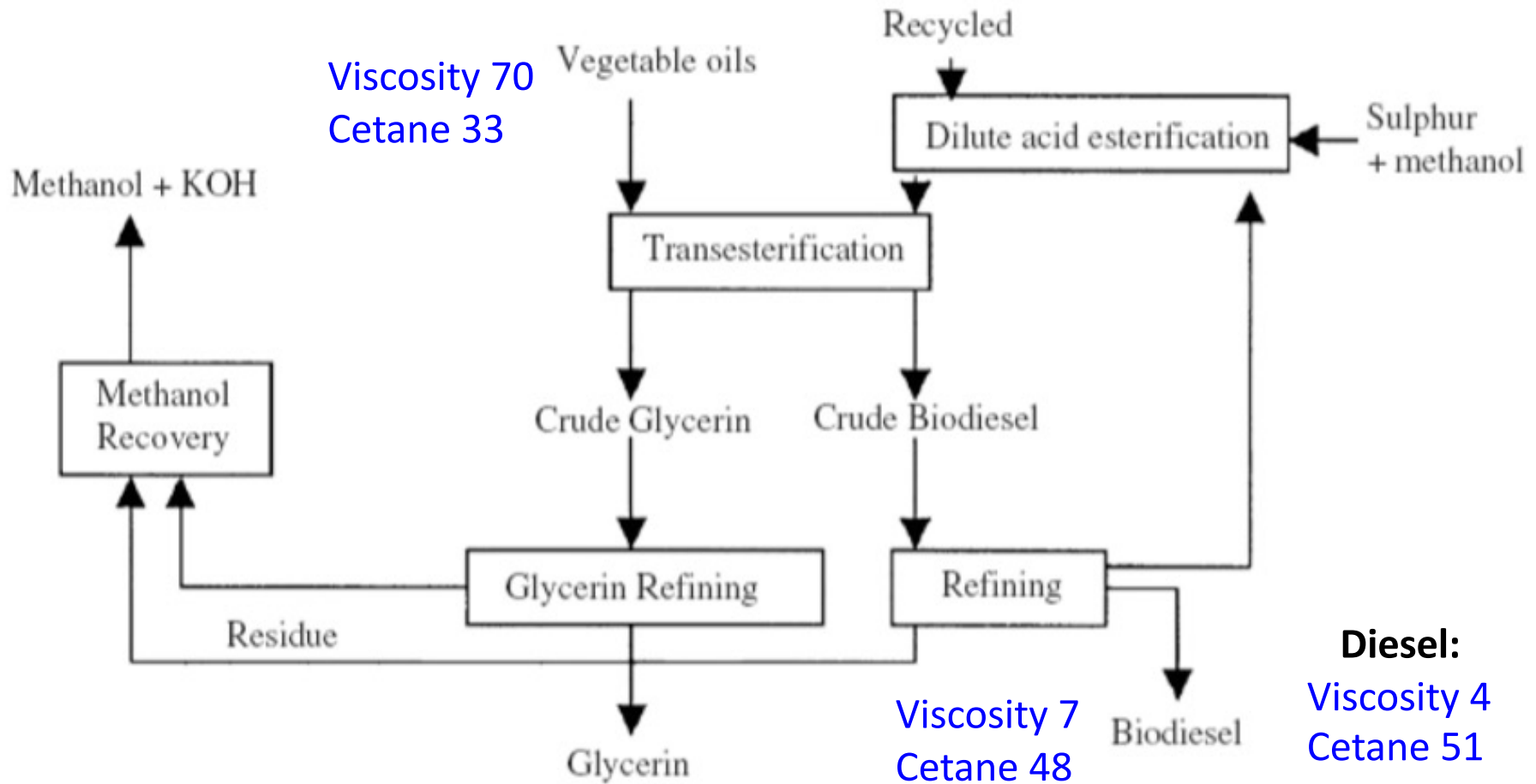
- most frequently used: methanol

- 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 ( <i>colza</i> )	1.49	40	264	661	680
Saf-flower ( <i>safran</i> )	0.856	35	268	766	340
Cynara ( <i>cardon</i> )	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**

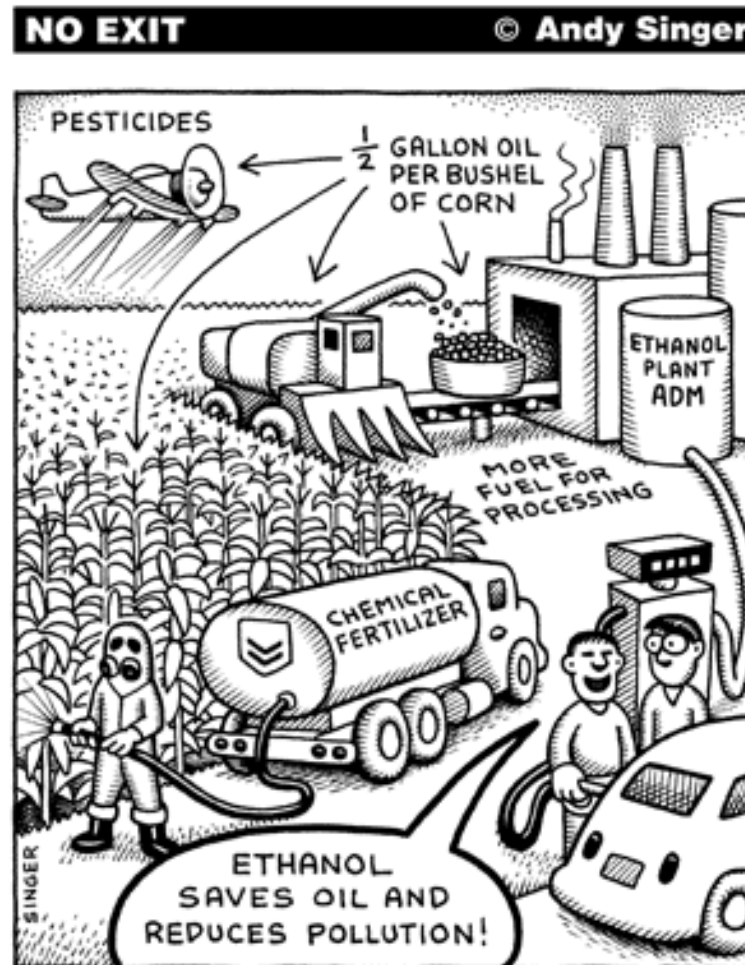


# Biodiesel vs. diesel

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

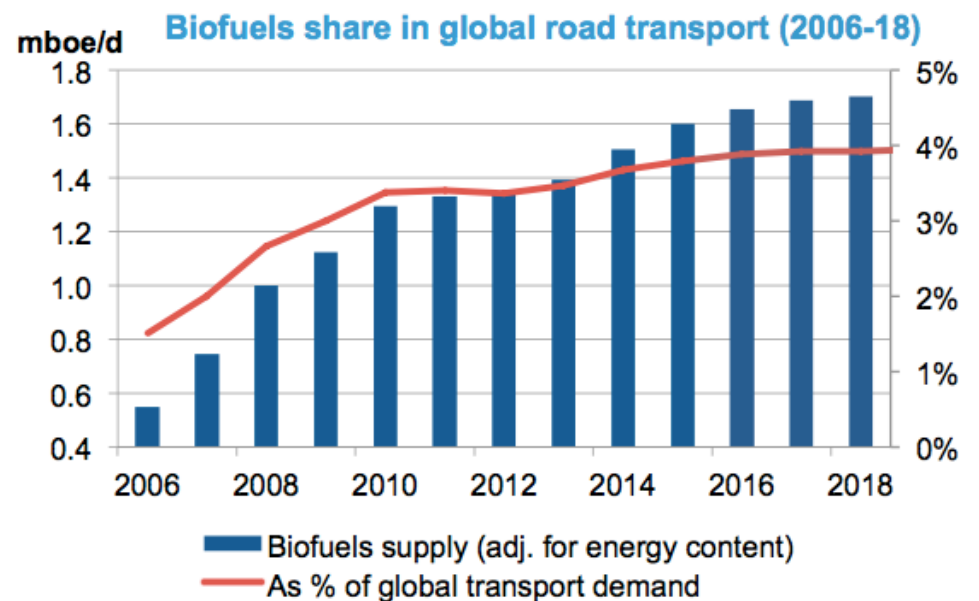
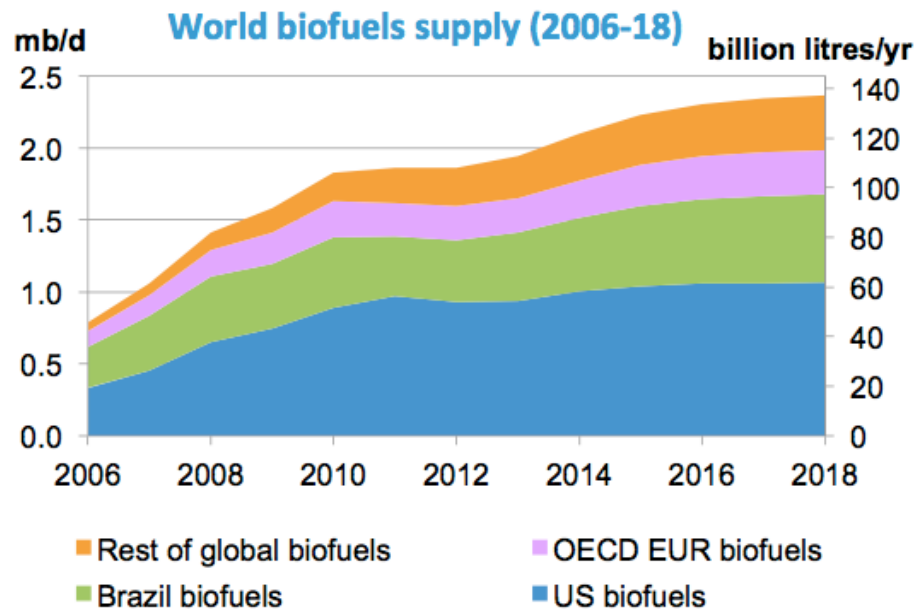
# Biodiesel comments

- its **low yield and high land use** are worse than for bioethanol
- it has no clear advantages in cost or efficiency over (fossil) diesel
- But: diesel is used in **many more engines** than gasoline



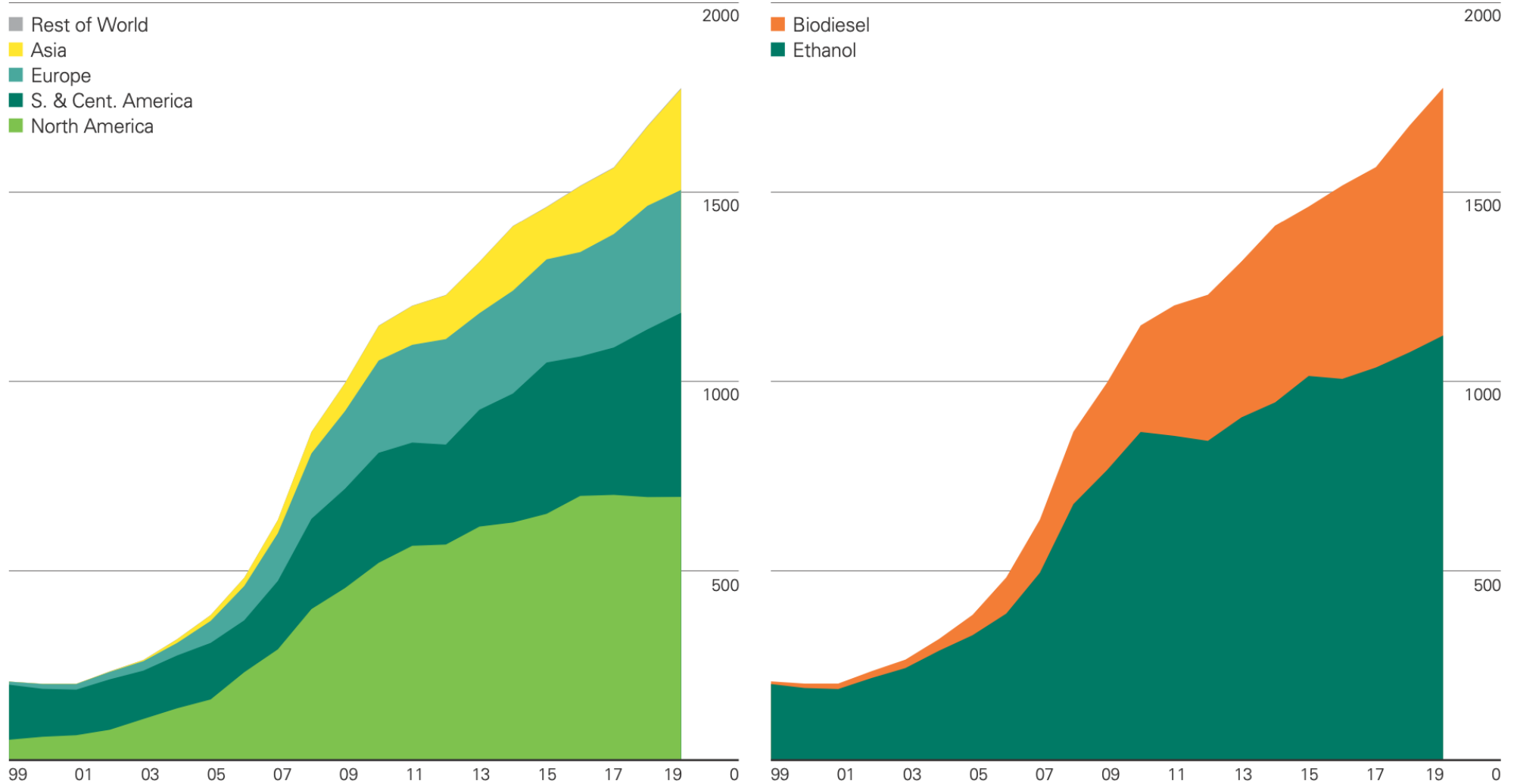
# IEA Facts on biofuels

- 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)



## World biofuels consumption

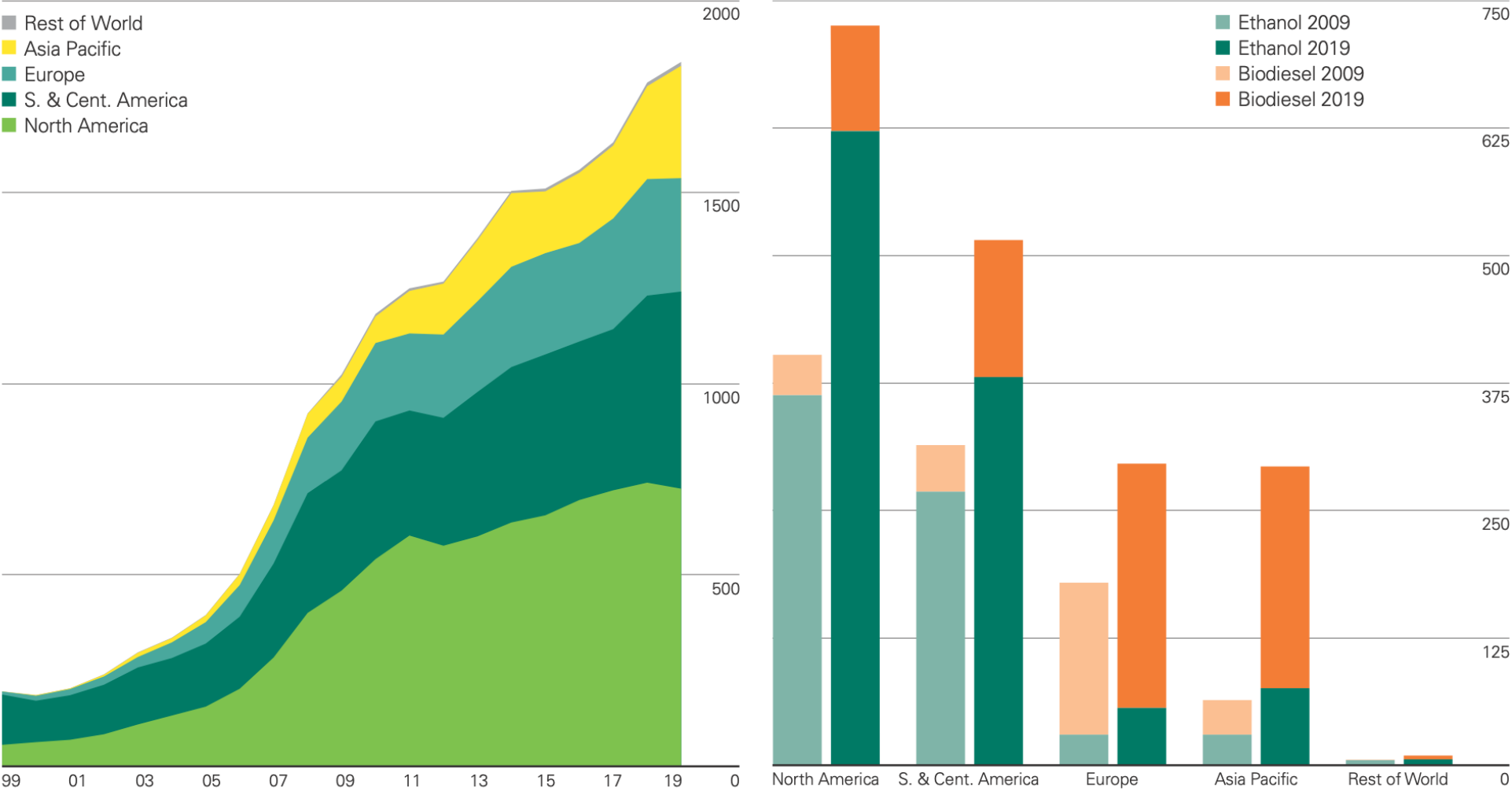
Thousand barrels of oil equivalent per day



Biofuels consumption rose by 6% (100,000 boe/d). As with production, growth was driven mainly by Brazil (42,000 boe/d), most of which was ethanol and Indonesia (56,000 boe/d), which was largely biodiesel. At the global level, ethanol made up 63% of biofuels in 2019, but the share of biodiesel has risen continually. For example, biodiesel's share was 23% in 2009 but rose to 37% last year.

**World biofuels production**

Thousand barrels of oil equivalent per day



Biofuels production growth averaged 3% (54,000 barrels of oil equivalent per day or boe/d, less than half the 10-year average). Growth was led by Brazil (31,000 boe/d) and Indonesia (32,000 boe/d) but US output declined by 19,000 boe/d. Growth was weighted towards biodiesel, which grew by 34,000 boe/d driven largely by Indonesia. Biodiesel is the dominant fuel in Europe and Asia Pacific (making up 81% and 74% of biofuels respectively in 2019), while ethanol is the main fuel in North America (86% of total) and S&C America (74%).

# Mobility fuels from wood: 'secondary' generation biofuels

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

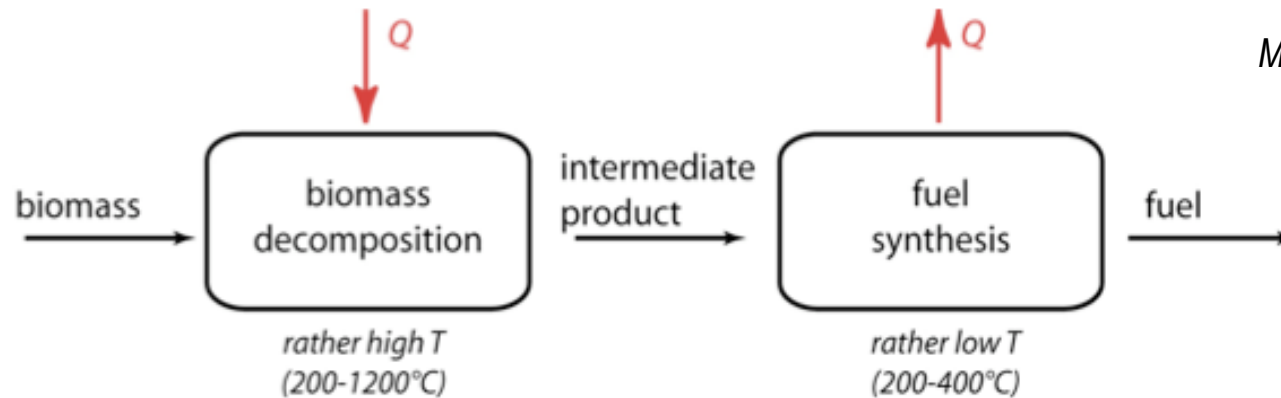
- Biogas
- Bioethanol
- Biodiesel
  
- limited conversion
- slow processes
- large residues

- **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:



- gasification
- pyrolysis

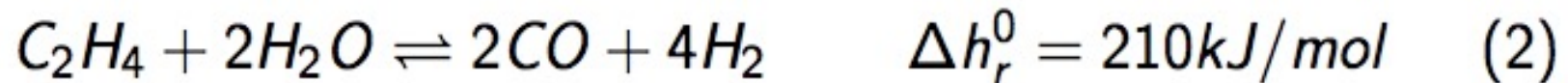
non-condensable/  
condensable  
substances  
( $H_2$ ,  $CO$ ,  $CO_2$ ,  $H_2O$ ,  
 $CH_4$ ,  $C_xH_y$ ,  
char, tars)

## Fuel synthesis step

- methanation
- FT synthesis
- DME synthesis
- methanol synthesis

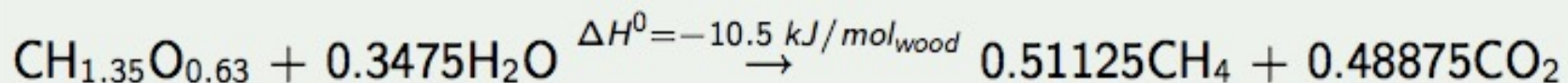
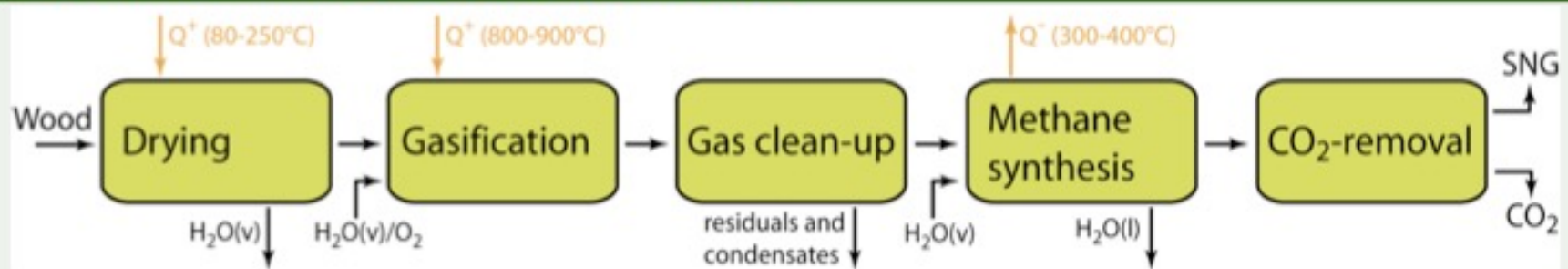
# Wood → syngas → methane

Gasification with producer gas to methane reforming:



M Gassner, EPFL

## Common wood to SNG route



→ CH<sub>4</sub>/CO<sub>2</sub> separation needed

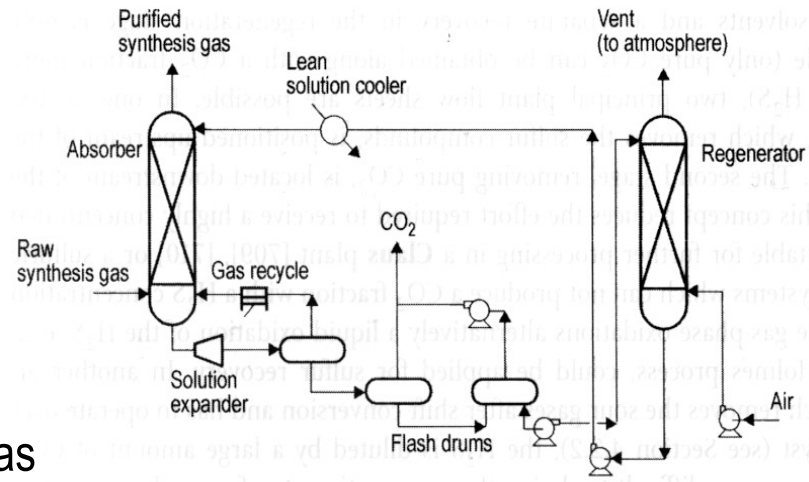


# CH<sub>4</sub> / CO<sub>2</sub> separation

M Gassner, EPFL

## Physical absorption

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

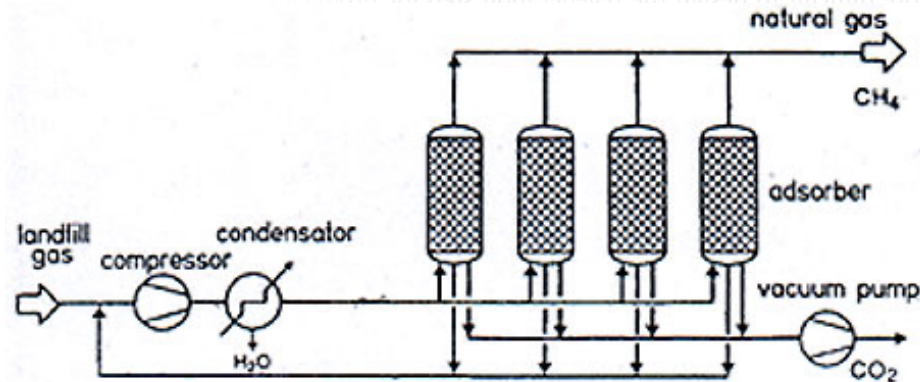


Appl, M.: Ammonia. Principles and Industrial Practice. Wiley, Weinheim, 1999.

P = 50 bar

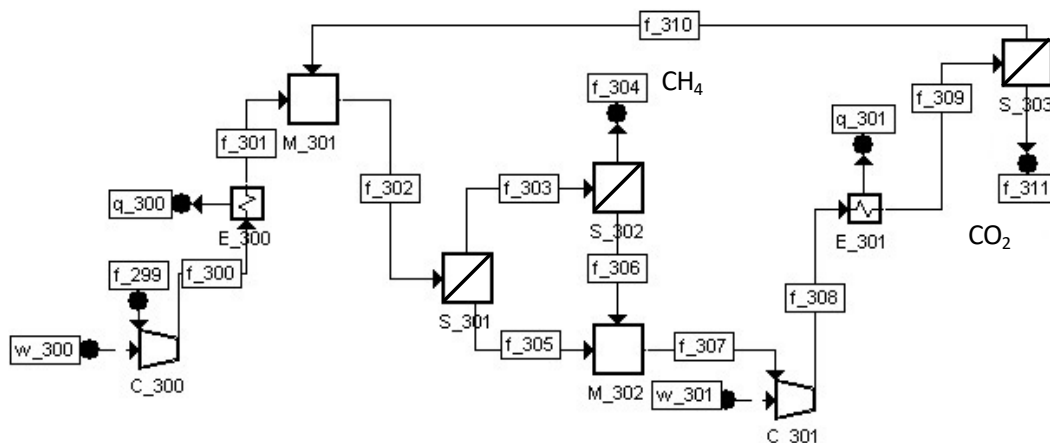
## Pressure Swing Adsorption

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



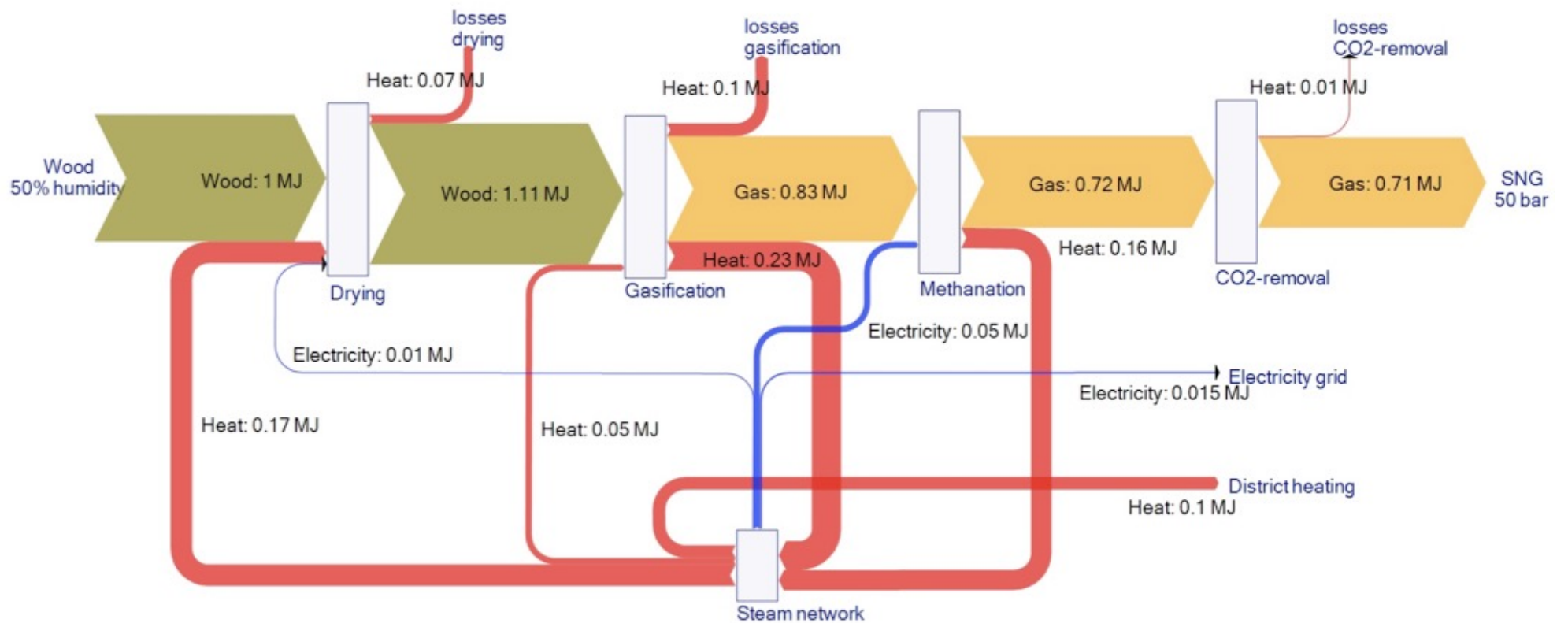
P = 50 bar

## 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%

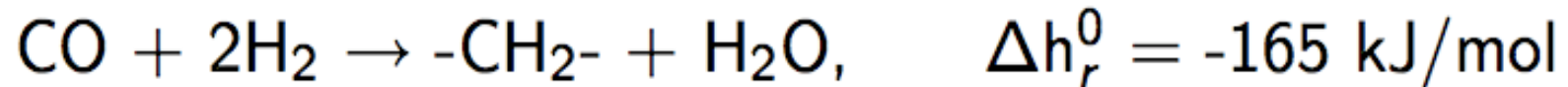


M Gassner, EPFL

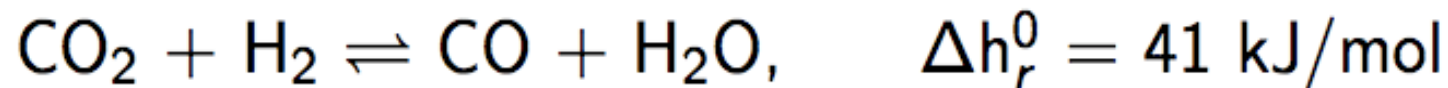
# Liquid synfuel fabrication from syngas

## **Fischer-Tropsch** synthesis:

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



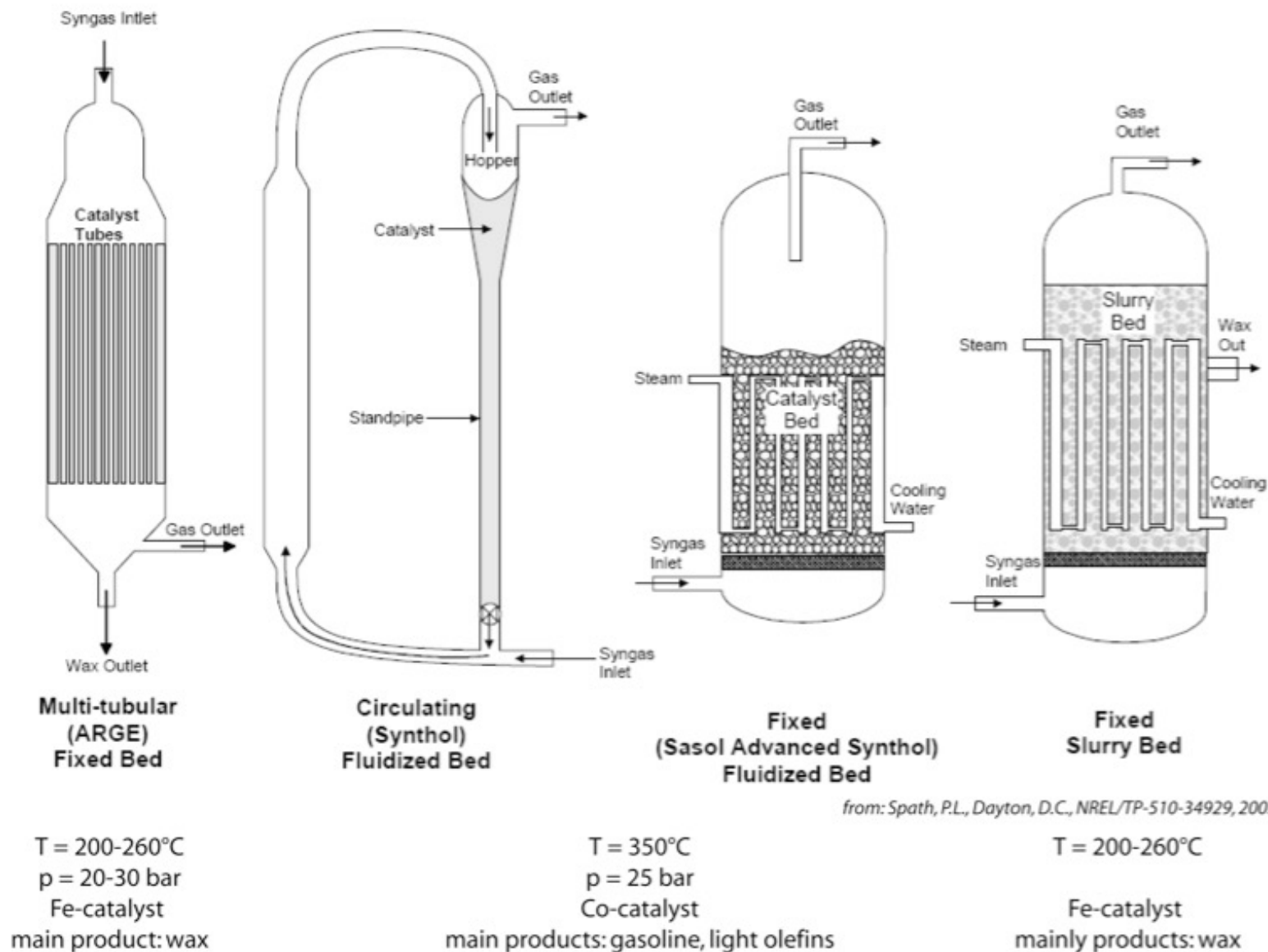
- building blocks:  $\text{H}_2$ ,  $\text{CO}$
- $\text{CO}/\text{H}_2$ -ratio adjustment via upstream water gas shift reaction:



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

*M Gassner, EPFL*

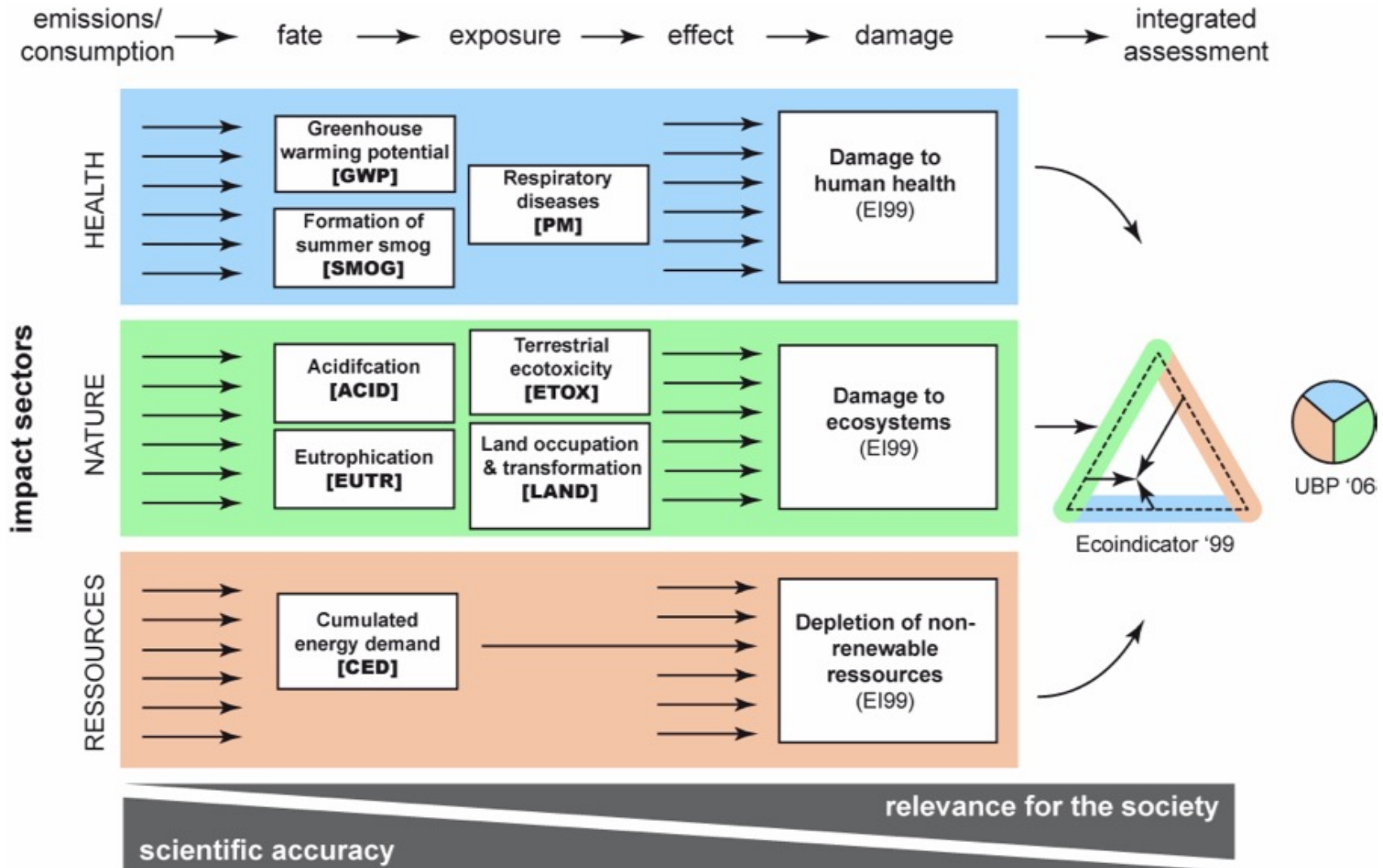
# F-T technology is well established



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

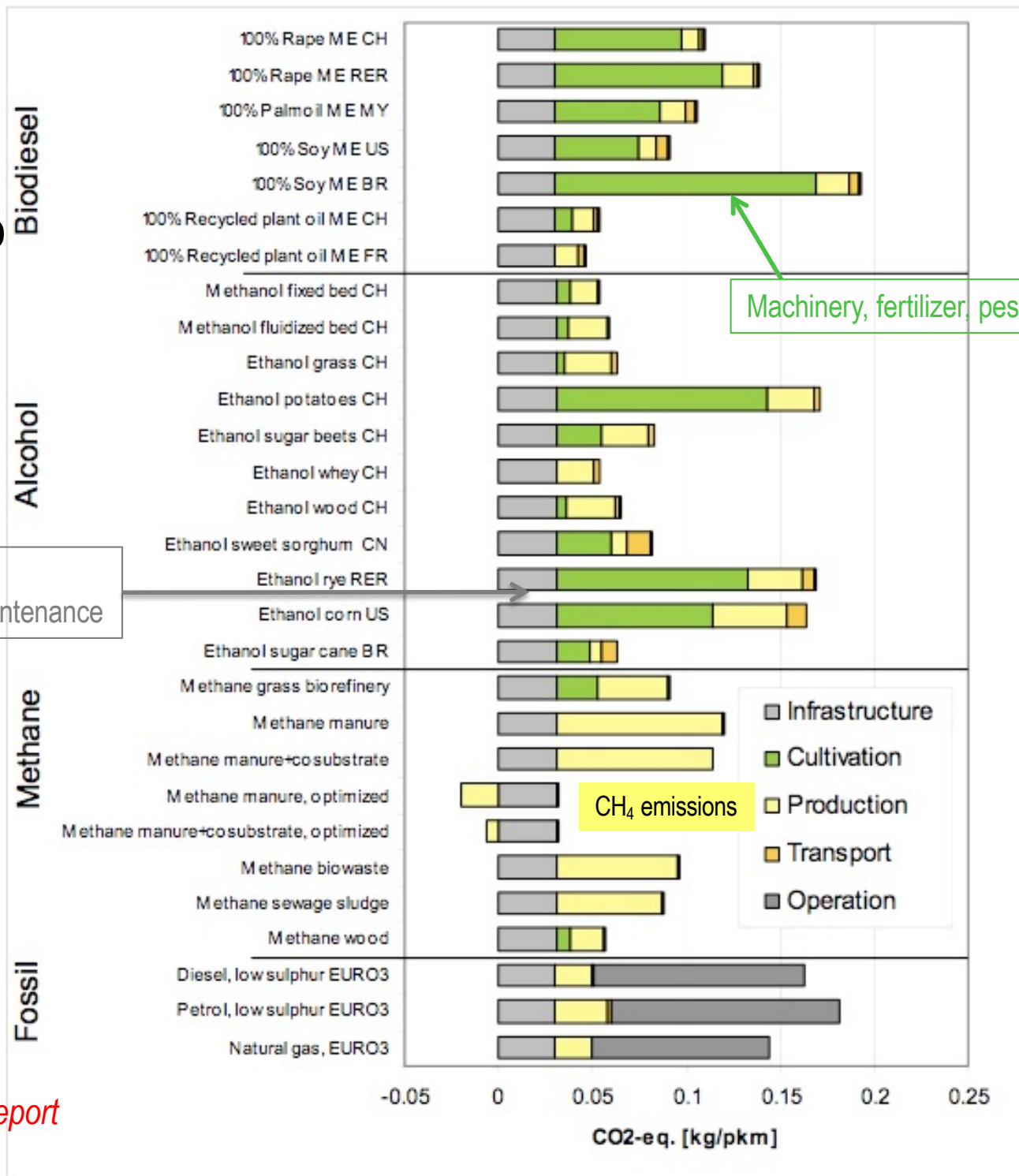
# EMPA report (2007/2013) on biofuel assessment

- 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

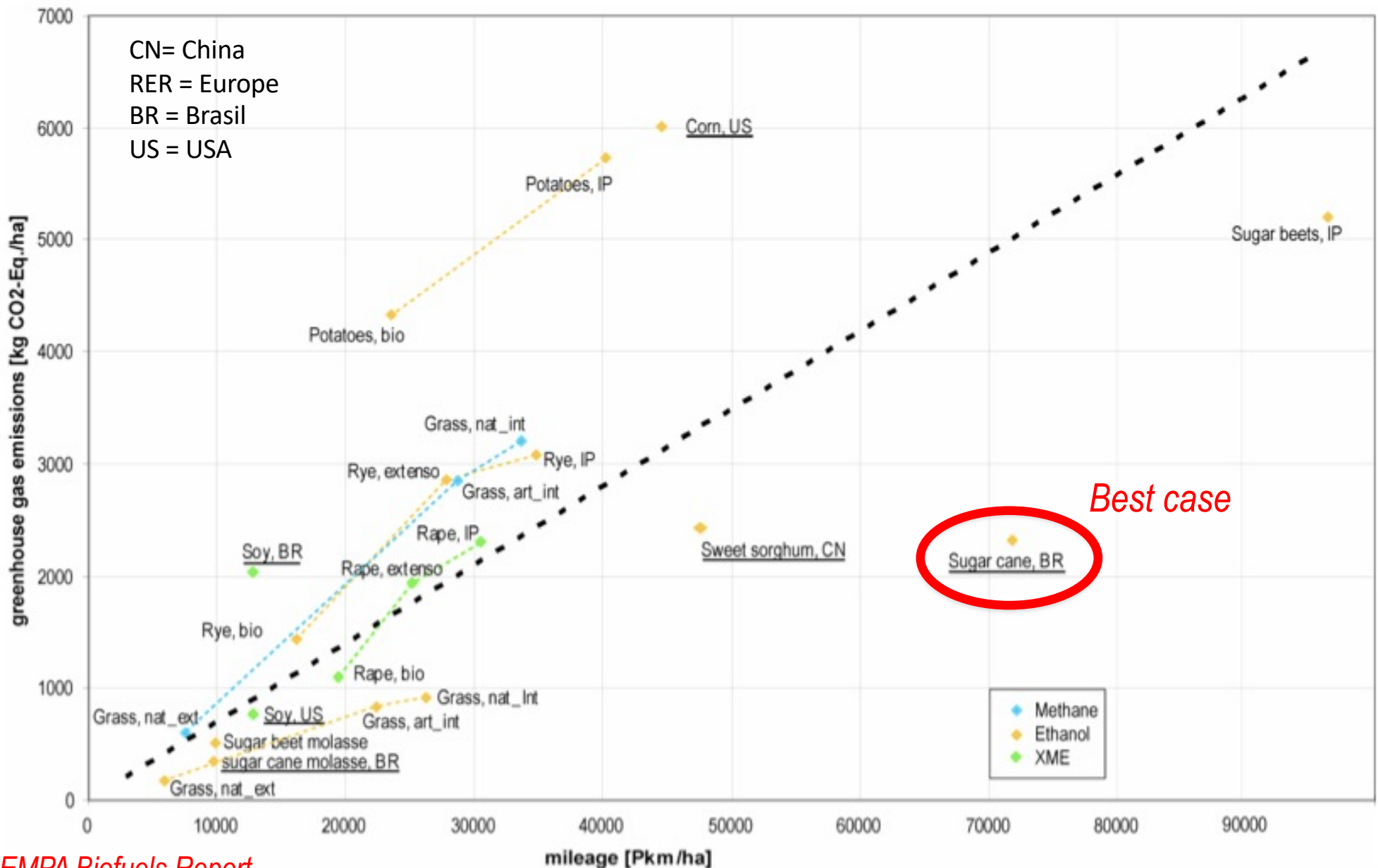


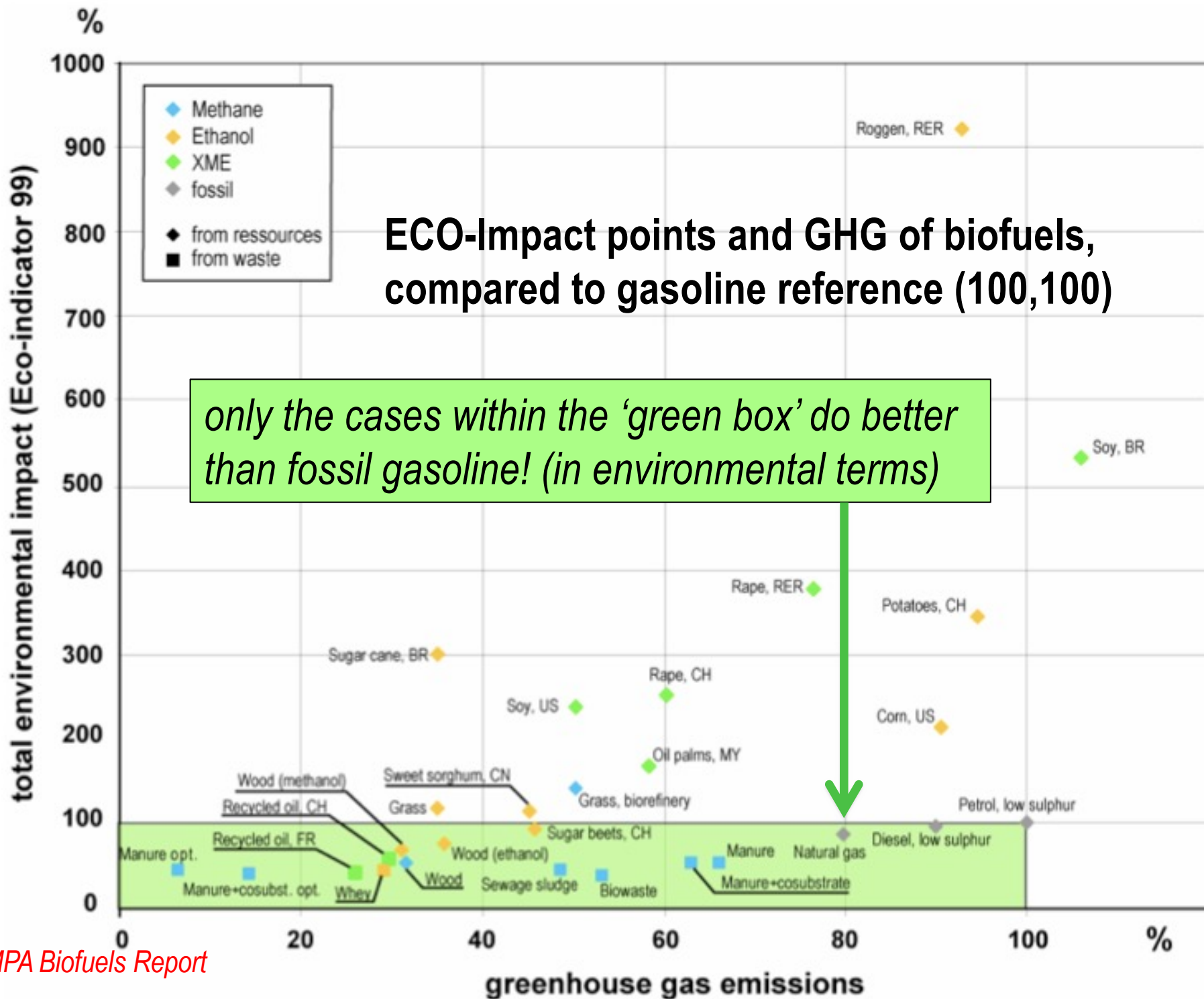
Machinery, fertilizer, pesticides, N<sub>2</sub>O

CH<sub>4</sub> emissions

- Infrastructure
- Cultivation
- Production
- Transport
- Operation

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



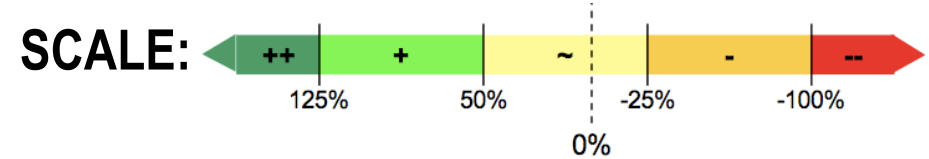




# GHG-impact

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*

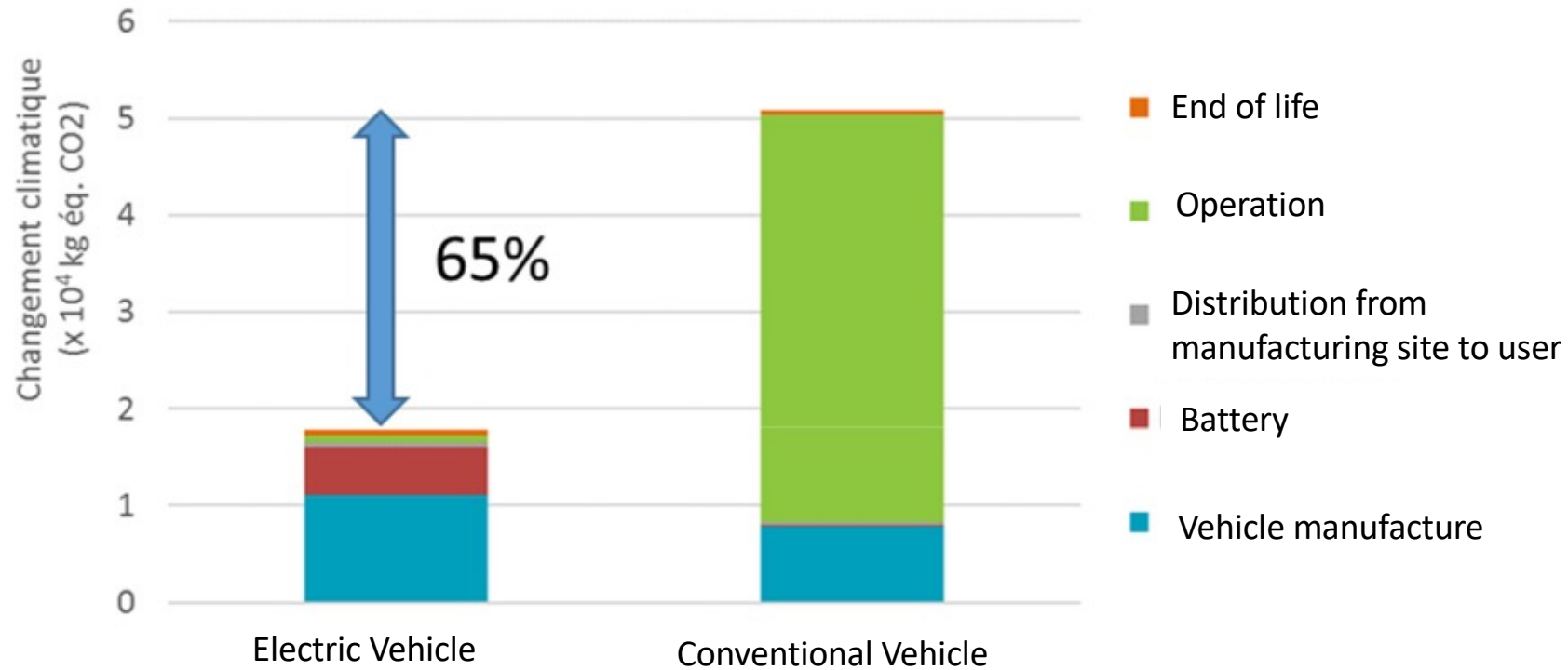
# ECO99'- impact

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							+	+					-	-

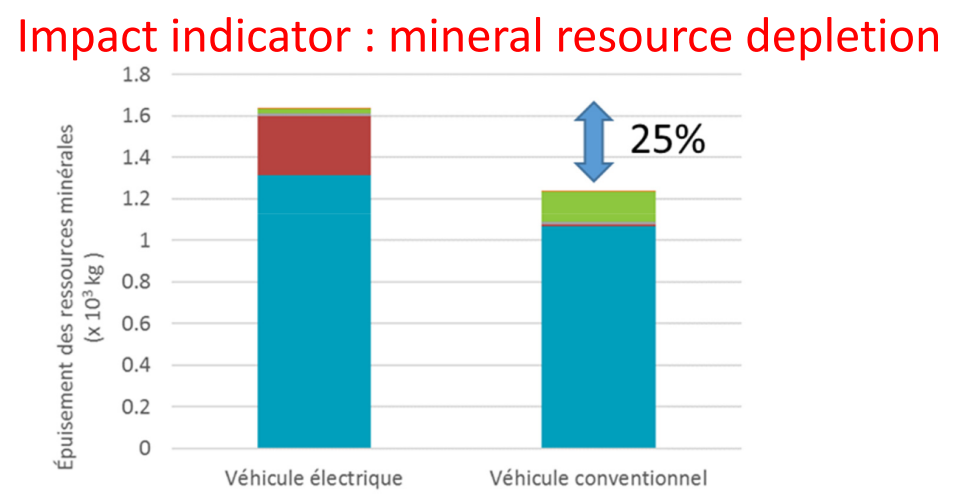
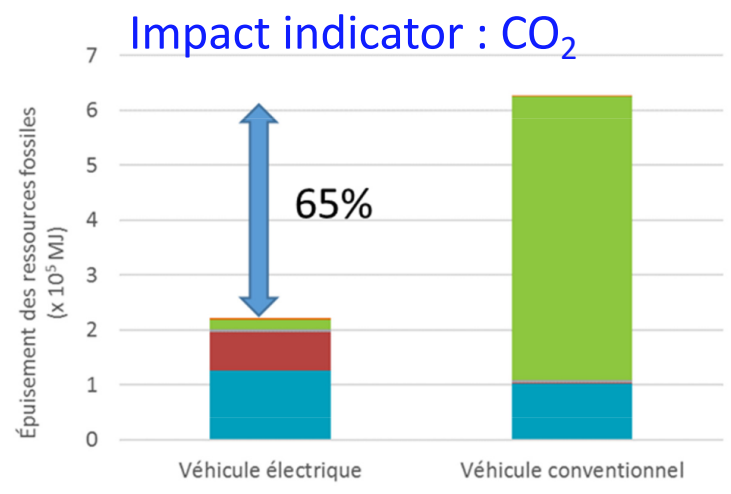
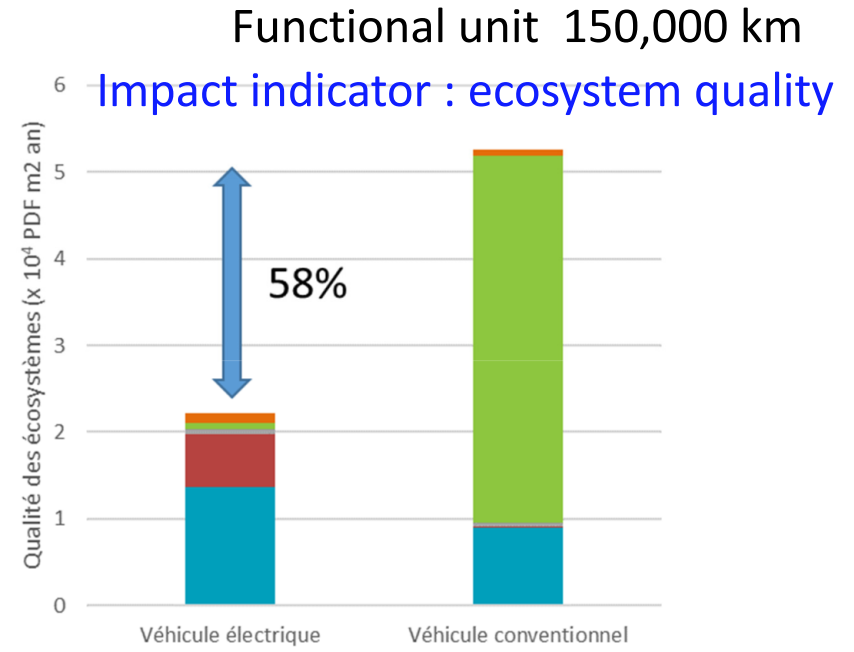
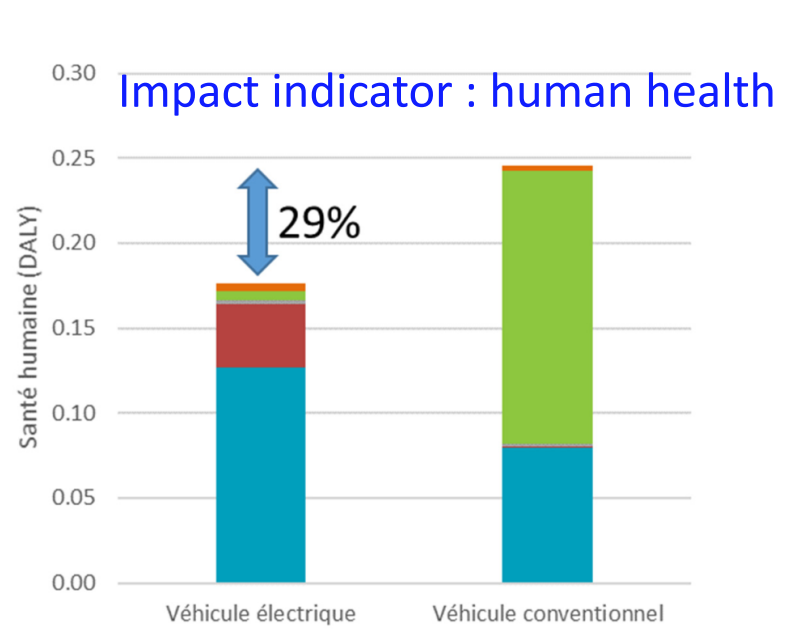
# Comparison electric vs. conventional car in Québec

Impact indicator : CO<sub>2</sub>

Functional unit: 150,000 km



# Comparison electric vs. conventional car in Québec



# 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, 1-20 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** of interest as diesel replacement (many more engines than for gasoline), but low production yield from land
- **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