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; 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 or renewable H_2*

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 /m^2

(1 m^2 of grapes vineyard yield 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

Yields a pure CO_2 output stream : perfect for CO_2 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 (→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)

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% 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 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**))

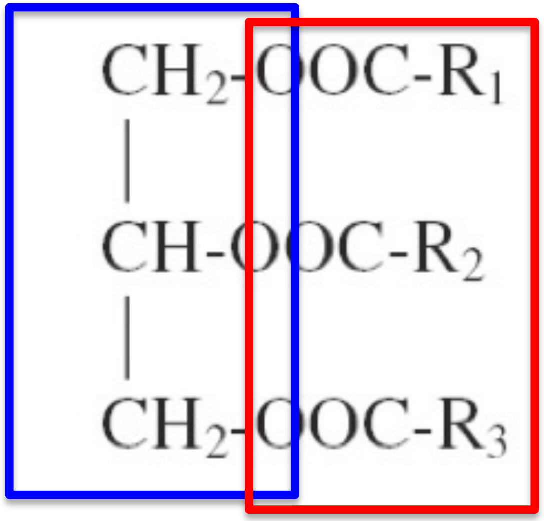
BIODIESEL

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 : oil-rich plants
  - rapeseed (*colza*), sunflower (*tournesol*), soyabean,…

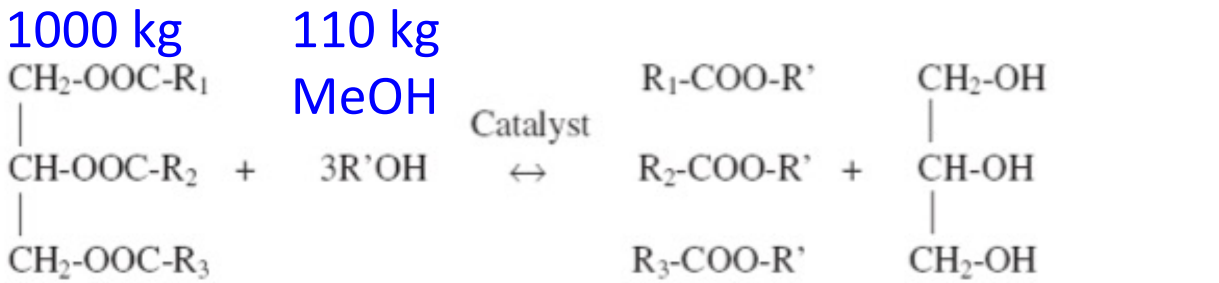
    Oil content = 40%
  - animal fats, frying oil
- Triglycerides : 1 mol glycerine + 3 mol fatty acids



Transesterification process

Transesterification (alkoholysis):

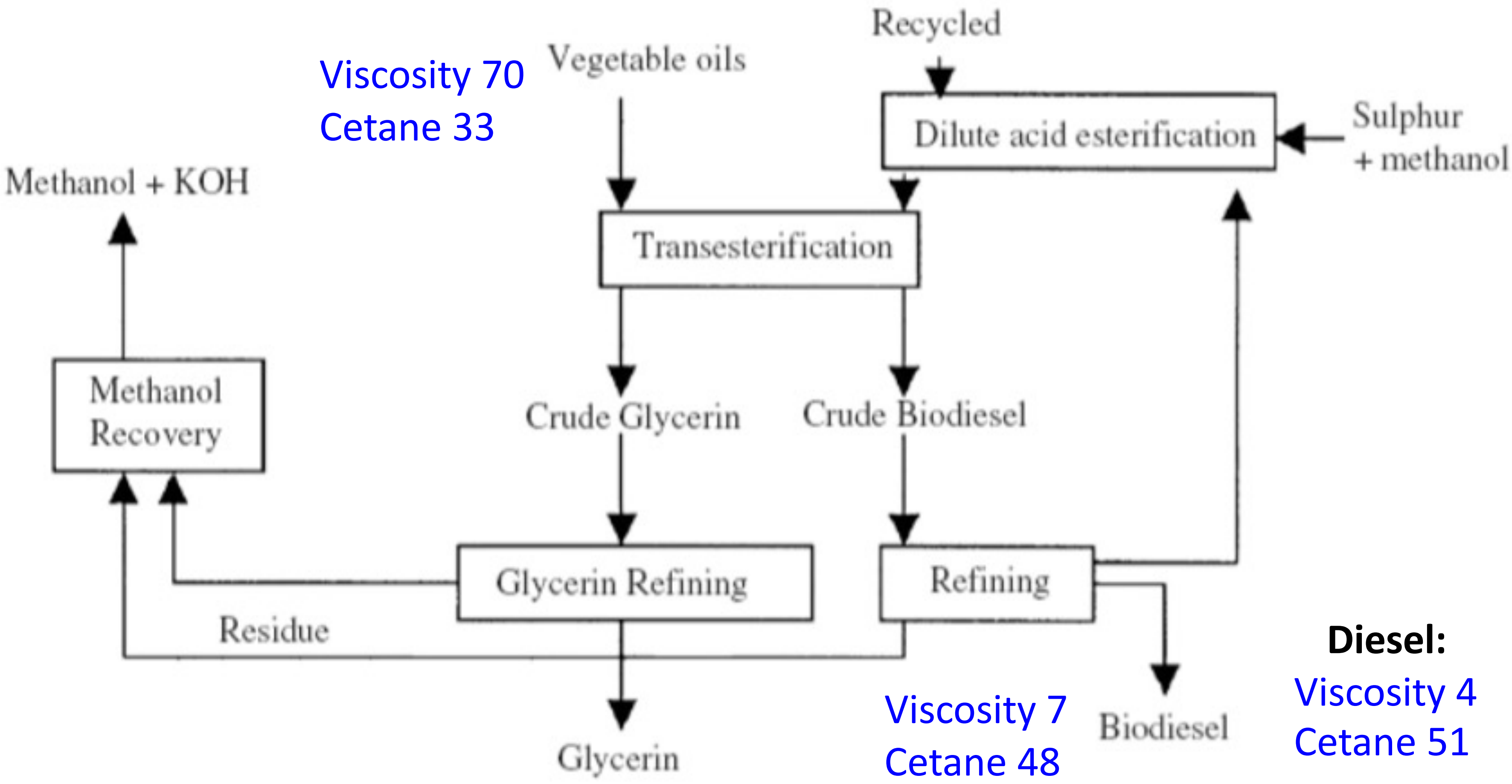
- reaction of triglyceride and alcohol to esters and glycerol:



- 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

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*

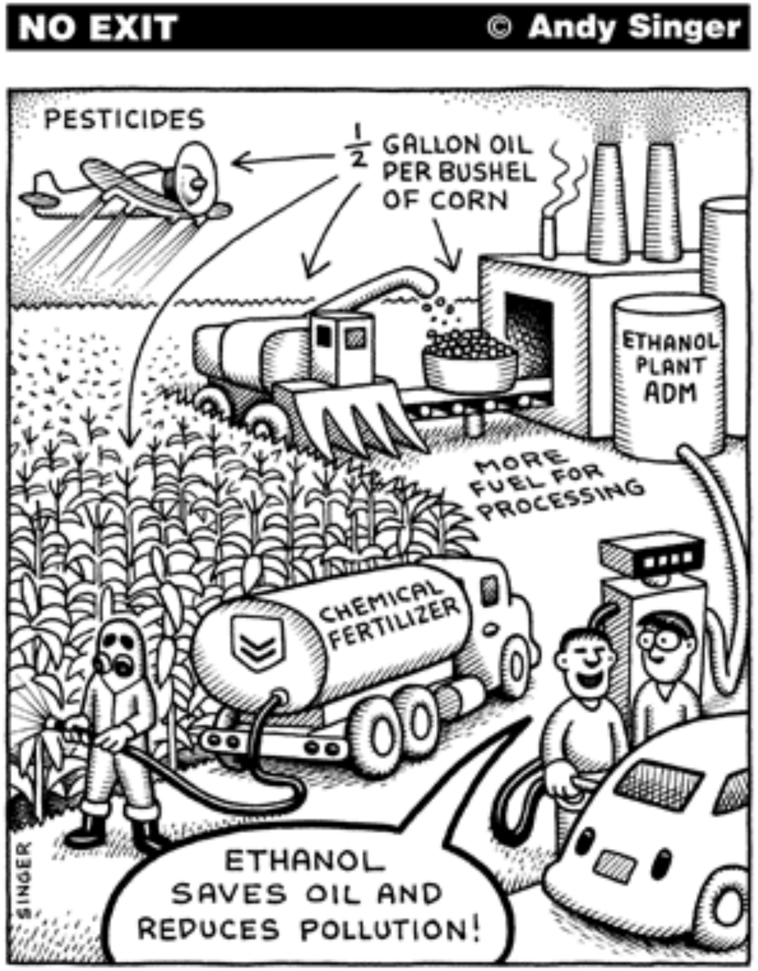
ca. 0.6 € / L

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

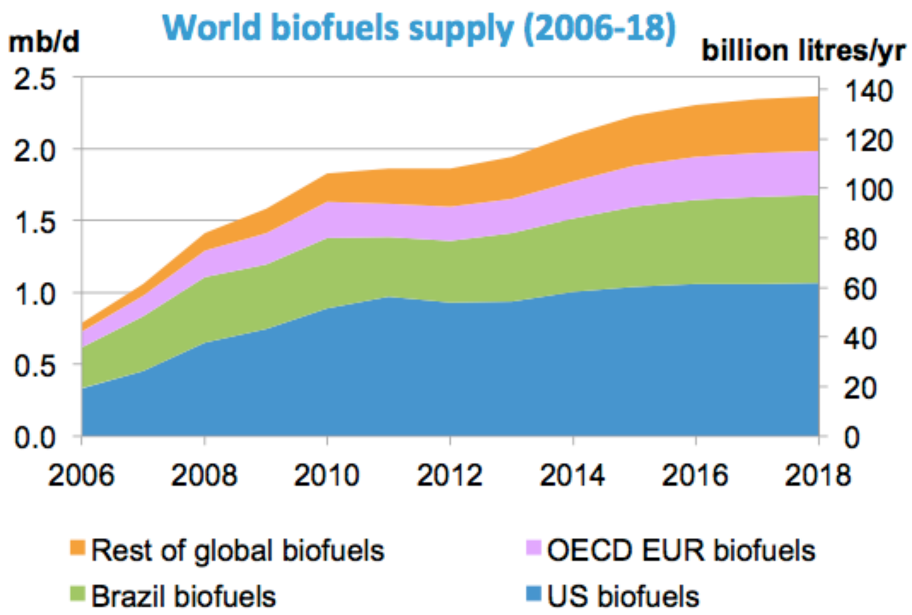
Biodiesel comments

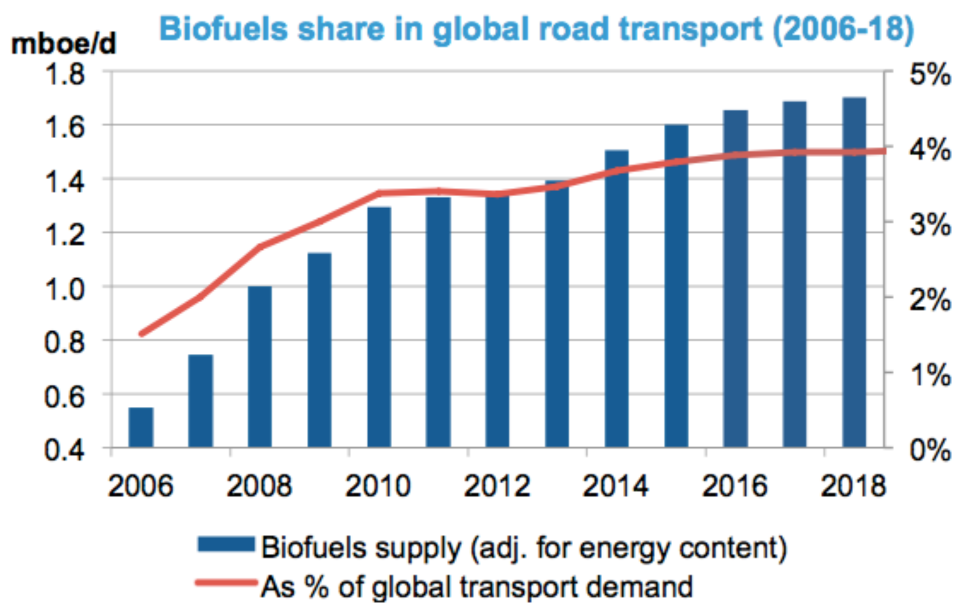
- its low yield and high land use are worse than for bioethanol
- it has no clear advantages in cost or efficiency over (fossil) diesel
- But: diesel is used in many more engines than gasoline



IEA Facts on biofuels

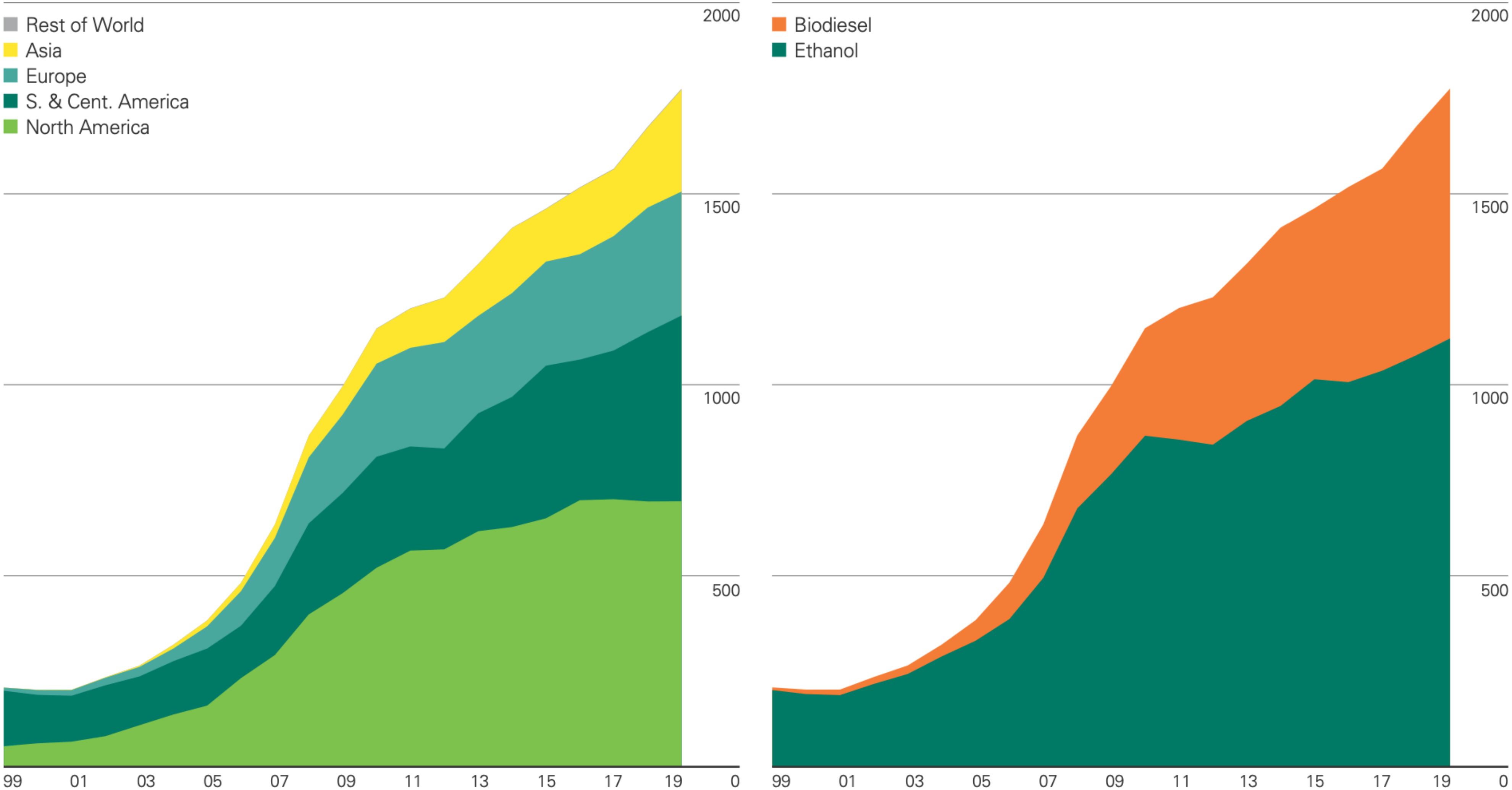
- Biofuels world output (**90%=ethanol**) grows from 20 Mtoe (2005) to 92 Mtoe (2030), to meet **4%** of road transport
- Current land use for biofuel production: 14 mio ha = 1% of arable land. By 2030 this would rise to 2.5% (i.e. the size of France+Spain).
- Cost of bioethanol production: 0.2 $/L (Brasil), 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 (2nd gen)





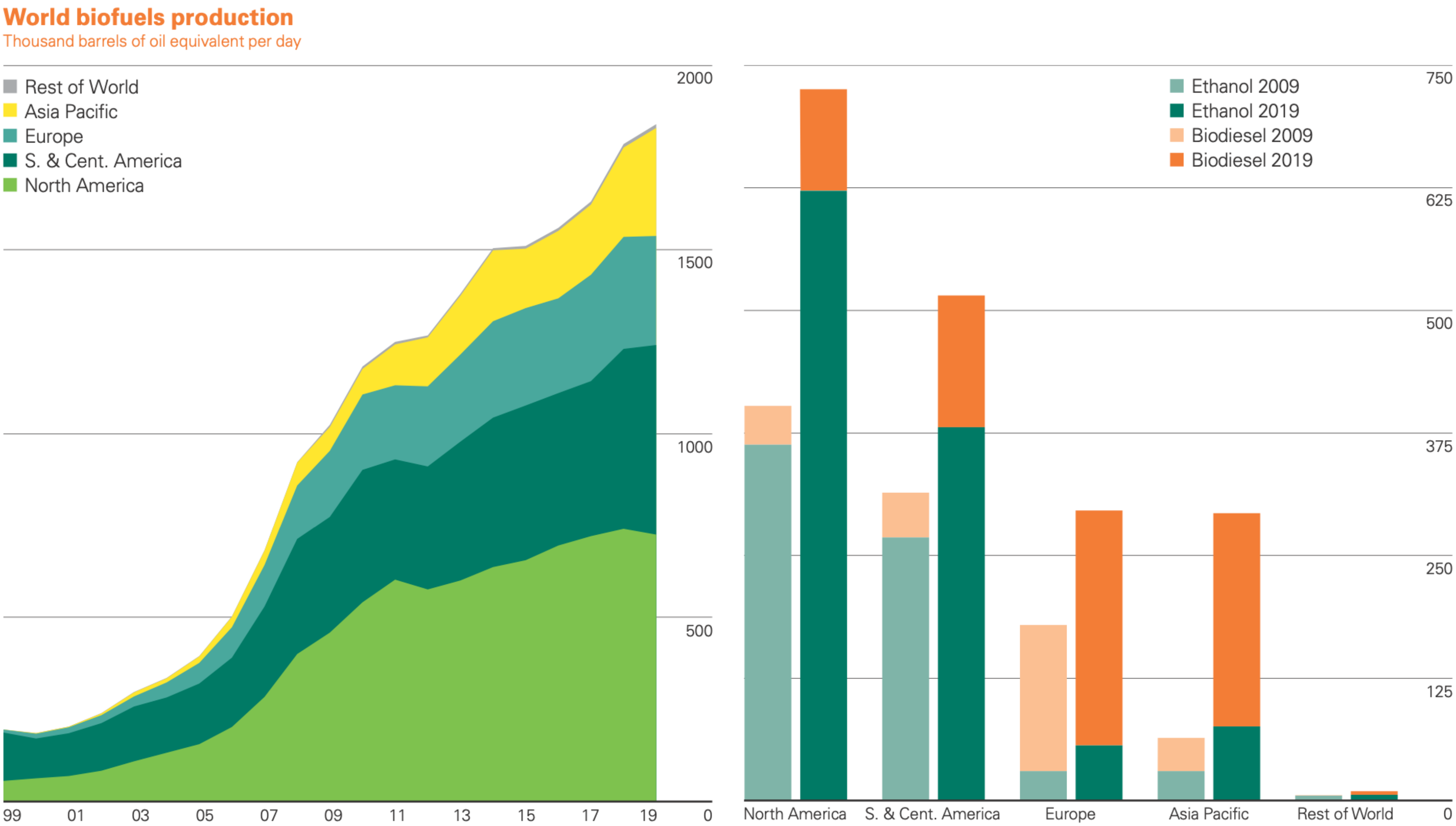
World biofuels consumption

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.

BP-energystats-review-2020



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

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

  - limited conversion
  - slow processes
  - large residues

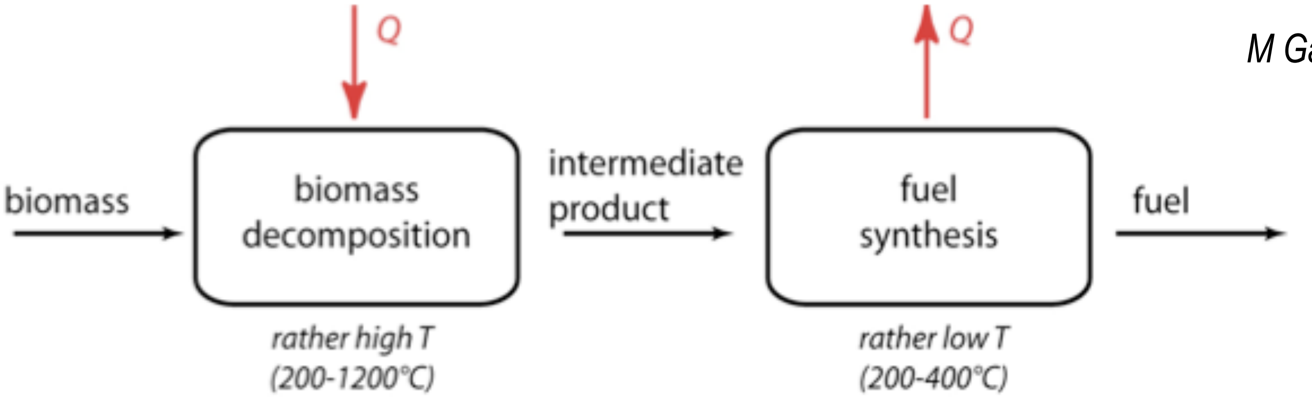
- **2nd generation**
  - **Wood** gas derivatives

  - 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:

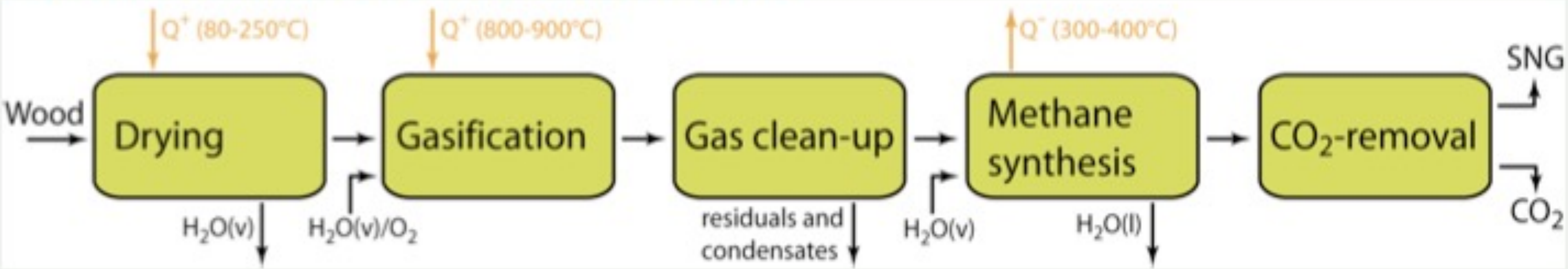
$$CO + 3H_2 \rightleftharpoons CH_4 + H_2O \qquad \Delta h_r^0 = -206 kJ/mol \qquad (1)$$

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

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

M Gassner, EPFL

Common wood to SNG route



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

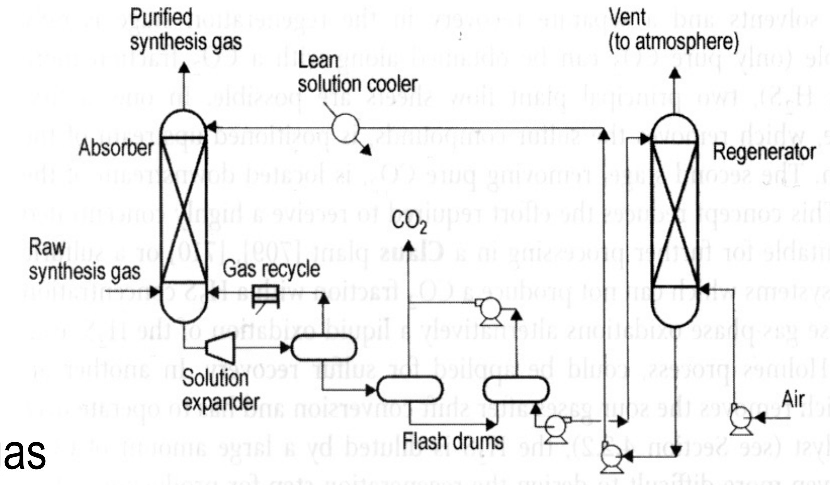
→ CH_4/CO_2 separation needed

CH_4 / CO_2 separation

M Gassner, EPFL

Physical absorption

Energy cost:
220 kWh_{el}/kg gas

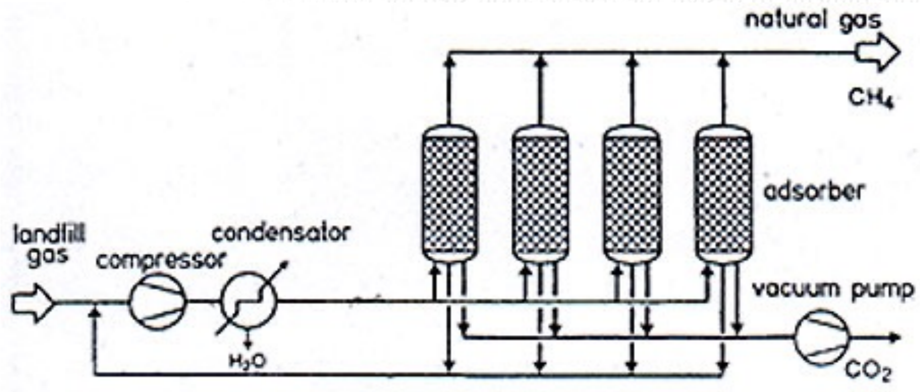


Appl, M.: Ammonia. Principles and Industrial Practice. Wiley, Weinheim, 1999.

P = 50 bar

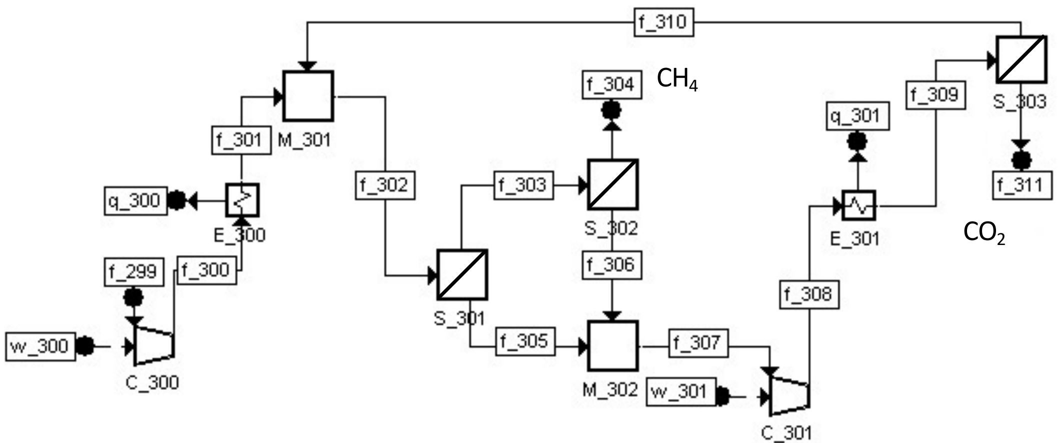
Pressure Swing Absorption

Energy cost:
70 kWh_{el}/kg gas



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

P = 5 – 6 bar



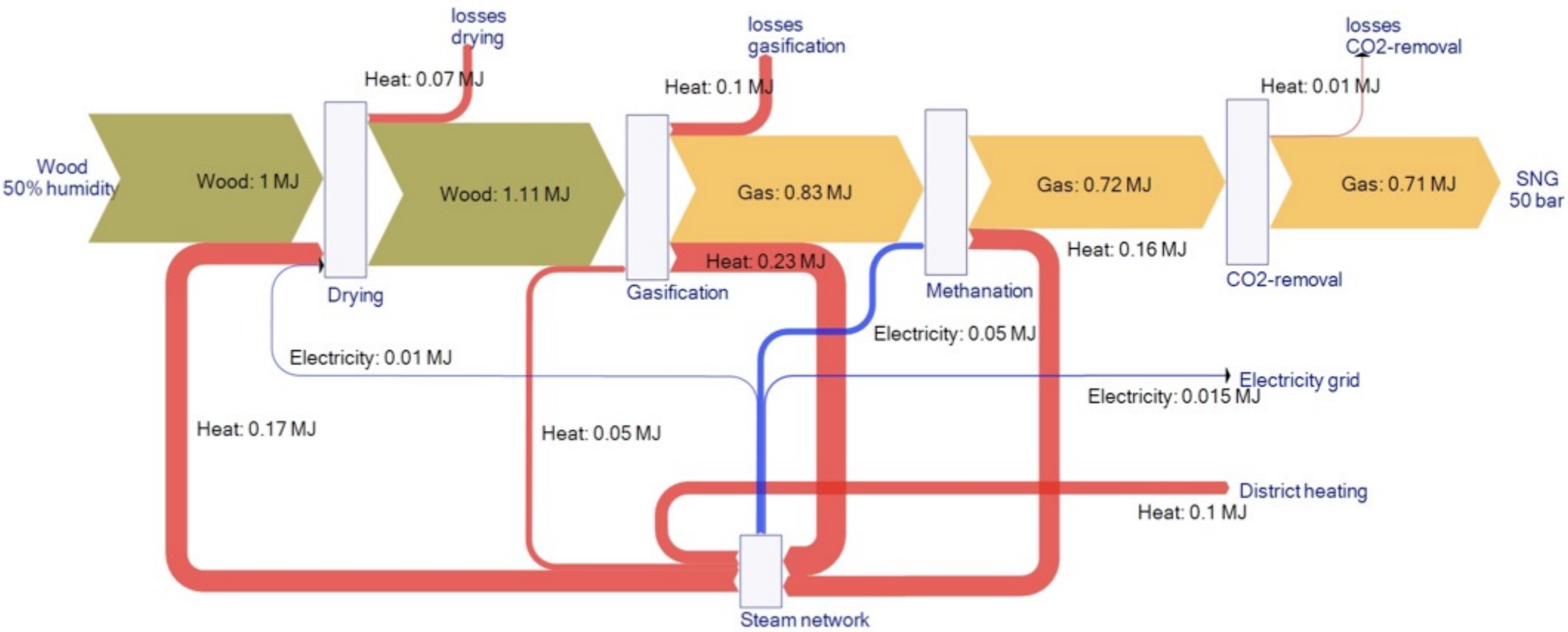
P = 50 bar

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

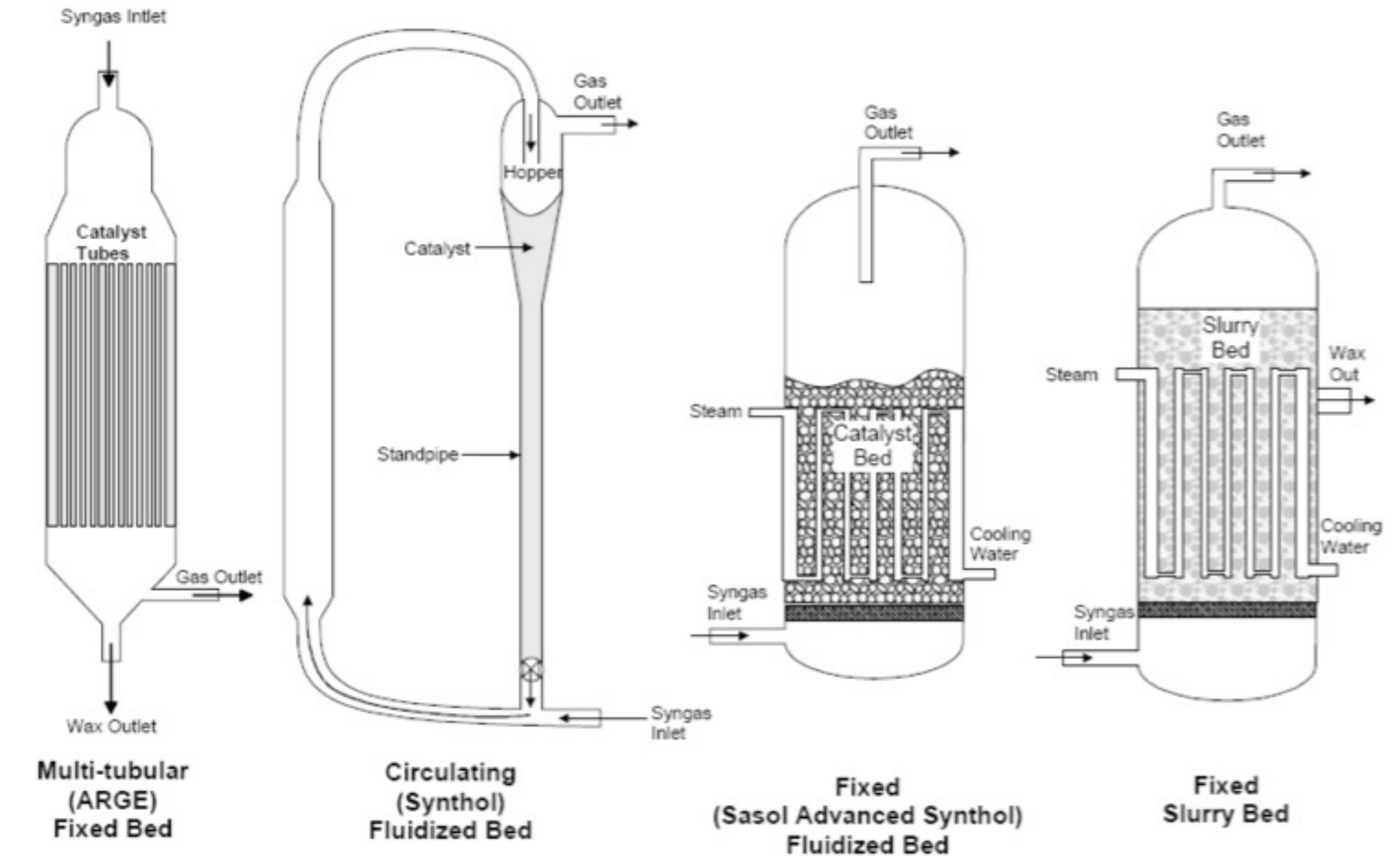
Liquid synfuel fabrication from syngas

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



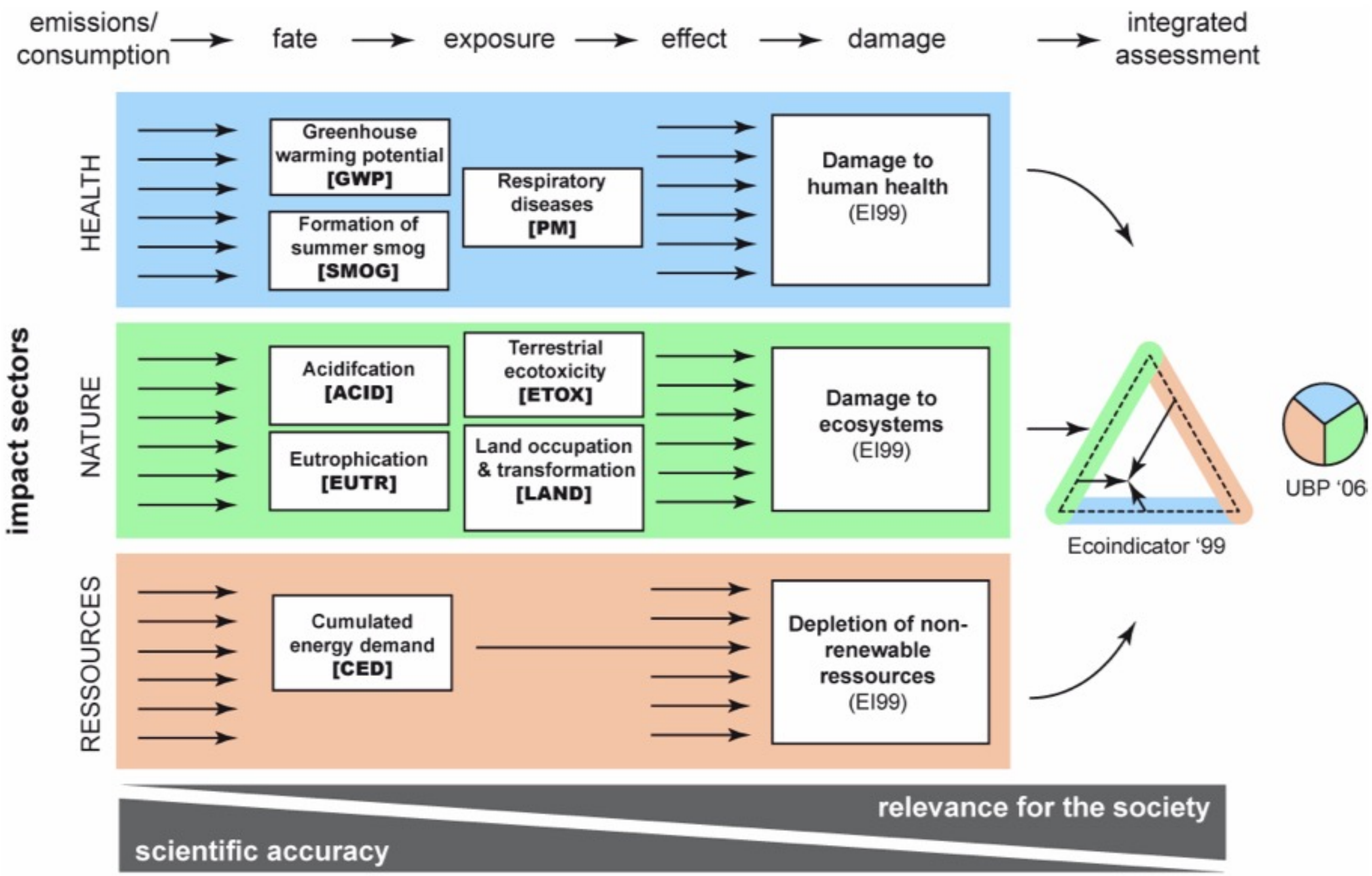
from: Spath, P.L., Dayton, D.C., NREL/TP-510-34929, 2003.

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

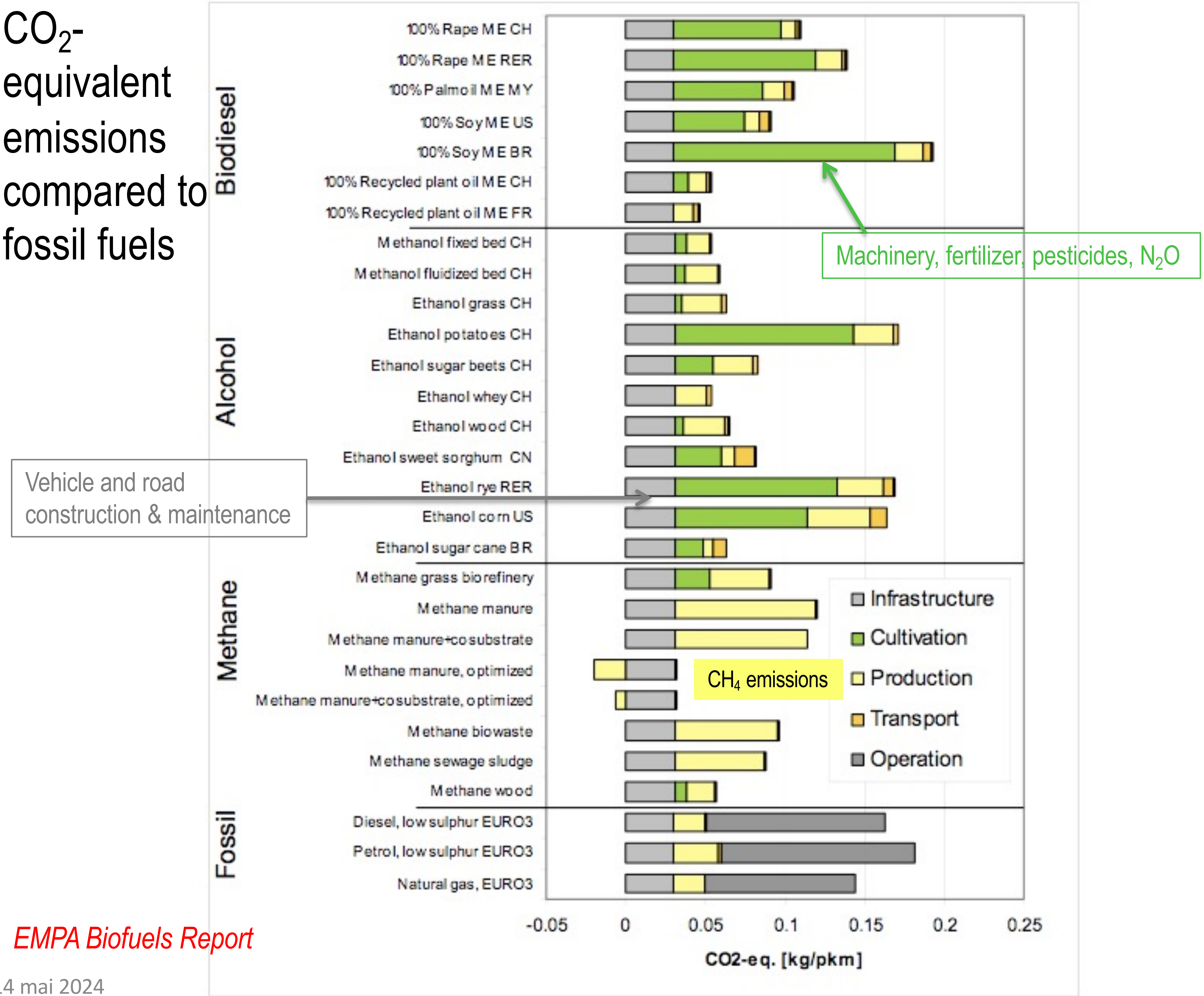
M Gassner, EPFL

EMPA report (2007/2013) on biofuel assessment

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

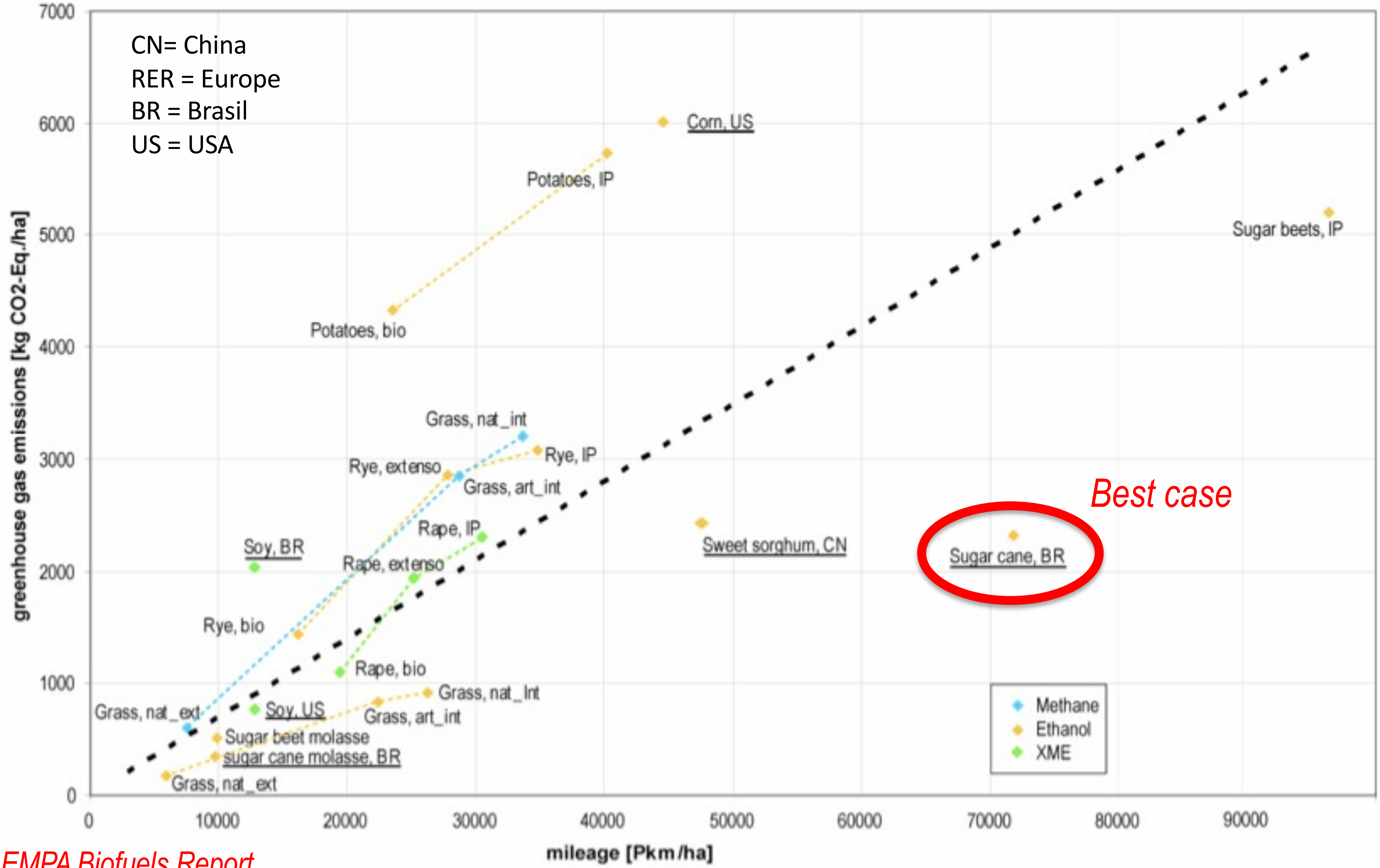


CO_2-equivalent emissions compared to fossil fuels



EMPA Biofuels Report

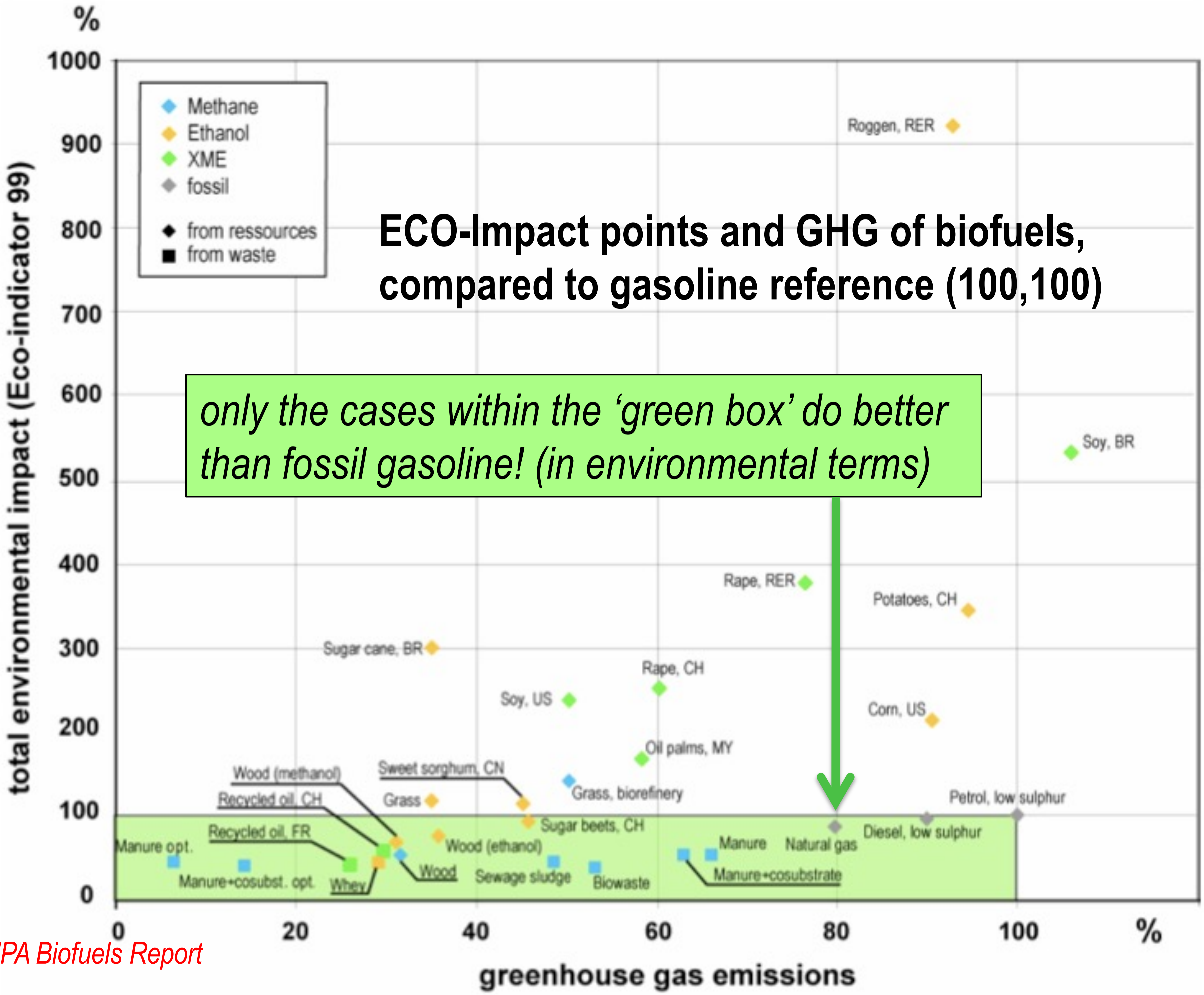
CO_2-equiv. emissions vs. transport-km (per ha land use)



EMPA Biofuels Report

ECO-Impact points and GHG of biofuels, compared to gasoline reference (100,100)

only the cases within the 'green box' do better than fossil gasoline! (in environmental terms)



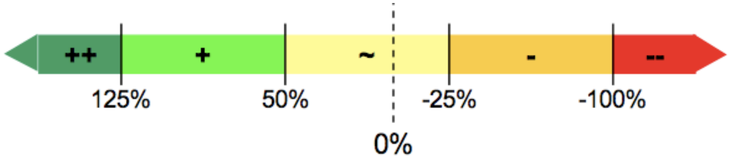
EMPA Biofuels Report

GHG-impact

energy carrier / use path	Wood min	Wood max	Grass min	Grass max	Manure min	Manure max	Waste wood min	Waste wood max	Whey min	Whey max	Biowaste min	Biowaste max	Sewage sludge min	Sewage sludge 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

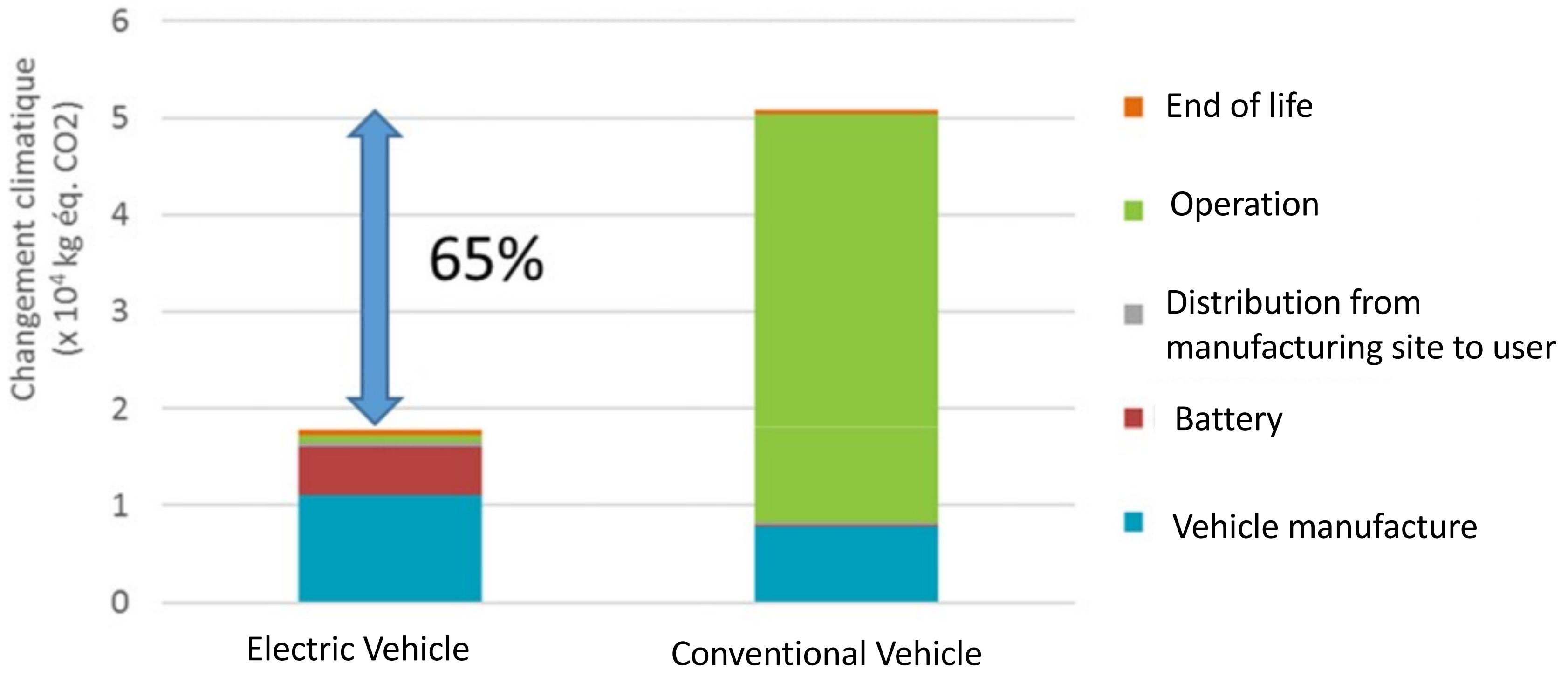
energy carrier / use path	Wood min	Wood max	Grass min	Grass max	Manure min	Manure max	Waste wood min	Waste wood max	Whey min	Whey max	Biowaste min	Biowaste max	Sewage sludge min	Sewage sludge max
Heating	~	++												
Cogeneration (CHP)	~	++	~	~	+	++			+	++	-	-	+	++
Car (methane)	+	+	~	~	++	++	+	+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

ECO99'-impact

Comparison electric vs. conventional car in Québec

Impact indicator : CO_2

Functional unit: 150,000 km

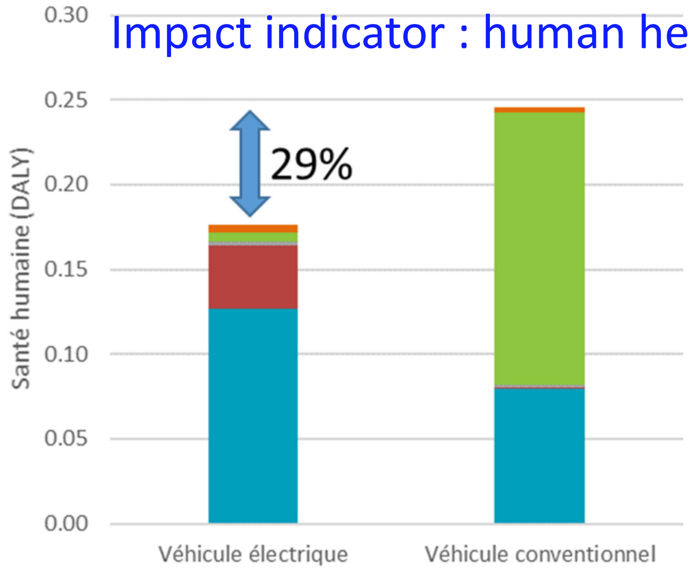


CIRAIG, 2016; https://www.hydroquebec.com/data/developpement-durable/pdf/analyse-comparaison-vehicule-electrique-vehicule-conventionnel.pdf

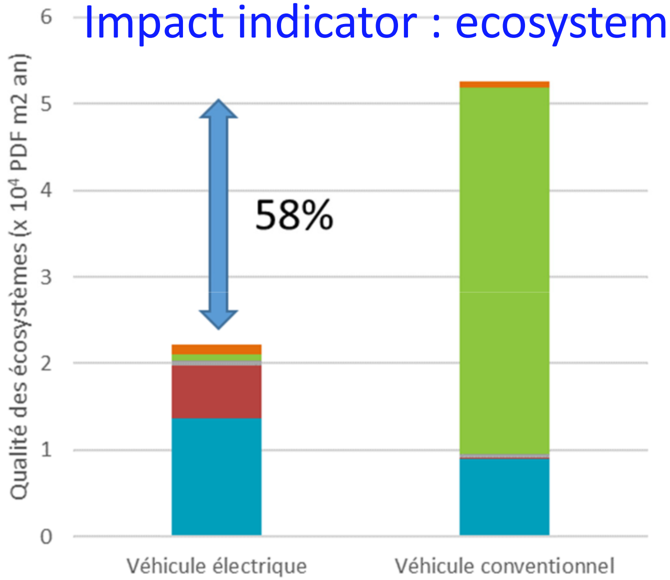
Comparison electric vs. conventional car in Québec

Functional unit 150,000 km

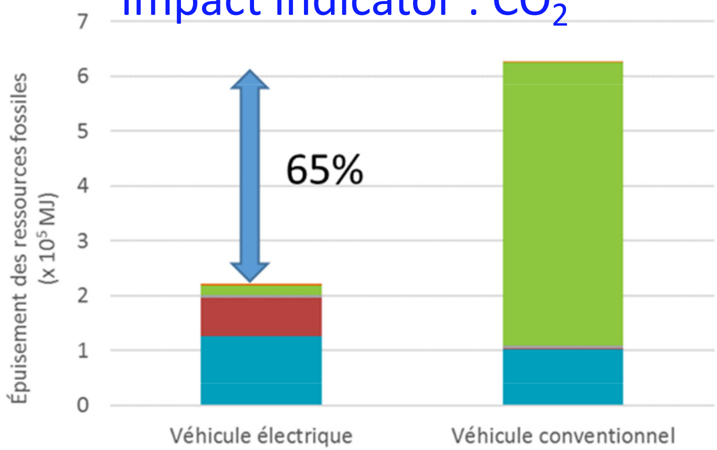
Impact indicator : human health



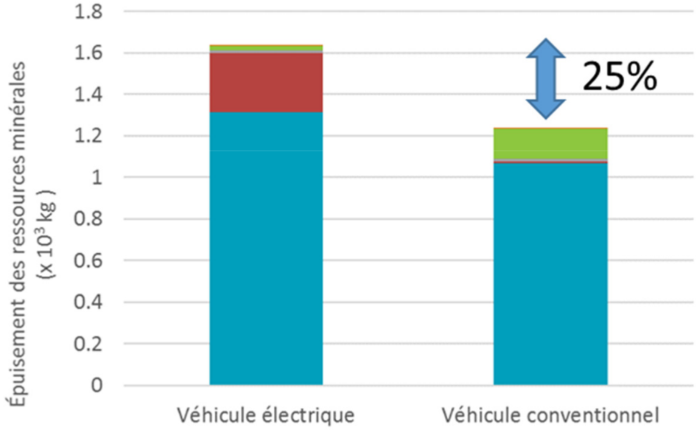
Impact indicator : ecosystem quality



Impact indicator : CO_2



Impact indicator : mineral resource depletion



CIRAIG, 2016; https://www.hydroquebec.com/data/developpement-durable/pdf/analyse-comparaison-vehicule-electrique-vehicule-conventionnel.pdf

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