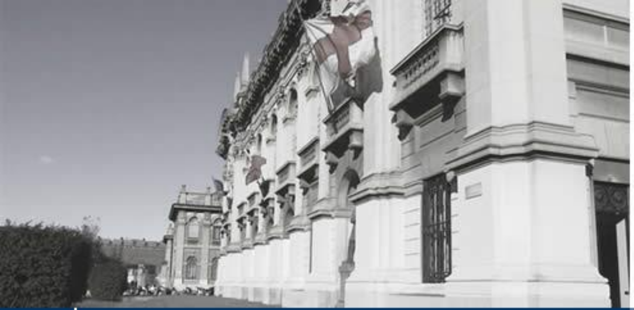


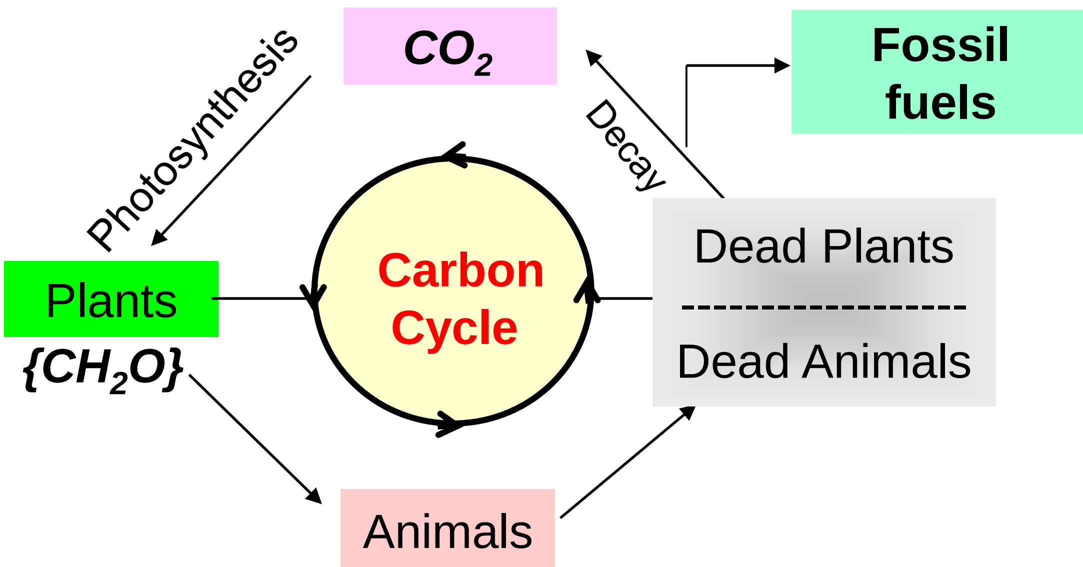
School of Industrial and Information Engineering
Course 096125 (095857)
Introduction to Green and Sustainable Chemistry

POLITECNICO DI MILANO

Biofuels.

Prof. Attilio Citterio
Dipartimento CMIC "Giulio Natta"
https://iscamapweb.chem.polimi.it/citterio/it/education/course-topics/

The Carbon Cycle.



$$C_XH_Y + (x + y/4)O_2 \rightarrow xCO_2 + (y/2)H_2O$$

Simplified Cycle of Carbon (Main Reactions)

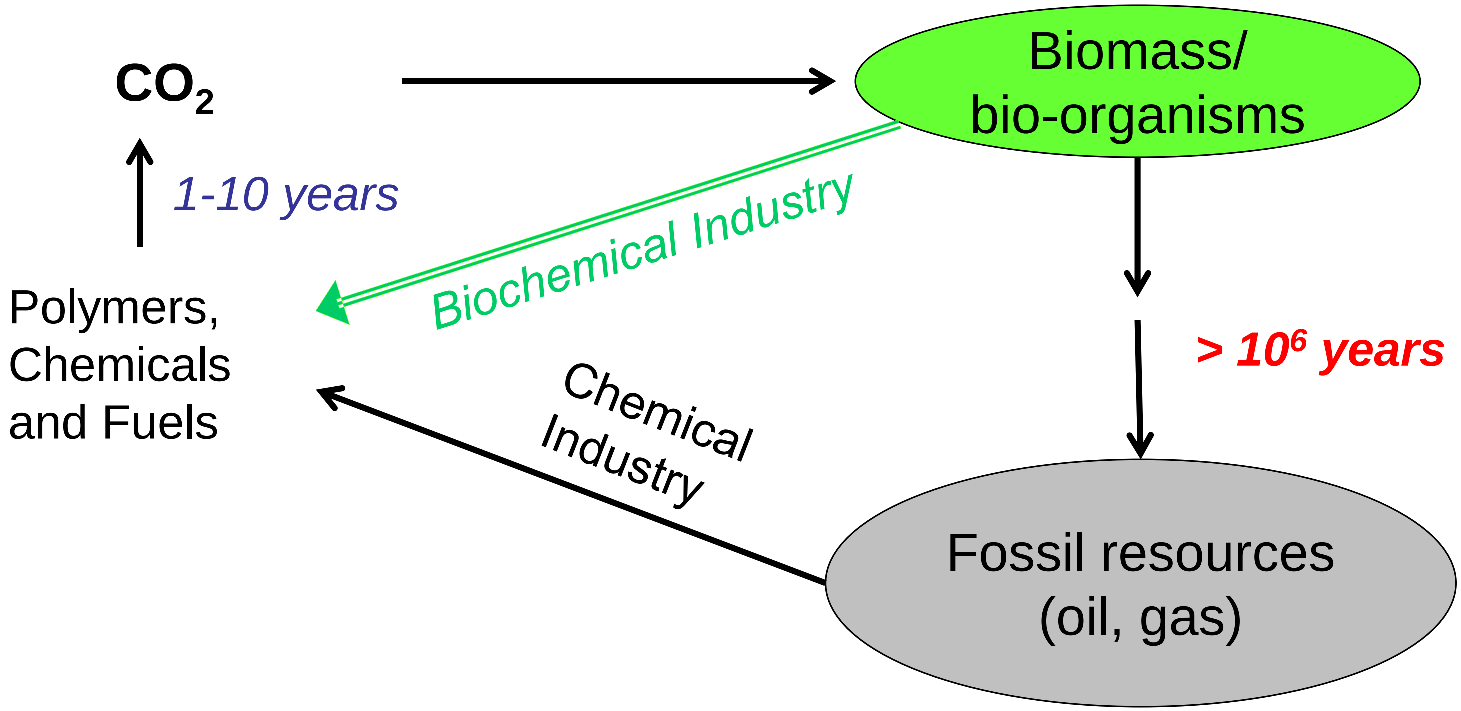
Combustion

$$\{CH_2O\} + O_2 \rightarrow CO_2 + H_2O \quad \Delta H = -440\ kJ$$

Photosynthesis

$$CO_2 + H_2O \xrightarrow{h\nu} \{CH_2O\} + O_2 \quad \Delta H = +440\ kJ$$

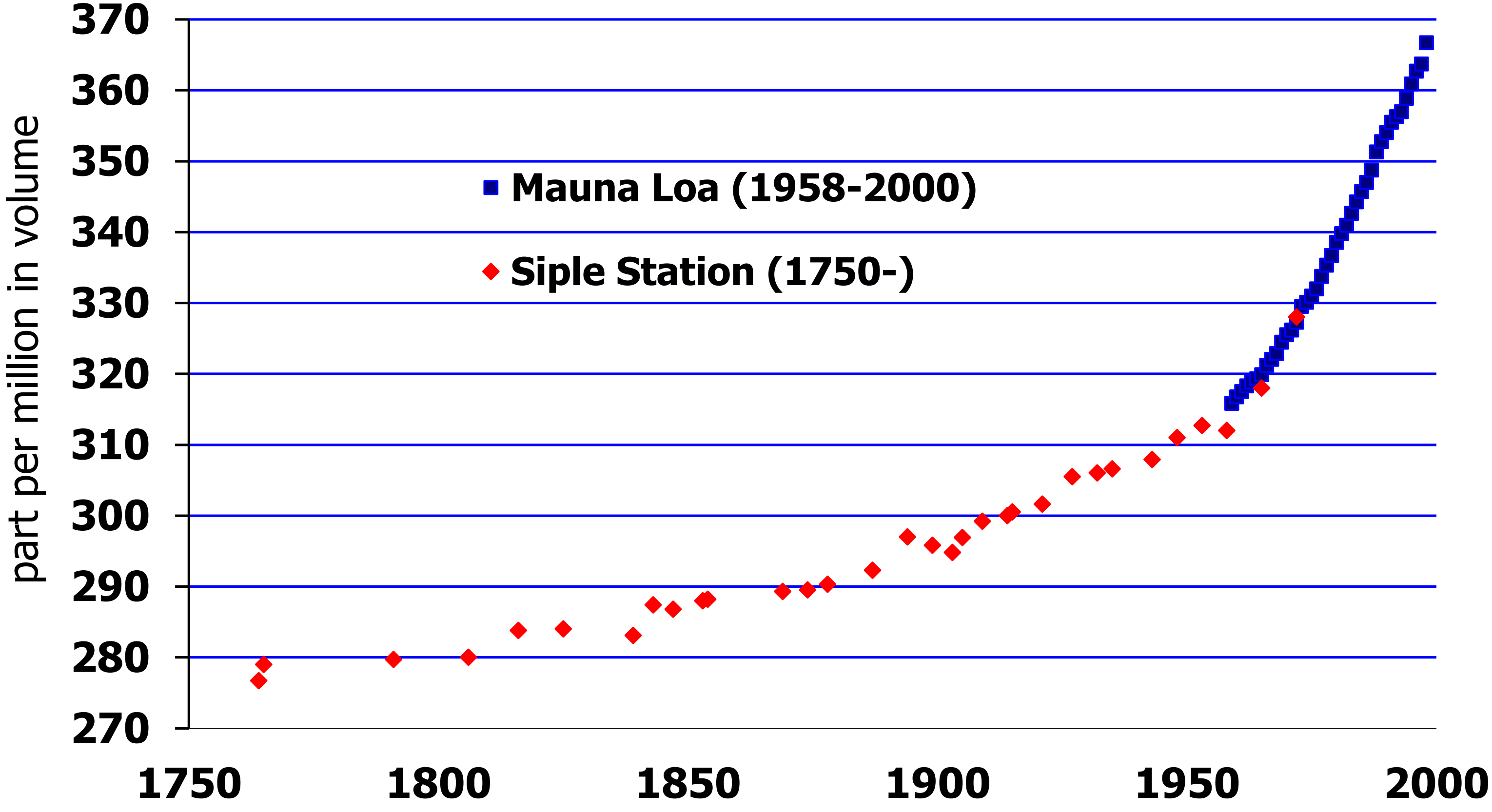
Carbon Cycle and Industry.



In photosynthesis, energy from sunlight drives the carbon fixation pathway. ~ 2×10^11 tons of carbon each year is involved in the process, with an equivalent energy content of 70 billion tons of oil, about 10 times the present world's energy demand.

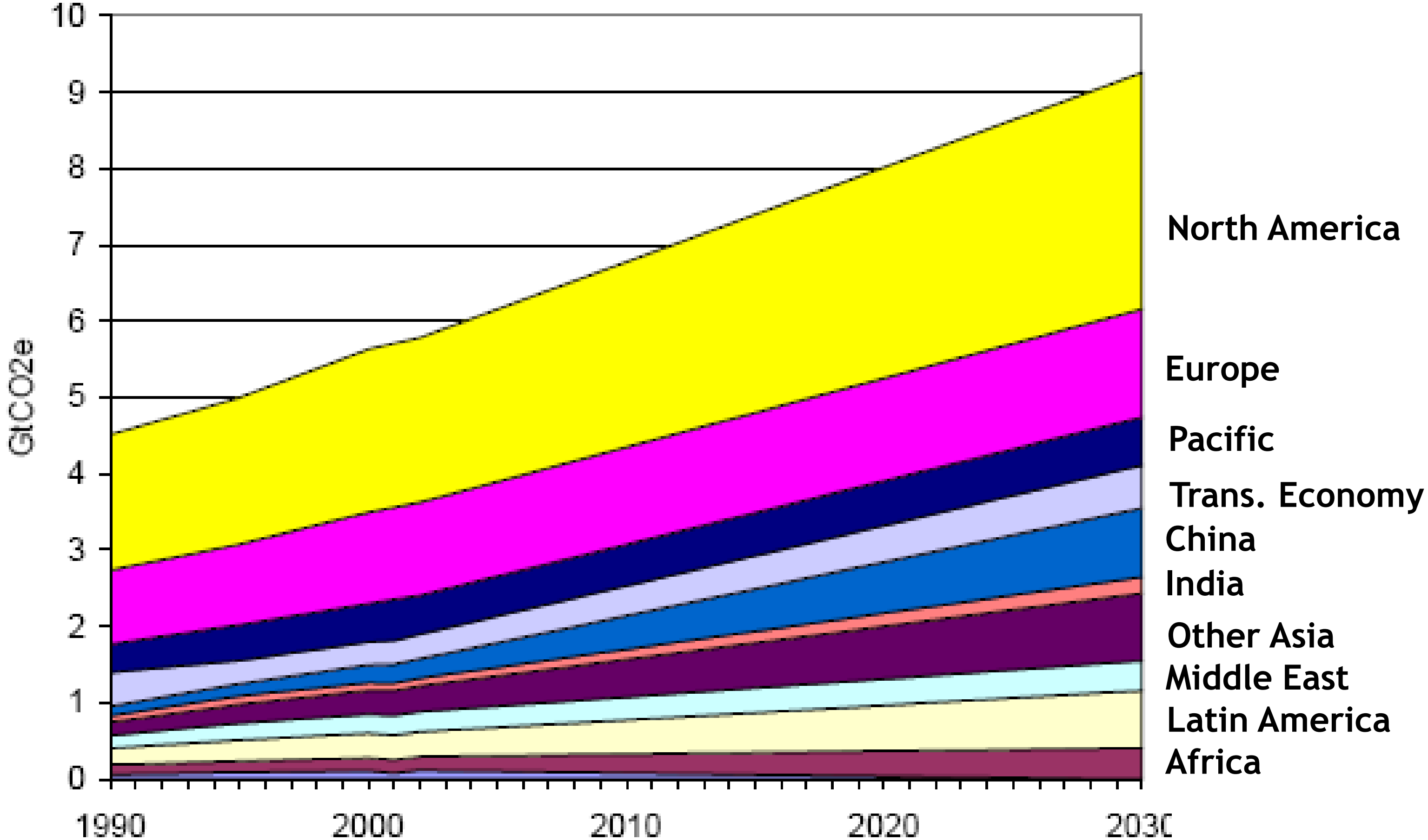
Global CO_2 Emissions.

Atmospheric carbon dioxide concentrations (from 1750 to 2000ac)



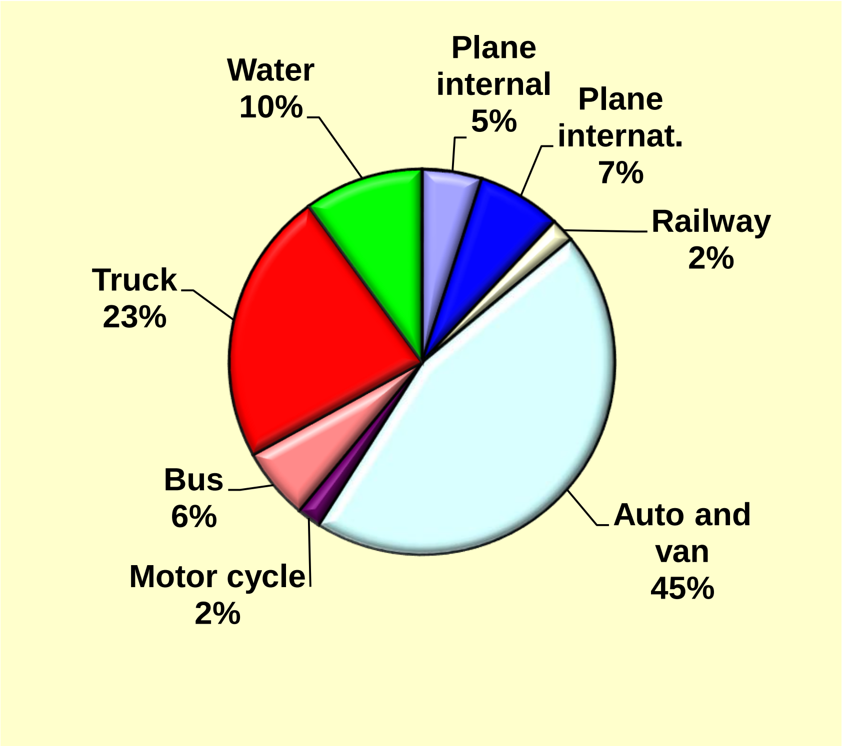
Source: C.D. Keeling and T.P. Whorf, Atmospheric CO_2 Concentrations (ppmv) derived from in situ air samples collected at Mauna Loa Observatory, Hawaii, Scripps Institute of Oceanography, 1998. A. Neftel et al, Historical CO_2 Record from the Siple Station Ice Core, Physics Institute, University of Bern, Switzerland, 1994.

Transport CO_2 Emissions by Country 1990-2030.

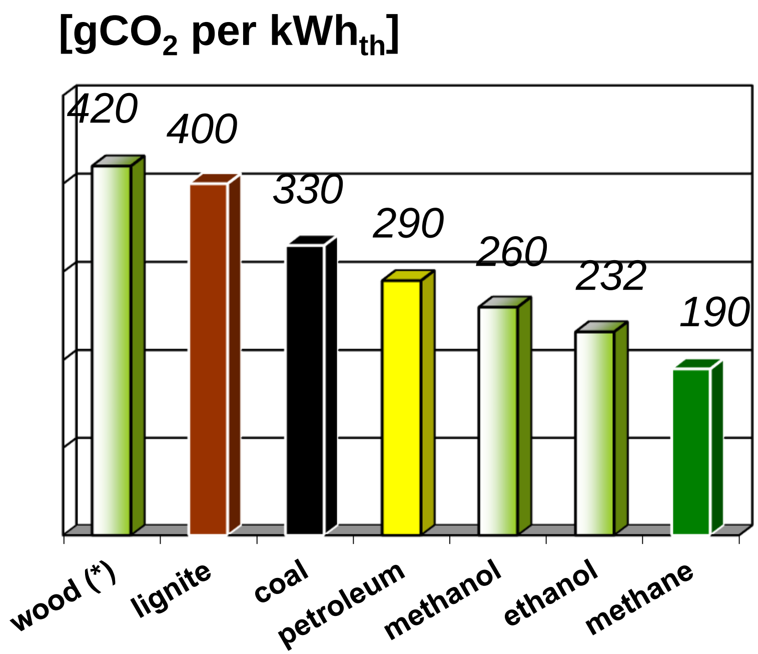


Source: Stern Review Report (2006)

Transport CO_2 Emissions by Mode and CO_2 Specific Emissions (in g of CO_2 per unit of thermal energy).



Source: Stern Review Report (2006)



(*) wood is neutral when used in sustainable way (reforestation)

Biomass.

"All plant and animal matter is 'Biomass'. Materials Produced by Living Organisms are Renewable Resources Used Goal-Oriented for Purposes Outside Food and Feed Production"

- Solar energy is stored in the chemical bonds of the biomass and this energy can be extracted, if burnt efficiently.
- Biomass resources include: dedicated energy crops (i.e. SRC willow/poplar; *miscanthus*); industrial crops; agricultural crop residues; forestry residues; animal waste; municipal wastes…
- Used either as a liquid or solid form of energy.

Biomass Feedstock.

Forest wood residues	Agricultural residues	Energy crops	Municipal waste residues
			
Thinning Residues Wood chips Wood waste • pallets • crate discards • wood yard trimmings	Corn Stover Rice hulls Sugarcane • bagasse Animal biosolids (CAFO)	Hybrid poplar switch grass Willow Rapeseed Algae	Municipal waste organic fraction

Fuel Composition and Characteristics of Oven-dry Biomass.

Biomass	Volatile (%)	Fixed C (%)	Ash (%)	Carbon (%)	Hydrogen (%)	HHV $MJ \cdot kg^{-1}$	LHV $MJ \cdot kg^{-1}$	Ash def. T (° C)	Ash fusion T (° C)
Arhar stalk	83.47	14.76	1.77	46.75	6.55	15.00	14.85	1250-1300	1460-1500
Bagasse	75.10	16.87	8.03	45.71	5.89	19.50	19.37	1300-1350	1420-1450
Bamboo dust	75.32	15.59	9.09	43.86	6.64	16.02	15.87	1300-1350	1400-1450
Cotton stalk	70.89	22.43	6.68	43.64	5.81	18.26	17.85	1320-1380	1400-1450
Coconut coir	70.30	26.77	2.93	47.17	6.54	18.20	17.79	1100-1150	1150-1200
Corn cob	80.20	16.20	3.60	45.31	7.16	15.58	15.23	800-900	950-1050
Dhaincha stalk	80.32	17.01	2.67	56.45	8.99	19.63	19.43	800	800-900
Groundnut shell	68.12	24.97	6.91	44.78	6.08	17.20	17.06	1180-1200	1220-1250
Jute stick	75.33	19.00	5.67	54.77	8.20	19.45	19.01	1300-1350	1400-1450
Kikar (Acacia)	77.01	22.35	0.64	45.89	6.08	20.25	19.79	1300-1350	1380-1400
Mustard shell	70.09	14.48	15.43	46.20	6.21	17.61	17.47	1350-1400	1400-1450
Pine needle	72.38	26.12	1.50	46.21	6.57	20.12	19.97	1250-1300	1350-1400
Rice hisk	60.64	19.90	19.48	40.10	6.03	13.38	13.24	1430-1500	1650
Sal seed leaves	60.03	20.22	19.75	46.74	6.72	18.57	18.42	1200-1250	1350-1400
Sal seed husk	62.54	28.06	9.40	48.12	6.55	20.60	20.13	1450-1500	1500-1550

Grover 1990

Calorific value of wood at different moisture contents:

Condition of wood	Calorific value ($kJ \cdot kg^{-1}$)
Freshly cut wood	8200
Air dry wood	15000
Oven dry wood	18800

Ref. FAO

Heating Values.

- Upper heating value (**UHV**), or Gross calorific value (**GCV**):

  The heating value for the dry fraction of the fuel. Heat of evaporation for water formed from H is not taken into account.

  UHV = $0.3491\chi_C + 1.1783\cdot\chi_H + 0.1005\cdot\chi_S - 0.0151\cdot\chi_N - 0.1034\cdot\chi_O - 0.0211\cdot\chi_{ash}$ [$MJ\cdot kg^{-1}$, dry basis], with χ_i in wt.%

- Lower heating value (**LHV**):

  LHV = UHV minus heat of evaporation for water (2.447 $MJ\cdot kg^{-1}$ water) formed from H [$MJ\cdot kg^{-1}$, dry basis]

- Effective heating value (**EHV**), or Net calorific value (**NCV**):

  EHV = LHV minus heat of evaporation for water in the fuel [$MJ\cdot kg^{-1}$, wet basis]

Fuel Composition and Heating Values.

C, H and O concentrations as well as amounts of volatile matter in different biomass fuels.

Glossary: d.b.....dry basis.

Fuel type	**C wt.% (d.b.)**	**H wt.% (d.b.)**	**O wt.% (d.b.)**	**volatiles wt.% (d.b.)**
Wood chips (spruce, beech, poplar, willow)	47.1 – 51.6	6.1 - 6.3	38.0 - 45.2	76.0 - 86.0
Bark (coniferous trees)	48.8 - 52.5	4.6 - 6.1	38.7 - 42.4	69.6 - 77.2
Straw (rye, wheat, triticale)	43.2 - 48.1	5.0 - 6.0	36.0 - 48.2	70.0 - 81.0
Miscanthus	46.7 - 50.7	4.4 - 6.2	41.7 – 43.5	77.6 – 84.0

Fuel Composition and Heating Values.

N, S and Cl concentrations in different biomass fuels

Glossary: d.b. ... dry base.

	Nitrogen N $mg \cdot kg^{-1}$ (d.b.)	Sulphur (S) $mg \cdot kg^{-1}$ (d.b.)	Chlorine (Cl) $mg \cdot kg^{-1}$ (d.b.)
Wood chips (spruce)	900 - 1,700	70 – 300	50 - 60
Wood chips (poplar, willow)	1,000 - 2,000		
Bark (spruce)	3,000 - 4,500	350 – 550	150 - 200
Straw (winter wheat)	3,000 - 5,000	500 - 1,100	2,500 - 4,000
Miscanthus	4,000 - 6,000	200 - 1,400	500 - 2,000
Triticale (cereals)	6,000 - 9,000	1,000 - 1,200	1,000 - 3,000
Hay	10,000 - 20,000	2,500	2,500 - 4,500
Needles (spruce)	12,000 - 15,000		
Grass	19,000 - 25,000	800	2,600

Fuel Composition and Heating Values.

Concentration ranges of combustion relevant elements in different biomass ashes

(d.b......dry basis)

Ash/element	Wood chips (spruce)	Bark (spruce)	Straw (wheat, rye, barley)	Cereals (wheat, triticale)
Si [wt% (d.b.)]	4.0 - 11.0	7.0 - 17.0	16.0 - 30.0	16.0 - 26.0
Ca [wt% (d.b.)]	26.0 - 38.0	24.0 - 36.0	4.5 - 8.0	3.0 - 7.0
Mg [wt% (d.b.)]	2.2 - 3.6	2.4 - 5.6	1.1 - 2.7	1.2 - 2.6
K [wt% (d.b.)]	4.9 - 6.3	2.4 - 5.6	1.1 - 2.7	1.2 - 2.6
Na [wt% (d.b.)]	0.3 - 0.5	0.5 - 0.7	0.2 - 1.0	0.2 - 0.5
Zn [$mg \cdot kg^{-1}$ (d.b.)]	260 - 500	300 - 940	60 - 90	120 - 200
Cd [$mg \cdot kg^{-1}$ (d.b)]	3.0 - 6.6	1.5 - 6.3	0.1 - 0.9	0.1 - 0.8

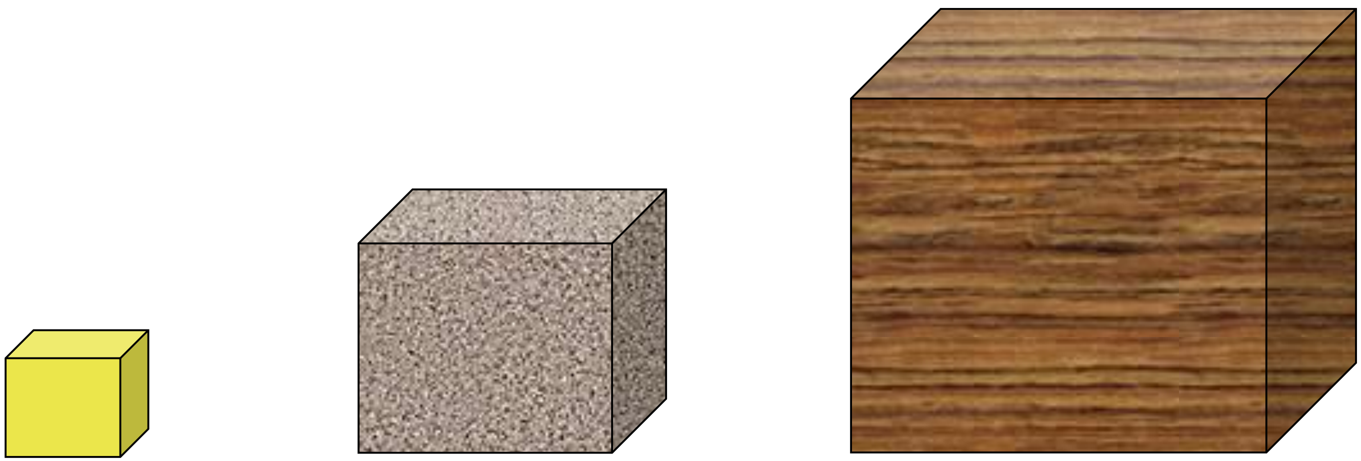
Fuel Composition and Heating Values.

Sample	Proximate analysis			Ultimate Analysis						HHV
	VM (wt%)	Fix-C (wt%)	Ash (wt%)	C (wt%)	H (wt%)	O[a] (wt%)	N (wt%)	S (wt%)	Cl (wt%)	(MJ·kg^{-1})
Cellulosic fr.:										
Newspaper	88.5	10.5	1.0	52.1	5.9	41.86	0,11	0.03	n.a.	19.3
Cardboard	84.7	6.9	8.4	48.6	6.2	44.96	0.11	0.13	n.a.	16.9
Recycled paper	73.6	6.2	20.2	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	13.6
Glossy paper	67.3	4.7	28.0	45.6	4.8	49.41	0.14	0.05	n.a.	10.4
Spruce	89.6	10.2	0.2	47.4	6.3	46.2	0.07	n.a.	n.a.	19.3
Plastics:										
HDPE	100	0	0	86.1	13.0	0.90	n.a.	n.a.	n.a.	46.4
LDPE	100	0	0 0	85.7	14.2	0.05	0.05	0.00	n.a.	46.6
PP	100	0	0	86.1	13.7	0.20	n.a.	n.a.	n.a.	
PS	99.8	0.02	0	92.7	7.3	0.00	n.a.	n.a.	n.a.	42.1
PVC	94.8	4.8	0.4	41.4	5.3	5.83	0.04	0.03	47.7	22.8
Multi material										
Juice carton	86.0	6.1	7.9	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	24.4

Fuel Composition and Heating Values.

	Moisture content [wt% w.b.]	GCV [kWh·kg^{-1} (d.b.)]	NCV [kWh·kg^{-1} (d.b.)]	Bulk density [kg(w.b.)·m^{-3}]	Energy density [kWh·m^{-3}]
Wood pellets	10	5.5	4.6	600	2,756
Wood chips - hardwood - pre-dried	30	5.5	3.4	320	1,094
Wood chips – hardwood	50	5.5	2.2	450	1,009
Wood chips - softwood - pre-dried	30	5.5	3.4	250	855
Wood chips – softwood	50	5.5	2.2	350	785
Grass- high-pressure bales	18	5.1	3.8	200	750
Bark	50	5.6	2.3	320	727
Triticale (cereals) - high-pressure bales	15	5.2	4.0	175	703
Sawdust	50	5.5	2.2	240	538
Straw (winter wheat) - high-pressure bales	15	5.2	4.0	120	482

Biomass having an energy content equivalent to
1 m^3 fuel oil.



Fuel oil
(0% moisture)
1 m^3
840 kg

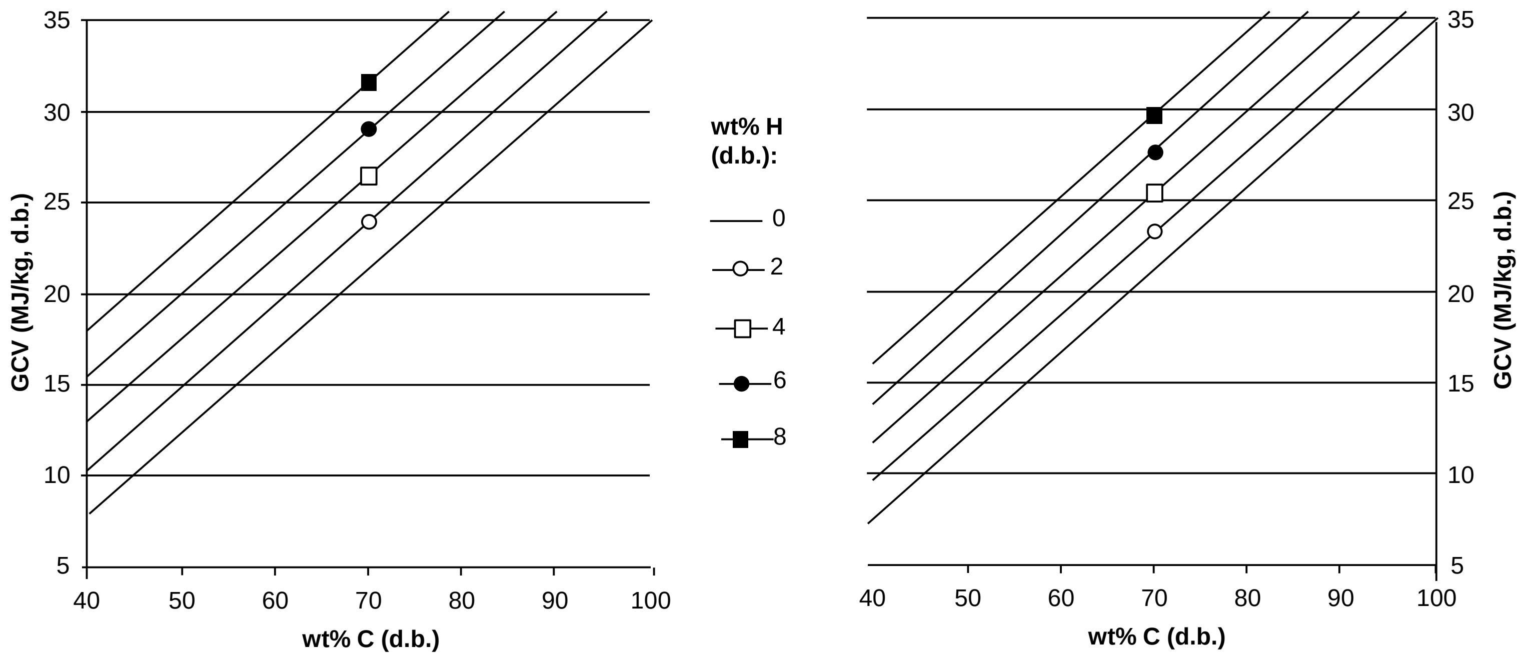
Pellets
(12% moisture)
3.2 m^3
2200 kg

Wood chips
(40% moisture)
12 m^3
3800 kg

Fuel Composition and Heating Values.

$$GCV = 0.3491 \cdot \chi_C + 1.1783 \cdot \chi_H + 0.1005 \cdot \chi_S - 0.0151 \cdot \chi_N - 0.1034 \cdot \chi_O - 0.0211 \cdot \chi_{ash} \text{ [MJ/kg, d.b.]}$$

where χ_i is the content of carbon (C), hydrogen (H), sulfur (S), nitrogen (N), oxygen (O) and ash in wt% (d.b.)

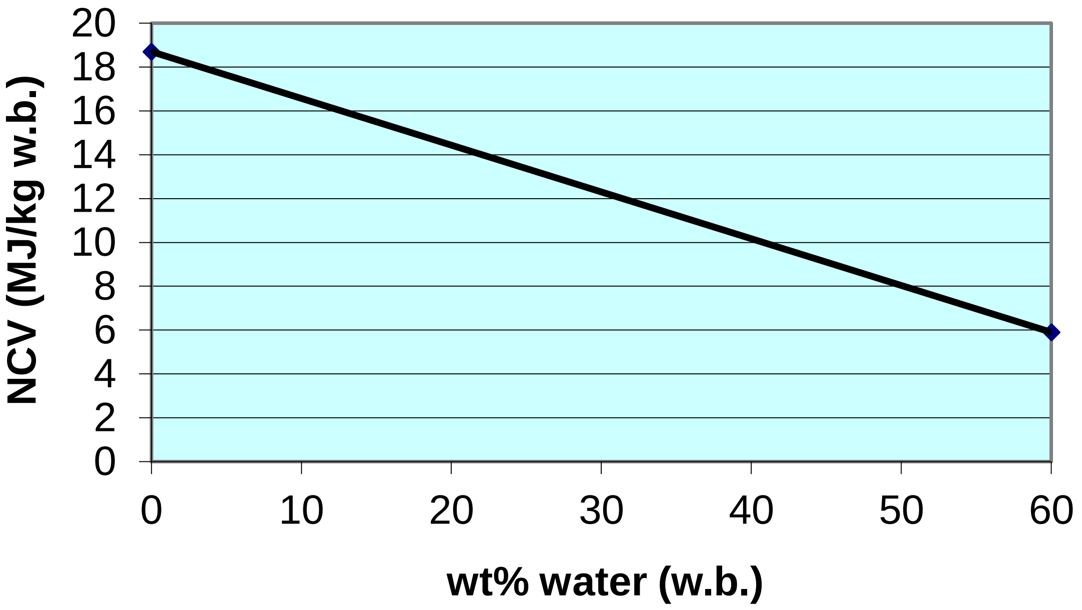


GCV and NCV (assuming zero wt% moisture) as a function of wt% C and H (d.b.), O is calculated by difference, neglecting the influence of N, S, and ash in the fuel.

Fuel Composition and Heating Values.

$$NCV = GCV \cdot \left(1 - \frac{w}{100}\right) - 2.447 \cdot \frac{w}{100} - 2.447 \cdot \frac{h}{100} \cdot 9.01 \cdot \left(1 - \frac{w}{100}\right) \quad [MJ/kg, w.b.]$$

w	moisture content of the fuel in wt% (w.b.)
h	hydrogen content of the fuel in wt% (d.b.)



NCV as a function of wt% moisture (w.b.) for a fuel composition of 50 wt% C, 6 wt% H, and 44 wt% O (d.b.).

Average Calorific Values, Energy Content.

		kJ (NCV)	kgoe (NCV)
Hard Coal	1 kg	17 200 – 30 700	0,411 – 0,733
Recovered Hard Coal	1 kg	13 800 – 28 300	0,330 – 0,676
Patent Fuels	1 kg	26 800 – 31 400	0,640 – 0,750
Hard Coke	1 kg	28 500	0,681
Brown Coal	1 kg	5 600 – 10 500	0,134 – 0,251
Black Lignite	1 kg	10 500 – 21 000	0,251 – 0,502
Peat	1 kg	7 800 – 13 800	0,186 – 0,330
Brown Coal Briquettes	1 kg	20 000	0,478
Tar	1 kg	37 700	0,9
Benzene	1 kg	39 500	0,943
Oil Equivalent	1 kg	41 868	1
Crude Oil	1 kg	41 600 – 42 800	0,994 – 1,022
Feedstock	1 kg	42 500	1,015
Refinery Gas	1 kg	50 000	1,194
LPG	1 kg	46 000	1,099
Motor Spirit	1 kg	44 000	1,051
Kerosene, Jet Fuel	1 kg	43 000	1,027
Naphtha	1 kg	44 000	1,051
Gas Diesel Oil	1 kg	42 300	1,01
Residual Fuel Oil	1 kg	40 000	0,955
White Spirit	1 kg	44 000	1,051
Lubricants	1 kg	42 300	1,01
Bitumen	1 kg	37 700	0,9
Petroleum Cokes	1 kg	31 400	0,75
Other Petro. Products	1 kg	30 000	0,717
Electrical Energy	1 kWh	3 600	0,086

NCV = Net Calorific Value
kgoe = kilogram of oil equivalent

Standards.

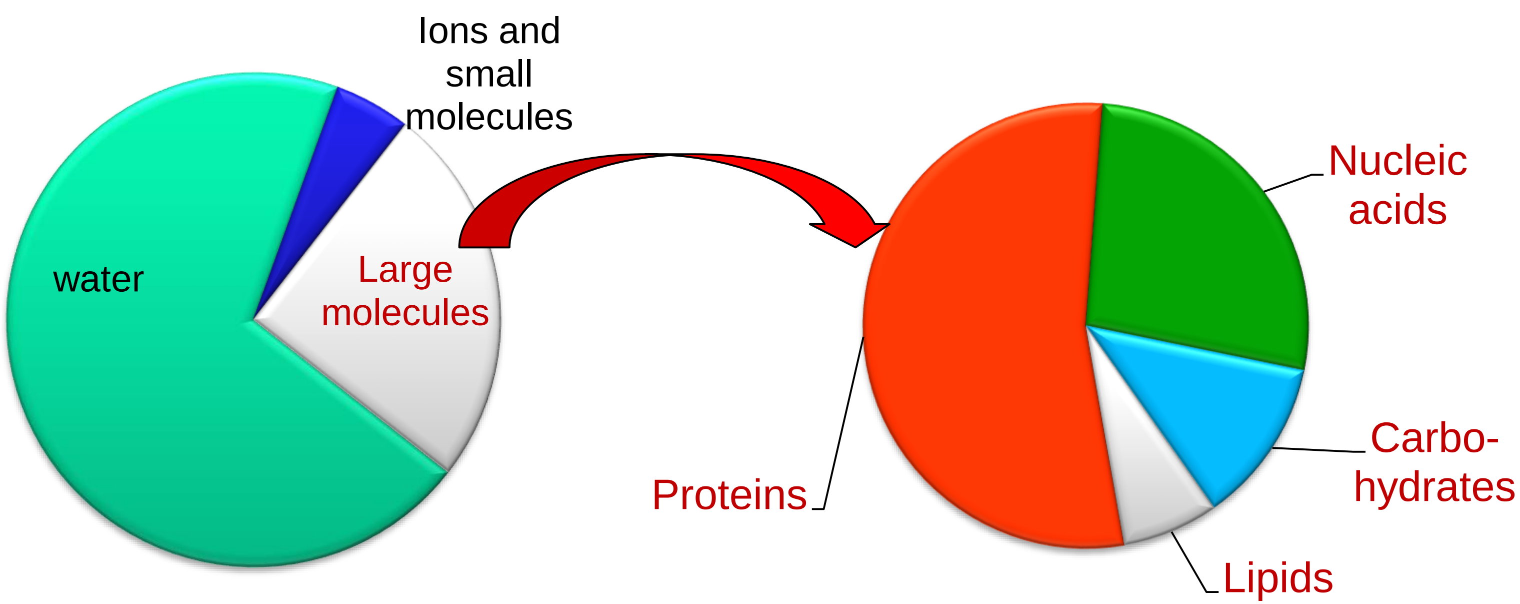
- ISO standard (http://www.iso.com/)
  - Insurance Service Office
- ASTM standard (http://www.astm.org/)
  - ASTM International
- DIN standard (http://www2.din.de/)
  - Deutsches Institut für Normung
- CEN standard (http://www.cenorm.be/)
  - European Committee for Standardization

Biofuel Certification (EU).

As of April 2015, the EC has approved 19 voluntary schemes that can certify biofuels for all MS. MS must accept these certification schemes and cannot demand anything more than what they cover. The approved voluntary certification schemes are:

1. ISCC (International Sustainability and Carbon Certification)
2. Bonsucro EU
3. RTRS EU RED (Round Table on Responsible Soy EU RED)
4. RSB EU RED (Round Table of Sustainable Biofuels EU RED)
5. 2BSvs (Biomass & biofuels voluntary scheme)
6. RBSA (Abengoa RED Bioenergy Sustainability Assurance)
7. Greenergy (Brazilian bioethanol verification program)
8. Ensus (Voluntary scheme under RED for Ensus bioethanol production)
9. Red Tractor (Farm Assurance Combinable Crops & Sugar Beet Scheme)
10. SQC (Scottish Quality Farm Assured Combinable Crops scheme)
11. Red Cert
12. NTA 8080
13. RSPO RED (Roundtable on Sustainable Palm Oil RED)
14. Biograce (GHG calculation tool)
15. HVO Renewable Diesel Scheme
16. Gafta Trade Assurance Scheme
17. KZR INIG
18. Trade Assurance Scheme for Combinable Crops
19. Universal Feed Assurance Scheme

Substances in Living Cells.



The functions of macromolecules are related to their shape and the chemical properties of their monomers. Some of the roles of macromolecules include:

- ❖ Energy storage
- ❖ Structural support
- ❖ Transport
- ❖ Heredity
- ❖ Protection and defence
- ❖ Means for movement, growth, and development
- ❖ Regulation of metabolic activities

Biomass Feeding Constituents.

Starch: 70-75% (wheat)

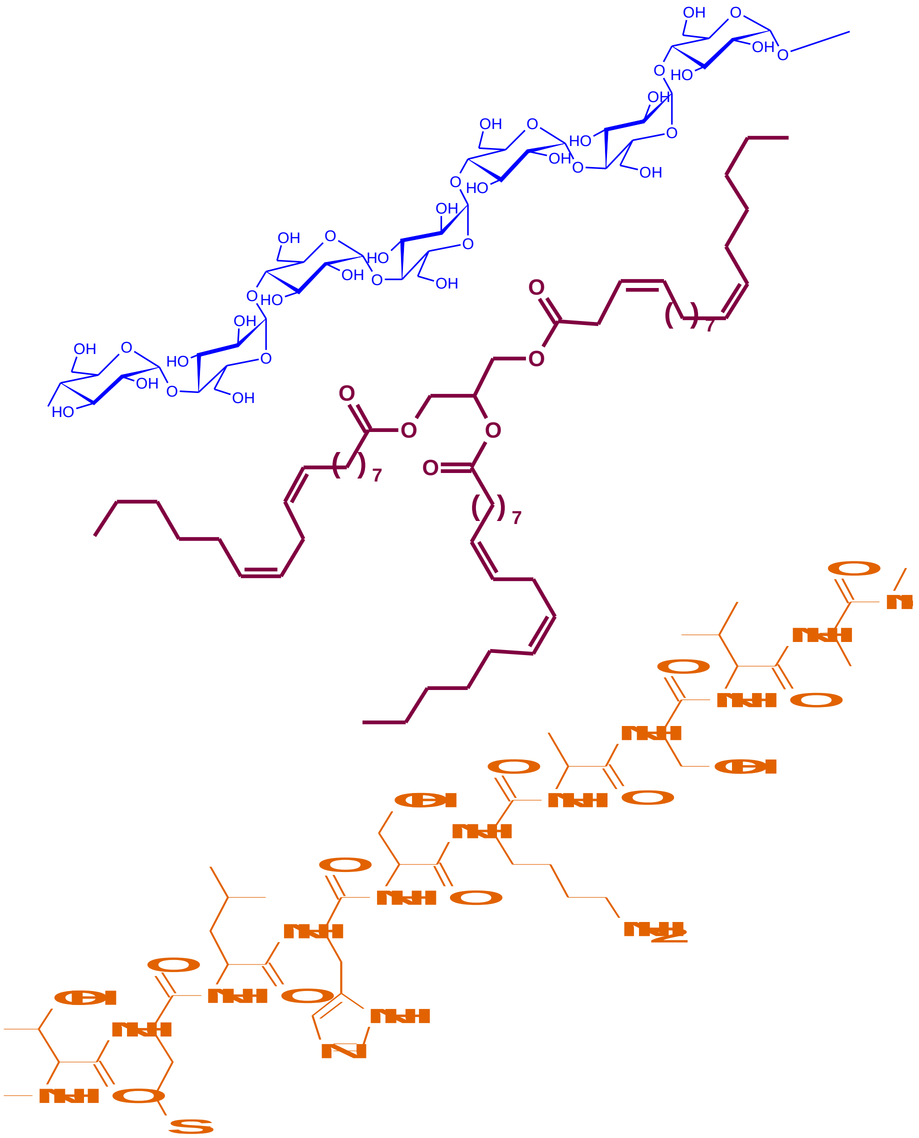
- Rapidly available and hydrolysable
- Basis for actual "*bio-refineries*"

Oils: 4-7% (wheat), 18-20% (soy)

- Rapidly separable from plant
- Basis for *oleochemistry* and for *biodiesel*

Proteins: 20-25% (wheat), 80% (soy)

- Key components of foods
- Applications in chemical products.



Biomass Non Feeding Constituents.

Lignin : 15-25%

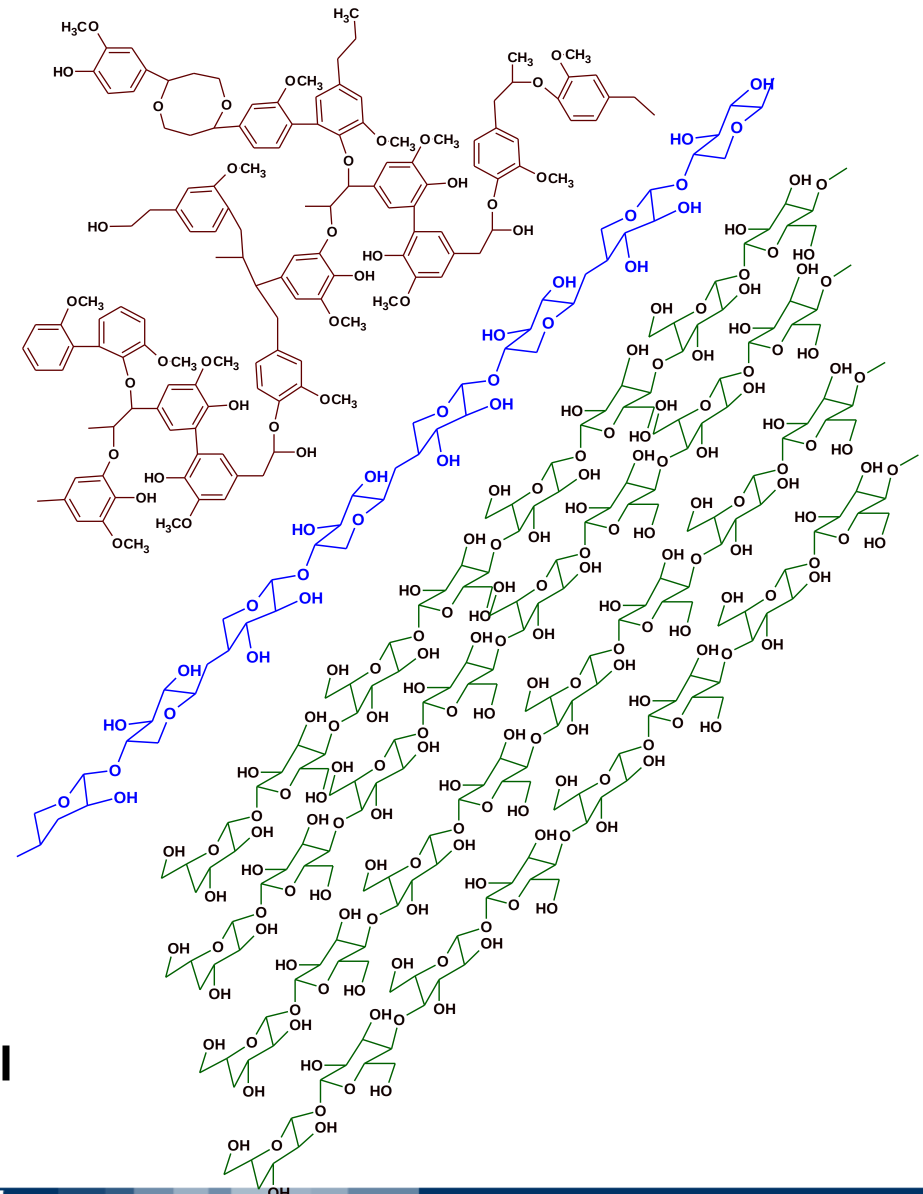
- **Complex network of aromatics**
- **High energy content**
- **Resists biochemical conversion.**

Hemicellulose : 23-32%

- **Xylose is the 2nd most abundant sugar in biosphere**
- **A collection of 5- and 6-carbon sugars linked together in long, substituted chains-branched, marginal biochemical feed.**

Cellulose : 38-50%

- **Most abundant carbon form in biosphere**
- **Long polymer chains of beta-linked glucose, good biochemical feedstock.**



Bioproducts Terminology.

Renewable Bioresource Feedstock

- Plants
  - crops
  - trees
  - algae
- Animals, fish
- Microorganisms
- Organic residues
  - municipal
  - industrial
  - agricultural
  - forestry
- Aquaculture

Bioprocess Technology

Biocatalysis (Enzymes)

Fermentation (Microorganisms)

Physical – Chemical Process Technology

Extraction

Pyrolysis

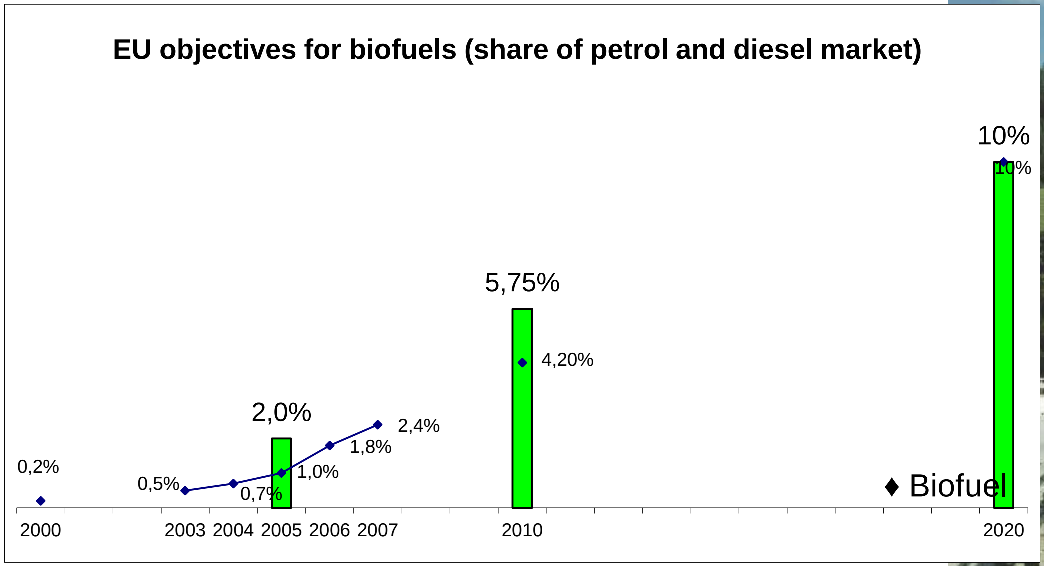
Gasification

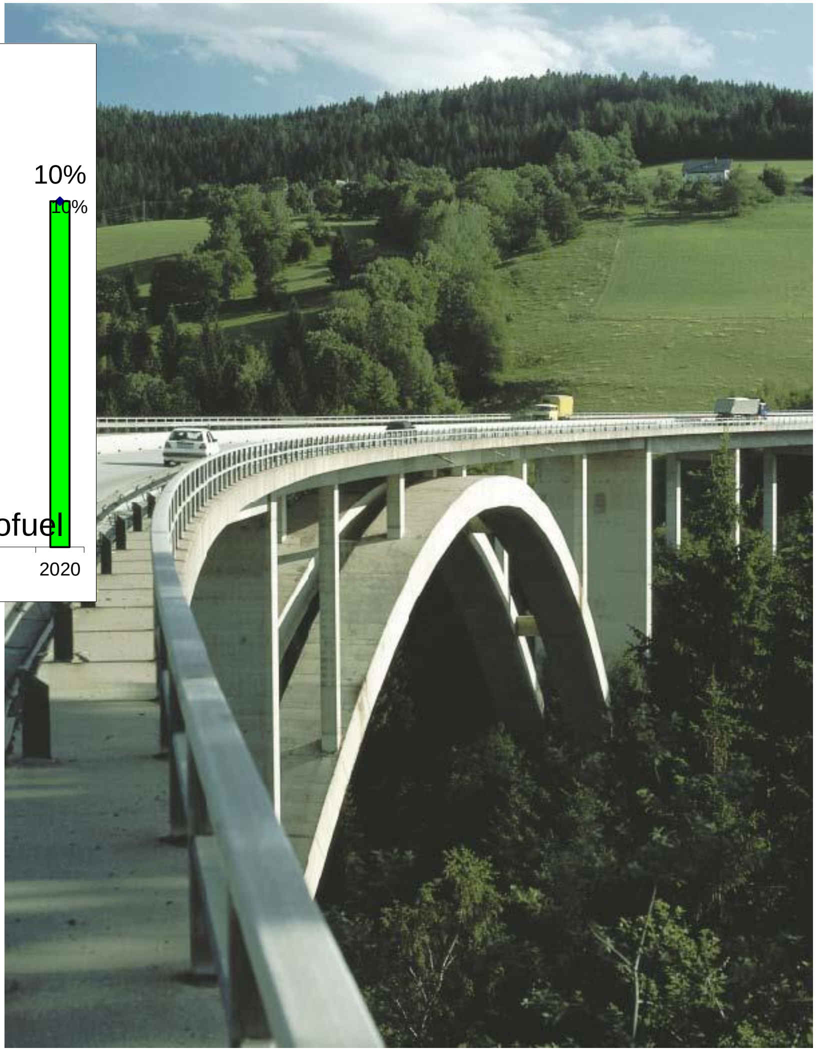
Etc.

Industrial Bioproducts

- Bioenergy and Biofuels
- Manufactured products:
  - biochemicals
  - biosolvents
  - bioplastics
  - ‘smart’ biomaterials
  - biolubricants
  - biosurfactants
  - bioadhesives
  - biocatalysts
  - biosensors

EU Targets on Transport Biofuels.





- European Directive 2003/30/CE
- Dlgs n. 128 (2005) – Allegato I – Biocarburanti.
- Finanziaria 2006– Law n.266 (2005)
- DLvo 3 aprile 2006 n. 152
- Finanziaria 2007– art. 26
- Directive 2009/28/EC

www.agra-net.com

EU Fuel Use Projections (Ktoe).

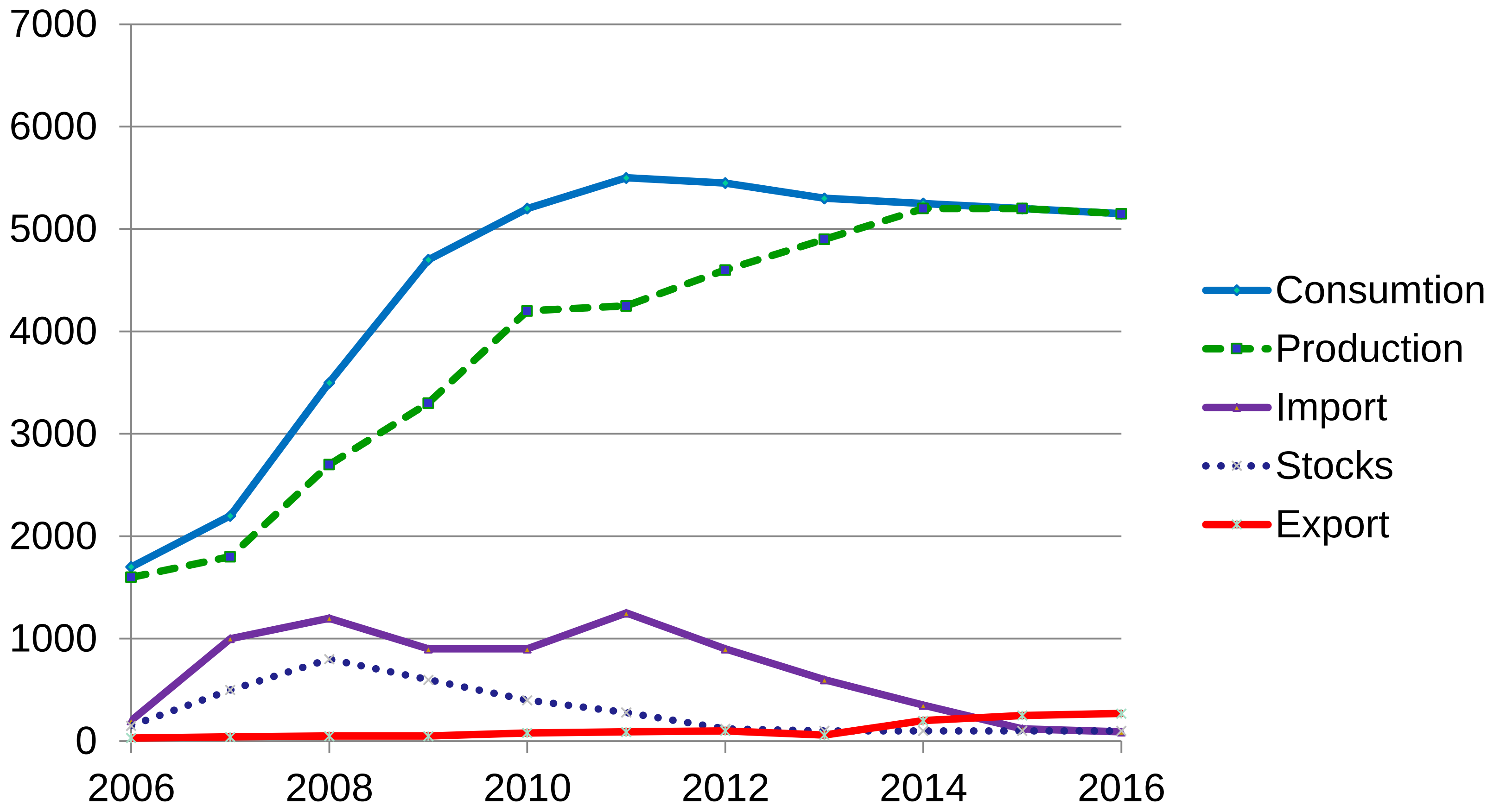
Calendar Year	2009	2010	2011	2012	2013	2014e	2015e	2016e
Gasoline Total	99,246	94,118	90,578	84,769	81,706	77,732	73,944	70,38
Diesel Total	256,026	260,305	255,185	250,647	249,906	250,2	250,75	251,3
On-road	190,695	194,864	195,502	191,39	191,68	192	192,4	192,8
Agriculture	12,64	12,387	12,074	11,491	11,669	11,8	11,9	12
Constr./mining	3,036	3,222	3,191	3,146	3,35	3,4	3,45	3,5
Shipping/rail	6,435	6,472	6,138	6,114	5,53	5,5	5,5	5,5
Industry	11,723	12,184	10,631	10,802	9,545	9,5	9,5	9,5
Heating	31,497	31,177	27,648	27,704	28,132	28	28	28
Jet Fuel Total	49,192	49,217	50,57	49,06	48,926	49	49	49
Total Fuel	404,464	403,64	396,333	384,475	380,539	376,932	373,694	370,68

Ethanol Used as Fuel and Other Industrial Chemicals (Million Liters - EU).

Calendar Year	2009	2010	2011	2012r	2013e	2014e	2015f	2016f
Beginning Stocks	872	621	440	315	88	161	230	170
Fuel Begin Stocks	839	588	407	282	55	128	197	137
Production	4,203	4,918	5,042	5,308	5,561	5,9	5,9	5,9
Fuel Production	3,553	4,268	4,392	4,658	4,911	5,25	5,25	5,25
-of which cellulosic (a)	0	0	0	0	0	75	75	75
Imports	1,136	1,284	1,663	1,245	676	447	270	270
Fuel Imports	899	880	1,285	886	595	367	190	190
-of which ETBE (b)	158	270	261	188	197	109	100	100
Exports	150	126	149	145	113	278	300	280
Fuel Exports	100	76	99	95	63	228	250	230
Consumption	5,44	6,257	6,681	6,635	6,051	6	5,93	5,93
Fuel Consumption	4,603	5,253	5,703	5,676	5,37	5,32	5,25	5,25
Ending Stocks	621	440	315	88	161	230	170	130
Fuel Ending Stocks	588	407	282	55	128	197	137	97
Production Capacity								
Number of Refineries	66	68	68	70	71	71	71	71
Capacity	6,234	7,57	7,759	8,468	8,48	8,48	8,48	8,48
Capacity Use (%)	57	56	57	55	58	62	62	62
Co-product Production (1,000 MT)								
DDG	2,119	2,594	2,664	2,752	2,953	3,229	3,172	3,187
Corn Oil	70	71	67	111	151	155	157	159
Feedstock Use (1,000 MT)								
Wheat	2,736	4,173	4,813	4,209	2,85	3,535	3,306	3,26
Corn	2,414	2,455	2,327	3,84	5,213	5,36	5,398	5,478
Barley	661	608	707	389	618	651	602	598
Rye	959	1,051	666	355	753	769	829	846
Sugar Beet	9,209	10,68	10,882	11,04	11,683	11,509	12,209	12,019
Market Penetration (1,000 TOE)								
Fuel Ethanol	2,327	2,656	2,883	2,87	2,715	2,69	2,654	2,654
Gasoline	99,246	94,118	90,578	84,769	81,706	77,732	73,944	70,38
Blend Rate (%)	2,3	2,8	3,2	3,4	3,3	3,5	3,6	3,8

The ethanol production and exports for industrial chemicals is estimated at respectively 650 and 50 million liters per year. r = revised / e = estimate / f = forecast EU FAS Posts. (a) For more information see section Advanced Biofuels. (b) ETBE in million liters of ethanol. HS code 29091910, ETBE contains 45 percent ethanol. Source: European Commission, Eurostat, Global Trade Atlas, ePURE and EU FAS Posts.

EU Supply & Demand of Bioethanol (in 10^6 L).



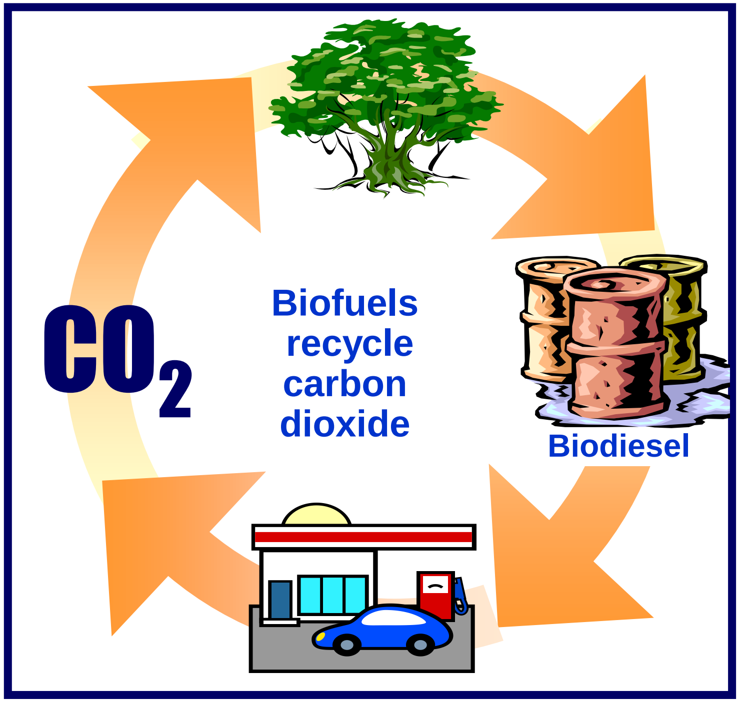
Source: *EUFAS Posts*

Drivers for the Use of Biomasses as Fuels.

1. Increase in the price of fossil fuels and decrease their reserves
2. Interest in diversifying agricultural production
3. Wider resource delocalization.

Environmental Protection:

4. Burning maintains the balance of CO_2 in the atmosphere
5. Lower sulfur content
6. Higher safety in use and storage.



Fuel from biomasses

A 60% reduction in CO_2 emission can be reached!

Heat of Combustion of Representative Biological Molecules.

	$kcal \cdot g^{-1}$	$kJ \cdot g^{-1}$
Carbohydrates	4.1	17.2
Fats	4.1	17.2
Proteins	9.3	38.9

Biofuels.

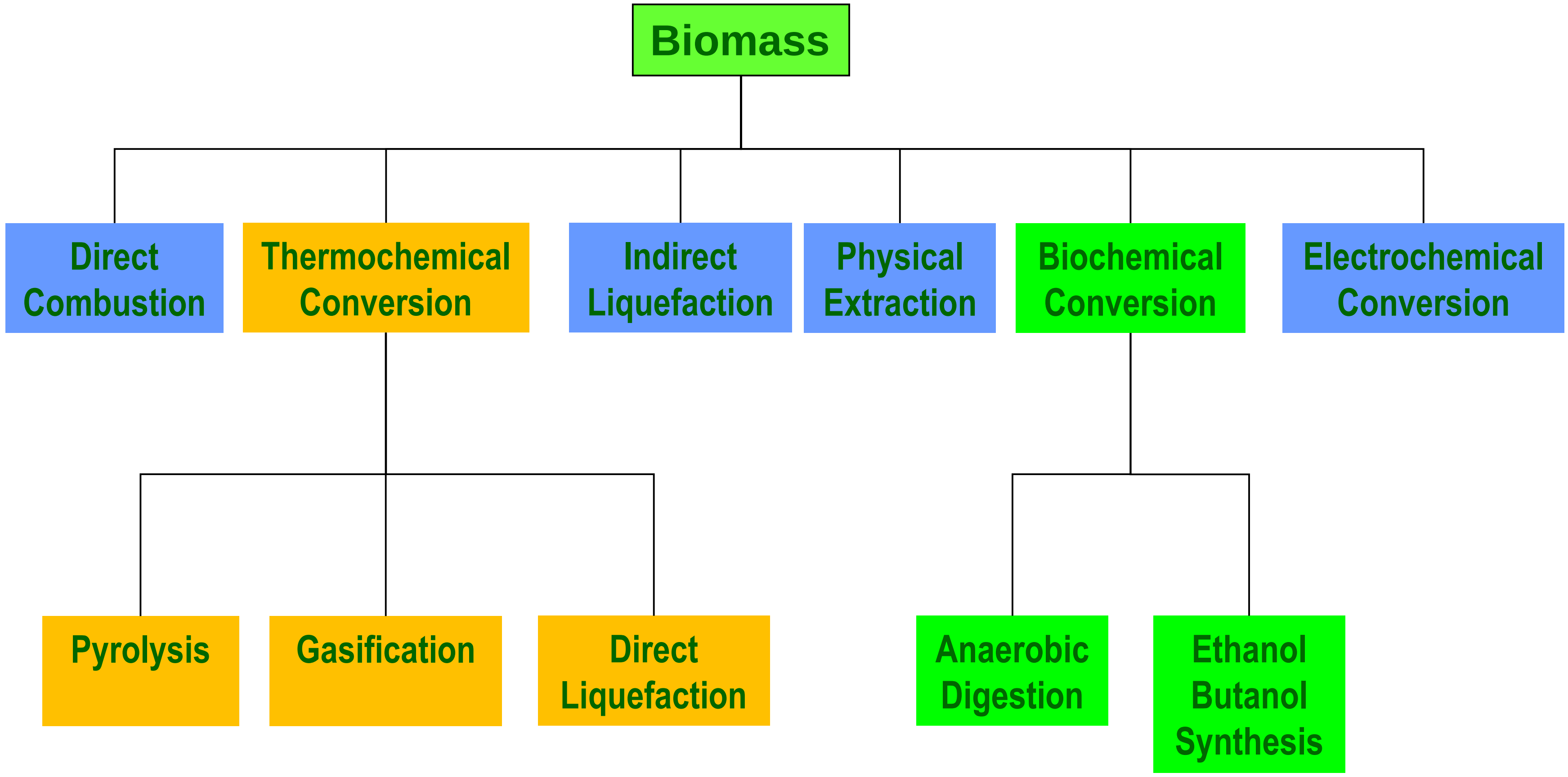
Biofuels are organic compounds (frequently in mixture - solid, gaseous or liquid) which can be used as fuels.

Type:

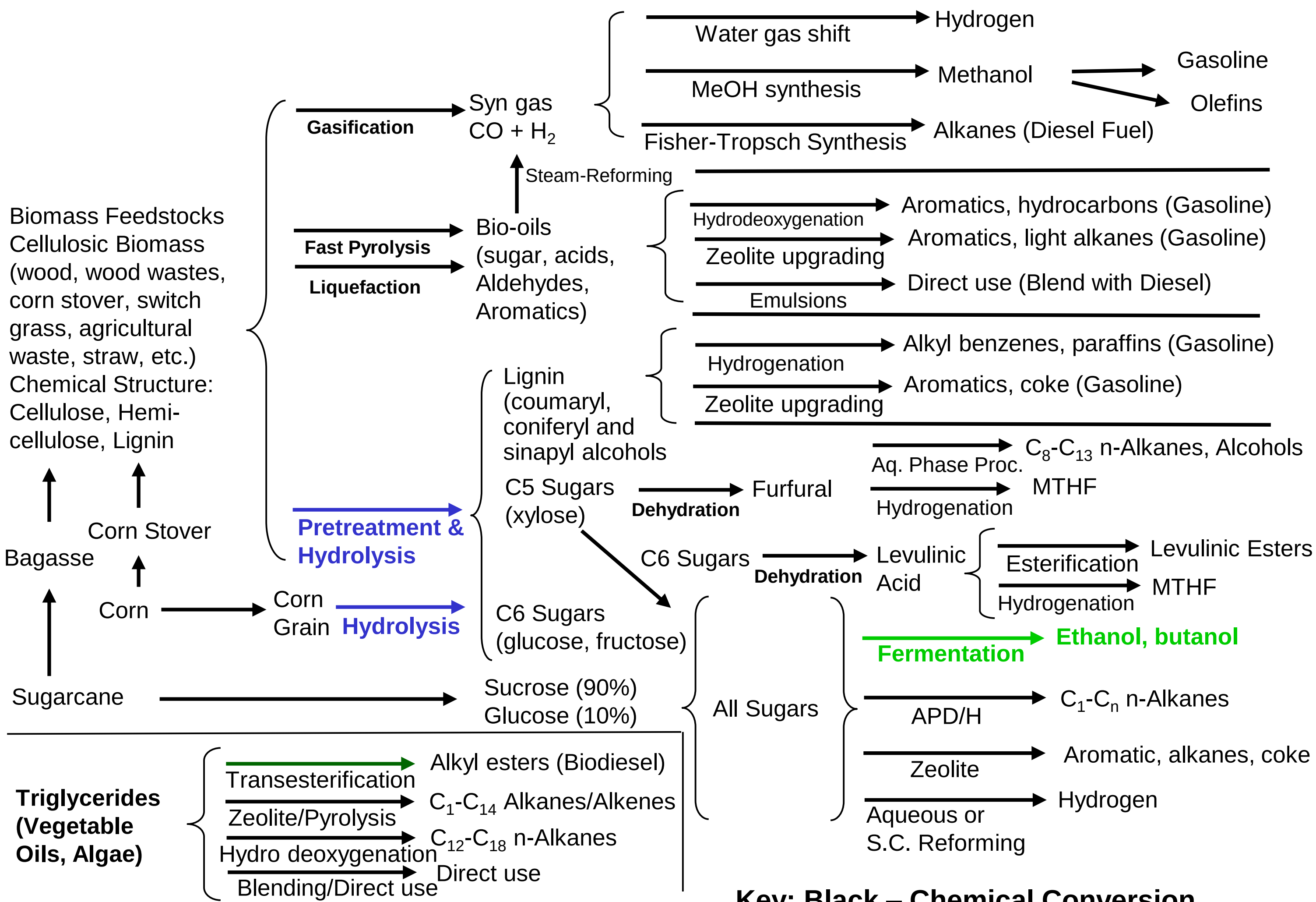
- Solid Biomass (mainly cellulosic)
  - Wood, pyrolytic coal, urban and agricultural wastes)
- Liquid Biofuels :
  - Biodiesel
  - Bioethanol
  - Biooil
  - Biomethanol
  - Biodimethylether
- Biogas (gas of organic waste processing by bacteria mainly anaerobic, in particular CH_4 and syngas)

Biofuels were used by men for a long time, but in a less processed way (wood, oils).

Biomass Conversion Technologies.



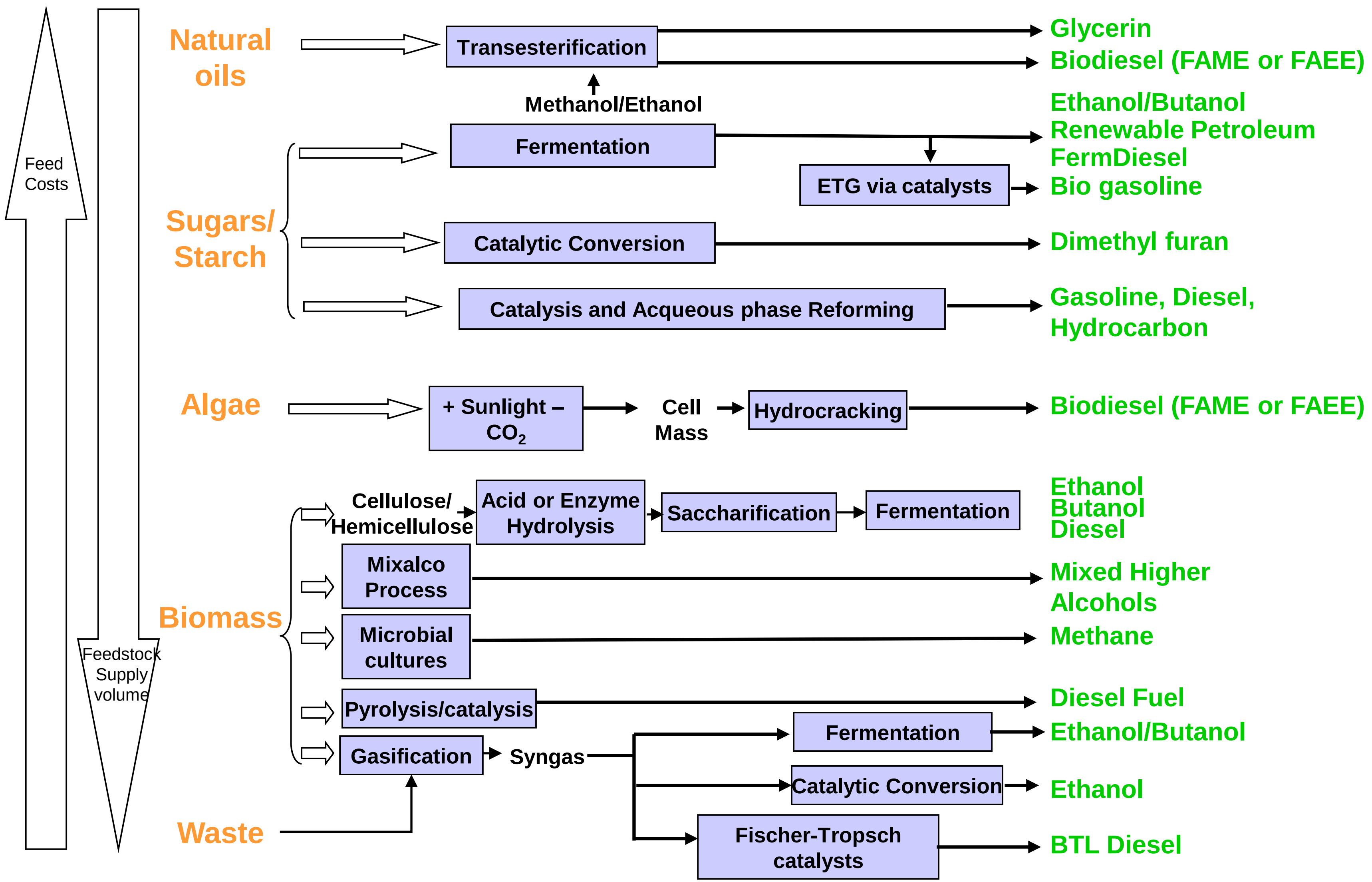
Routes to Make a Biofuel.



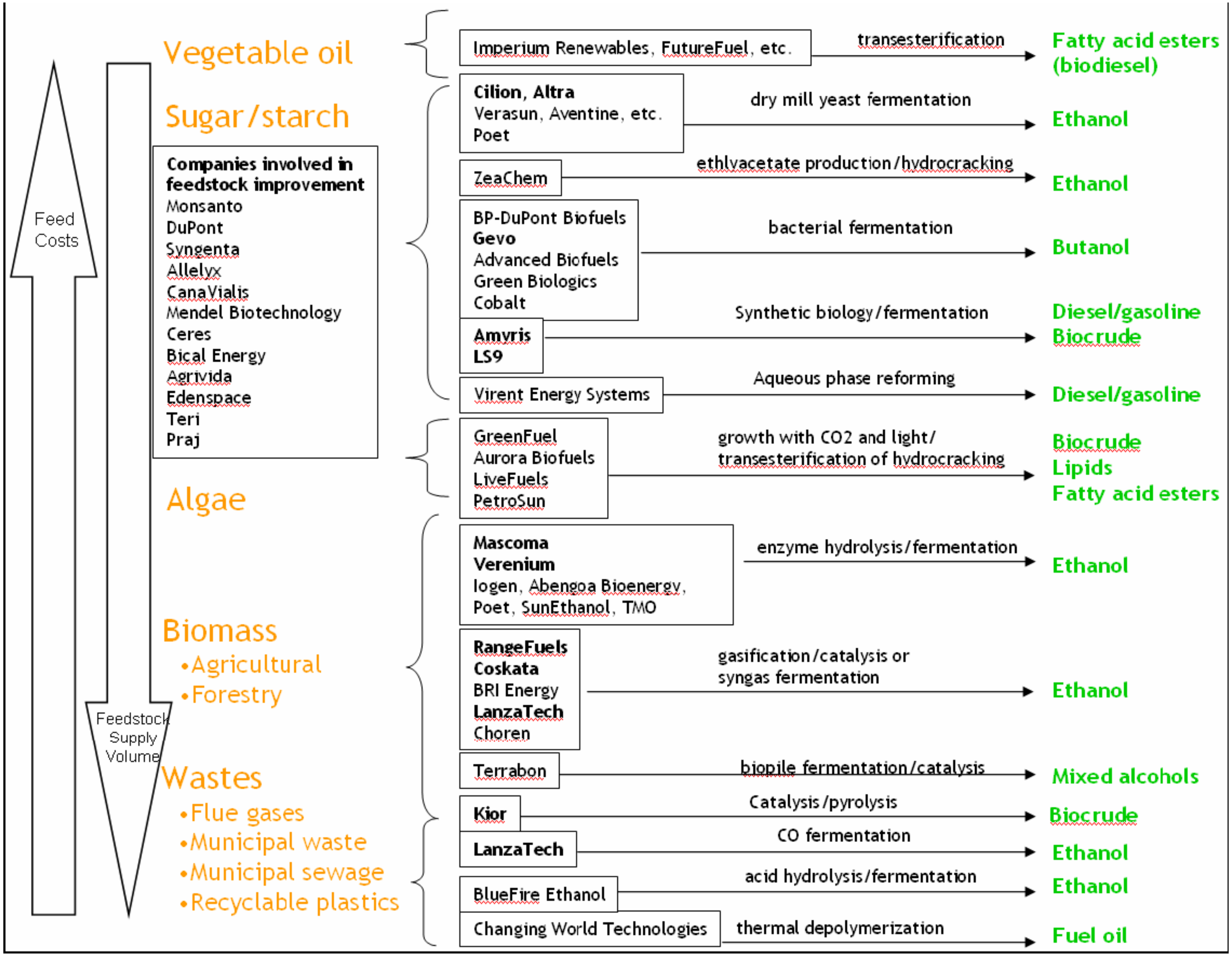
Key: Black – Chemical Conversion
Green – Biological Conversion
Blue – Both Chemical & Biochemical Conv.

Adapted from Huber at al. [2006]

Current Pathways ….



Representative Companies Working on Biofuels.



Biomass – Available Tonnage and MW.

Source	Forest Wastes	Agri Wastes	Urban Organic Wastes
Ton. of material/year	**4500000**	**200000**	**95000**
MW	**300**	**18**	**9.5**
Installed Cost (€·kW^{-1})	**1600**	**1900**	**1600**
Operative Cost (€·kW^{-1})	**0.06**	**0.06**	**0.06**

Biofuel Sources (see Energy Crops).

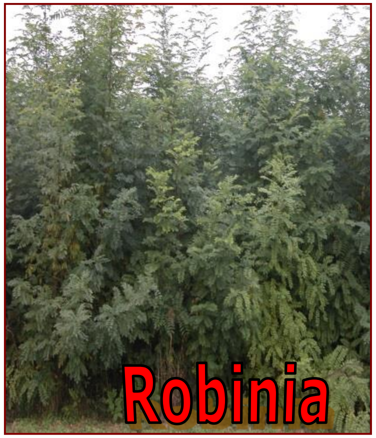
Cereals

Sugar cane

Potato

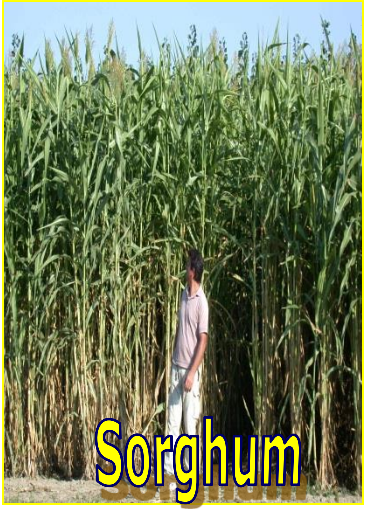
Sugar beet

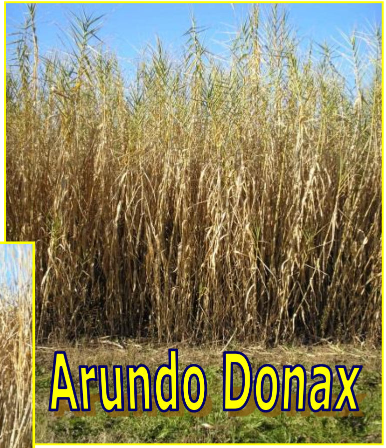
Biomass Sources.

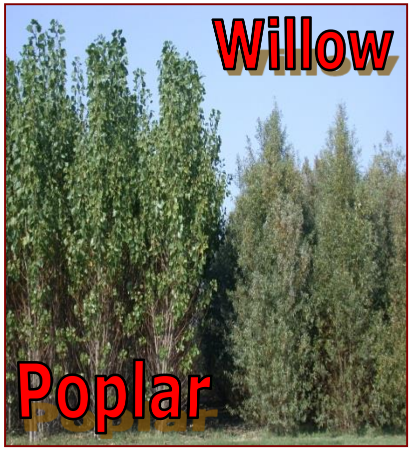


Grass

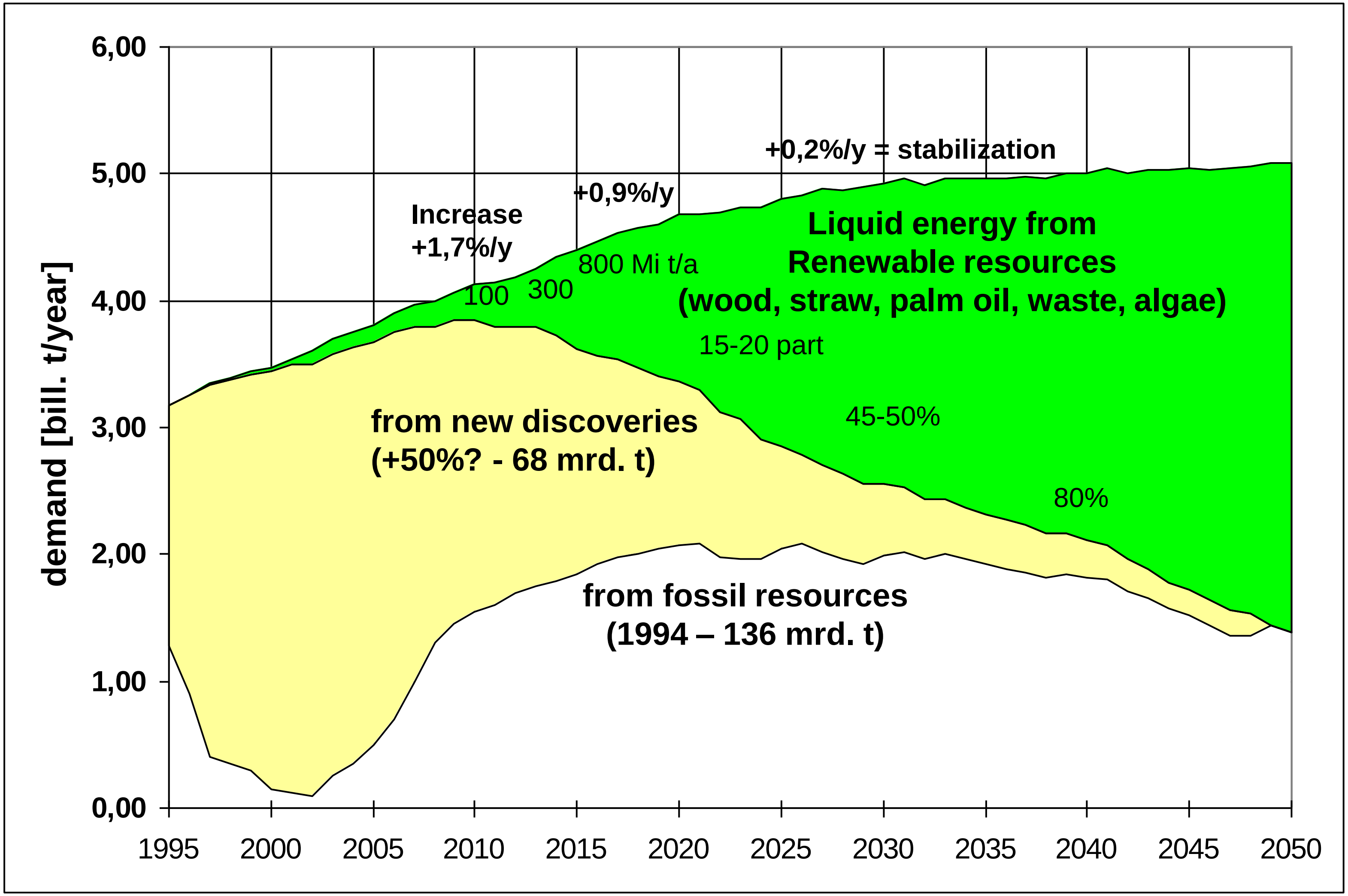
Woody





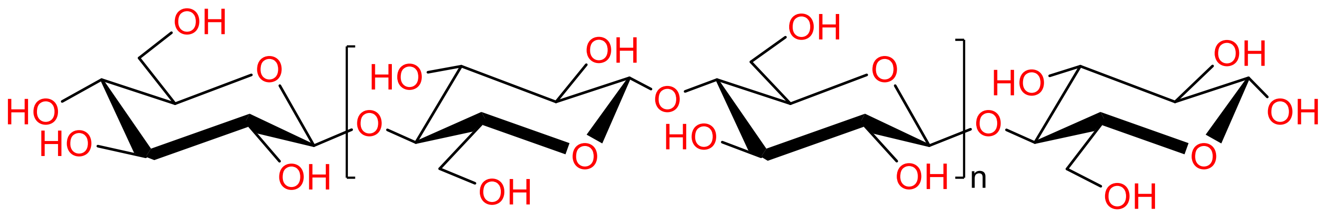


Total Consumption of Liquid Energy Carriers.



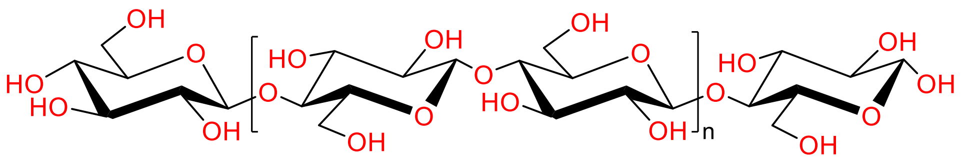
Solid Biomass – Cellulose.

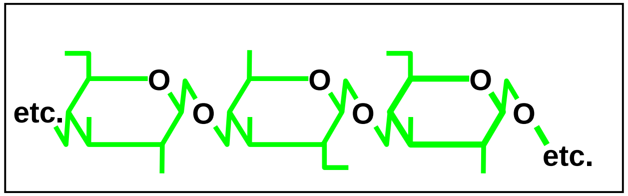
Cellulose: A polymer of glucose units in β–1,4 linkages. Cellulose is a linear molecule consisting of 1,000 to 10,000 β-D-glucose residues with no branching. Neighboring cellulose chains may form hydrogen bonds leading to the formation of microfibrils with partially crystalline parts. Hydrogen bonding among microfibrils can form microfibers and microfibers react to form cellulose fibers. Cellulose fibers usually consist of over 500,000 cellulose molecules.



cellulose

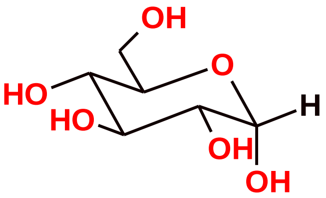
Cellulose

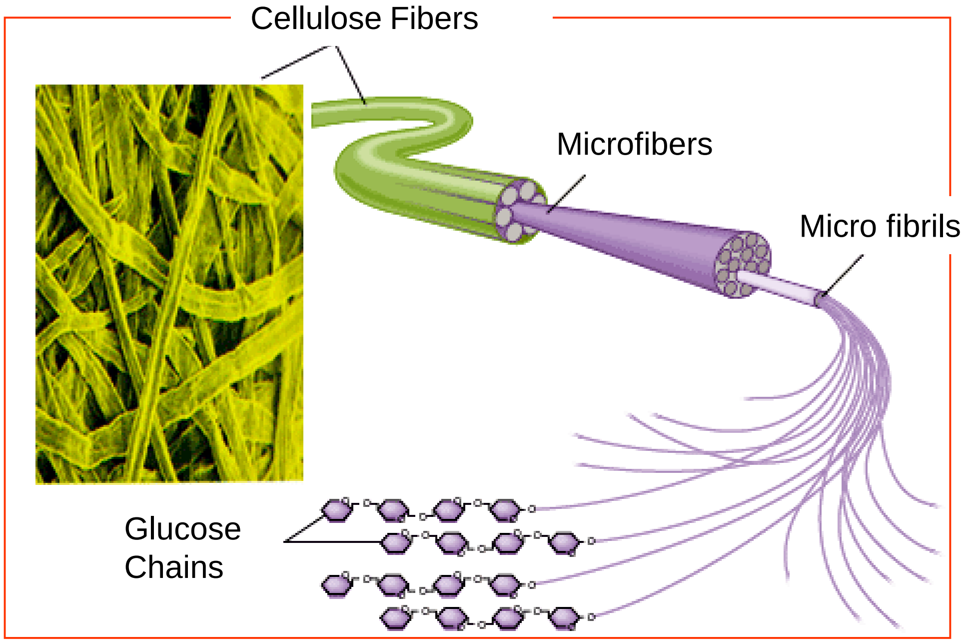




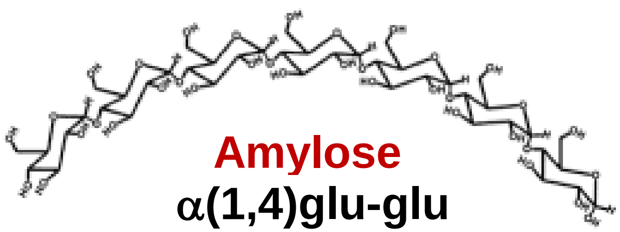
β(1,4)glu-glu

- Main structural component of terrestrial plants
- Polymer made from molecules of glucose monomer
- The acetal bridges can be hydrolyzed to glucose.



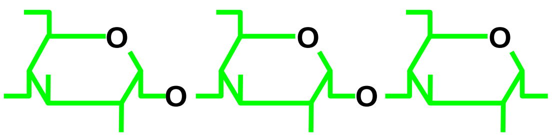


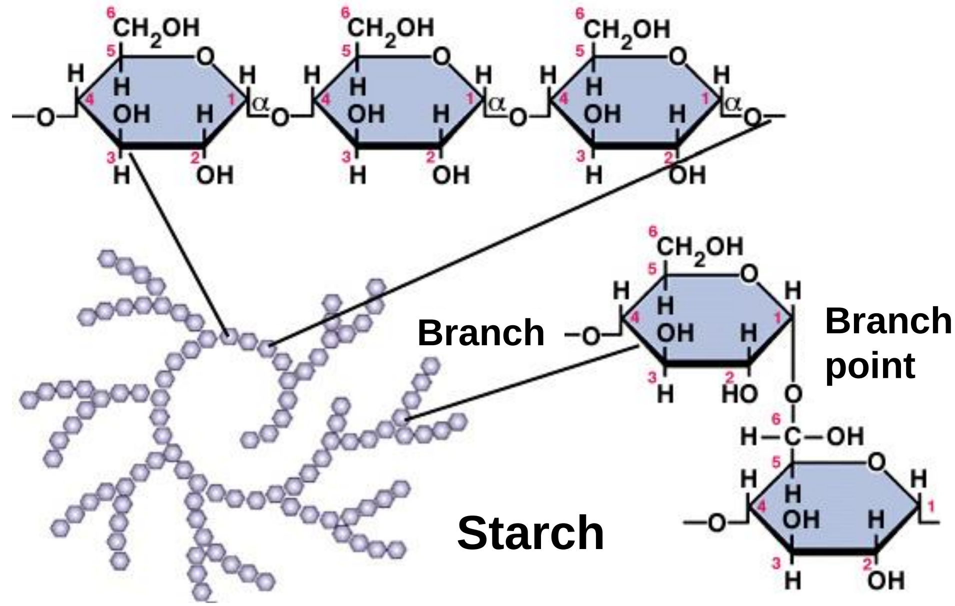
Solid Biomass: Starch.

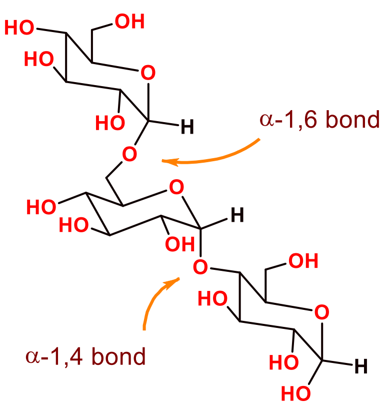


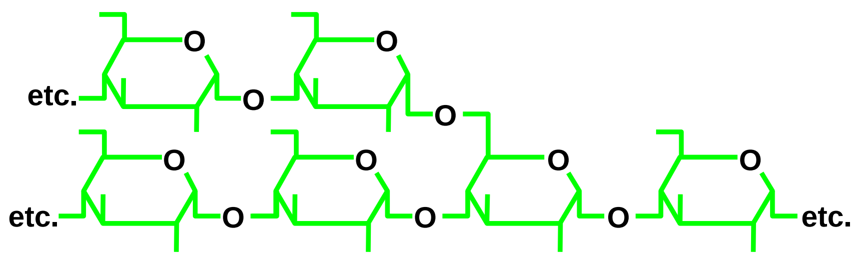
Amylose

α(1,4)glu-glu

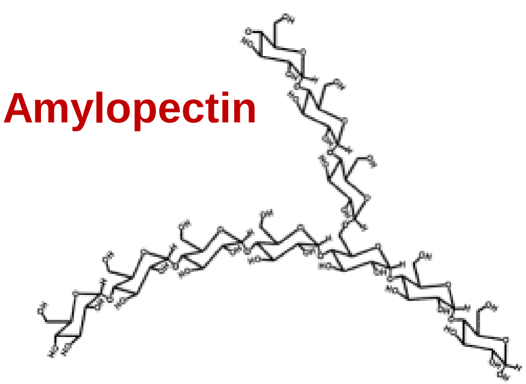








Amylopectin



Amylopectin (starch) **Glycogen (body reserve)**

α(1,4) + α(1,6)glu-glu

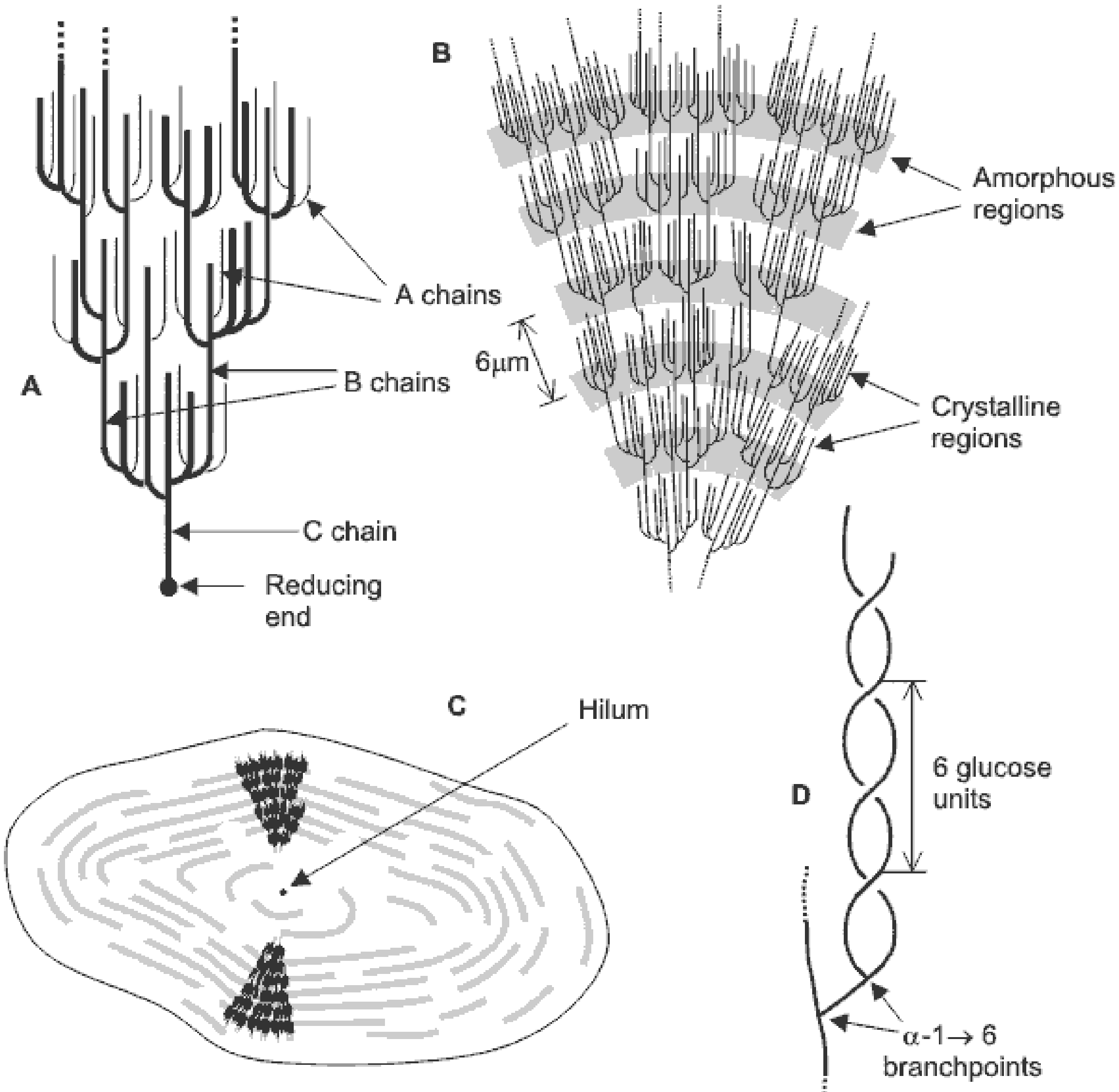
Starch Composition.

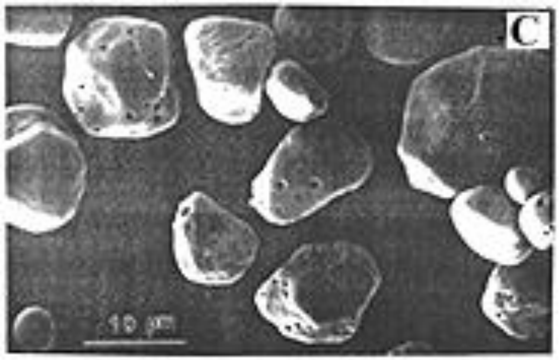
A polymer of α-D-glucose in α-1,4 linkages. Starch consists of two types of molecules, amylose and amylopectin. Amylose is a single chain of glucose units whereas in amylopectin at about every twenty glucose units there is a branch with an α-1,6 linkage. The relative proportions of amylose to amylopectin depend on the source of the starch, *e.g.* normal corn contains over 50% amylose whereas 'waxy' corn has almost none (~3%). Amylose has lower molecular weight with a relatively extended shape, whereas amylopectin has large but compact molecules.

Amylose molecules consist of single mostly-unbranched chains with 500-20,000 α-(1,4)-D-glucose units with a few α-1,6 branches. Amylose can form an extended shape. Hydrogen bonding occurs between aligned chains. The aligned chains may form double stranded crystallites that are resistant to amylases.

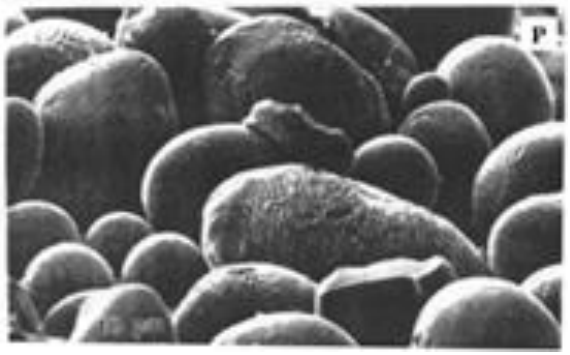
Amylopectin is formed by non-random α-1,6 branching of the amylose-type α-(1,4)-D-glucose structure. This branching is determined by branching enzymes that leave each chain with up to 30 glucose residues. Each amylopectin molecule contains one to two million residues, about 5% of which form the branch points, in a compact structure forming granules. The molecules are oriented radially in the starch granule and as the radius increases so does the number of branches required to fill the space, resulting in concentric regions of alternating amorphous and crystalline structure.

Amylopectin Structure.





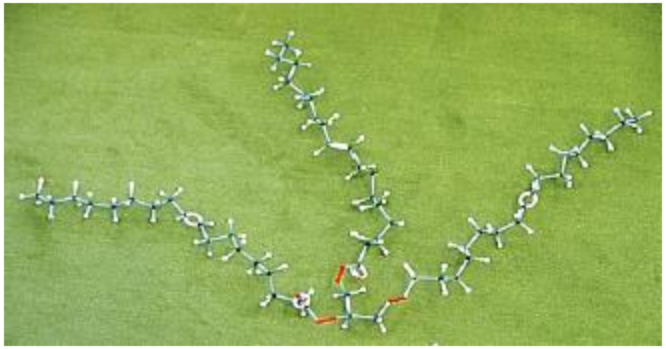
Corn starch



Potato starch

Oils and Fats – Structure.

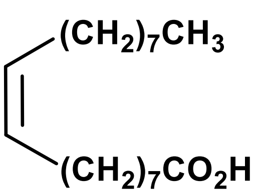
- Esters of fatty acids with glycerol
- Liquids or solids depending on the chain length and unsaturations



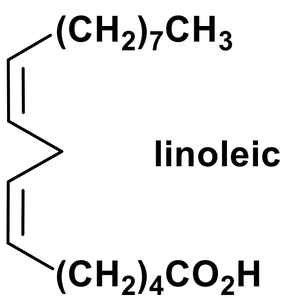
(Long Organic Acids)

Saturated
- $H_3C(CH_2)_{18}CO_2H$ — Stearic acid
- $H_3C(CH_2)_{10}CO_2H$ — Lauric acid

Unsaturated



oleic acid



linoleic acid

(Ester)

$H_2C—COOR'$
$HC—COOR''$
$H_2C—COOR'''$

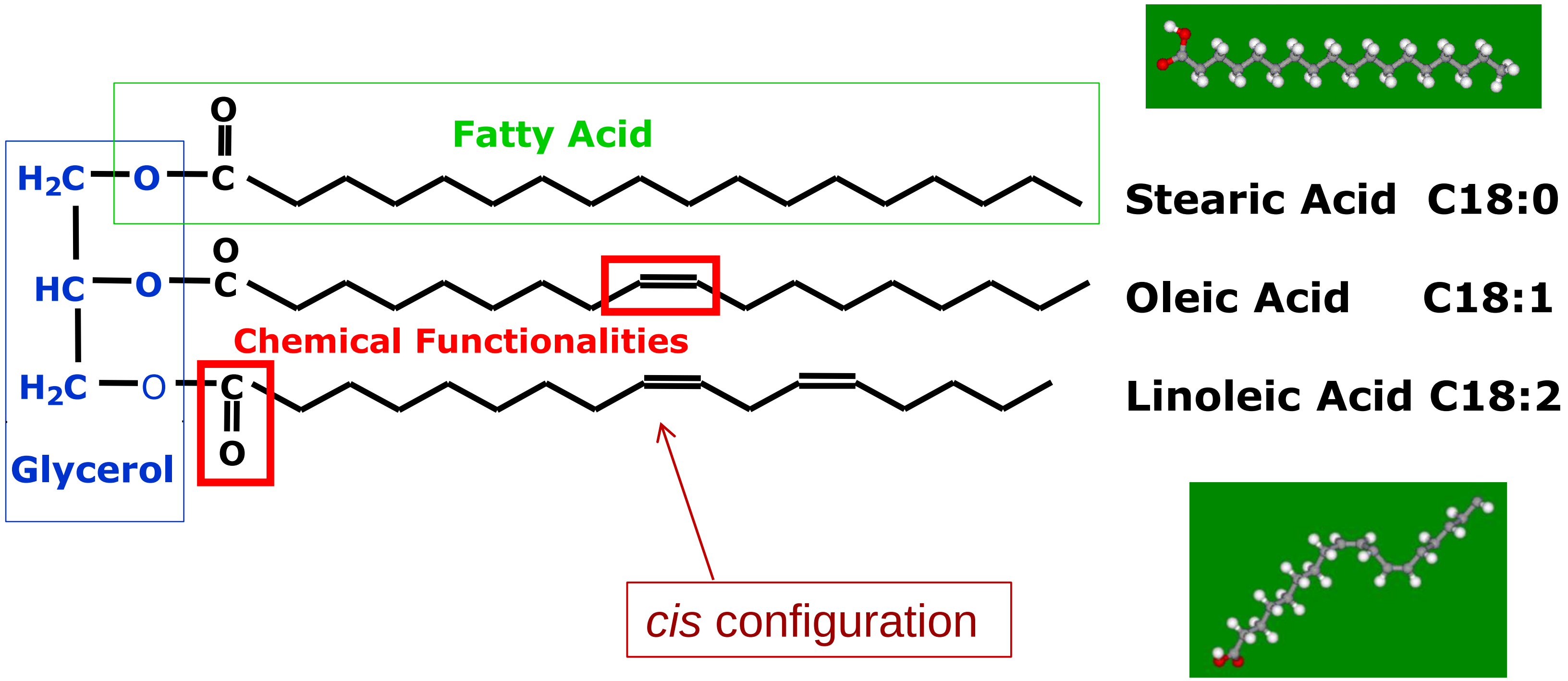
Gliceride

(Polyol)

$H_2C—OH$
$HC—OH$
$H_2C—OH$

Glycerol

Oils and Fats – Structure.



- **Ordinary oils & fats have a mixed fatty acid composition**
- **HO Oils (Definition): > 80 % Oleic Acid (C18:1)**

Fatty Acid Characterization.

Fatty Acid		Low-Temp. Behaviour	High-Temp. Behaviour	Oxidative Stability	Avail-ability	Costs
Caprylic	C8 :0	+ / o	+	++	o	--
Capric	C10:0	+ / o	+	++	o	--
Lauric	C12:0	o	++	++	+	o / -
Myristic	C14:0	-	++	++	+	o / -
Palmitic	C16:0	-	++	++	++	+
Stearic	C18:0	--	++	++	++	++
Oleic	**C18:1**	**+ / o**	**+**	**+**	**++**	**+**
Linoleic	C18:2	+	-	-	+	o / -
Linolenic	C18:3	++	--	--	o	o

$\Rightarrow$ **C18:1 - Convincing compromise between technical & economical constraints**

What are Liquid Biofuels.

- Liquid biofuels are esters, alcohols, ethers, and other compounds derived from biomass.
- They are renewable fuels which can be made in all climates by using agricultural practices jet developed.
  - *Bioethanol:* ethanol produced from biomass and/or from biodegradable fraction of wastes
  - *Biodiesel:* a liquid with a diesel quality made from biomass, oil seeds or from used oils
  - *Biomethanol:* methanol from biomass and/or from biodegradable fraction of wastes
  - *Biodimethylether:* a fuel produced similarly to methanol.
  - *Biooil:* a petrol type fuel made by pyrolysis and/or hydrogenation of biomass.

Evolution of Biofuels.

First generation Biofuels :	Corn and sugar to ethanol Chemical trans-esterification of veg. oils
Second Generation Biofuels :	Lignocellulose to ethanol Enzymatic bioconversion of Vegetable oil Fisher-Tropsch syngas to HC oil
Third generation Biofuels:	Energy crops for bio-alcohol Algal Hydrogen Algal Oil/Biodiesel
Fourth generation Biofuels :	GMO carbon-negative Energy crops

Evolution of Biofuels (2).

Loser in Food vs. Fuel

First generation Biofuels :	Corn and sugar to ethanol Chemical transesterification of veg oils
Second Generation Biofuels :	Lignocellulose to ethanol Enzymatic bioconversion of Vegetable oil Fisher-Tropsch syngas to HC oil
Third generation Biofuels:	Energy crops for bio-alcohol Algal Hydrogen Algal Oil/Biodiesel
Fourth generation Biofuels :	GMO carbon-negative Energy crops

Evolution of Biofuels (3).

Still struggling with technologies !!

First generation Biofuels :	Corn and sugar to ethanol Chemical transesterification of veg oils
Second Generation Biofuels :	Lignocellulose to ethanol Enzymatic bioconversion of Vegetable oil Fisher-Tropsch syngas to HC oil
Third generation Biofuels:	Energy crops for bio-alcohol Algal Hydrogen Algal Oil/Biodiesel
Fourth generation Biofuels :	GMO carbon-negative Energy crops.

Evolution of Biofuels (4).

First generation Biofuels :	Corn and sugar to ethanol Chemical transesterification of veg oils
Second Generation Biofuels :	Lignocellulose to ethanol Enzymatic bioconversion of Vegetable oil Fisher-Tropsch syngas to HC oil
Third generation Biofuels:	Energy crops for bio-alcohol Algal Hydrogen Algal Oil/Biodiesel
Fourth generation Biofuels :	GMO carbon-negative Energy crops

Future : Distant or near !!

Liquid Fuel Scenario.

- Significant Energy from Petroleum feedstock
  - World Petroleum consumption

    85 million barrels·day^{-1}

    13.5 million tons·day^{-1}

    4000 million ton·day^{-1}

  - 70% goes into transportation : 3000 million tons·year^{-1}.

- World grain production : 2000 million tons·year^{-1}
  - Agricultural biomass production : 10,000 million tons·year^{-1}
  - Potential bioethanol production : 2500 million tons·year^{-1} [at 0.25 ton·(ton biomass)$^{-1}$]

Transport Biofuels – 1st and 2nd Generation.

Fuel	Feedstock	Regions where currently produced	GHG reduction v. petroleum	Production cost	Biofuels yield per hectare	Land types
1st generation biofuels, commercially available						
Ethanol	**grains (wheat, maize)**	**US, Europe, China**	**low-moderate**	**moderate**	**moderate**	**cropland**
Biodiesel (SVO, FAME)	**oil seeds (rape, soy, sunflower)**	**US, Europe**	**low-moderate**	**moderate**	**low**	**cropland**
1st generation biofuels (commercially available mainly in developing countries)						
Ethanol	**sugar cane**	**Brazil, India, Thailand**	**high**	**low-moderate**	**high**	**croplands**
Biodiesel/SVO	**palm oil**	**Southeast Asia**	**moderate**	**low-moderate**	**moderate-high**	**coastal lands**
Biogas (CNG)	**wastes, crops**	**Europe, India**	**high**	**low-moderate**	**high**	**all land**
2nd generation biofuels (not yet commercially available)						
Ethanol	**cellulose, residues**	**none**	**high**	**moderate-high***	**high**	**croplands, marginal lands**
Biodiesel (BTL)	**cellulose residues**	**none**	**high**	**moderate-high***	**high**	**croplands, marginal lands**
other						
Biodiesel/SVO	**jatropha**	**South Asia, Africa**	**high**	**moderate-high****	**low-moderate**	**degraded lands**
Biogas (SNG, GtL)	**biomass, residues**	**all**	**high**	**moderate**	**high**	**all land**

First Generation Biofuels.

Vegetable oils;
e.g. rapeseed oil;
sunflower oil,
palm oil

[esterification+]

Production Processes

[fermentation+]

Sugar:
Sugar beet; sugar cane;
Starch: corn

Biodiesel → **Blended with or replaces diesel**

Yield: 1,300 l·hectare^{-1} per year diesel equivalent
Net CO_2: -(40-60)%

Bio-ethanol → **Blended with or replaces petrol**

Yield: 2,500 l·hectare^{-1} per year diesel equivalent
Net CO_2: -(30-80)%

Biomass to liquid (BtL) and cellulosic ethanol (processes under development)

Biomass, e.g. wood, straw

[gasification and Fischer-Tropsch synthesis +]
Production processes

Biodiesel

Yield: > 3 times that of 1st generation
Net CO_2: > -90%

[enzymes+ fermentation+]

Bio-ethanol

Yield: 1.7 to 2 times that of 1st generation
Net CO_2: -(80-90)%

Potential Advantages of 2nd Generation Biofuels.

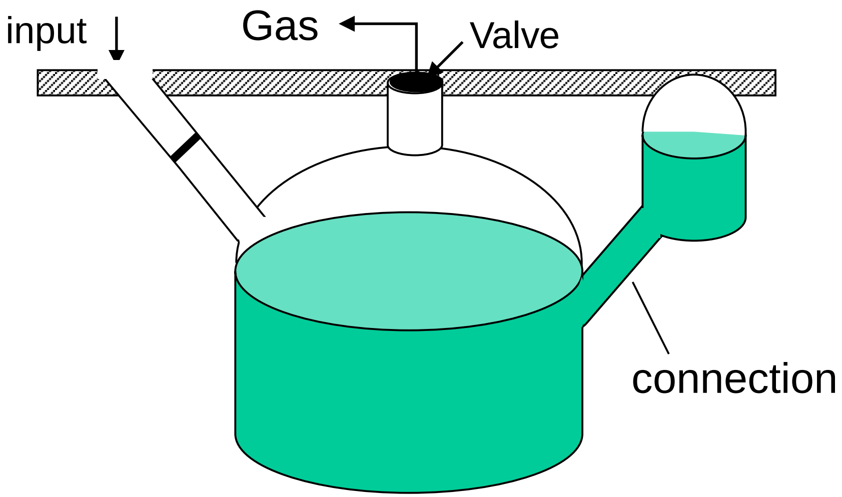
- Potential CO_2 reduction of >90% (compared to conventional diesel measured over fuel cycle)
- More efficient use of land, as 2nd generation feedstock can be produced more intensively (higher yields)
- Lower quality of land can be used for 2nd generation feedstock – so more fuel can be produced
- Can be used in all blends in existing engines without need for modification
- Improved performance compared to 1st generation and conventional diesel, e.g. lower freezing point, higher energy content.

Gas Biofuels (Biogas).

1. Anaerobic digestion of organic wastes (also landfills)
   - Fragmentation induced by Microorganisms (mainly *methanogens*) of solid wastes in an anaerobic atmosphere
2. Produce a methane rich gas
   - Typically 60% CH_4 and 40% CO_2
   - Energy content 20-25 $MJ \cdot kg^{-1}$
   - (natural gas = 36 $MJ \cdot kg^{-1}$)
3. Municipal wastes treatment plants (e.g. Montello S.p.A. plant)
   - Plant with 100 MGD input (12 MW)
4. CAFOs
   - Pigs - 135,000 animals (8 MW)
   - Cows - 318,000 animals (30 MW)

Biogas – Sources and Production.

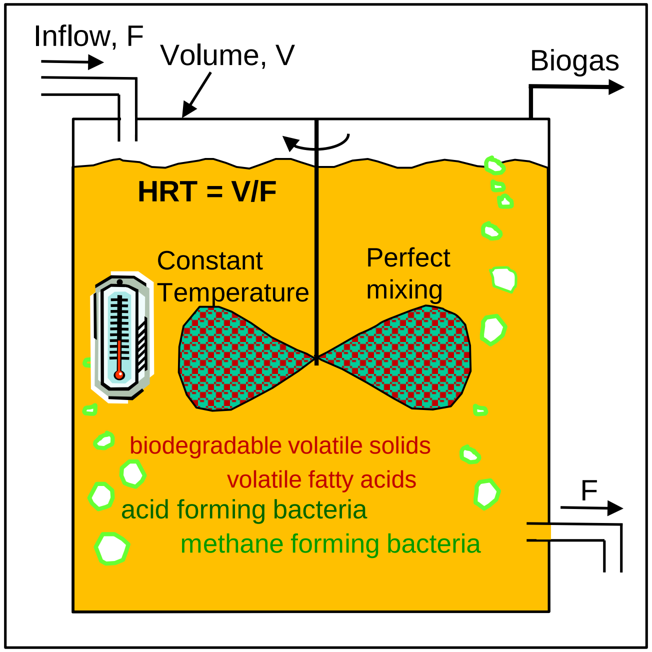
Substrate	*Biogas ($m^3 \cdot m^{-3} \cdot day^{-1}$)*	*Retention Time (h)*
Primary wastes	**0.9-3.0**	**4-22**
Secondary wastes	**0.7-2.4**	**5-22**
Municipal wastes	**2.4-3.6**	**19-30**
Non-recyclable municipal wastes	**0.3-0.6**	**20**
Primary and secondary wastes	**1**	**10**
Manure	**1**	**10**



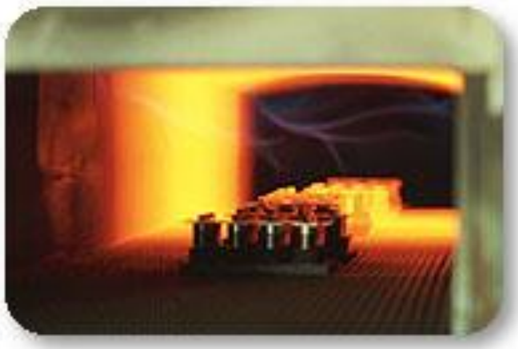
Scheme of a submerged small dimension plant for biogas production at low pressure.

Anaerobic Digestion Technology: Process Components.

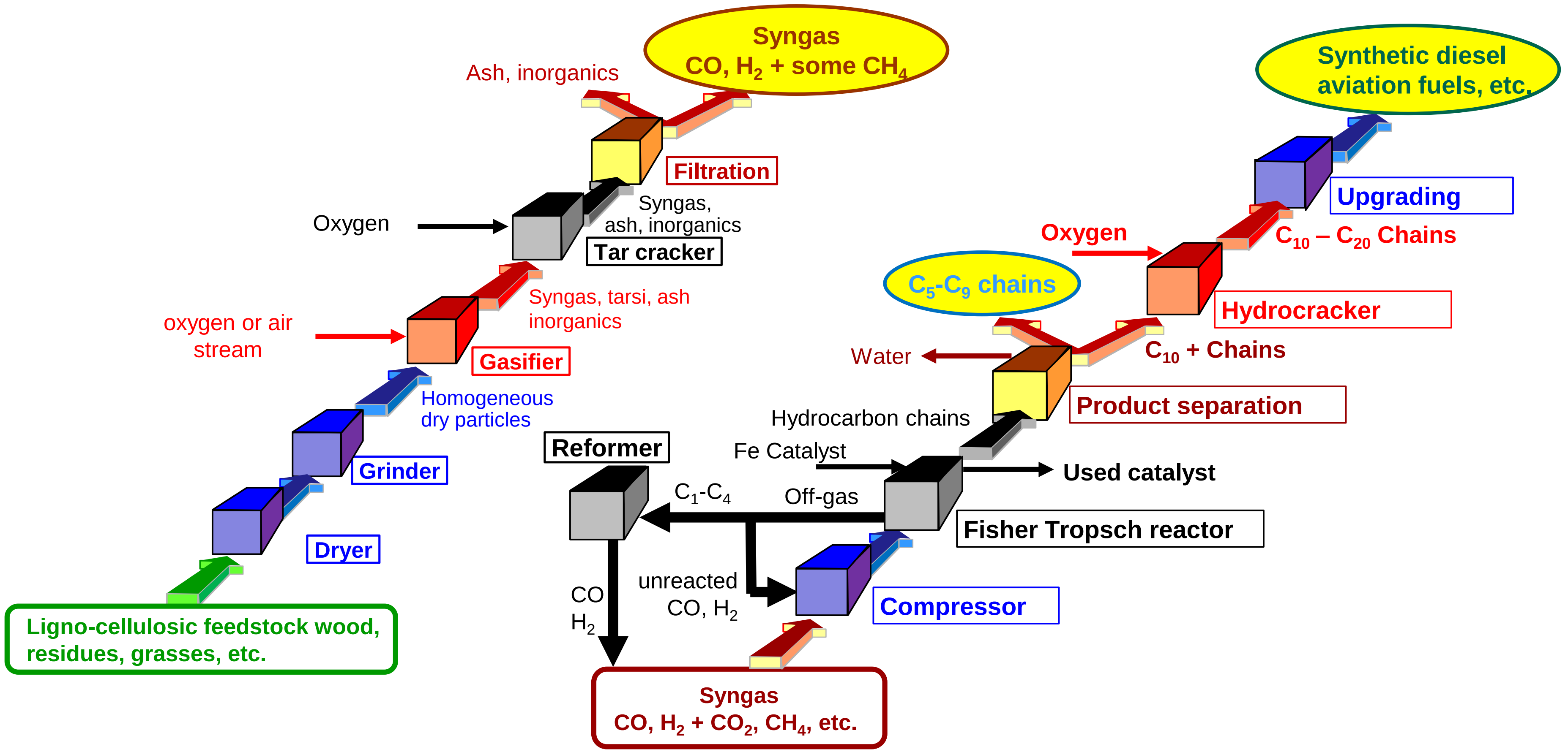
- Pretreatment (contaminant removal)
- Nutrient balancing (Ni, Fe, Co, Mo, N, P, K, S)
- Water / alkalinity re-use (effluent recycle, strong waste)
- Biomass recycle (high rate)
- Contacting/mixing (digester tank)
- Heating (digester tank)
- Biogas flare
- Fuel management (purification/compression)
- Biogas end use (heat, CHP, transport fuel, fuel cell)
- Fertilizer recovery
- Residue management



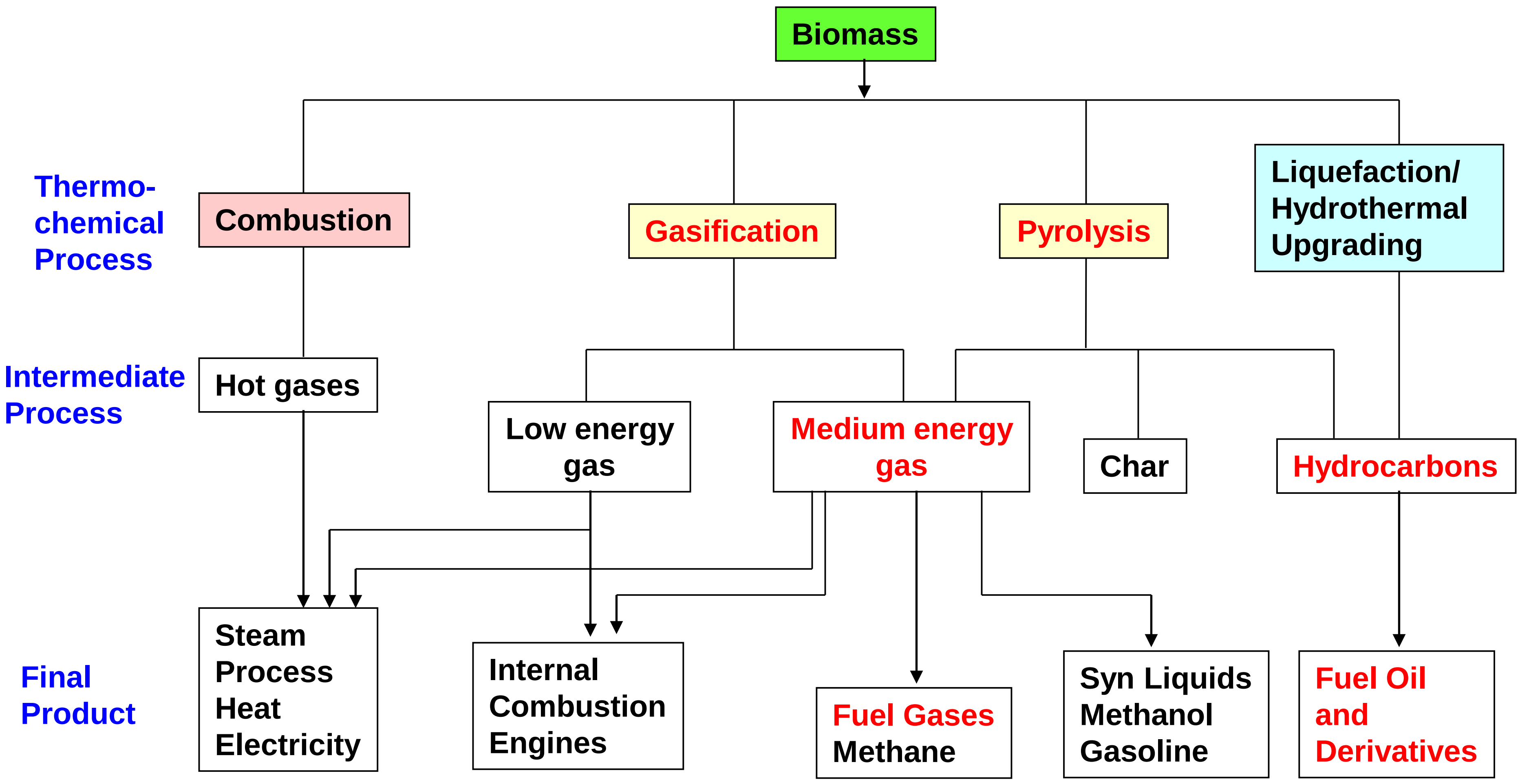
Biofuel Production
Thermal Methods



“Thermo-chemical Conversion“.

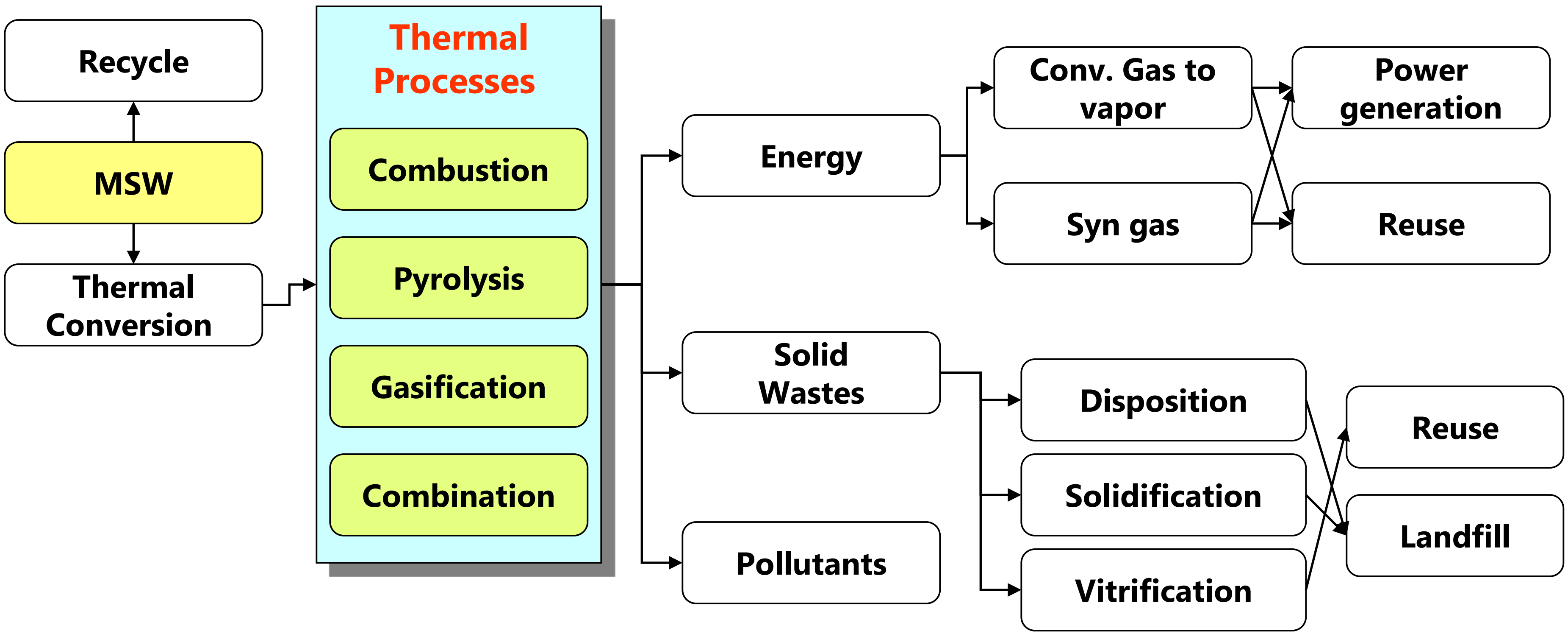


Biomass Thermal Conversions.

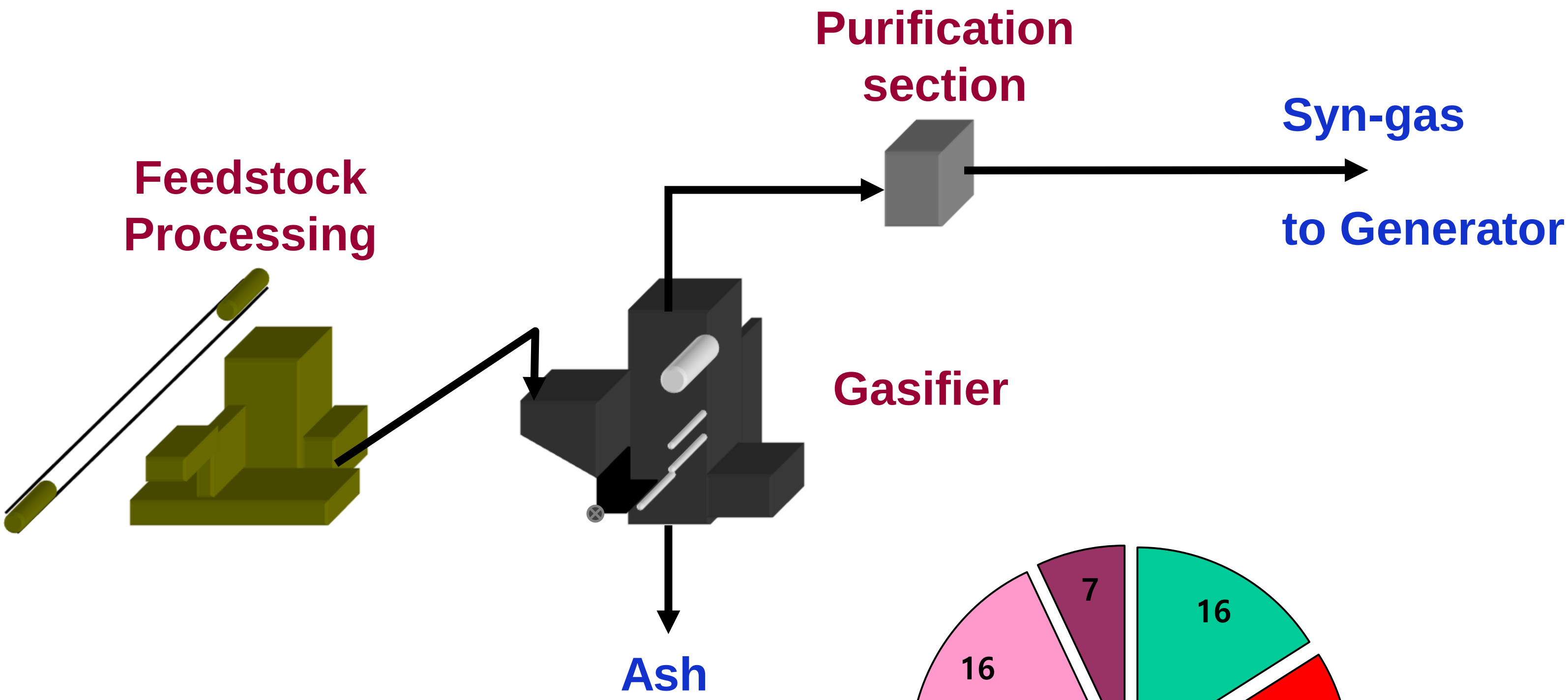


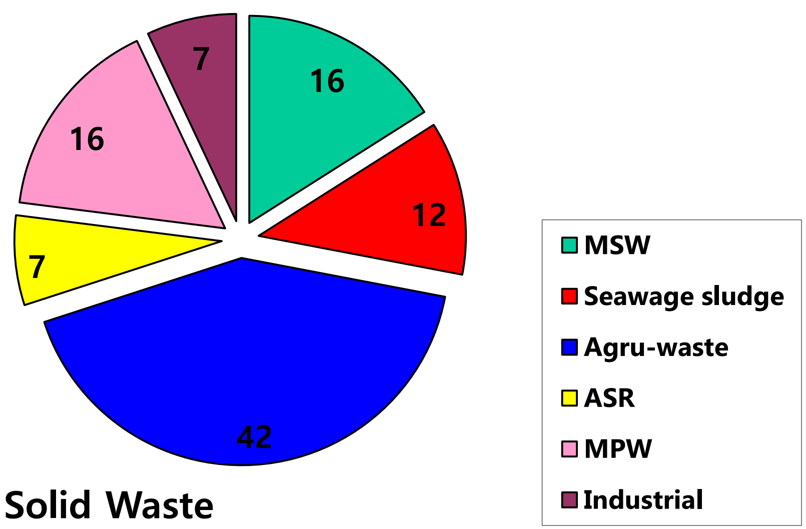
P. McKendry, Bioresource Technology, 83, (2002), 47-54

Thermal Treatment of Municipal Solid Wastes (MSW).



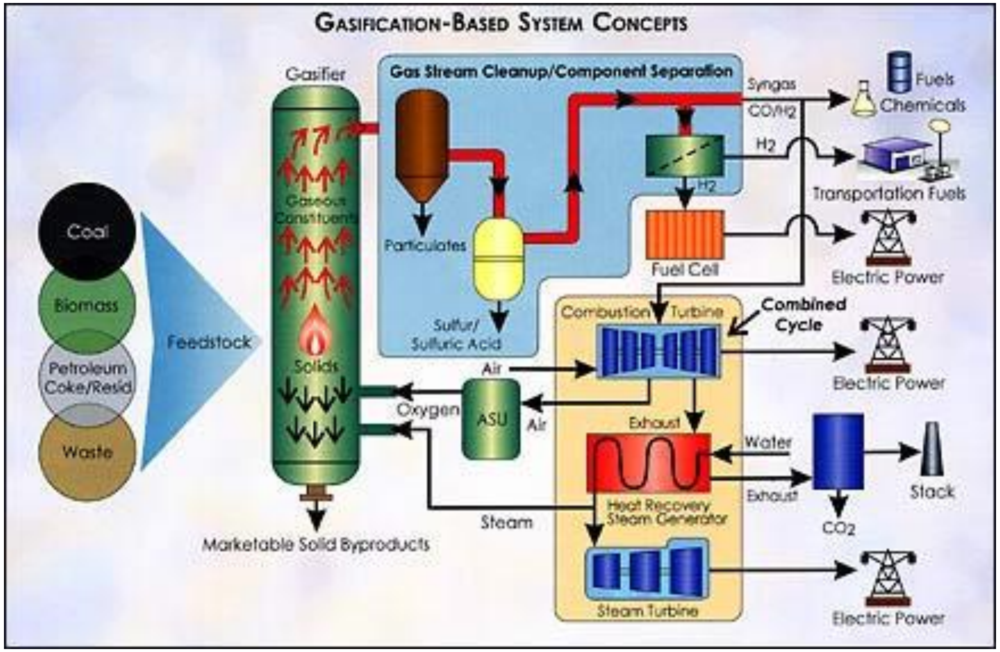
Gasification Technologies.

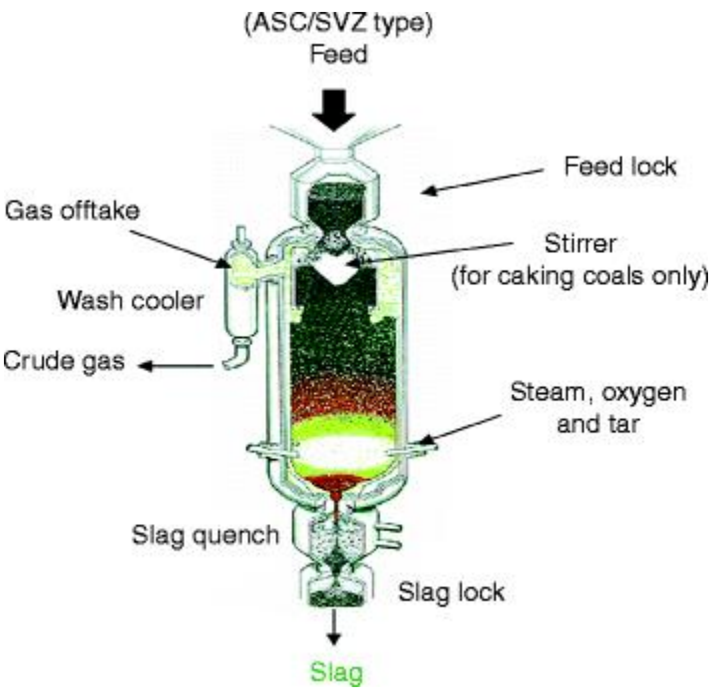




MSW : Municipal Solid Waste
ASR : Auto Shredder Residues

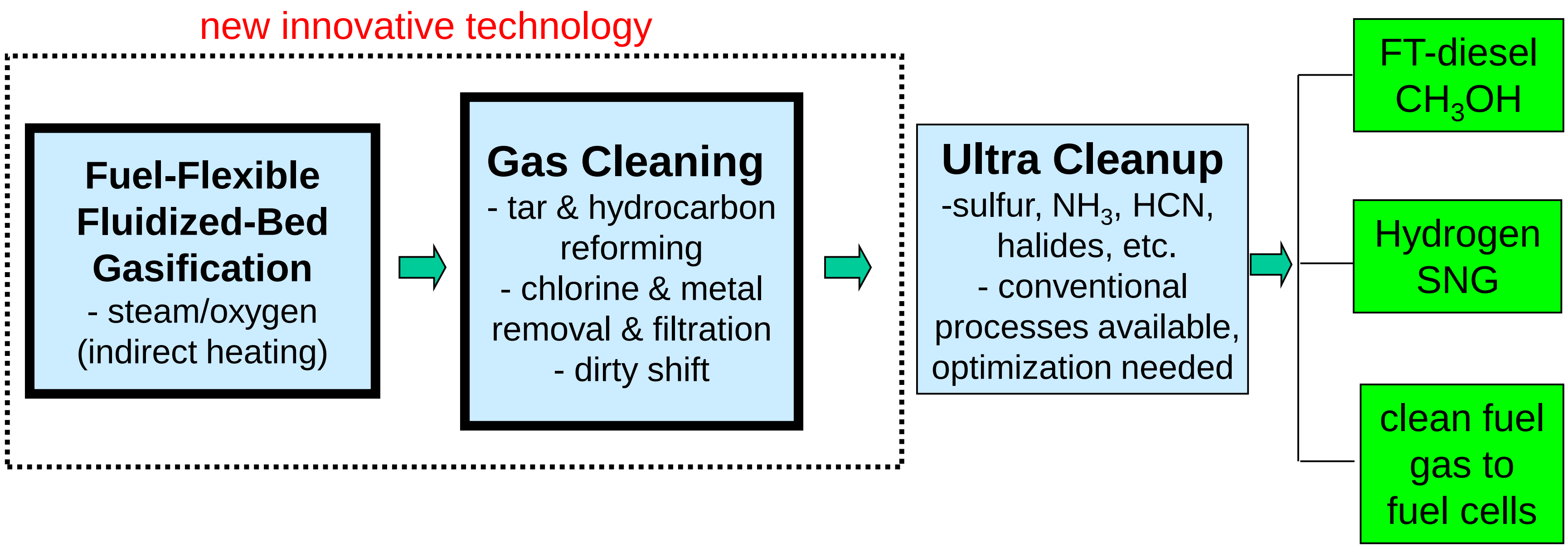
Gasification Bases Systems.





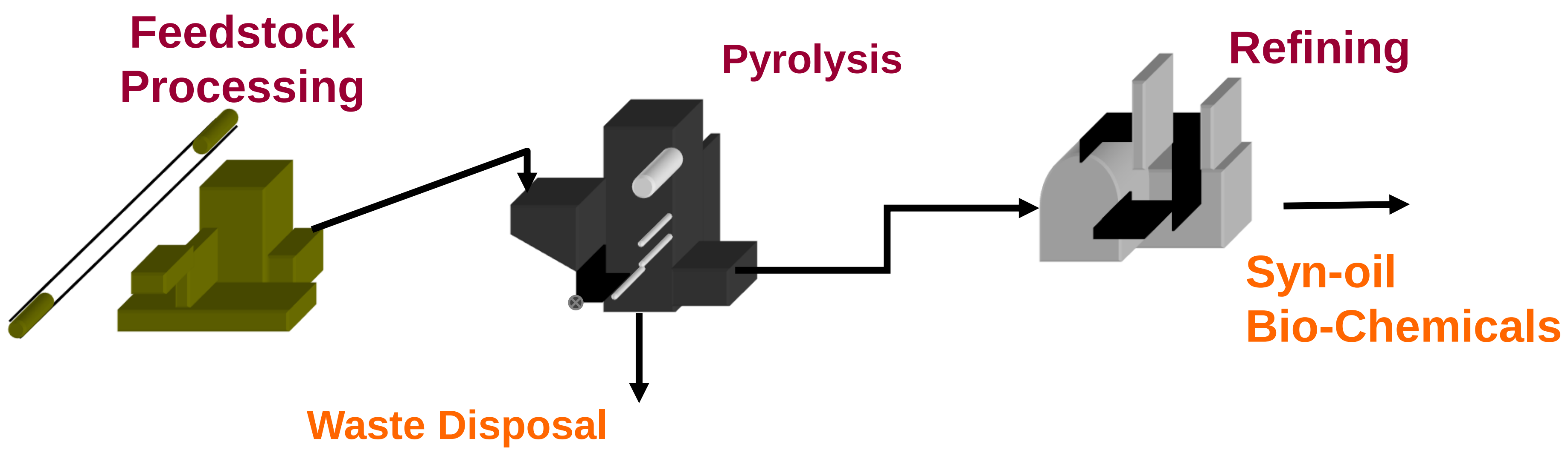
Gasification may be one of the best ways to produce clean-burning hydrogen for tomorrow's automobiles and power-generating fuel cells. Hydrogen and other coal gases can also be used to fuel power generating turbines or as the chemical "building blocks" for a wide range of commercial products.

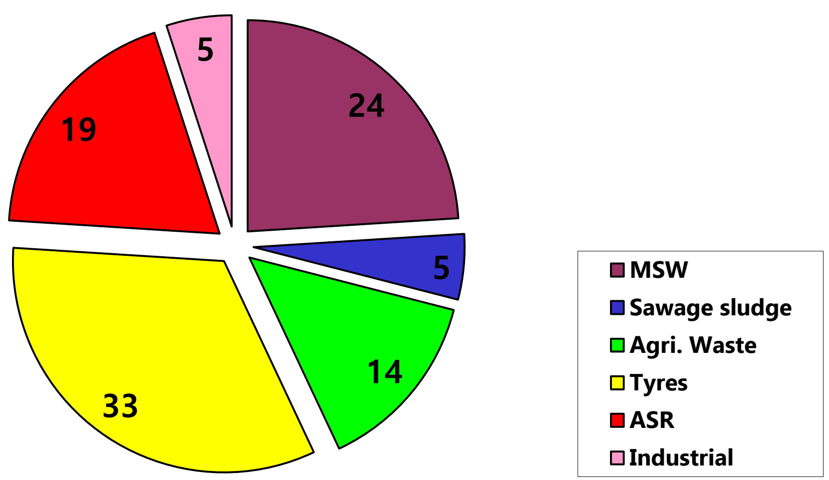
Biomass Gasification Process Development.



Gas cleaning targets:
- complete tar and benzene decomposition
- over 95 % methane reforming
- H_2/CO ratio suitable to FT-synthesis
- reliable operation
- minimum overall gas cleanup train costs.

Pyrolysis.





MSW : Municipal Solid Waste
ASR : Auto Shredder Residues

Flash Pyrolysis.

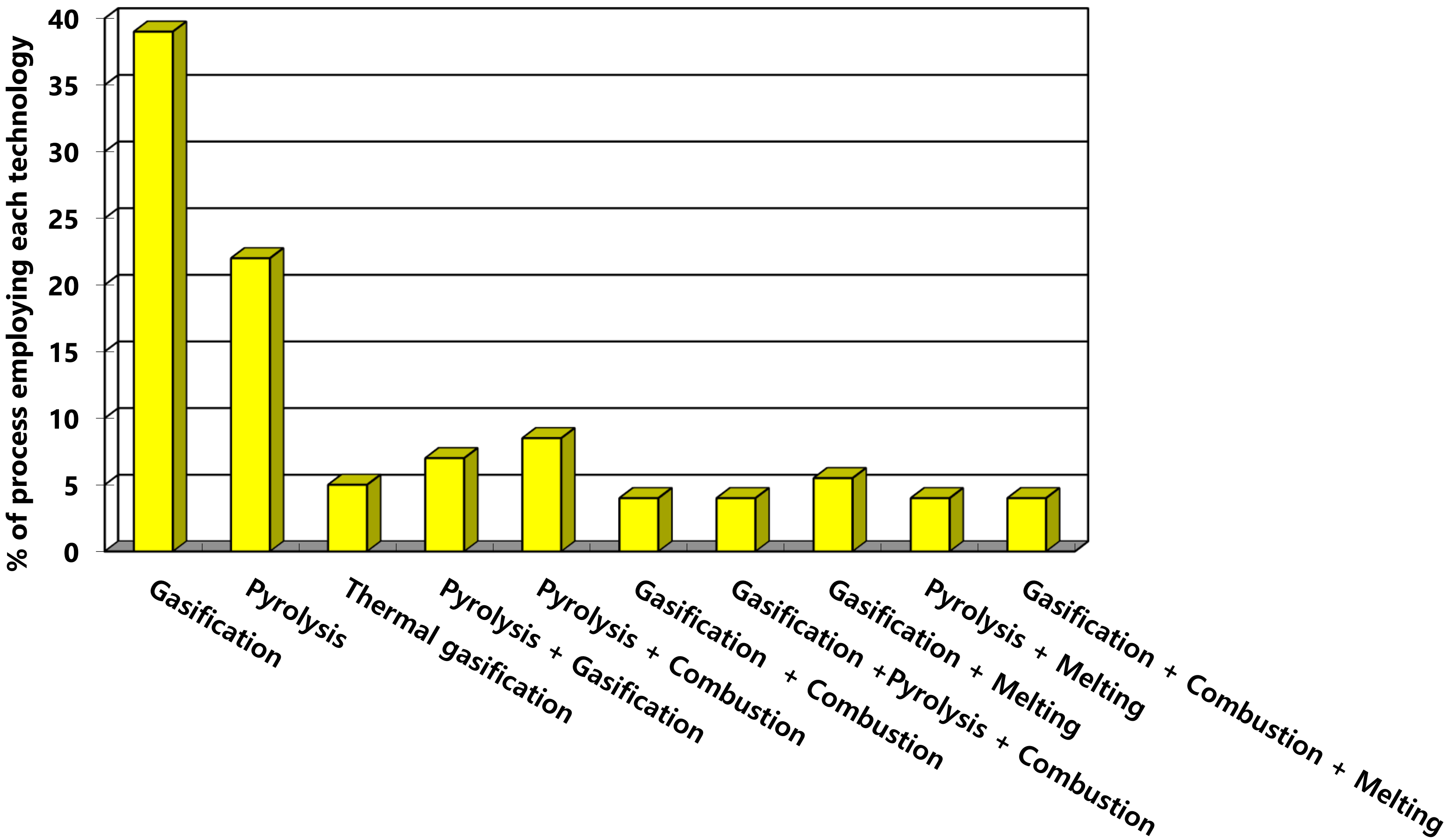
Flash pyrolysis.

- Also known as short residence time pyrolysis.
- Involves rapid heating rates and very short contact time for biomass.
- Results in large amounts of liquid product which are quenched out of the system to prevent them going on to react further.
  - Temperature below that required to gasify organic products.
  - Heating to higher temperature (above 650 °C) results in maximisation of gaseous product.
- Liquid products are classed as highly oxygenated, acidic and unstable over time.

Parameter	Conventional Pyrolysis	Flash Pyrolysis
Temperature (°C)	400 - 900	400 - 900
Residence time	Hours	Seconds
Heating rate	Low	High
Product composition (wt %)		
Gas	17	10
Charcoal	35	10
Pyrolytic liquid	25	65
Water	22	12

Property	No. 6 fuel oil	Liquid fuel from RDF
Heating Value ($MJ \cdot kg^{-1}$)	42.3	24.6
Density ($kg \cdot L^{-1}$)	0.98	1.3
Pour point (°C)	15-30	32
Flash point (°C)	65	56
Viscosity at 87.8 °C (SU's)	90-250	1150
Pumping temperature (°C)	46	71
Atomisation temperature (°C)	104	116
Analysis dry wt %		
C	85.7	57.5
H	10.5	7.6
O		33.4
S	0.5-3.5	0.1-0.3
Cl		0.3
N	2.0	0.9
Ash	0.5	0.2-0.4

Type of Technology Combination.

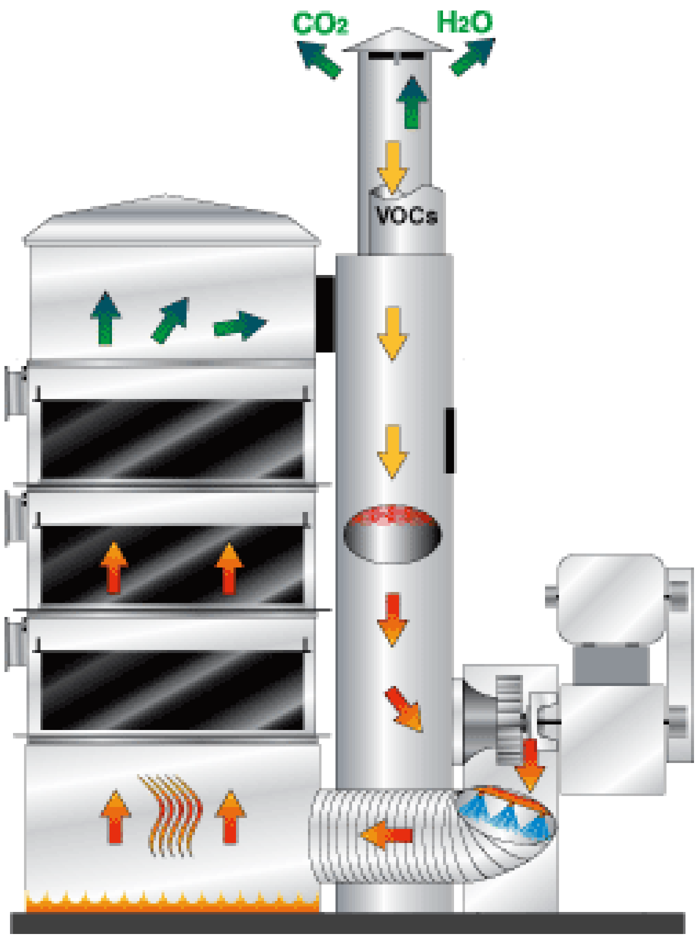


Combustion Emissions Control.

The presence in the combustion wasted gas of pollutants imposes control technologies to cut down:

- NO_X
- SO_2 /metals
- VOC (volatile organic compounds)

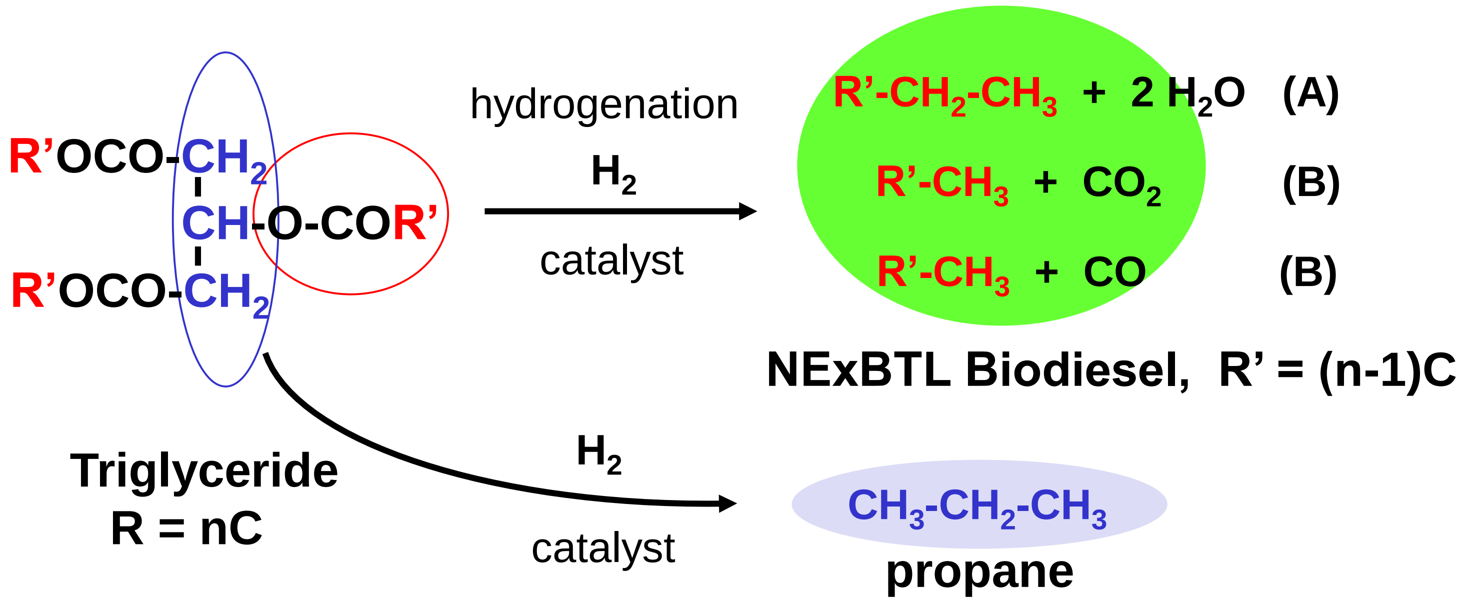
Commonly are used catalytic post combustors and filters able to convert VOC into CO_2 and trap physically or chemically other compounds.



NExBTL Process by Hydrogenation.

Feedstock

Reactions and Products



NExBTL is a stable and pure hydrocarbon

Biofuels Production

Non-thermal Methods

Biodiesel

History of Liquid Biofuels: Biodiesel.

Dr. Rudolph Diesel designed a particular engine in 1894 to run on peanut oil or other fuels of vegetal origin.

Diesel presented its engine at the Word Exposition in 1900.

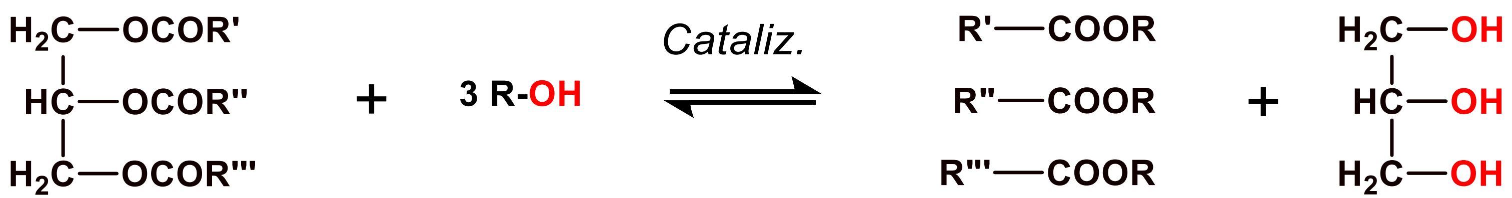
Diesel died mysteriously in 1913. After its death, the Diesel engine was adapted for the use of a by-product of the refining process of gasoline, for this named diesel fuel.

The use of vegetable oils as engine fuels may seem insignificant today but the such oils may become, in the course of time, as important as petroleum and the coal tar products of the present time.

-Rudolph Diesel, 1912

Biodiesel.

- The use of vegetable oils fuel is old (Cyprus metal production 2000 BC), but only in 1900 R. Diesel proposed peanuts oil as fuel for its diesel engine.
- The nowadays attention for biodiesel is limited to fatty acid lower alkyl esters from vegetable oils or, to a minor extent, to animal fats.
- In particular, the more investigated liquid fuel is **FAME** (**fatty acid methyl esters)** made by catalyzed trans-esterification of oils with methanol (R = CH_3).

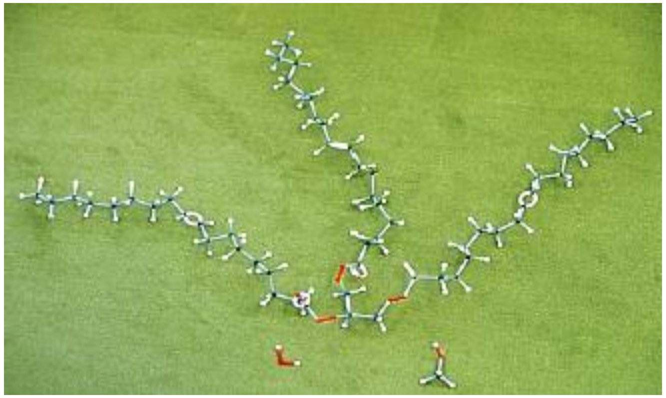


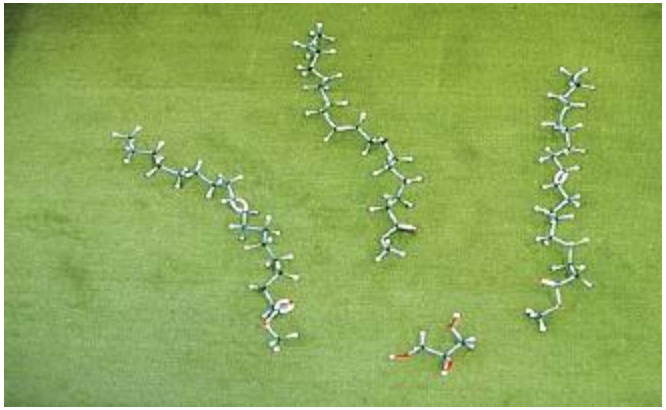
Gliceride | Alcol | Esteri | Glicerolo

60 Kg **Oil**	**6.78 Kg** **Ethyl Alcohol**	**0.60 Kg** **NaOH**	**58 Kg** **Biodiesel**	**6.5 Kg** **Glycerol**

Oil or Fat to FAME.

- Triacylglycerol +
  - methanol (from biomass?)
  - + catalyst gives
  - ester + glycerol
- the hooked tripod molecule
  - is changed to
    slippery ester chains, thus
- viscosity is reduced from
  - 60 to 4 cSt (like diesel fuel)





FAME = Fatty acid methyl esters

Production of Raw Oil.

- The production of crude oil from the plant seeds can be performed by two completely different procedures. In larger oil processing plants these are usually used in combination. The steps are:
  - **Pre-pressing**: The oil is pressed mechanically. Nowadays screw presses (expellers) are used. Depending on the size of the press and preheating of the seed, the oil can be pressed out down to a residual oil content of 5% in the feed-stuffs. Pressing without heating allows a very simple oil production from high oil-content oil seeds (e.g. sunflower, rapeseed). However for a better oil yield, preheating of the seed is a necessary pretreatment.
  - **Extraction**: Here the oil will be removed from the seed nearly 100% by the action of a solvent. Only extraction is used for oil production from low oil-content oil seeds (e.g. soybean). Extraction is much more energy intensive than pressing, it is therefore used in combination with pre-pressing to remove only the residual oil from the expeller feed-stuff.
  - **Byproducts of raw oil production**: Expeller and extraction meals are very valuable protein feedstuffs for animal feeding. They contribute to cover the processing costs.

Further Processing.

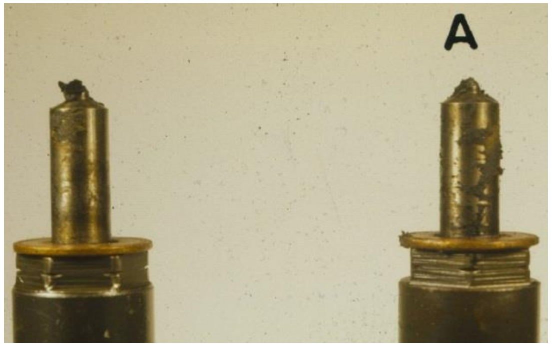
Refining of crude oil: Fuel utilization of vegetable oils requires a refining of the raw oil. After some industrial treatments, the so-called "semi-refined-oil" is available. Further processing steps (like deodorization and bleaching) common in oil refining are not necessary for fuel application.

Transesterification: As early as 1938 a need for chemical modification of vegetable oils was indicated by Walton (1938), who noted that ... "to get the utmost value from vegetable oils as fuels it is necessary to split off the glycerides which are likely to cause an excess of carbon in comparison". During World War II Chinese scientists developed a batch-cracking procedure for refining "veg-gasoline" and 'beg-diesel" from plant oil feedstock, using Tung and rapeseed oils in particular (Chang and Wang, 1947). Some military equipment was kept moving this way.

Problems of Vegetable Oil Application in Combustion Engines.

- The major problem when using pure plant oils in direct-injected diesel engines is coke **deposition at the injector** and at the combustion chamber, piston, valves, ... that impedes the engine running in short- or long-term use. The amount of time before power loss and engine deterioration becomes obvious varies with engine time, loading and condition, and the type of vegetable oil. It may be as brief as 10 hours for linseed oil or more than 100 hours for sunflower oil in direct injected engines.

- Problems with buildup of deposits around injector tips are caused by much higher viscosity and carbon content of vegetable oils in comparison with diesel fuel or oil esters.



Issues in the Use of Biodiesel.

- **Engine oil dilution**: the greatest problem associated to the fact that the methyl ester passes beyond the piston rings into the engine oil. Problems can then arise with inadequate lubrication and gumming of the top piston surface, piston ring and inlet valve.
- **Material compatibility**: Paints can be dissolved by biodiesel, and asphalt is made soft. Rubber components, such as pipes and seals, may also be affected. On the contrary there is no indication of corrosion of metallic components.
- **Winter performance**: supply of bio-diesel from the tank (e.g. in the fuel filter) and cold starting are problems. Increase of methanol content can be used but this is impractical for safety reasons (the flash point drops below 55°C). Additives, like flow enhancers, can make the operation safe at temperatures down to -10°C.

Feedstock for Biodiesel Production.

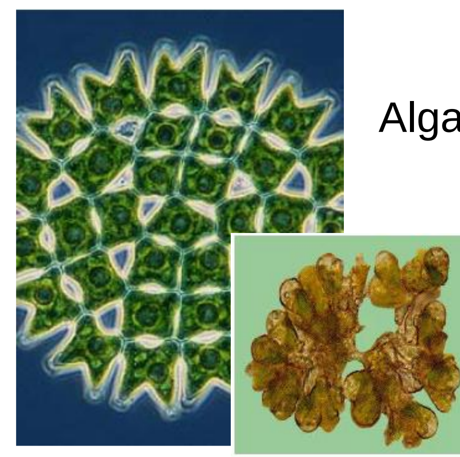
Jathropa: 2-6,000 liters·ha^{-1}·year^{-1}

Rapeseed: 1000 liters·ha^{-1}·year^{-1}

Soy: 400 liters·ha^{-1}·year^{-1}

Palm oil: 5,900 liters·ha^{-1}·year^{-1}

Castor: 1.200 liters·ha^{-1}·year^{-1}



Algae

Botryococcus braunii: 5000 liters·ha^{-1}·year^{-1}

Feedstock for Biodiesel Production.

Safflower: 2,500 liters·ha^{-1}·year^{-1}

Sunflower: 1,500 liters·ha^{-1}·year^{-1}

Flax: 1,000 liters·ha^{-1}·year^{-1}

Macaúba: 4,000 liters·ha^{-1}·year^{-1}

Yellow mustard: 1500 liters·ha^{-1}·year^{-1}

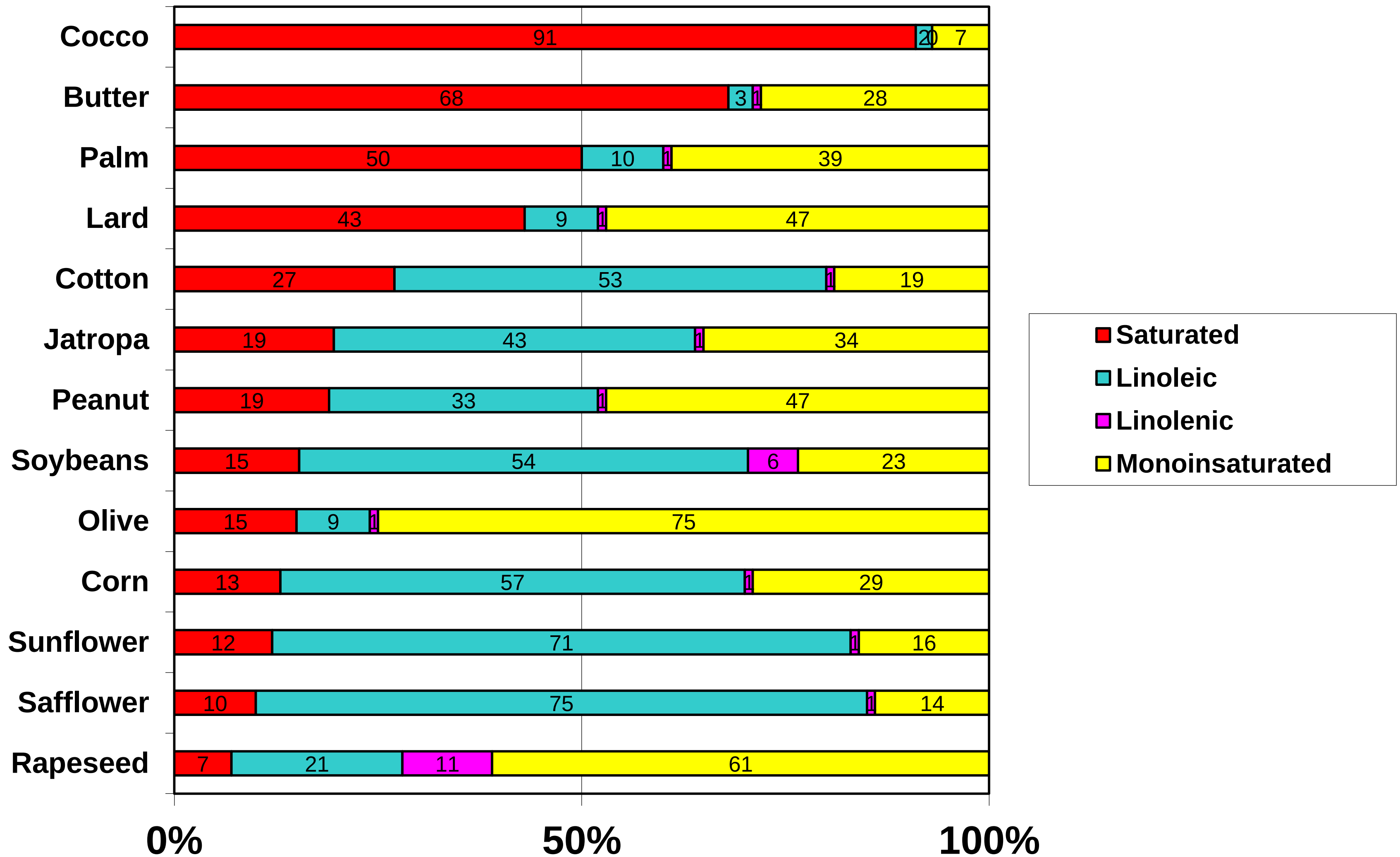
Peanuts: 890 liters·ha^{-1}·year^{-1}

Babaçú: 1,600 liters·ha^{-1}·year^{-1}

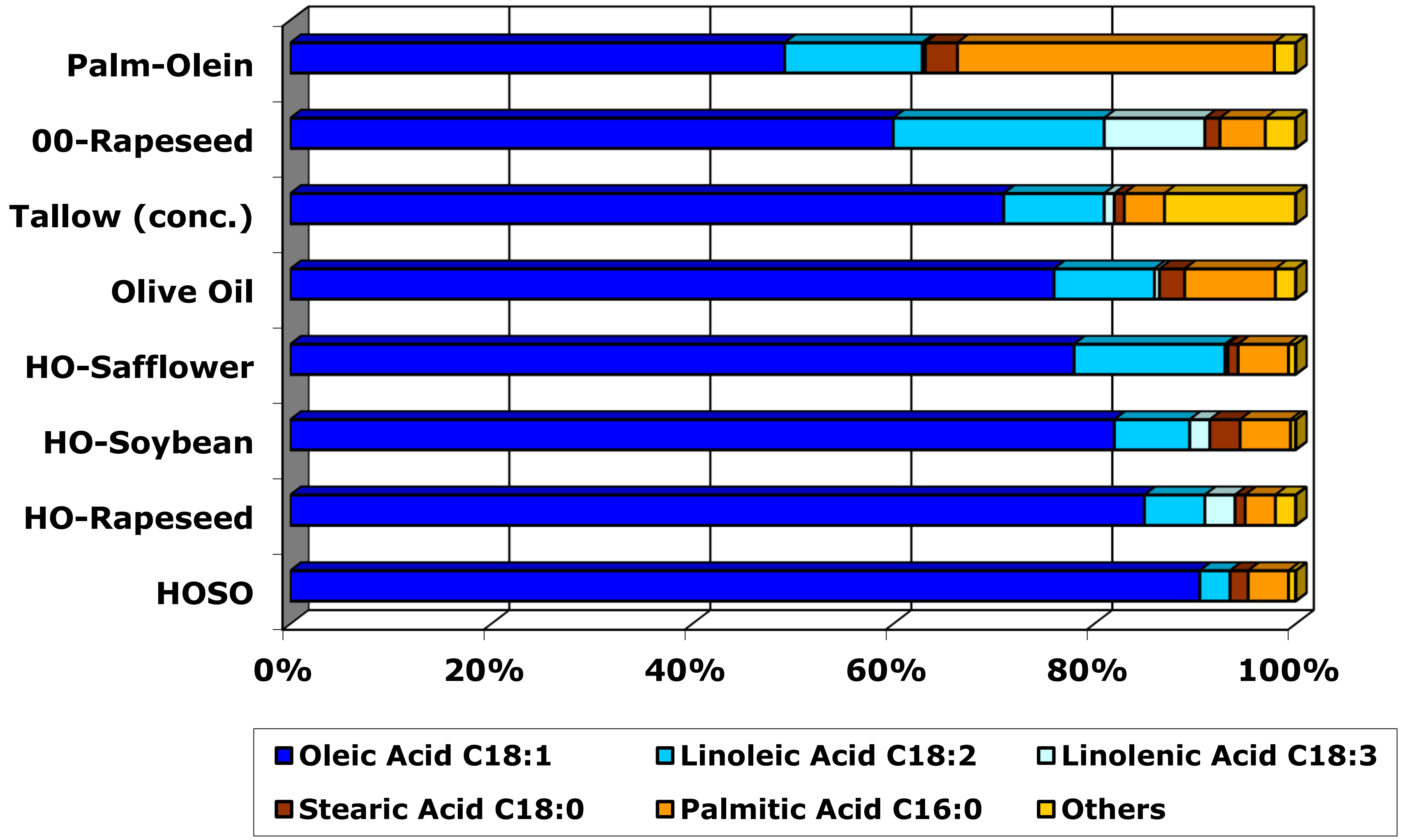
Some Properties of Fatty Acids.

Name (s)	Acronym	Molecular Weight	Melt°C/°F	Boil°C/°F	Cetane Number	Combustion Heat (kcal·mol^{-1})
Caprylic acid	8:0	144.22	16.5/61.7	239.3/462.7	-	-
Capric acid	10:0	172.27	31.5/88.7	270.0/518.0	47.6	1453.07
Lauric acid	12:0	200.32	44.0/111.2	131.0/267.8	-	1763.25
Myristic acid	14:0	228.38	58.0/136.4	250.5/482.9	-	2073.91
Palmitic acid	16:0	256.43	63.0/145.4	350.0/662.0	-	2384.76
Stearic acid	18:0	284.48	71.0/159.8	360.0/680.0	-	2696.12
Oleic acid	18:1	282.47	16.0/60.8	286.0/546.8	-	2657.40
Linoleic acid	18:2	280.45	-5.0/23.0	230.0/446.0	-	-
Linolenic acid	18:3	278.44	-11.0/12.2	232.0/449.6	-	-
Erucic acid	22:1	338.58	33.0/91.4	265.0/509.0	-	-
Methyl caprylate	8:0	158.24	-	193.0/379.4	33.6	1313.00
Methyl caprate	10:0	186.30	-	224.0/435.2	47.7	1625.00
Methyl laurate	12:0	214.35	5.0/41.0	266.0/510.8	61.4	1940.00
Methyl myristate	14:0	242.41	18.5/65.3	295.0/563.0	66.2	2254.00
Methyl palmitate	16:0	270.46	30.5/86.9	418.0/784.4	74.5	2550.00
Methyl stearate	18:0	298.51	39.1/102.4	443.0/829.4	86.9	2859.00
Methyl oleate	18:1	296.49	-20.0/-4.0	218.5/425.3	47.2	2828.00
Methyl linoleate	18:2	294.48	-35.0/-31.0	215.0/419.0	28.5	2794.00
Methyl linolenate	18:3	292.46	-57.0/-70.6	109.0/228.2	20.6	2750.00
Methyl erucate	22:1	352.60	-	222.0/431.6	76.0	3454.00

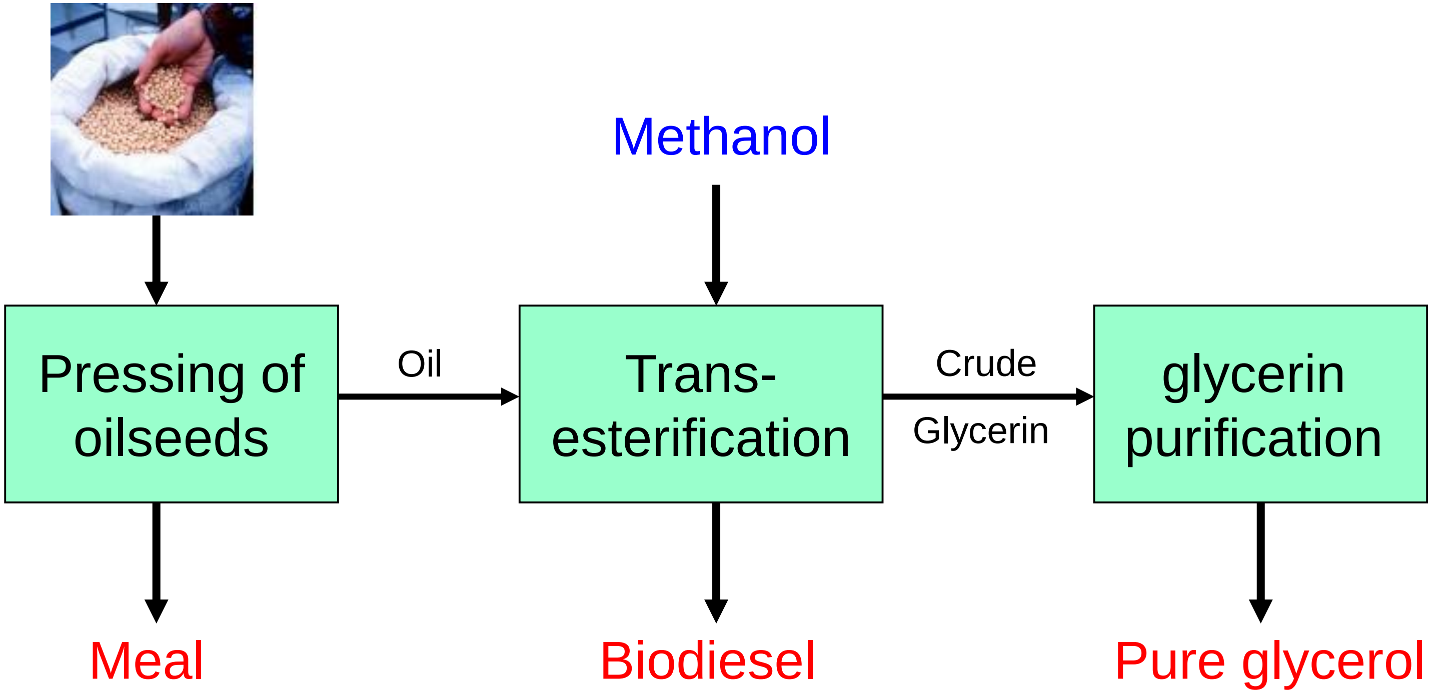
Content of Fatty Acids in Common Oil Seeds.



Fatty Acid Composition.



Biodiesel Chain.

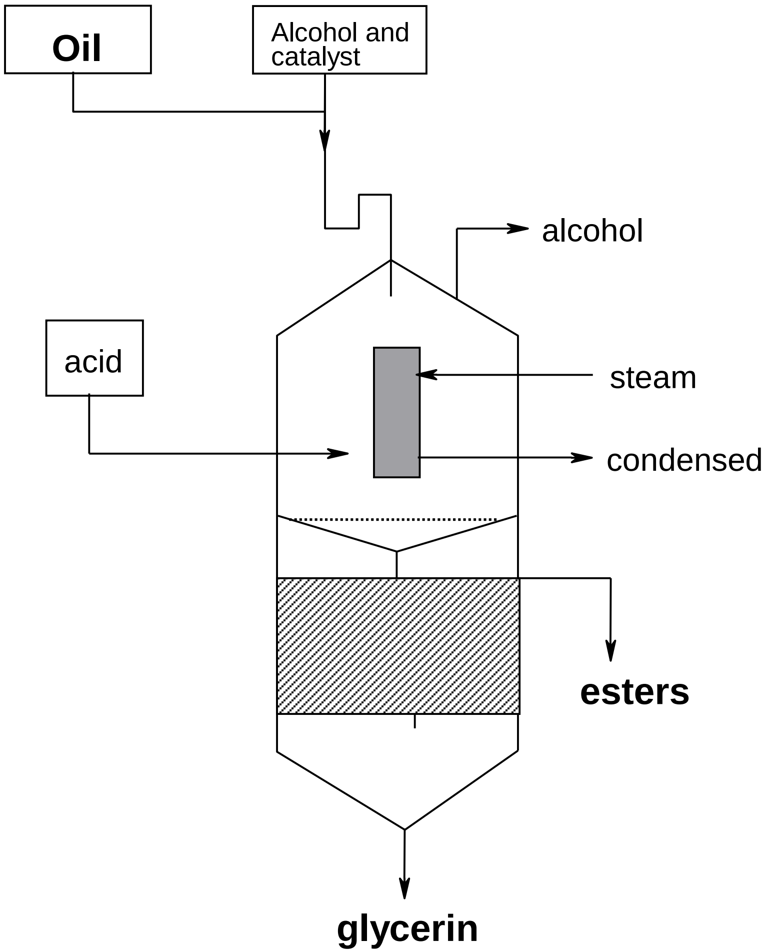


Biodiesel (Synthesis).

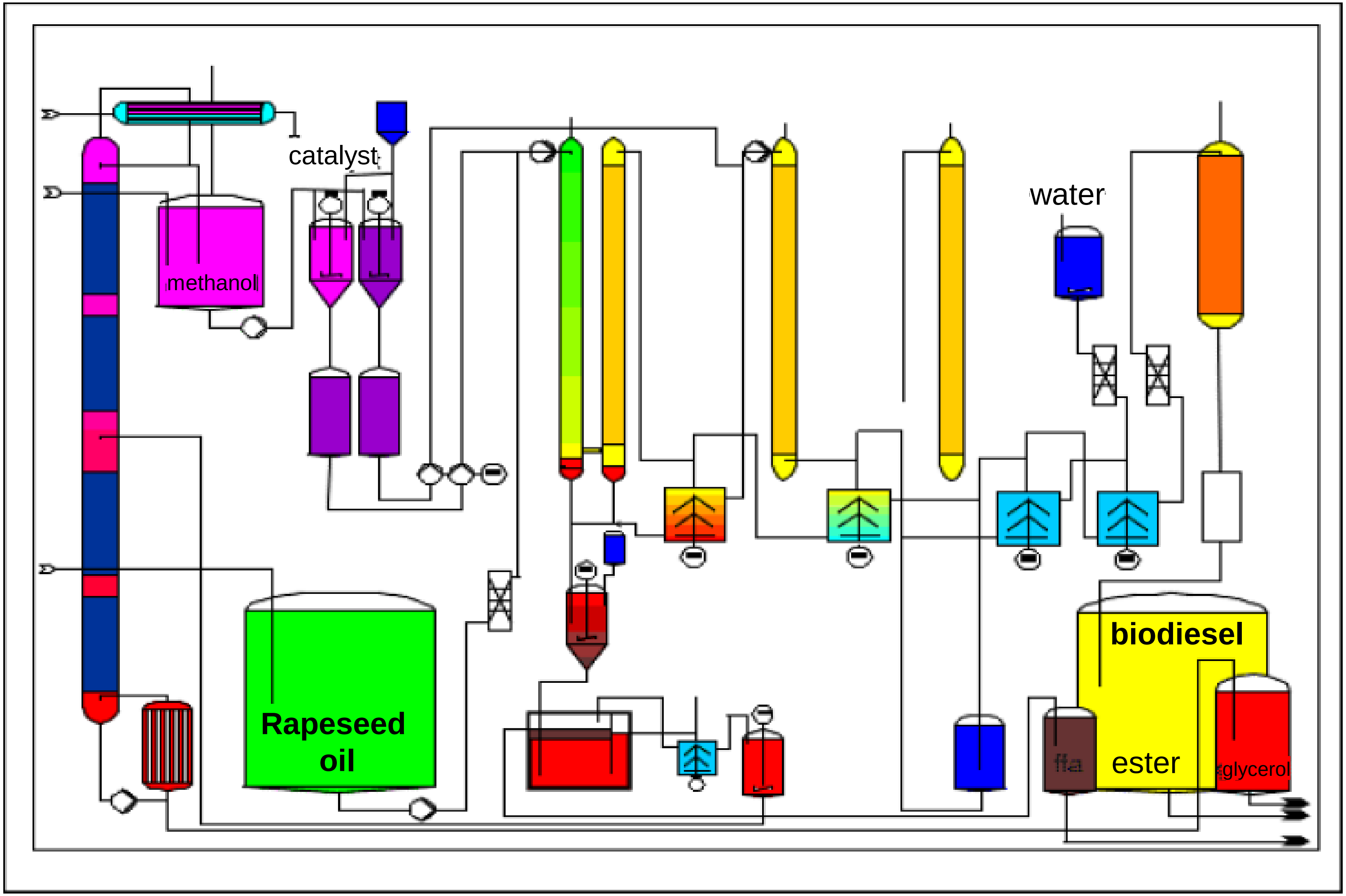
Methanol (CH_3OH) is used as alcohol.

A catalyst is used to speed the process (1 % w/w):

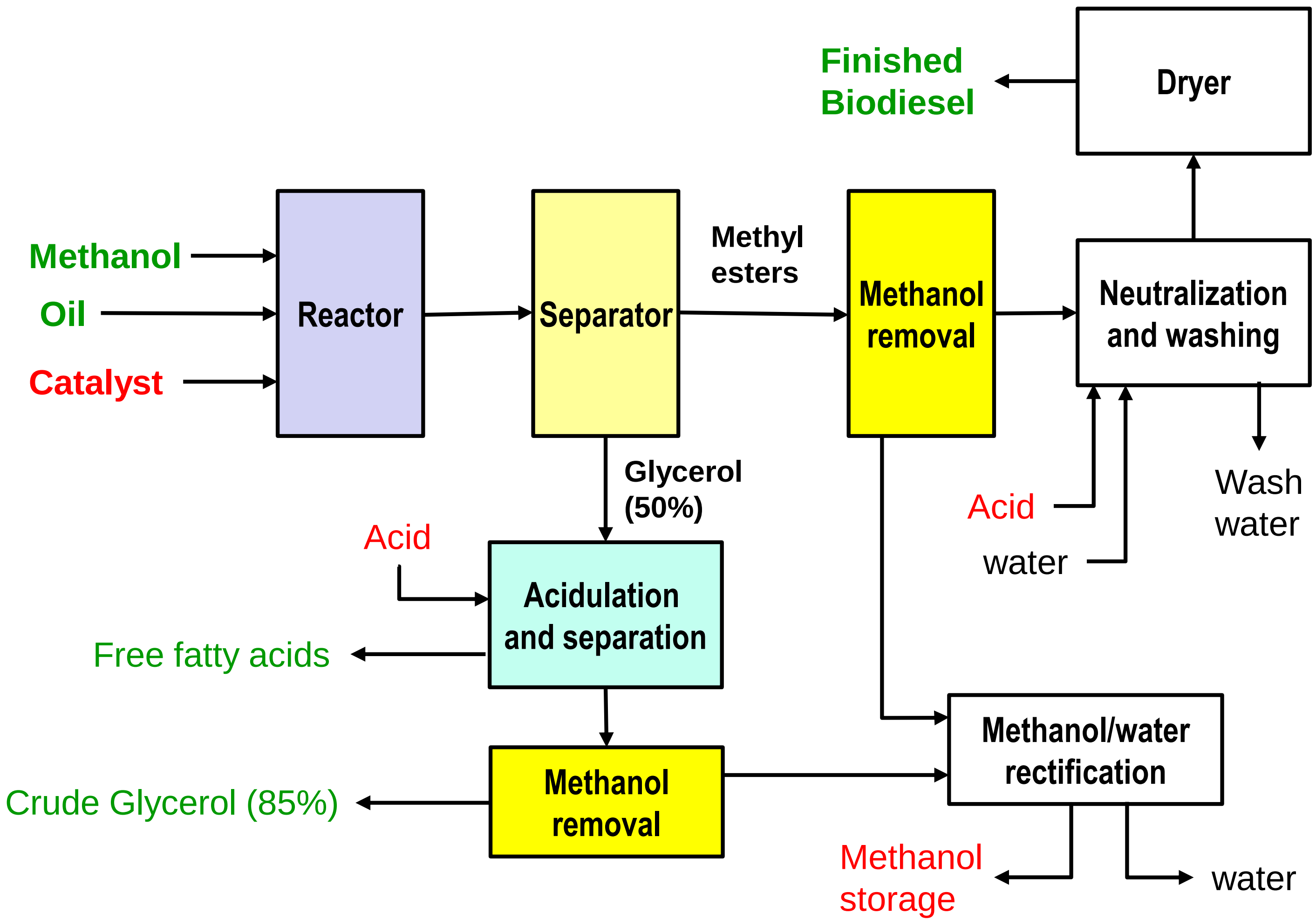
- Commonly a basic catalysis is used (i.e. sodium hydroxide) – because a lower ratio alcohol to glyceride is necessary (6:1). Supported guanidines were used successfully.
- Also acid catalysts can be used but with an higher ratio alcohol/glyceride (30:1) - however, the system tolerate more water and humid substrates.
- Heterogeneous catalysis is quite investigated owing the easy separation and the higher purity reached.
- Also the enzymatic catalysis was proposed – it needs a lower reaction temperature.



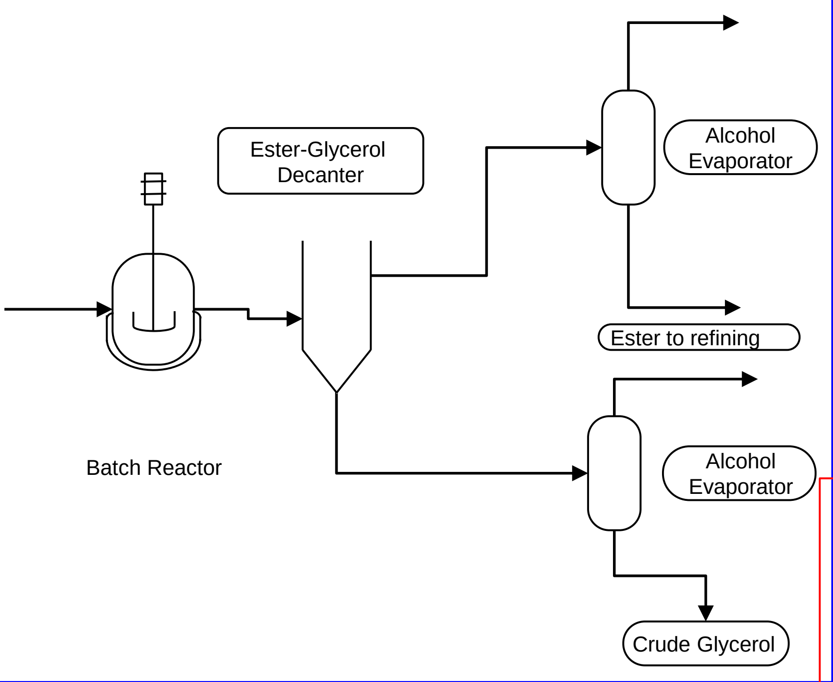
Biodiesel Process -
Transesterification of Biogenic Oils and Fats.



Process Flow Schematic for Biodiesel Production.



Categories of Biodiesel Processes.

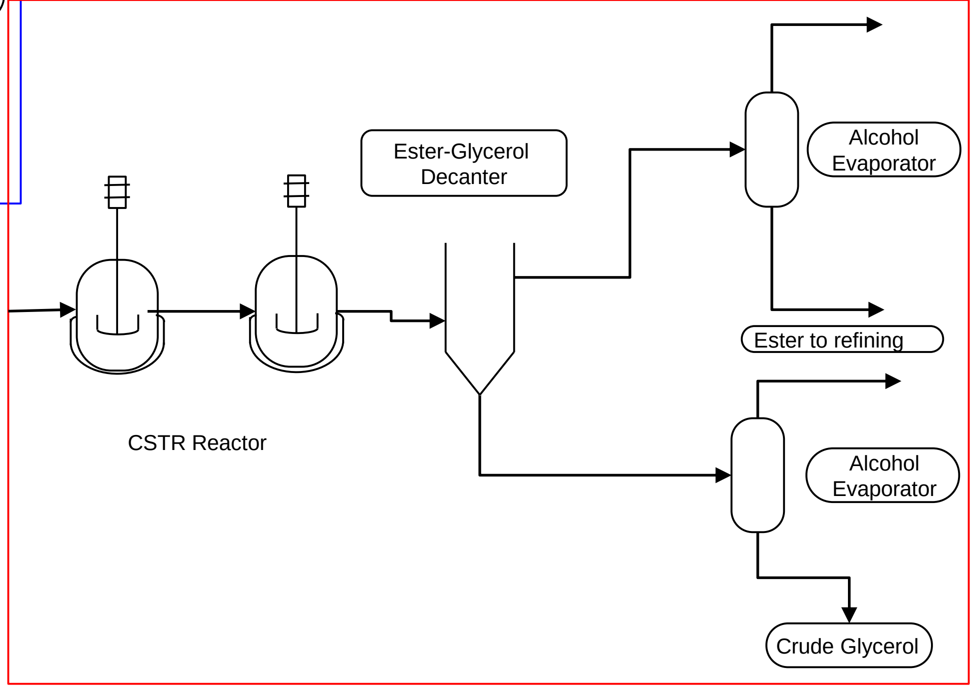


Base Catalyzed Batch System

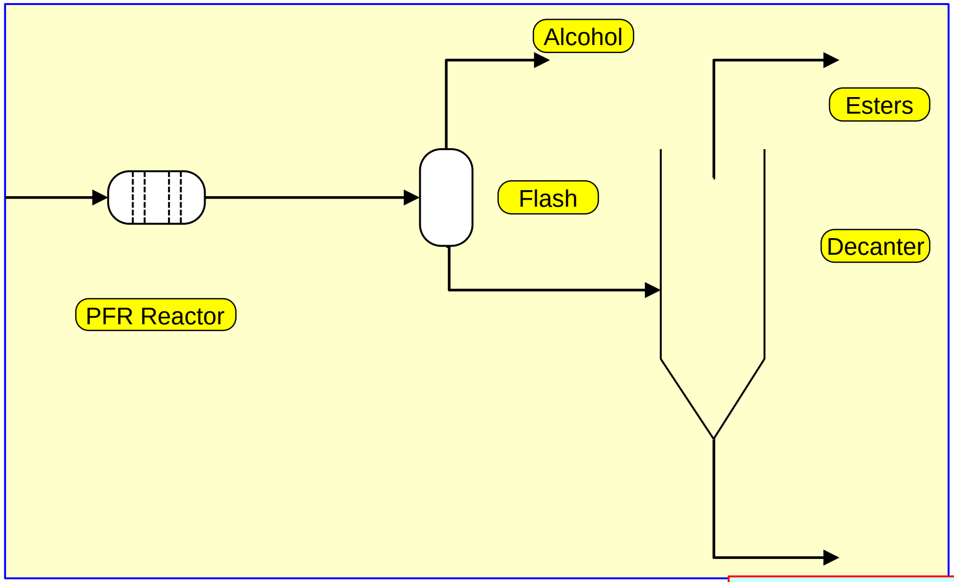
(indicated for small capacity or long residence times)

Continuous CSTR System

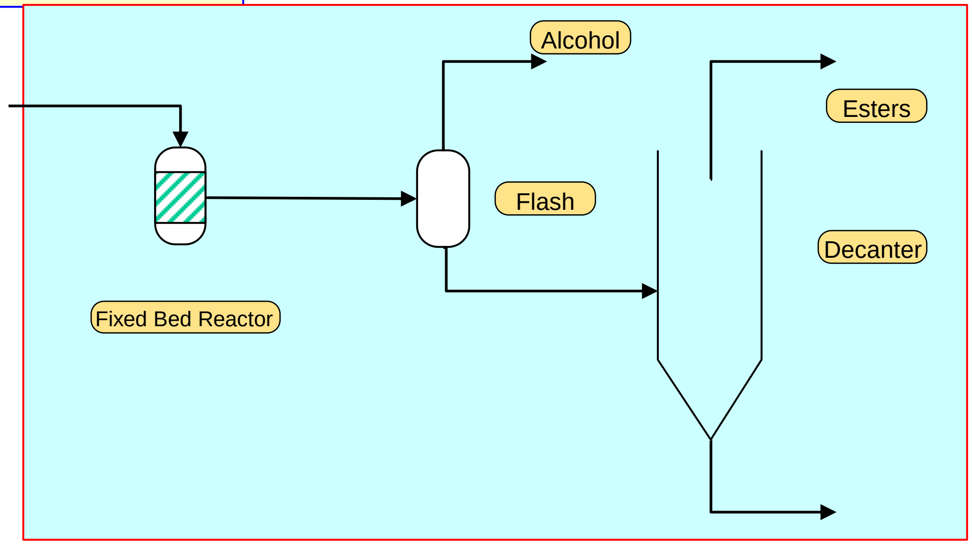
- indicated for large capacity systems
- longer residence times can be accommodated using sequential CSTRs or PFRs
- Residence time can be optimized using multiple parameters



Categories of Biodiesel Processes (2).

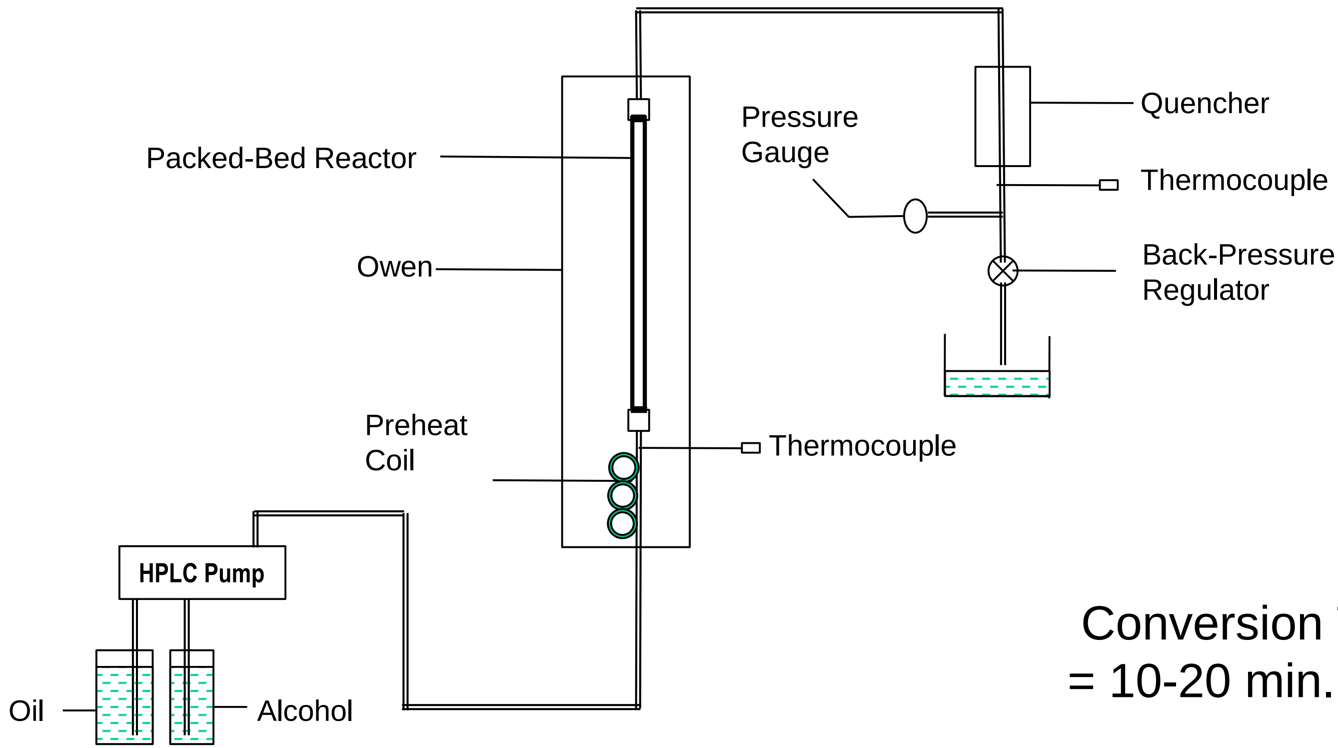


Base Catalyzed PFR System



Heterogeneous Catalyst System

Continuous Packed-Bed Reactor.



Conversion Time
= 10-20 min.

Schematic Diagram of Lab-Scale Reactor

Biodiesel Production Chemistry.

Esterification is a three step reaction:

- Solubility limited
- Rate limited
- Product inhibition (glycerol) limited

Temperature:

- Solubility Limited: Increasing T increases solubility
- Rate Limited: Reaction rate doubles with a 10 °C increase in T
- Product Inhibition Limited:

  GL $\rightarrow$ MG rate near MG $\rightarrow$ DG rate

Pressure: Operate 10 to 15 psig above alcohol vapor pressure

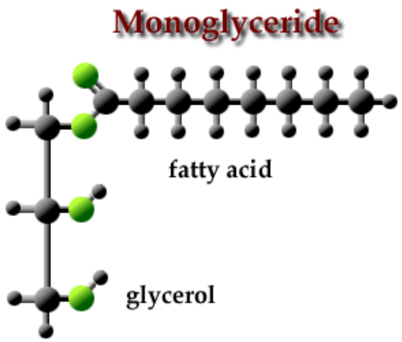
Biodiesel Production Chemistry (2).

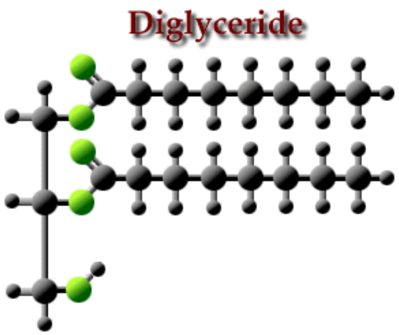
The reaction must be complete

- Incomplete reactions leave behind Mono-glycerides and Di-glycerides
  - They can't be seen, nor can they be washed out
  - They can cause engine problems such as Injector clogging, valve coking, poor emissions and corrosion of some metals.

Undesirable components in Biodiesel

Mono-glyceride showing 1 remaining fatty acid attached to the glycerin	Di-glyceride showing 2 remaining fatty acid attached to the glycerin





Product Recovery Steps.

- Ester – Glycerol Separation
  - Separation is based upon Ester-Glycerol immiscibility and density differ.
  - Separation is affected by:
    - Glycerol dispersion in ester phase
    - Presence of mono-, di-, triglycerides
    - Presence of un-reacted alcohol
    - pH of the two phases
- Ester Washing and Drying
  - Primary purpose – removal of soaps (deionized H_2O free of iron/copper)
  - Secondary purposes: Removal of free glycerol, Removal of catalyst residues, Removal of trace methanol (Spray drying, Vacuum drying, Evaporators, Absorbents)
- Glycerol Recovery
  - Recover methanol by spray drying
  - Neutralize catalyst using mineral acid
  - Removal of catalyst using ion exchange
  - All glycerol processing should take place at > 50 °C
- Methanol Management (> 98%; emission issues)
- Wastewater Considerations: Soapy wash-water contains about 25,000 ppm BOD5.

Biogenic Esters for Technical Purposes.

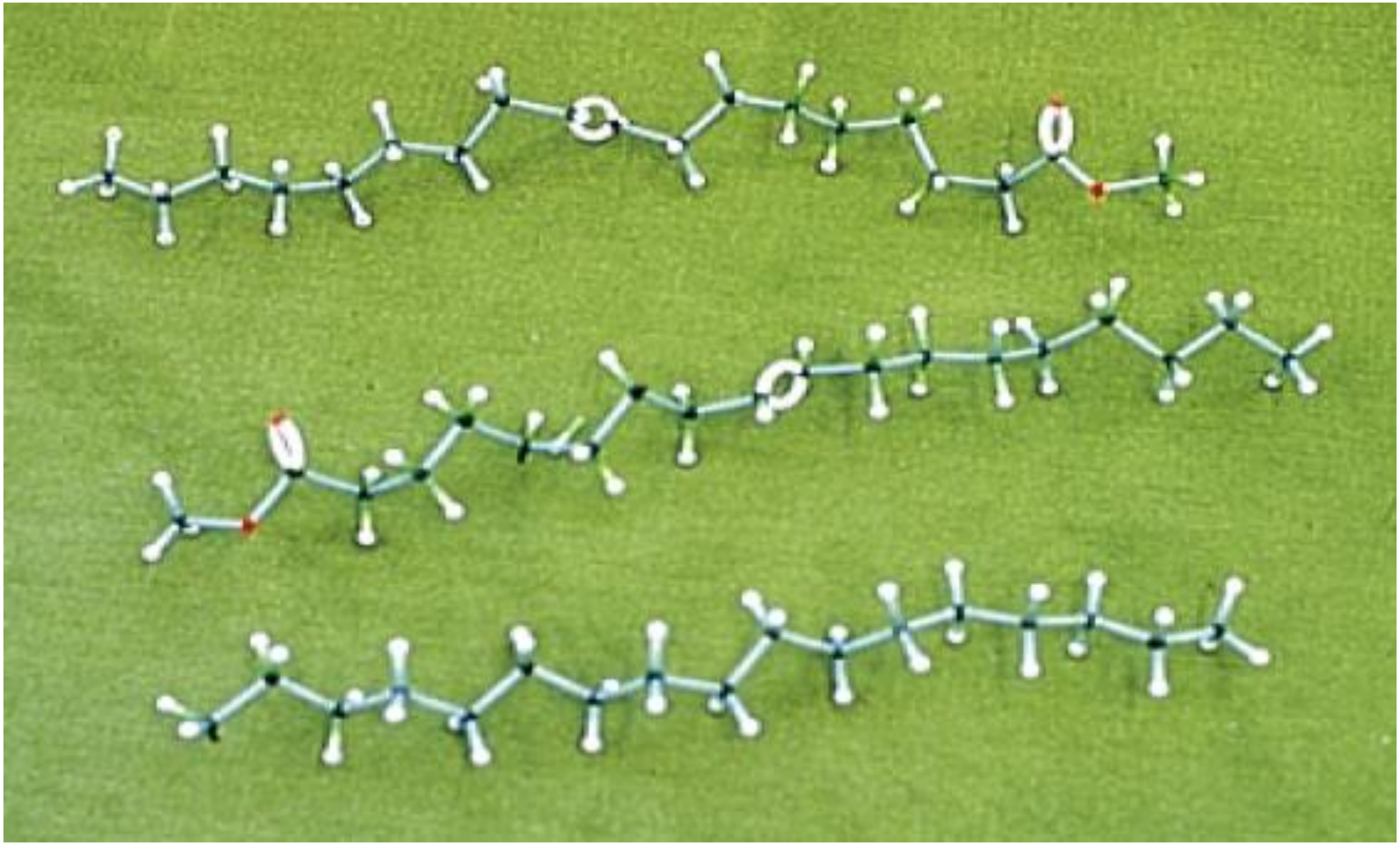
	Melting range °C				
	Oil/Fat	Me. Ester	Et. Ester	Iodine N.°	Cetane N.°
Rapeseed oil, h. eruc.	5	0	-2	97-105	55
Rapeseed oil, l. eruc.	**-5**	**-10**	**-12**	**110-115**	**58**
Sunflower oil	**-18**	**-12**	**-14**	**125-135**	**52**
Olive oil	-12	-6	-8	77-94	60
Soybean oil	**-12**	**-10**	**-12**	**125-140**	**53**
Cotton seed oil	0	-5	-8	100-115	55
Corn oil	-5	-10	-12	115-124	53
Coconut oil	20-24	-9	-6	8-10	70
Palmkernel oil	20-26	-8	-8	12-18	70
Palmoil	**30-38**	**14**	**10**	**44-58**	**65**
Palm oleine	20-25	5	3	85-95	65
Palm stearine	35-40	21	18	20-45	85
Tallow	**35-40**	**16**	**12**	**50-60**	**75**
Lard	32-36	14	10	60-70	65

Fuel Properties of Vegetable Oils and their Methyl Esters in Comparison with Diesel Fuel.

Fuel properties	Diesel Fuel	Sunflower oil	Sunflower methyl ester	Linseed oil	Linseed oil methyl ester	Rape oil	Rape oil methyl ester
Specific Gravity ($kg \cdot cm^{-3}$)	0.835	0.924	0.88	0.932	0.896	0.916	0.88
Viscosity (cSt) at 20°C at 50°C	 5.1 2.6	 65.8 34.9	 4.22	 50.5	 8.4	 77.8 25.7	 7.5 3.8
Heat of Comb. Gross ($KJ \cdot L^{-1}$) Net ($KJ \cdot L^{-1}$)	 38.4 35.4	 36.5 34.1	 35.3 33.0	 36.9	 35.6	 37.2 34.3	 33.1
Cetane Number	>45	33	45-51			44-51	52-56
Carbon residue (%)	0.15	0.42	0.05		0.22	0.25	0.02
Sulfur (%)	0.29	0.01	0.01	0.35	0.24	0.0001	0.002

Source: Guibet 1988, Pernkopf 1988 and Schsfer and Heinrich, 1990, modified

Biodiesel is a High Cetane Diesel Fuel.

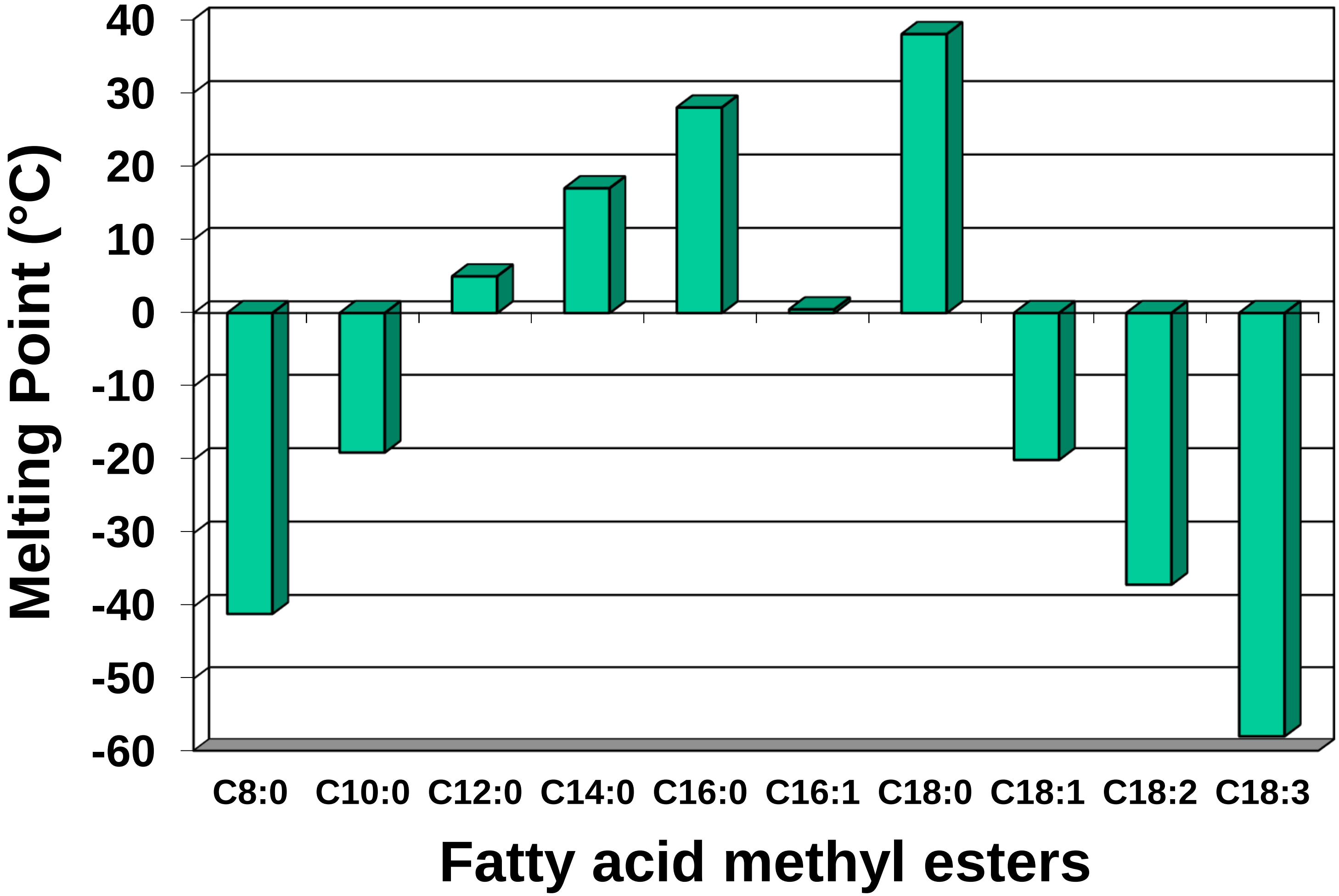


FAME is an ideal compression-ignition fuel

Biodiesel as Super-Diesel.

- Cetane Number : 54-58
- Sulfur below 10 ppm
- No aromatics, no benzene
- Stabile and long lasting (if ox. inhibitors present)
  - efficiency of catalytic converters
- Very low CO, HC, PAH,
  - lower PM_{10}, NO_x better +2°,
- Exorbitant lubricity = additive,
  - Less wear (-50%)
- CFPP -22°C, operability -20°C

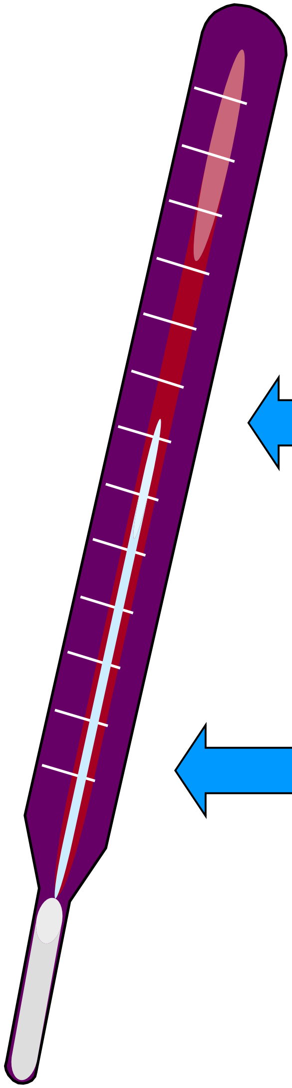
Melting Points of Some Methyl Esters of Fatty Acids.



Drawbacks to Biodiesel.

Cold weather performance

- Biodiesel starts gelling about 10°F higher than petrol diesel (depending on the feedstock).
- Currently not any additives to lower the gel point:
  - Can be overcome by blending
  - Future additives will likely be available
  - Can be improved by using different feedstock.



Cloud Point

"Temperature at which the paraffin wax falls out of the liquid phase.

CFPP

"The absolute lowest operating temperature a vehicle will operate"

Pour Point

"Temperature which fuel ceases to flow, more a storage flow temperature used by pipelines and terminals"

Biodiesel Standards:
Properties Specific to Esters.

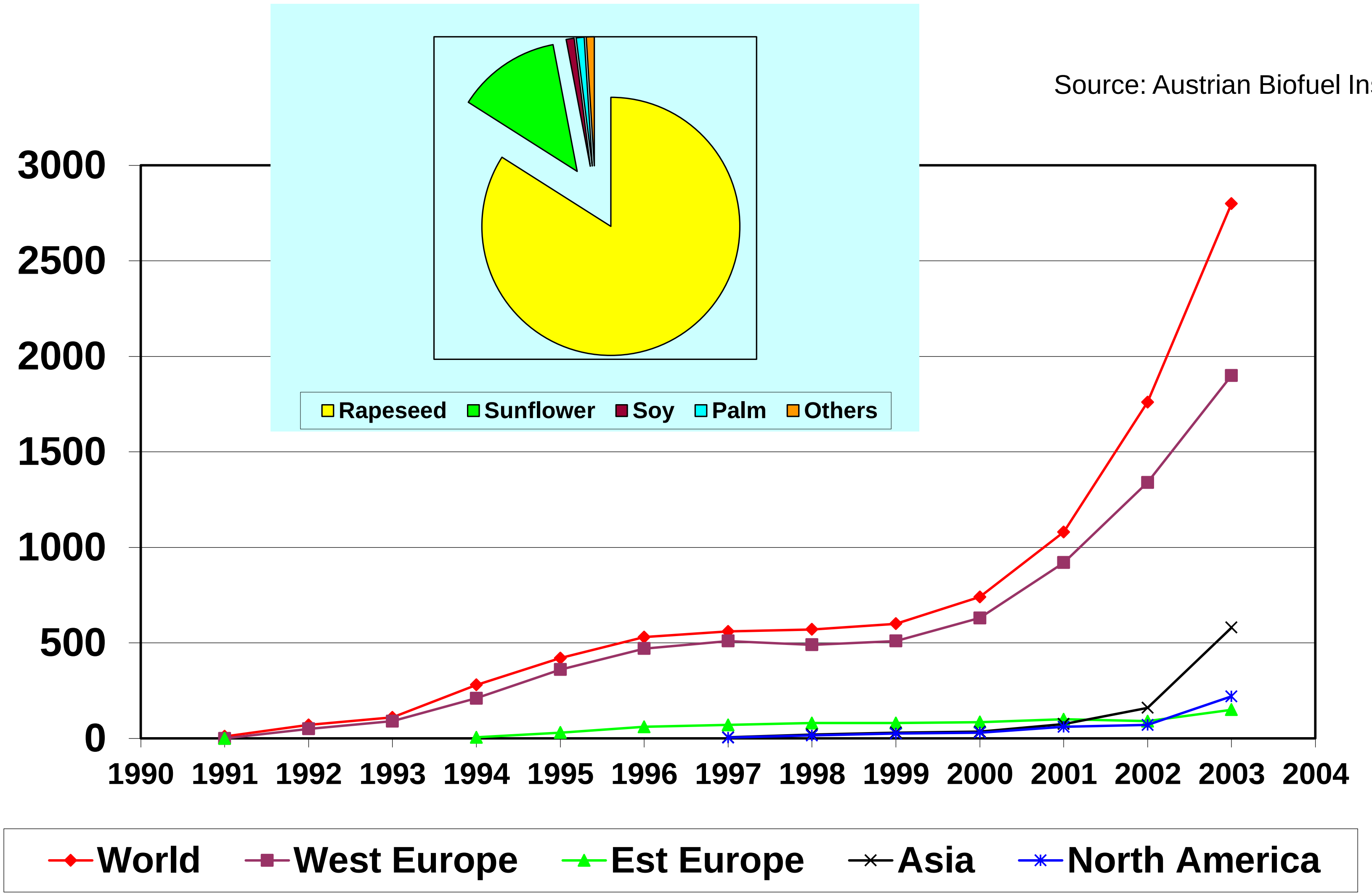
		Target data Diesel fuel E DIN 51606	Actual data
Density 15°C	$g \cdot ml^{-1}$	0.875-0.890	0.883
Flashpoint	°C	110	Above 170*
Moisture	ppm	300	200
Neutr. number	$mg\ KOH \cdot g^{-1}$	0.500	0,200
Total glycerol	%	0.250	0,100
Free glycerol	%	0.020	0,001
Phosphorous	ppm	10	Less than 2
Methanol	%	0.300	Less 0.005
CFPP	°C	-20. -10. 0	Winter: -22
Viscosity 15°C	$mm^2 \cdot s^{-1}$ (cSt)	3.5-5.5	1.9-6.0
Description: *same flashpoint		Biodiesel from FAME 99/-20(-10. 0)	

Influence of Fatty Acid Composition on Biodiesel Properties.

Fatty Acid (FA)	Positive Effects	Negative Effects
Saturated	• Cetane number • Oxidation stability	• Cold stability
Polyunsaturated	• Cold stability	• Oxidation stability
Short chain FA	• Distillation Curve	• Flash point
Long chain FA		• Viscosity • Cold stability

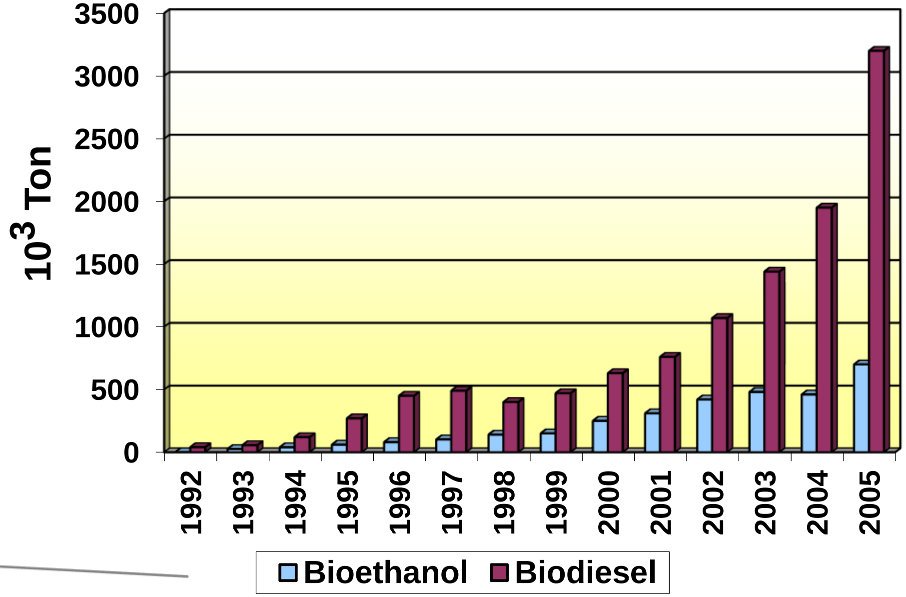
Biodiesel Sales.

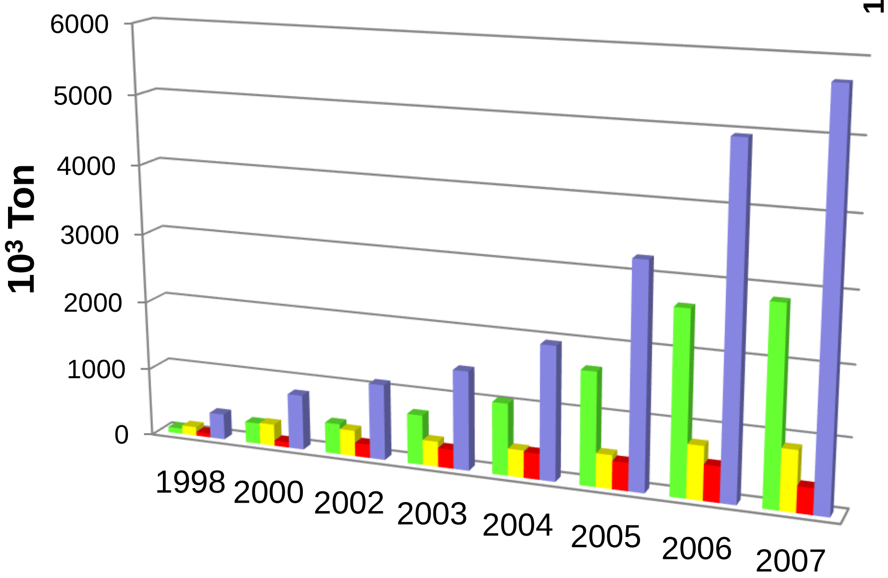
Source: Austrian Biofuel Institute



Biofuels Production in the European Union (EU).

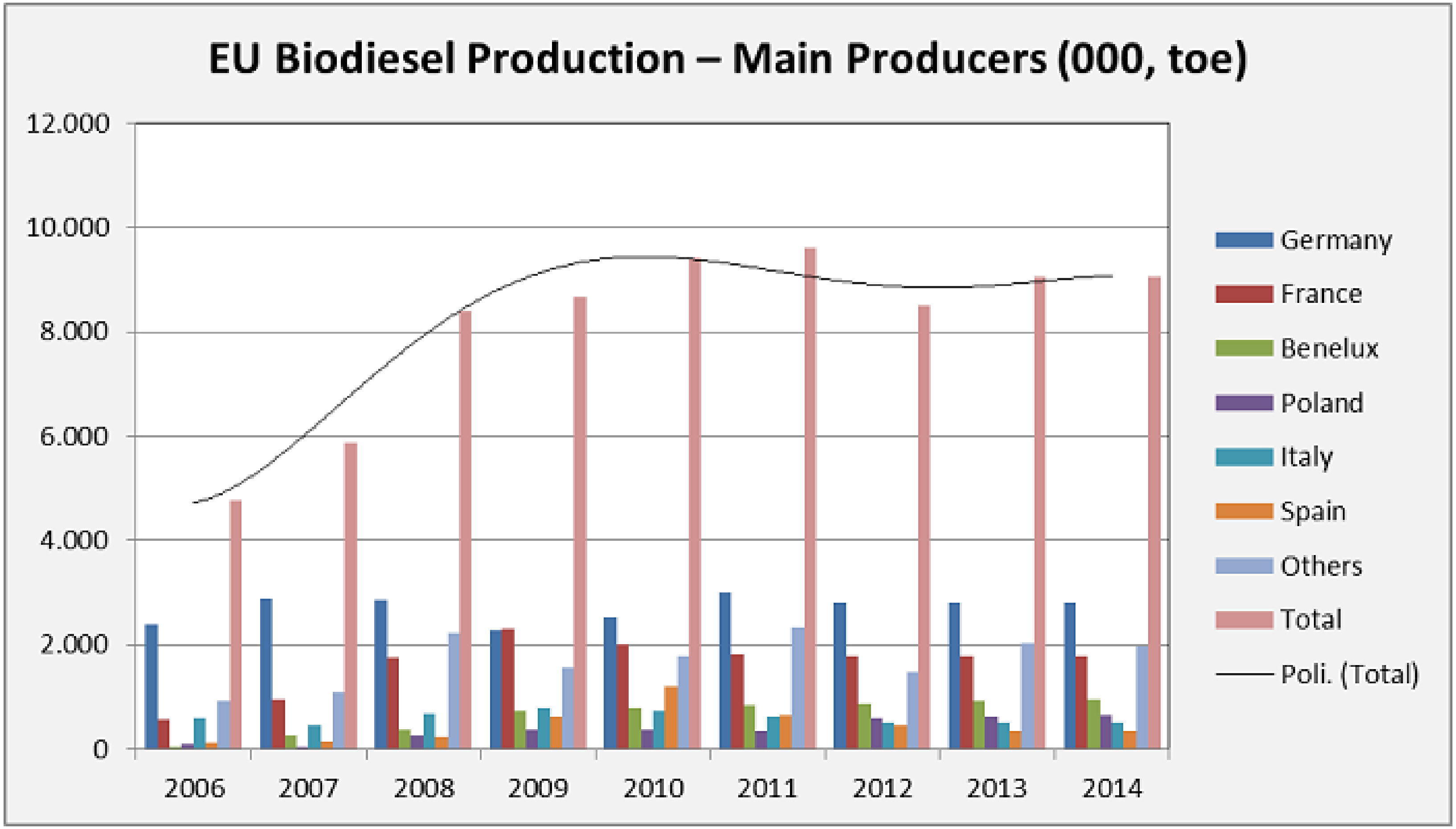
in the EU 25





in the EU 27)
by 2007 (×10^3 t)

Biodiesel Production in the European Union (EU 27) by 2006-2014 ($\times 10^3$ t).



Source: EurObserver – Biofuels Barometer, May 2014

Some Biodiesel Specifications.

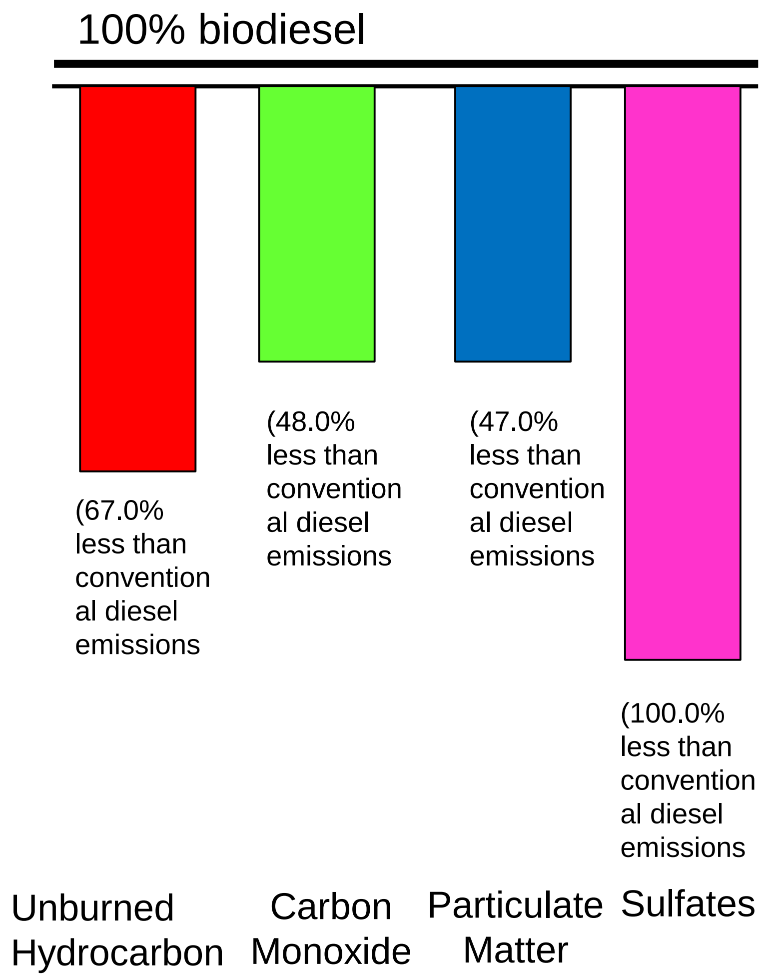
Fuel specifications

	1st series of tests			Petrodiesel						B 100	Limits	D6751-02
	B 100 Soy			D23	B5/D23	B20/D23	B5/D23	B20/D23	B20/D40		D100 B-FTS	B 100
	Blended at		°C		-5	-5	20	20	20		-	
1	Flash point	ASTM D 93A	°C	46			46	47		184	40 min.	100 min.
2	Water & sediments	ASTM D 2709	vol. %	0.005						0.035	0.05 max.	0.05 max.
3	Viscosity at 40°C	ASTM D 445	cSt	2.024			2.096	2.332		4.1	1.70 à 4.10	1.9 à 6.0
4	Sulfur	ASTM D 2622	% mass								0.05 max.	.05 max.
5	Sulfated ash	ASTM D 874	% mass									.02 max.
6	Copper strip corrosion	ASTM D 130		1a				1A		1a	n°1 max.	n° 3 max.
7	Cetane number	ASTM D 613		41.1			44.0	46.7		52.0	40.0 min.	
8	Cloud point	ASTM D 2500	°C	-25	-21	-15	-21	-15	-23	-3 à +4	-23 max.	note d
9	Carbon residue at 10%	ASTM D 4530	% mass	0.03			0.06	0.11			0.16 max.	
9	Carbon residue at 100%	ASTM D 4530	% mass							0.03		.050 max.
10	Free Glycerin	ASTM PS 121	% wt.							0.002		.02 max.
10	Total Glycerin	ASTM PS 121	% wt.							0.188		.240 max.
11	Acid number	ASTM D 974 / D 664	$mgKOH \cdot g^{-1}$	0.10				0.10		0.3	0.10 max.	0.80 max.
12	Water by Karl Fisher method	ASTM D 6304	$mg \cdot Kg^{-1}$	39.0						776		
13	Energy content	ASTM D 240	$BTU \cdot lbs^{-1}$	19554						17119		
14	Lubricity (180 minutes	ASTM D 6079	mm	0.420			0.225	0.180		0.145		
15	Carbon content		% wt.	86						78		
	Hydrogen content		% wt.	14						13		
	Oxygen content		% wt.	0						9		
16	Density ay 15°C	ASTM D 4052	$kg \cdot m^{-3}$	840.4			842.6	849.0				
17	LTFT	ASTM D 4539	°C	-22	-22	-14	-22	-14	-21	2		
18	Thermal Stability	ASTM D 6468	% riflect.					98				
19	Distillation at 90%	ASTM D 86	°C	315.0			322.0	334.0			360 max.	
20	Conductivity at 23°C	ASTM D 2624	$pS \cdot m^{-1}$	253				604			25 min.	
21	Ash	ASTM D 482	% mass								0.010 max.	

Biodiesel Emissions Performances.

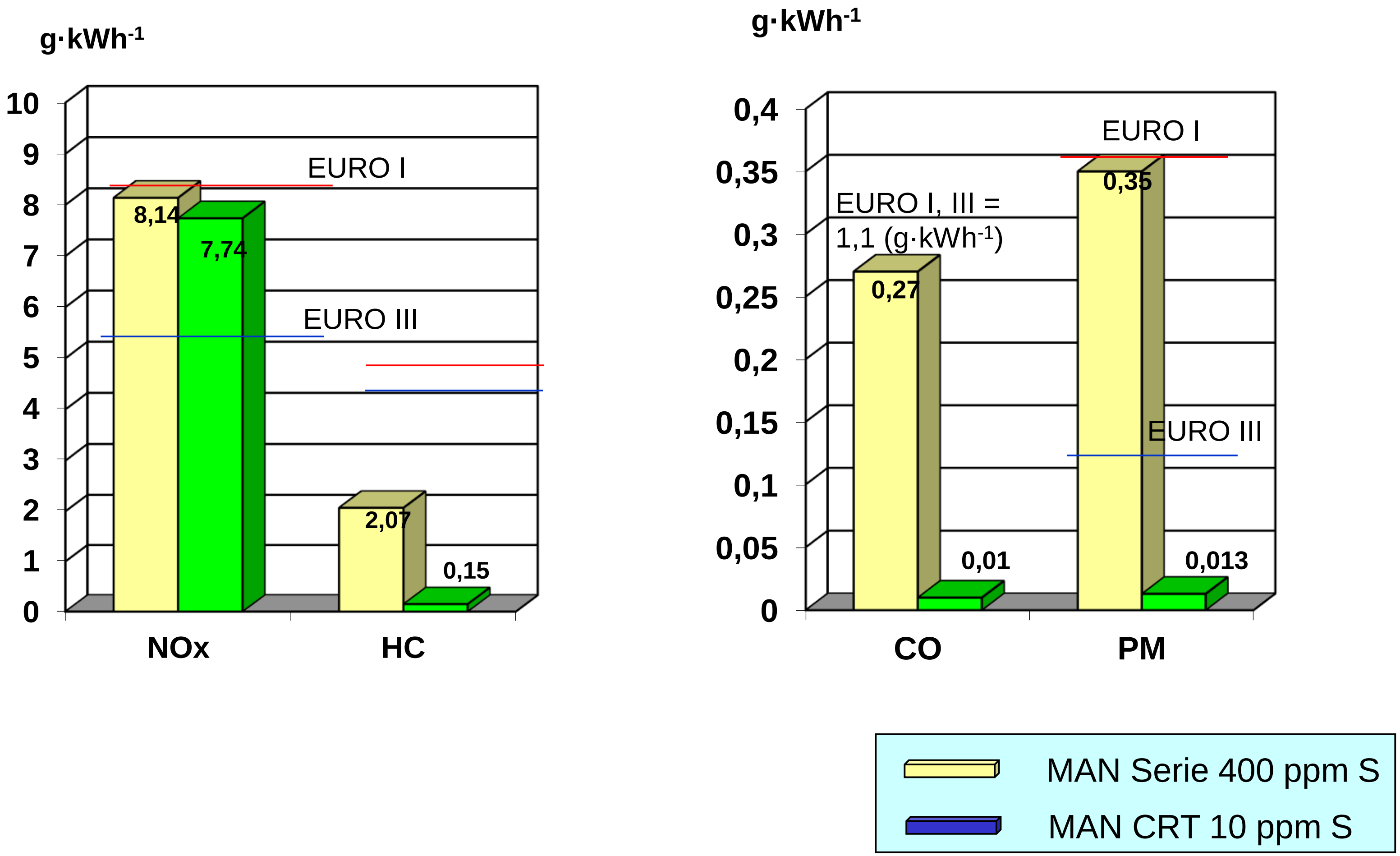
Lower Emission of Exhaust Smoke. Biodiesel is a clean burning fuel and provides a number of benefits in terms of emissions and environmental effect when compared to conventional petroleum-based diesel, including:

- close-to-zero sulfur content
- significantly lower exhaust particulates and hydrocarbons
- significant reduction of CO
- significantly lower lifecycle greenhouse gas emissions.
- no significant decrease of NO_x is observed.
- non-toxic



Source: US National Biodiesel Board

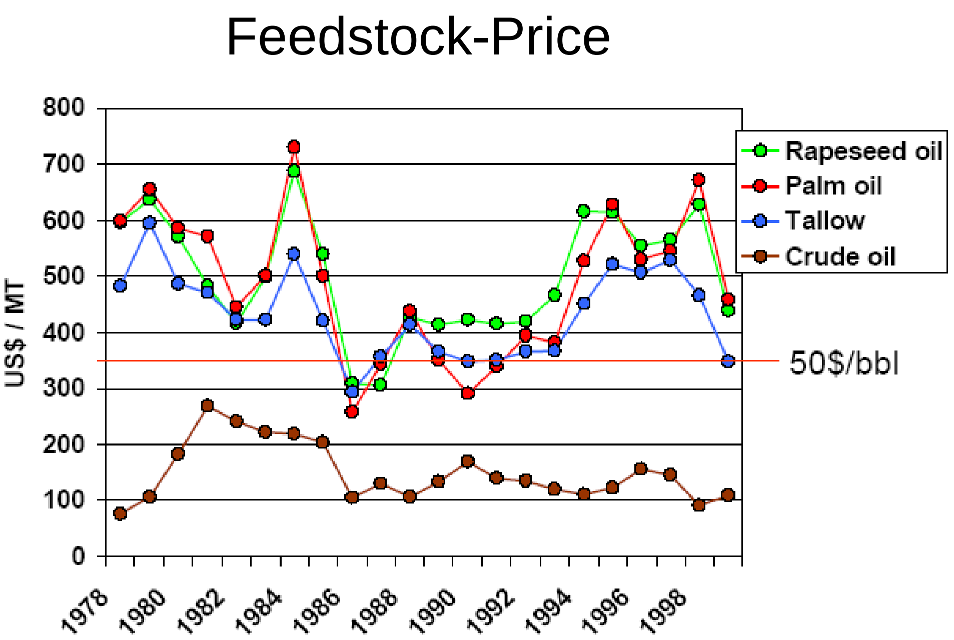
Exhaust Emissions in 13-mode test on Biodiesel - EURO I.



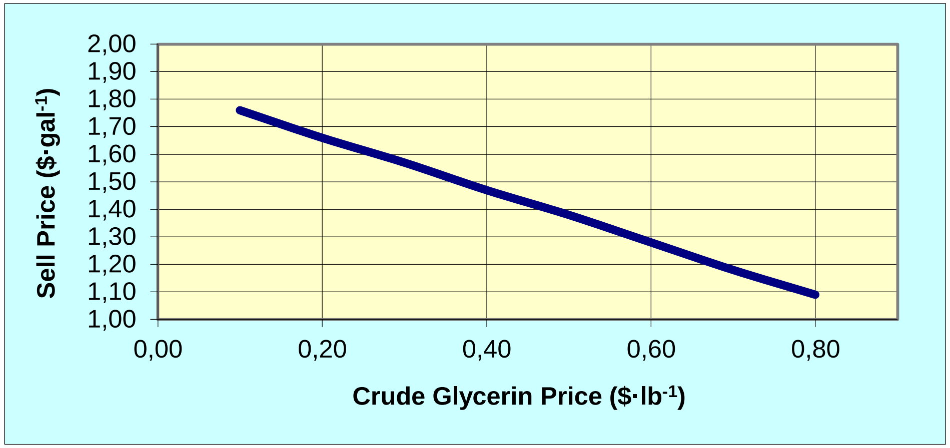
Barriers in the Development of Biodiesel.

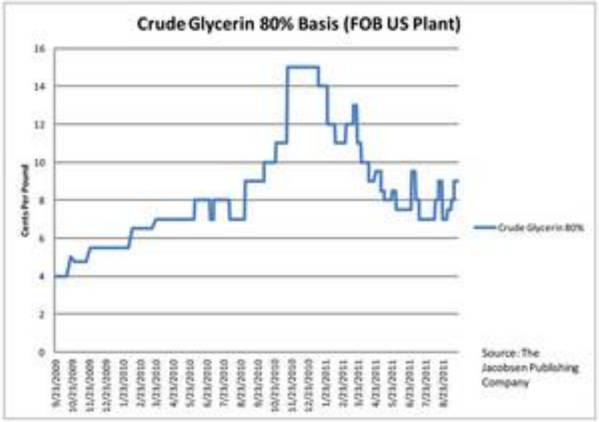
- **Feedstock prices very high**
- **Stability of oil price**
- **Fluctuations of prices of vegetal oils and minerals**
- New precursors for biodiesel production?
- **The glycerin issue**

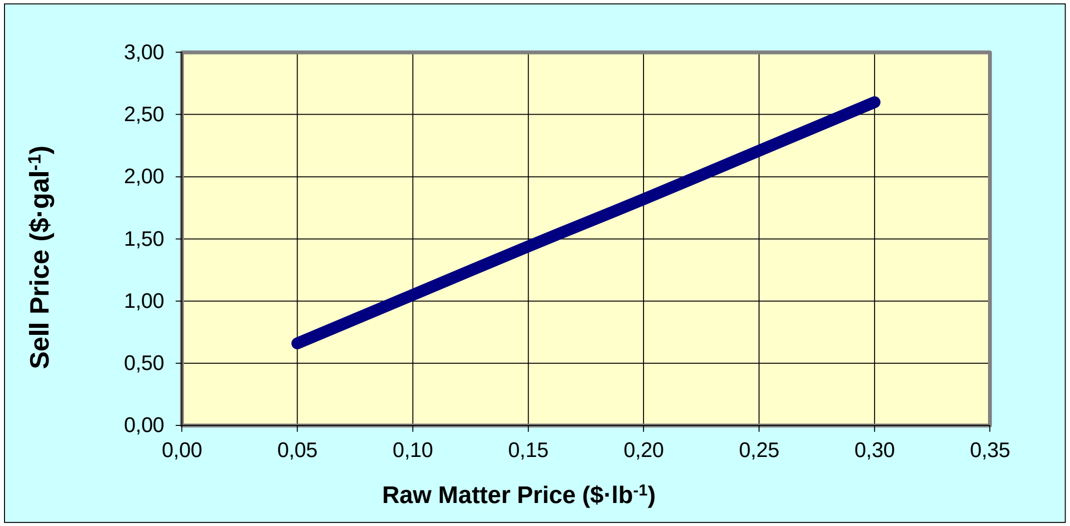
In Italy the «Finanziaria 2005 (art. 43)» have defined a six year program to 2010, for the use of biodiesel, exempting from excise for an annual share of 300.000 tons. Mixtures of gasoil-biodiesel with a biodiesel content ≤5% can be sell to consumption both to extra network users and in network, whereas those ≥25% can be sell only extra network. The law limits the possibility to use in Italy neat biodiesel (i.e. 90% rapeseed oil, 10% alcohol) without excise exemption.



Biodiesel Price vs. Raw Material and Co-product.







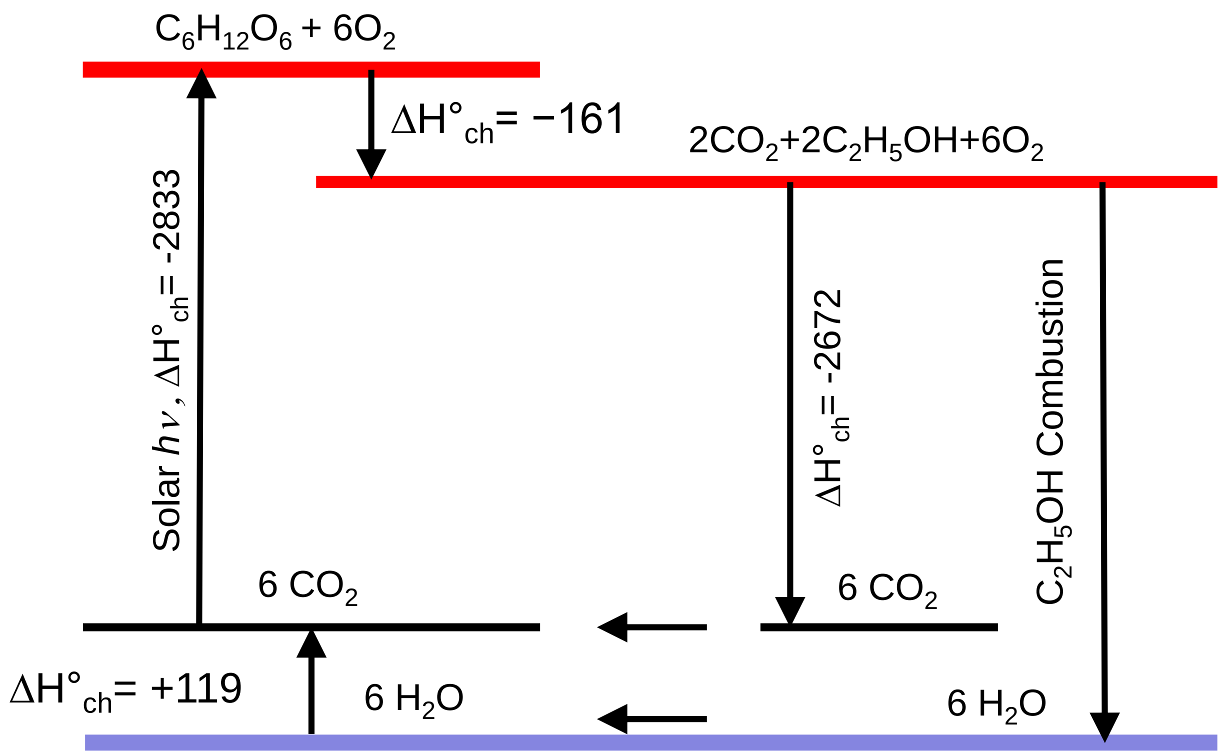
Biofuels Production

Non-thermal Methods

Bioethanol

Bioethanol Energetic.

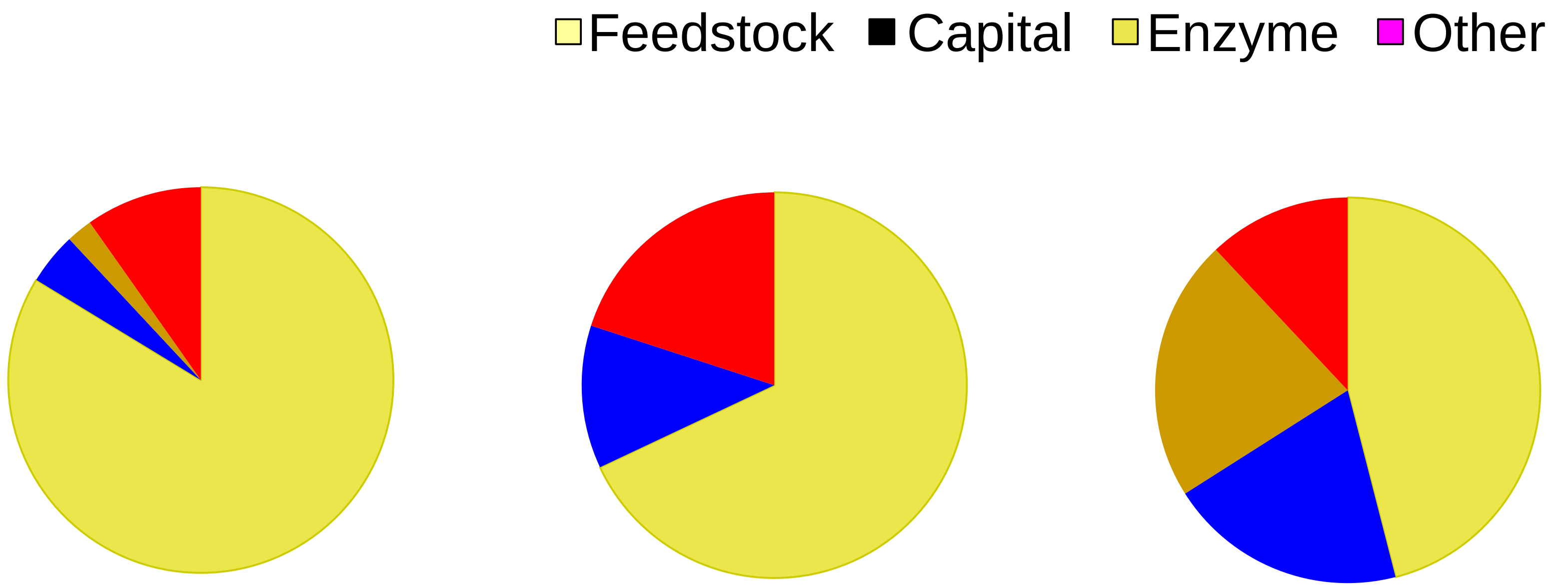
Energy diagram of the ideal CO_2-Glucose-EtOH cycle.



First generation: bioethanol from starch or sugars

Second generation: bioethanol from cellulose and hemicellulose

Illustrative Example – Cost Distribution by Type of Ethanol.



1G ethanol (corn)
Assumptions:
- Corn @ USD 5.25/bushel
- Depreciations (Plant cost USD 2.00/gal)
- Other = energy, water, yeast, chemicals & labor
- Enzymes: USD 0.04/gal

Sugarcane ethanol
Assumptions:
- Sugar cost equiv. to USD 0.18/lb.
- Depreciations (Plant cost USD 6.50/gal)
- Other = energy, water, yeast, chemicals

2G ethanol (biomass)
Assumptions:
- Biomass @ USD 50/ton
- Depreciations (Plant cost USD 7.50/gal)
- Other = energy, water, yeast, chemicals & labor
- Enzymes: USD 0.50/gal

Source: Novozymes - 2014

Biofuel History: Bioethanol.

- H. Ford designed the engine Model T in 1908 to be used with ethanol as anti-knock agent. Ethanol blends (E75 - 25% ethanol, 75% gasoline) account for 25% of sales in Midwest (DOE) until 1940 with more than 2,000 stations. Ethanol was mainly from wheat.
- 1940s - Low priced, Middle-East oil eliminate ethanol from market, with consequences on rural world.
- 1970s World energy crisis: US subsidies for ethanol blends. Some countries (i.e. Brazil) becomes main producers.
- 1978 MBTE become oxygenate of choice and ethanol use dropped.
- Eco-environmental regulations in 1990' stimulate the demand for ethanol as oxygenated fuel (MBTE in 2000 phased-out)
- Ethanol is commercialized blended with gasoline (E10, E85, E95)
- Ethanol production capacity was 10-12 billion gallons by 2010.

Bioethanol (2).

Ethyl alcohol can be obtained from a wide variety of plants sugar rich via fermentation processes.

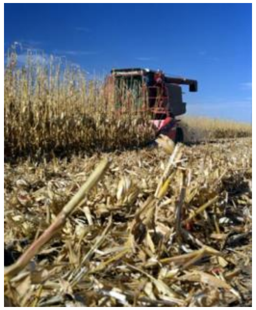
$$C_6H_{12}O_6 \rightarrow 2\ CH_3CH_2OH + 2\ CO_2$$

Fermentation is a disproportionation reaction of glucose to ethanol and CO_2

Sources:

- **Starch** (from seeds)
- **Sucrose** (from sugar cane, sugar beet, etc.)
- **Cellulose** (from hardwood and softwood).

Despite some problem of food competition and land use, ethanol industry can solve issues of soil preservation and rural overproduction.



Corn

Sugar cane

Arundo donax

Potential Biofuels Feedstocks.

ECONOMICAL ↑

Sugar Cane

Corn Fiber

Corn Starch

Cottonwoods

Switch Grass

Stover

Wood Chips

Paper

ABUNDANT & AVAILABLE →

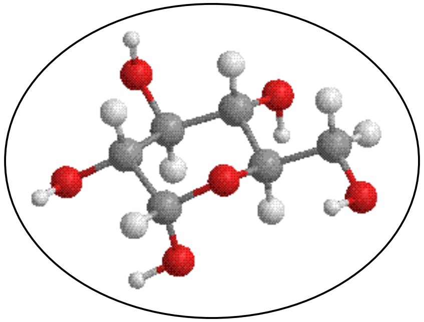
Dry-Grind Corn-to-Ethanol Fermentation: Summary of Inputs and Outputs.

1 bushel of corn (25.4 kg)

+ yeast

+ amylase enzyme

+ 89,940 kJ



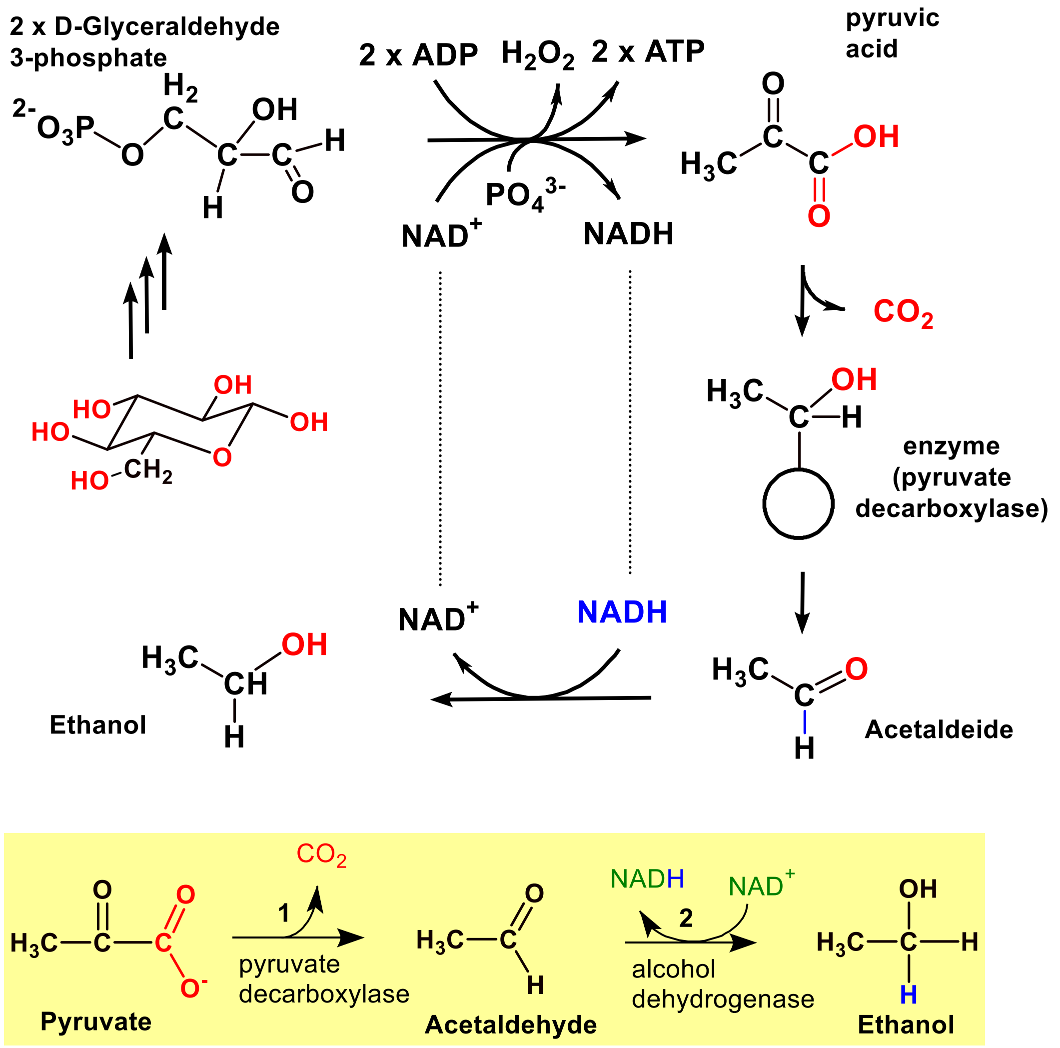
=

8.16 kg of ethanol

+ 8.16 kg CO_2

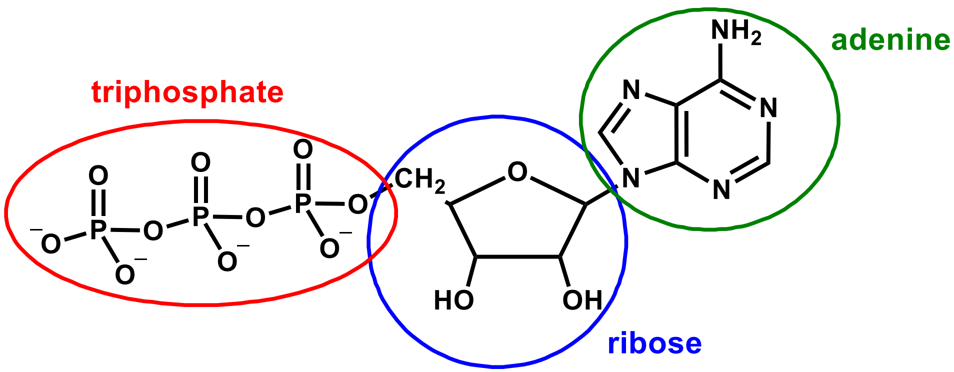
+ 8.16 kg of DDGS

Chemistry of Ethanol Fermentation.



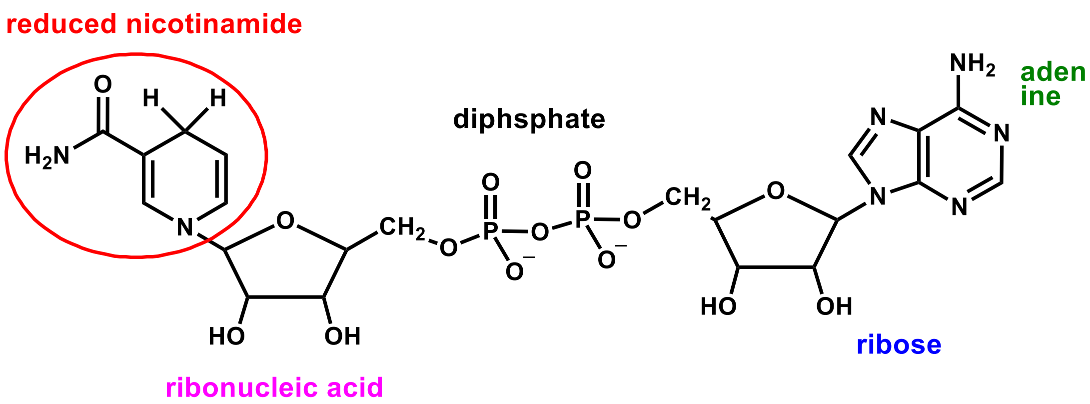
Essentially the fermentation is a way used by organisms to extract energy from the environment. The quite complex biochemical process occurs in cells. In simplified form can be summarized as depicted in the annexed scheme, the main intermediates involved are pyruvic acid (or pyruvate) and acetaldehyde.

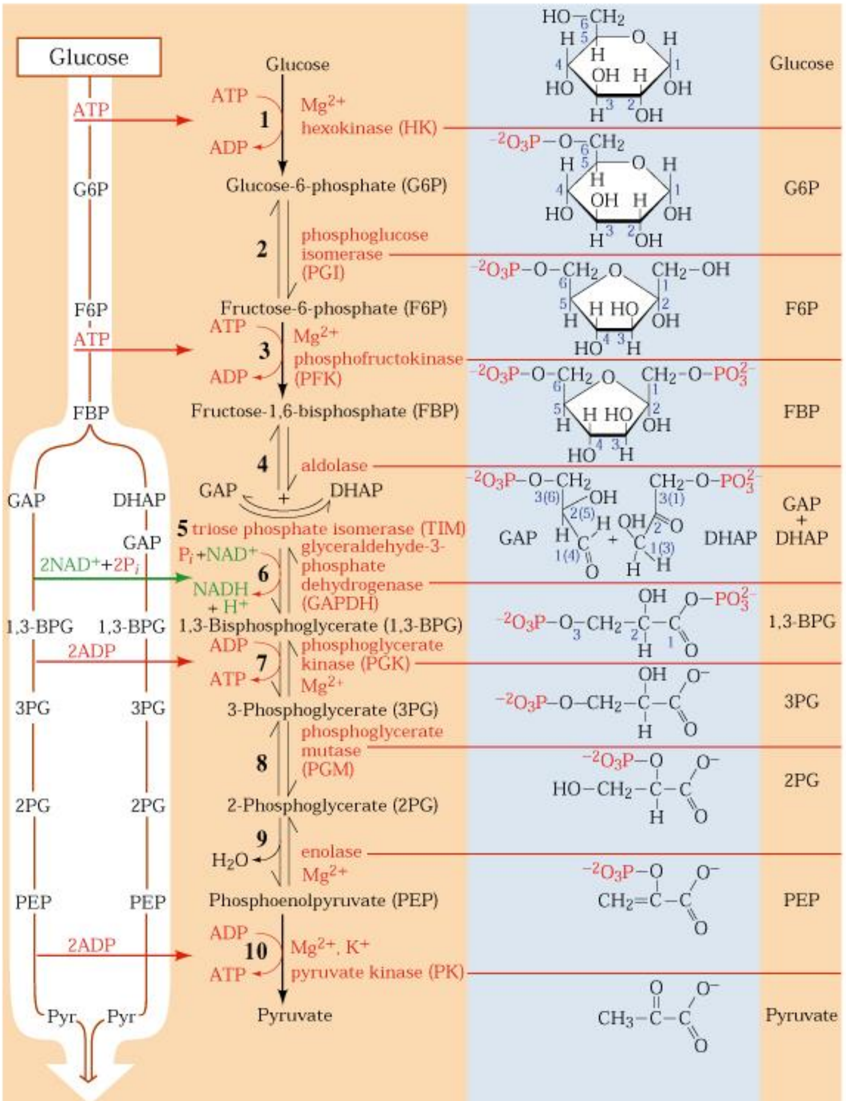
Chemistry of Ethanol Fermentation (2).



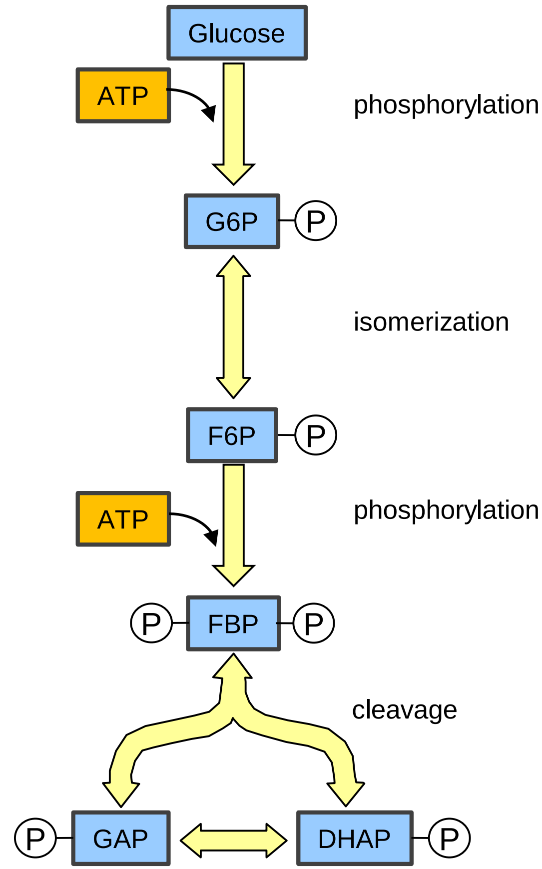
Adenosine Triphosphate (ATP) is considered to be the energy currency of life. It is the high-energy molecule that stores the energy we need to do just about everything we do. It consists of adenine (a DNA base) bonded to ribose (a 5 atom sugar) to form adenosine, with three phosphate units linked to the terminal OH group of ribose.

Nicotinamide adenine dinucleotide (NADH) is an essential cofactor in some reactions catalyzed by enzymes (is the reduced form of NAD). Generate hydrogen for reductive reactions.



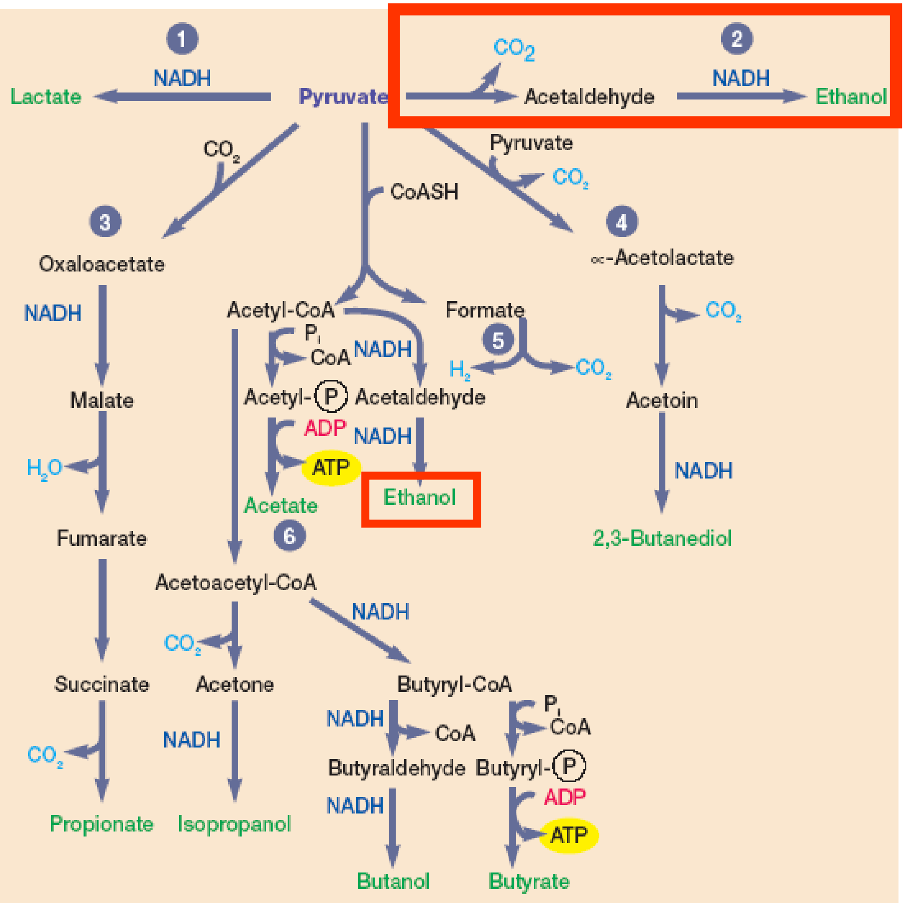


Glucose
Glucose-6-phosphate (G6P)
Fructose-6-phosphate (F6P)
Fructose-1,6-bisphosphate (FBP)
GAP
DHAP
1,3-Bisphosphoglycerate (1,3-BPG)
3-Phosphoglycerate (3PG)
2-Phosphoglycerate (2PG)
Phosphoenolpyruvate (PEP)
Pyruvate
ATP
ADP
Mg2+
hexokinase (HK)
phosphoglucose isomerase (PGI)
phosphofructokinase (PFK)
aldolase
triose phosphate isomerase (TIM)
glyceraldehyde-3-phosphate dehydrogenase (GAPDH)
Pi+NAD+
NADH + H+
2NAD+ + 2Pi
phosphoglycerate kinase (PGK)
phosphoglycerate mutase (PGM)
enolase
H2O
Mg2+, K+
pyruvate kinase (PK)
2ADP
G6P
F6P
FBP
1,3-BPG
3PG
2PG
PEP
Pyr
GAP + DHAP



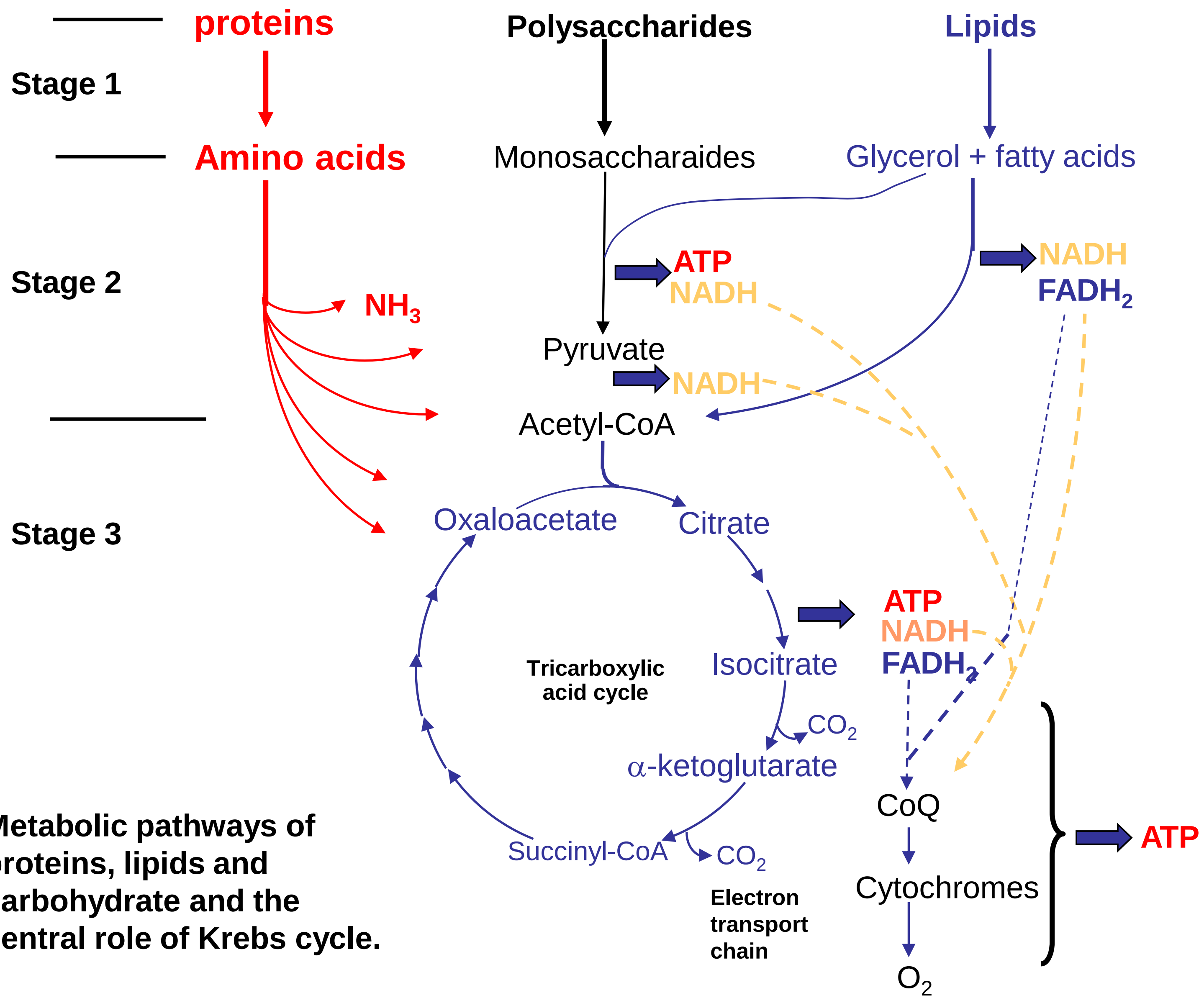
Glucose
ATP
phosphorylation
G6P
P
isomerization
F6P
ATP
phosphorylation
FBP
cleavage
GAP
DHAP

Reduction Phase.



1. Lactic acid bacteria (*Streptococcus, Lactobacillus*), *Bacillus*
2. Yeast, *Zymomonas*
3. Propionic acid bacteria (*Propionibacterium*)
4. *Enterobacter, Serratia, Bacillus*
5. Enteric bacteria (*Escherichia, Enterobacter, Salmonella, Proteus*)
6. *Clostridium*

The Three Stages of Catabolism.



Metabolic pathways of proteins, lipids and carbohydrate and the central role of Krebs cycle.

Ethanol Producing Bacteria and Yeast.

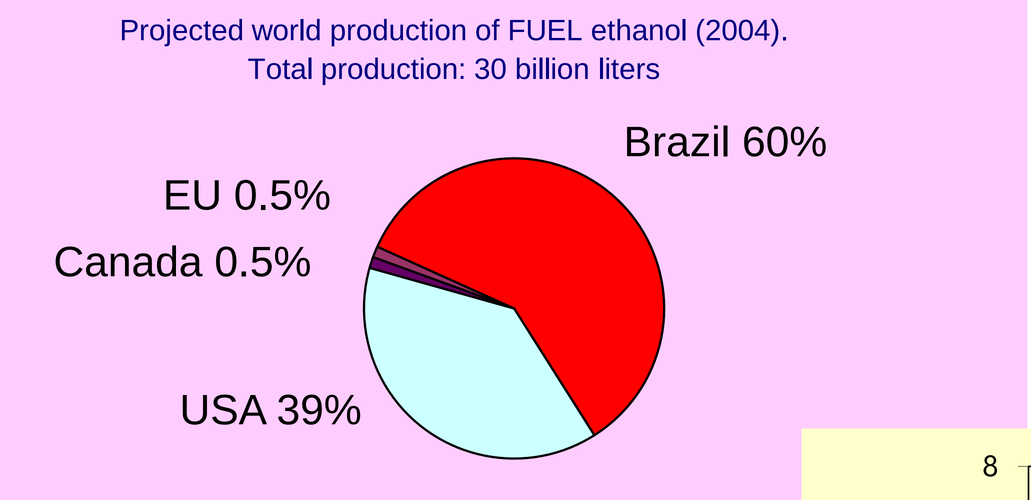
Organism	Substrate used
Yeast	
Saccharomyces cerevisiae	Glucose, fructose, galactose, maltose, maltotriose and xilulose
S. carlsbergensis	Glucose, fructose, galactose, maltose, maltotriose and xilulose
Kluyeromyces fragilis	Glucose, galactose and lactose
Candida tropicalis **Bacterium**	Glucose, xylose and xilulose
Zymomonas mobilis	Glucose, fructose and sucrose
Clostridium thermocellum	Glucose, cellobiose and cellulose

Ethanol Yield: 91% at 10-18% max. concentration.

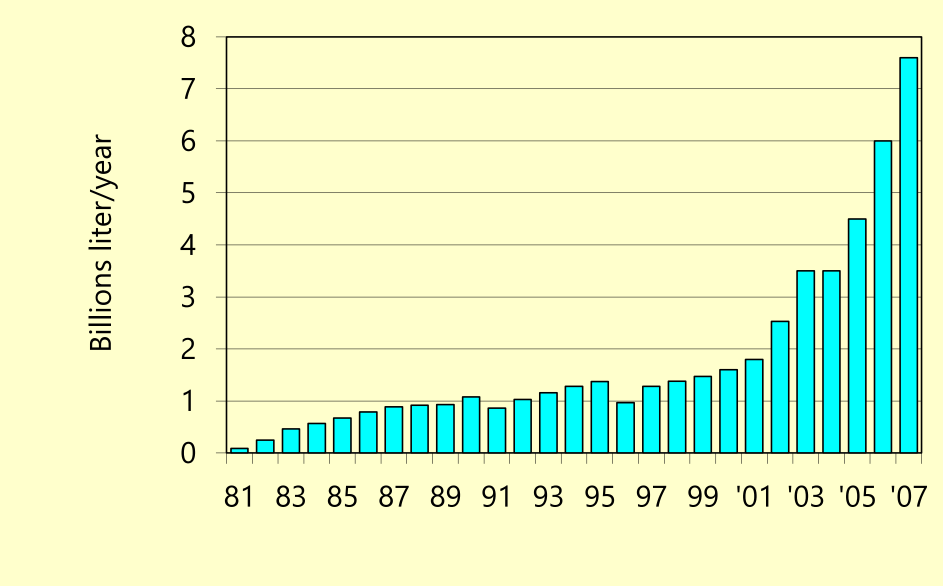
Ethanol recovery from bioreactor:

- High temperature evaporation/distillation
- Selective filtration through hydrophobic membranes.

Production of fuel ethanol is already a large business (10% of Liquid Fuels in 2015).



Bioethanol production trend in USA

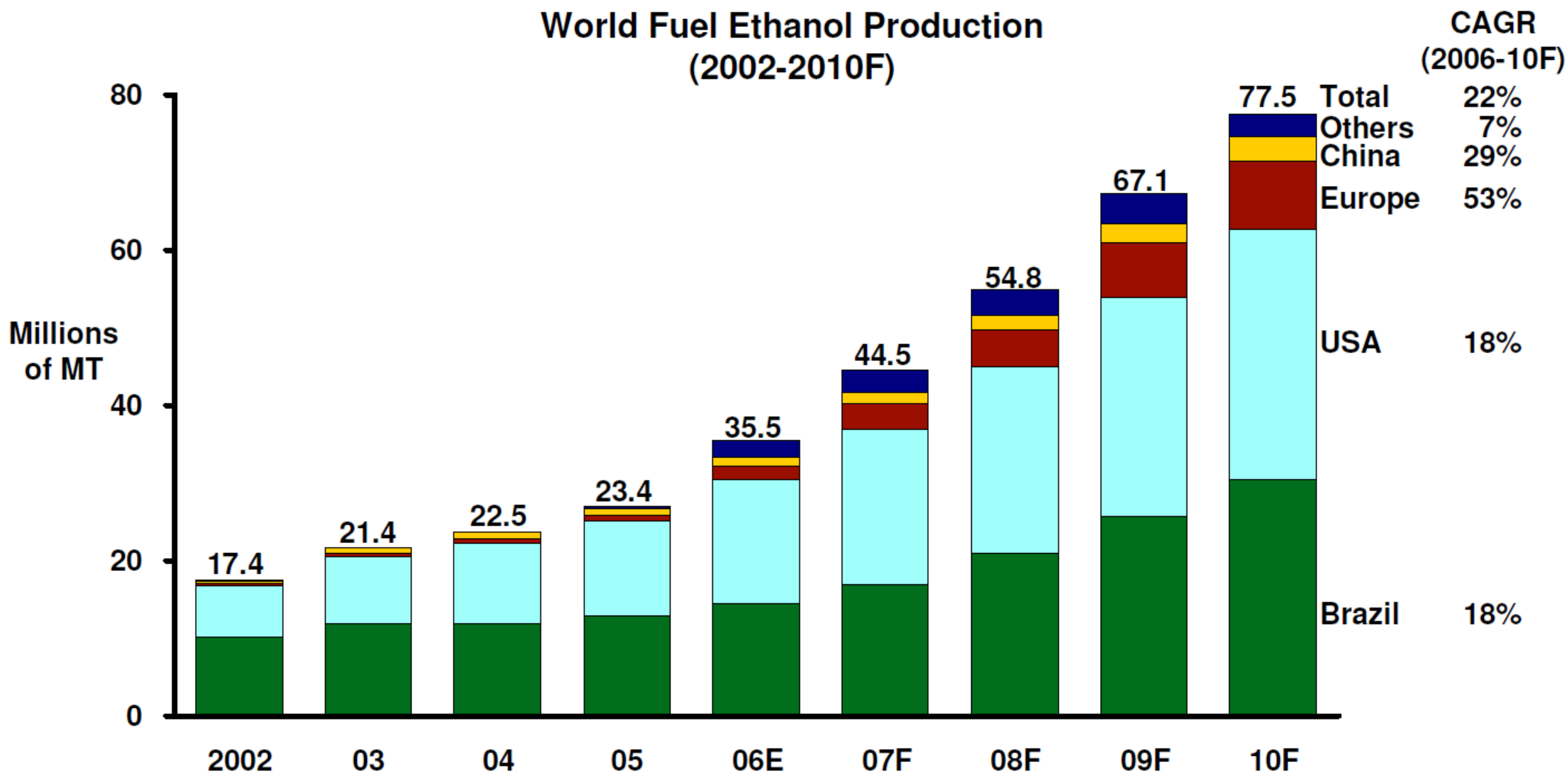


Europe

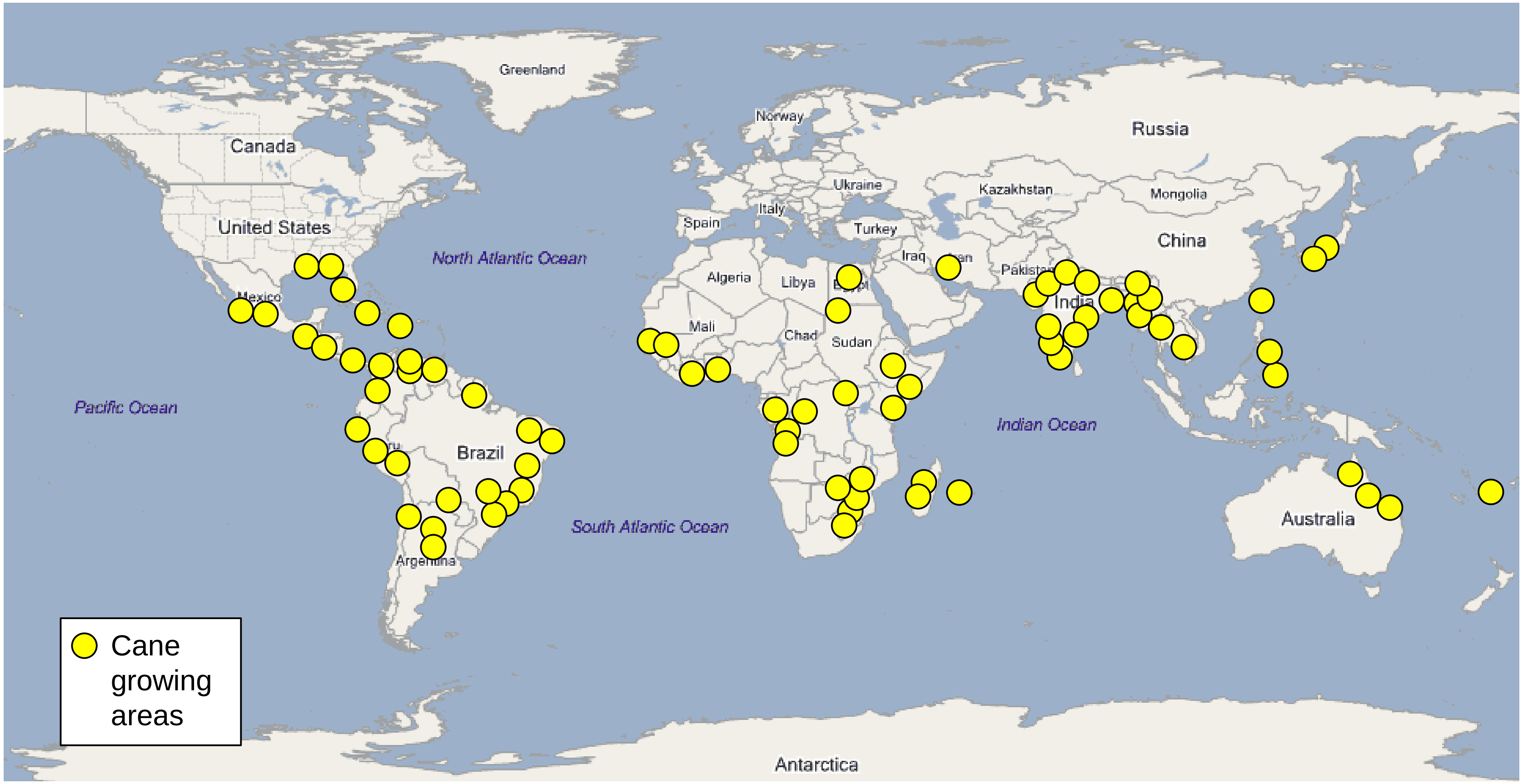
Ethanol production 0.7 billion liters
For potable ethanol: 4.2 billion liters
Recent directive from the EU Com. is 20% alternative sub. in 2020 on biofuels (mix of biodiesel and bioethanol)

- 2% in 2005, 6% in 2010, 8% in 2020
- estimated bioethanol (2014) from corn based sources: 3.5 billion liters.

World Fuel Ethanol Production (2002-2010).



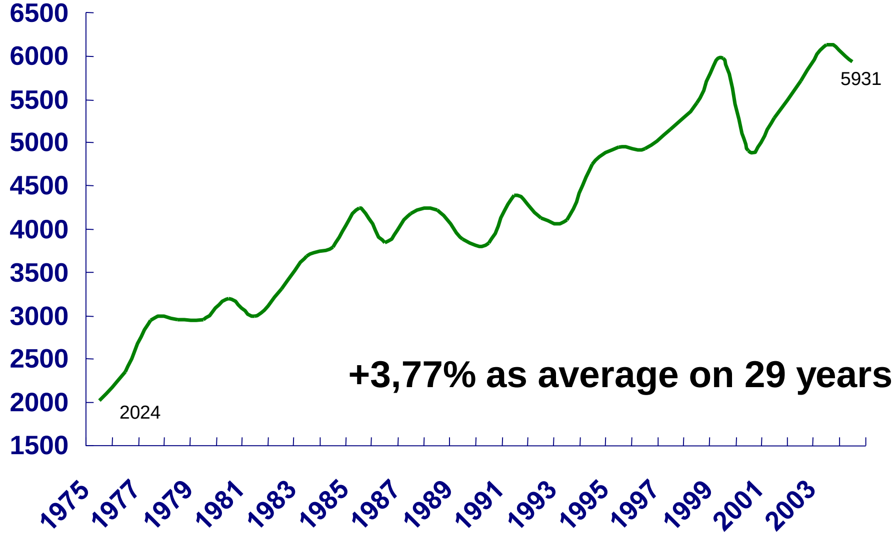
World Map of Sugar Cane.



Brazil Sugar-cane/Ethanol Learning Curve.

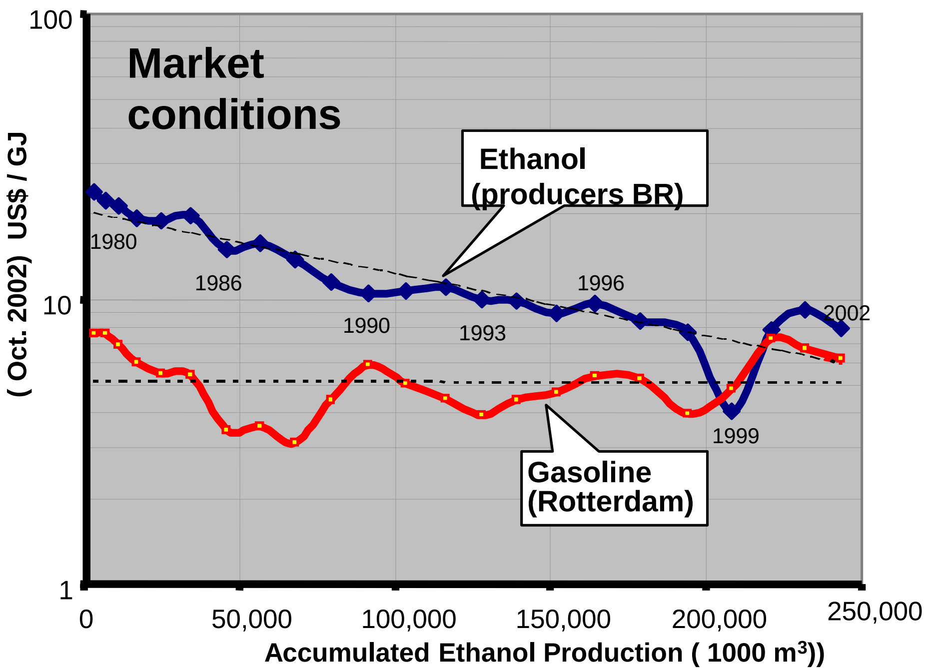
Liters of ethanol produced per hectare since 1975 to 2004.

(in liters of dry alcohol equivalent per ha)



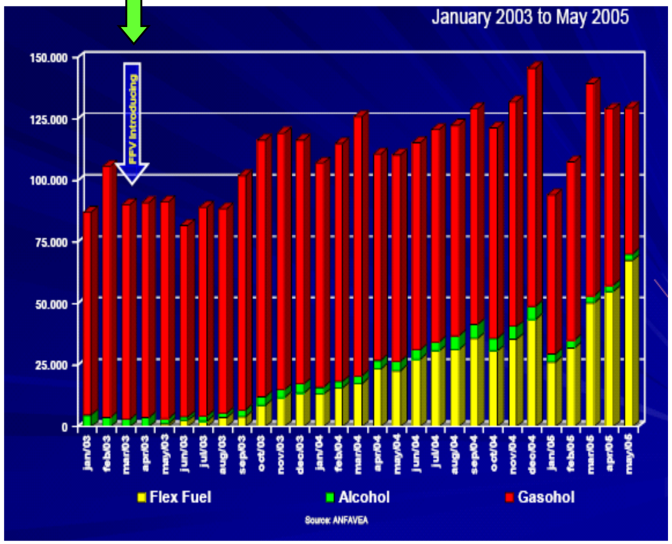
Fonte: Detagro

Price ($) per GJ

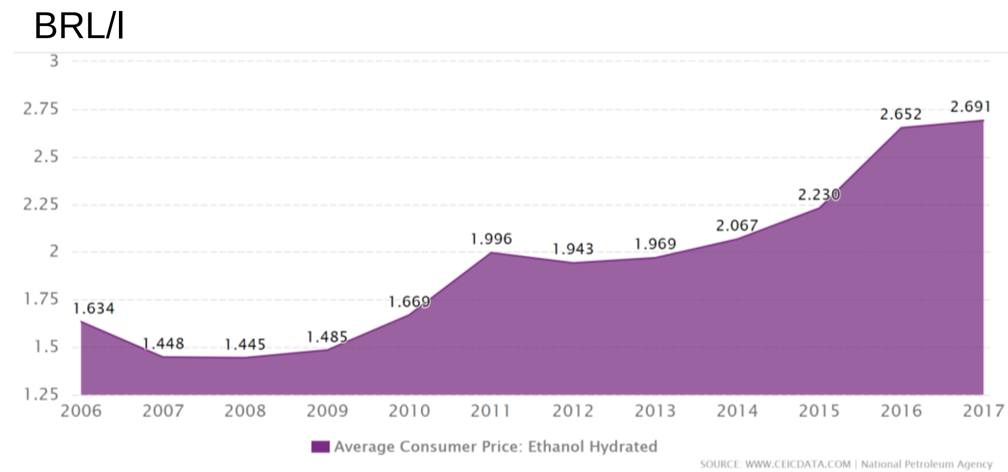


Bioethanol in Brazil.

Introduction of **FFV Technology**



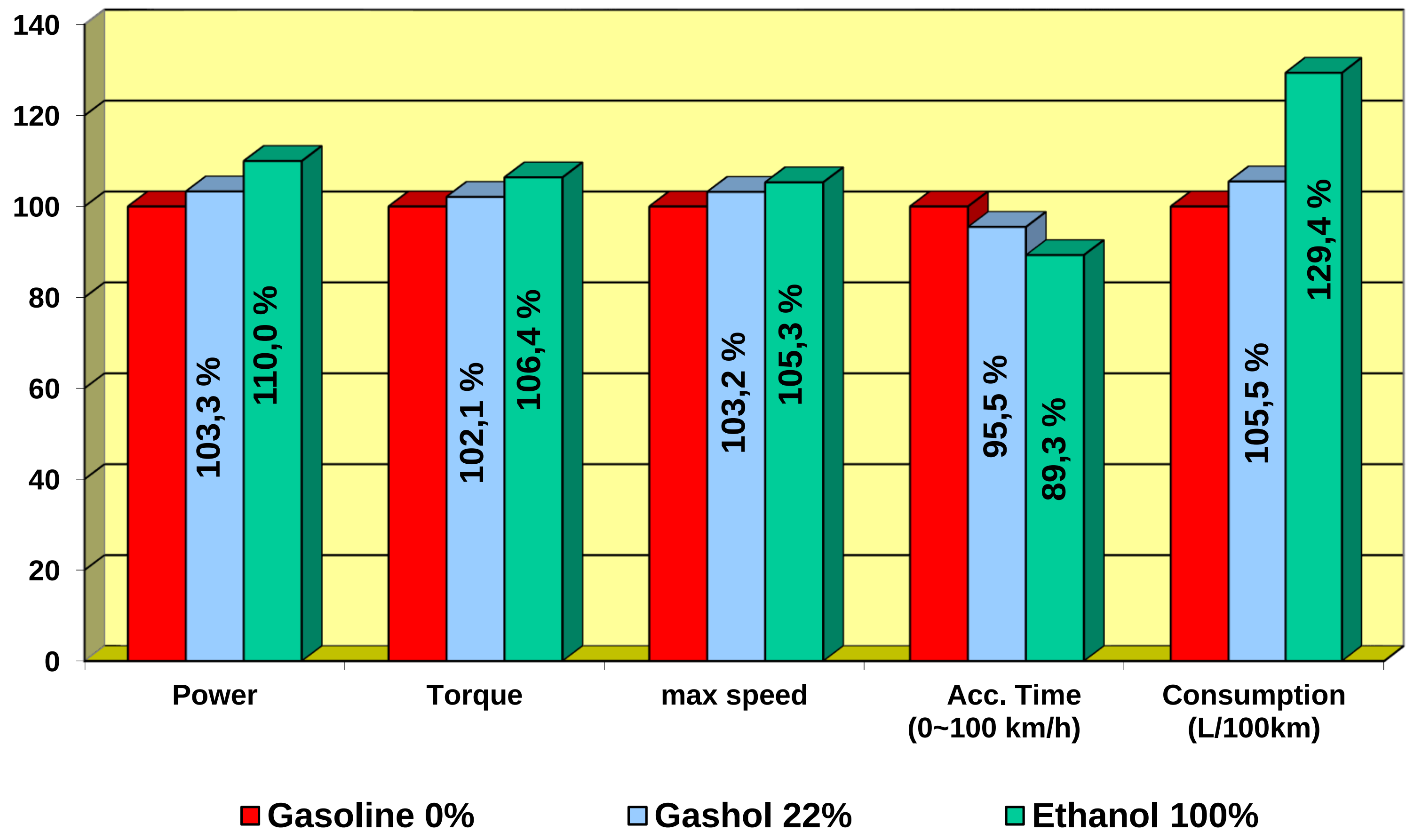
Consumer price



Brazilian Fuel Ethanol Statistics
(*in billion liters)

	2010	2011	2012	2013	2014
Production*	24.52	20.21	20.74	23.72	25.91
Imports*	0.074	1.1	0.055	0.2	0.24
Exports*	0.56	1.08	2.5	2.8	3
Consuption*	22.16	19.59	18.59	21.53	23.68
Nameplate Capacity*	41.3	42.8	41.6	40.7	40.7
Number of Refineries	430	418	408	399	399

Relative Performance of Ethanol Engines.



Potential Ethanol Yields from Some Raw Materials Based on Starch or Cellulose.

Feedstock	Yield ($L \cdot ton^{-1}$)
Apple	61
Barley	330
Buckwheat	348
Cellulose	259
Corn	355-370
Oats	265
Potato	96
Sugar beet	88
Sugar cane	160-187
Paper	416

Feedstock	Yield ($L \cdot ton^{-1}$)
Wheat	355
Green waste	176
Paper mill waste	204.4-309
Wood / furnishing	173
Paper waste	252
Herb Straw	229
Wheat straw	227
Forestry residues	250
Agricultural wastes	189
Urban solid waste	68

Composition of Waste Paper and Municipal Solid Waste (% Dry Basis).

Substrate	Cellulose %	Hemi-cellulose %	Lignin %
Newspaper	59.6	18.5	18.8
Cardboard	60.0	14.1	11.3
Regular newspaper	69.3	10.4	14.4
Office	80.3	10.4	0.9
Municipal Solid Waste	33.0	9.0	17.0

Drivers for Global Fuel Ethanol Development.

Global Fuel Ethanol Drivers

Environmental Drivers

- A sustainable and renewable source of Energy
- Reduce Greenhouse gas emission, reduce global Warming
  - ✓ CO_2, CO, NO_X
  - ✓ Total reduction approximately 30% of overall pollutants
- Replace MTBE as octane booster

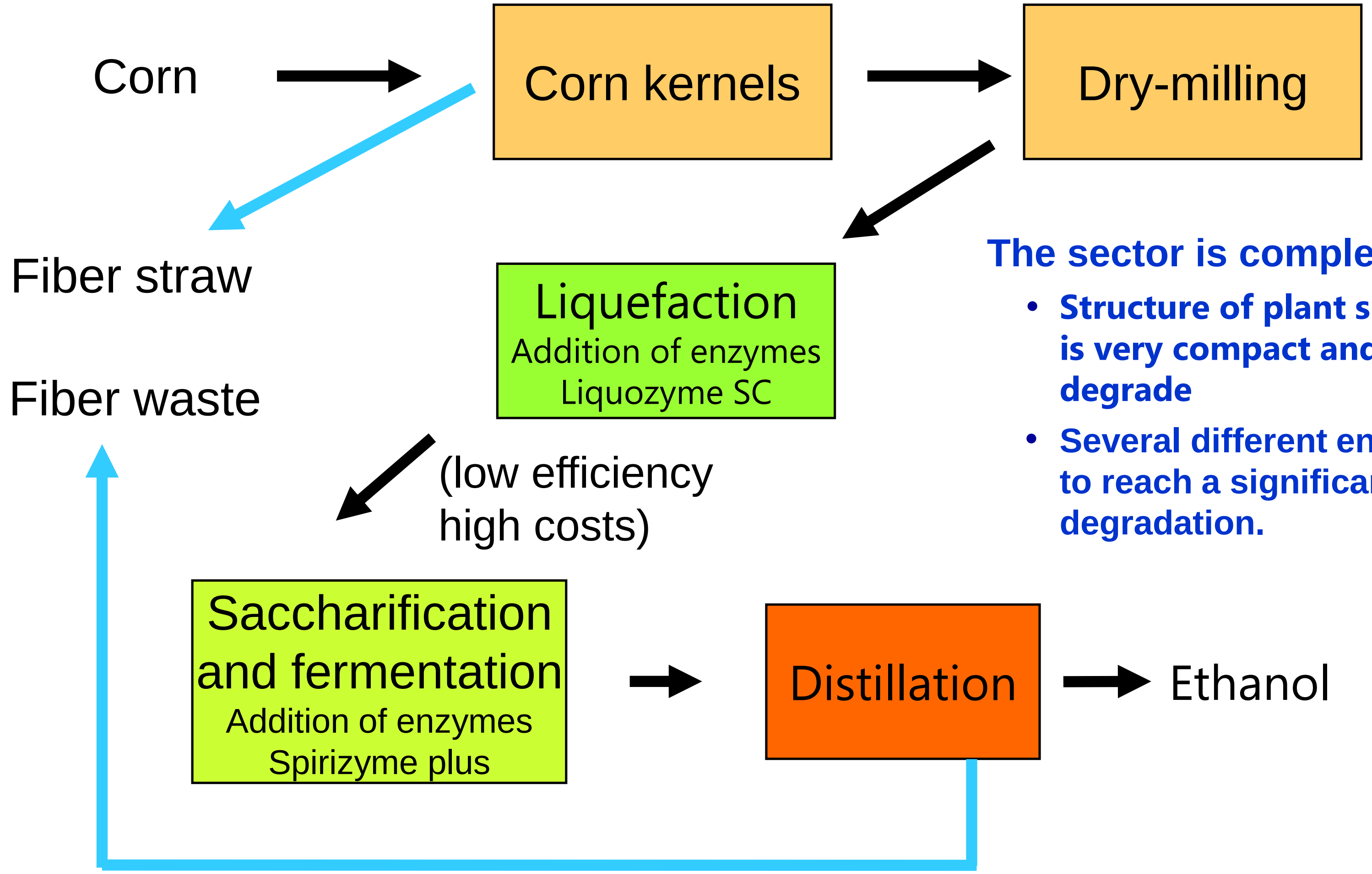
Economical Drivers

- Stimulate the development of agricultural areas
  - ✓ in USA ethanol industry expansion has added 155,000 new jobs and more than $32 billion to the gross output of the American economy
- Create a “new industry”
  - ❖ Value creation along the whole value chain
- High oil prices

Political Drivers

- Reduce the fossil fuel dependence and enhance energy security
- Benefit the trade balance.
- International treaties (Kyoto Protocol)
  - ✓ Impact the international goal of emission

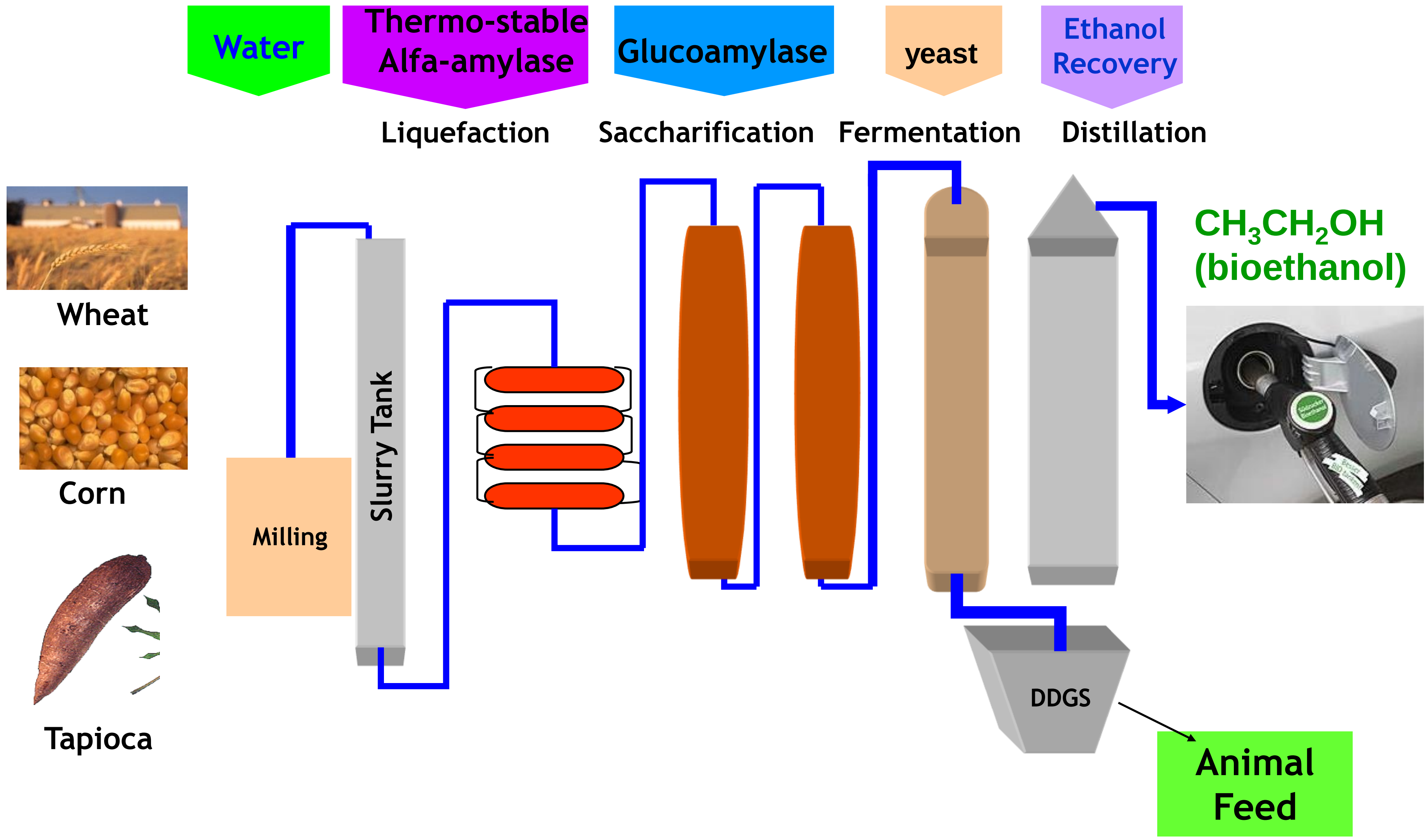
Simplified Dry-milling Process-Diagram Converting Starch to Ethanol.



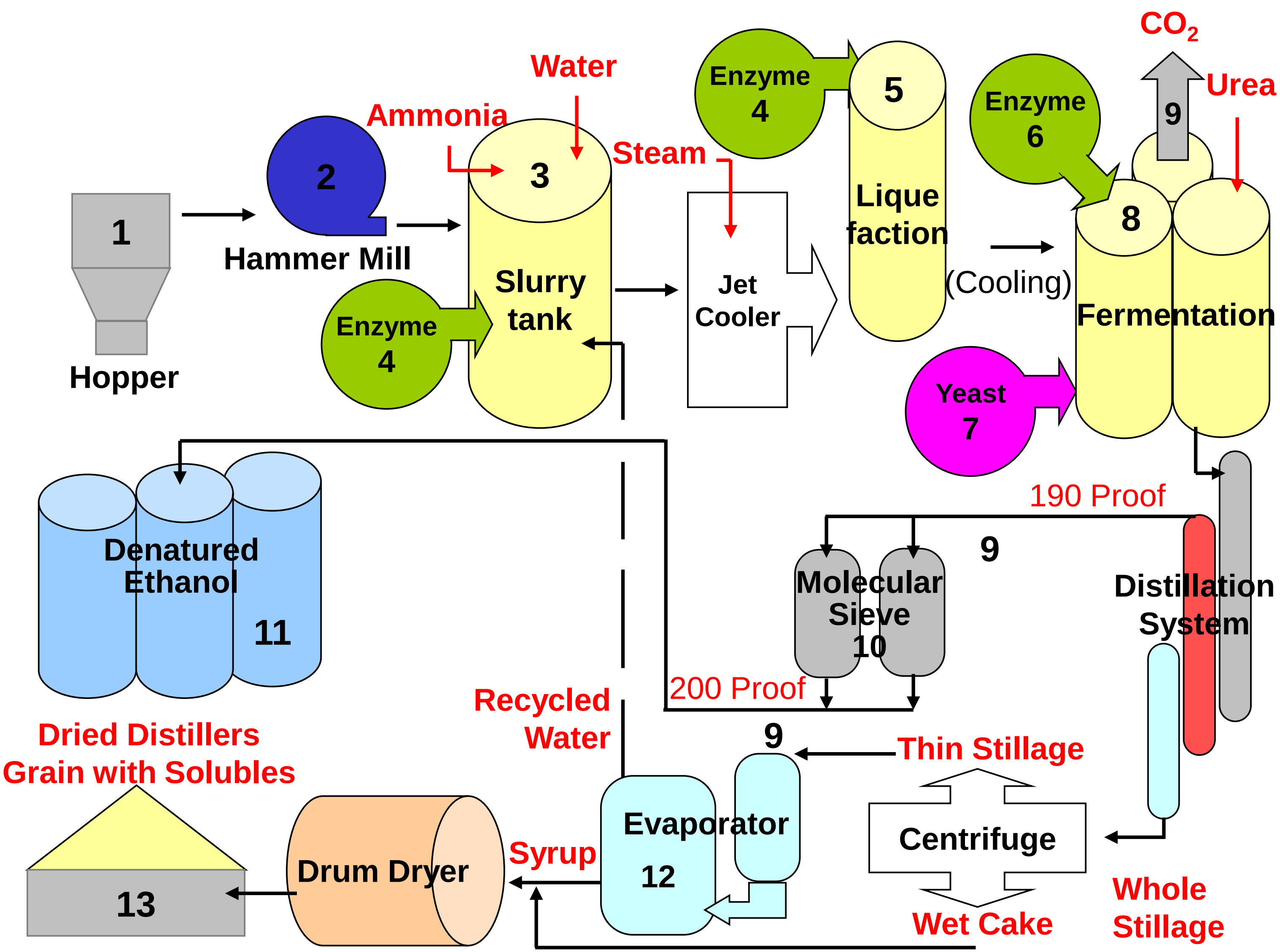
The sector is complex because:

- **Structure of plant skeletal fibers is very compact and difficult to degrade**
- **Several different enzymes need to reach a significant degradation.**

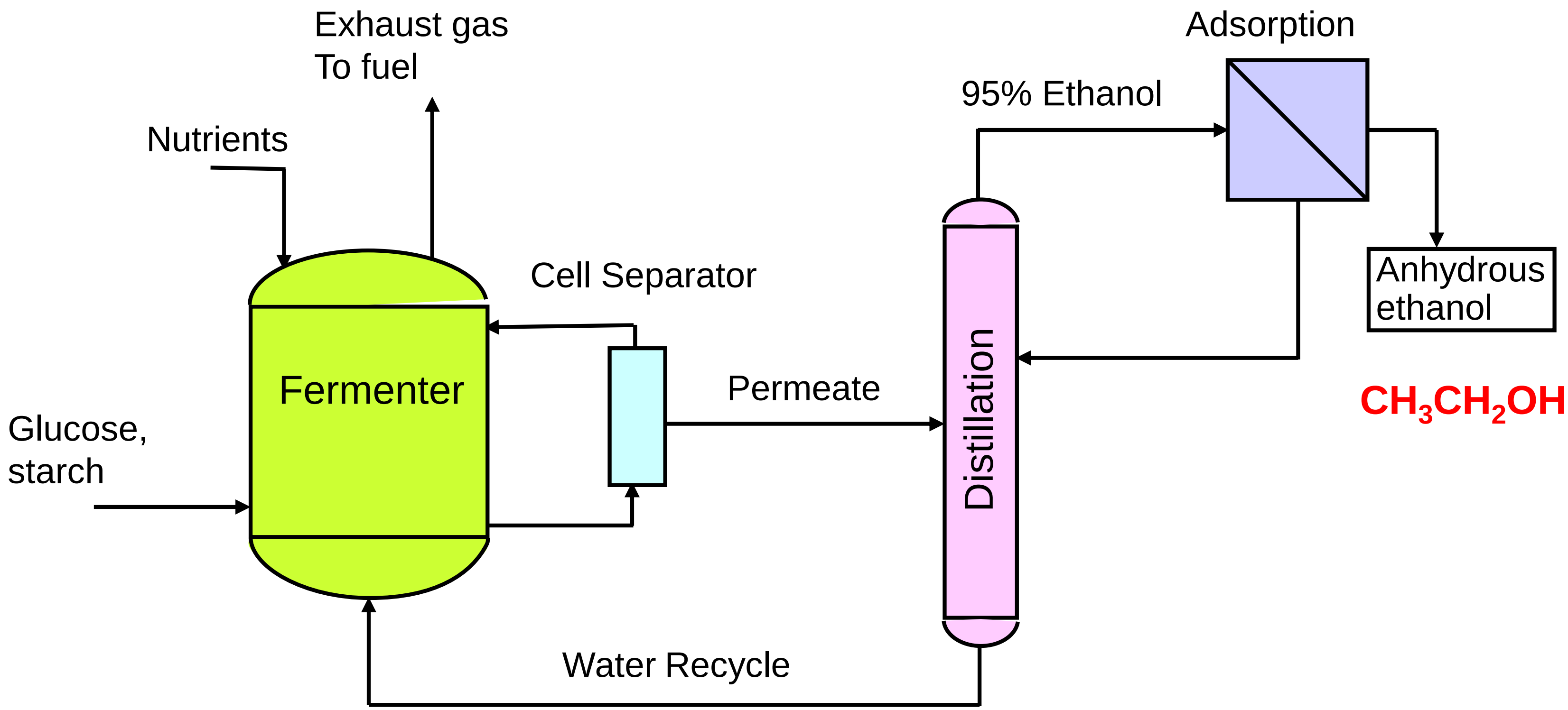
Bioethanol from Starch.



The Corn to Ethanol Process.



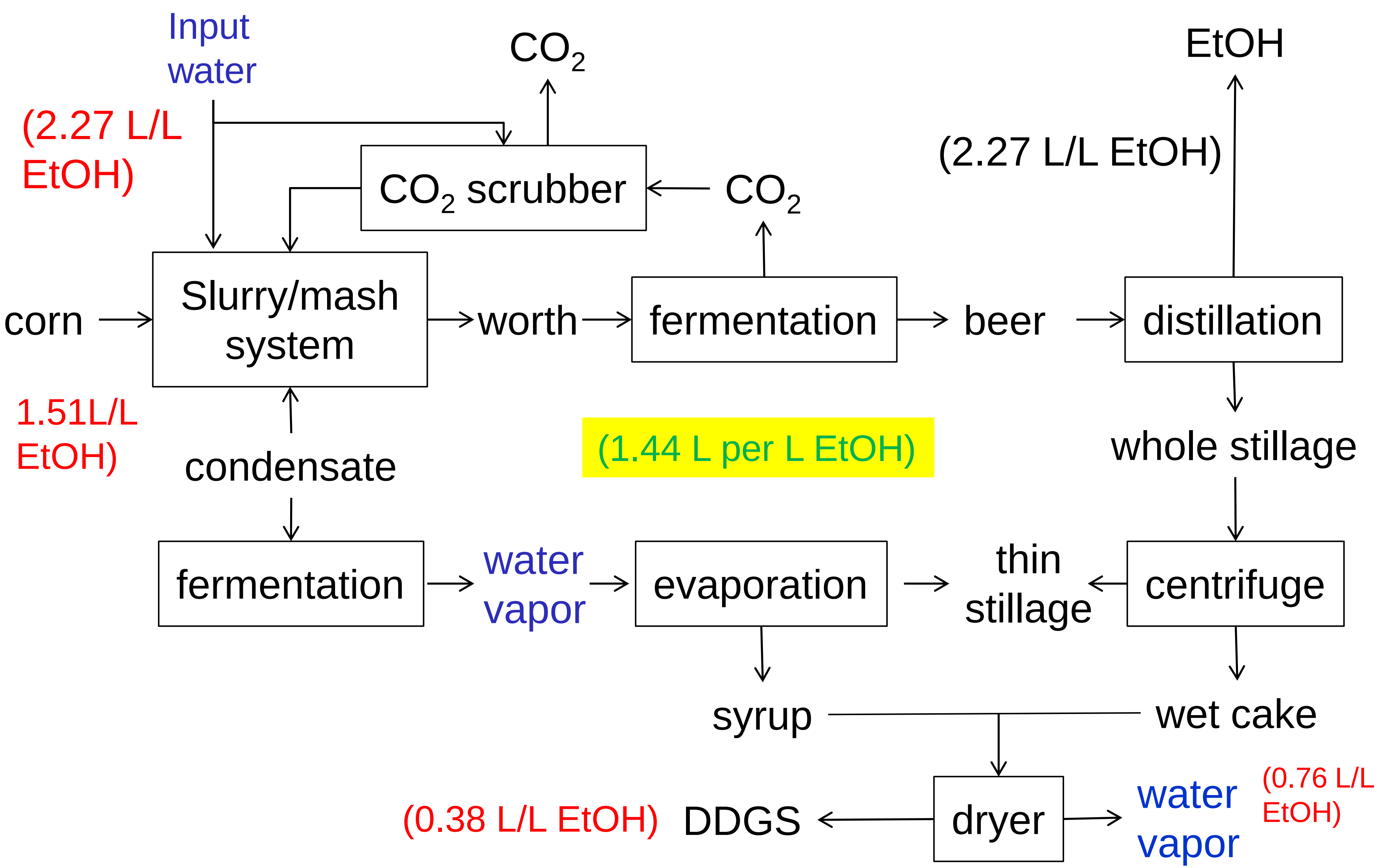
Microbial Conversion – Ethanol Fermentation.



CH_3CH_2OH

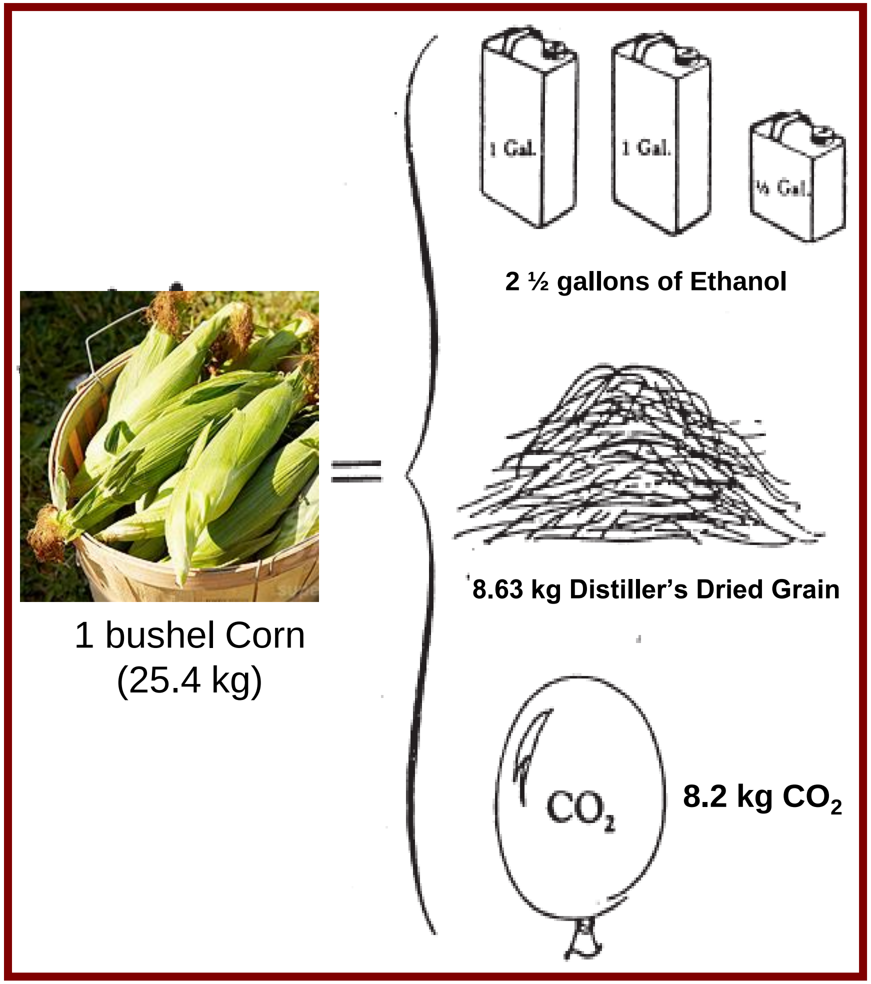
$$C_6H_{12}O_6 \rightarrow 2\ CH_3CH_2OH + 2\ CO_2$$

Process Water System and Balance.



DDGS (Distiller's Grain and Solubles).

- From a corn bushel (25.4 kg) about 8.63 kg of distiller's grains and solubles (DGS) can be obtained as by product of ethanol bioprocess.
- DDGS con be useful to increase the corn potentiality in the ethanol production because it is a good feeding for animals (10-40%).
- Its content in proteins, carbohydrates, phosphorus and fibers are higher than corn.



DDGS (Distiller's Grain).

However:

- Calcium and potassium content are lower than original seeds.
- Nitrogen and phosphor content can be higher.

It is important to take in consideration:

- The effect of seed nature on quality and nutrient profile.
- The effect of different manufacturing techniques on nutrient content.
- The effect of feeding with humid DDGS instead dry on growth, health and other characteristics of animals.

Ethanol Production Costs from Starch (per Gallon).

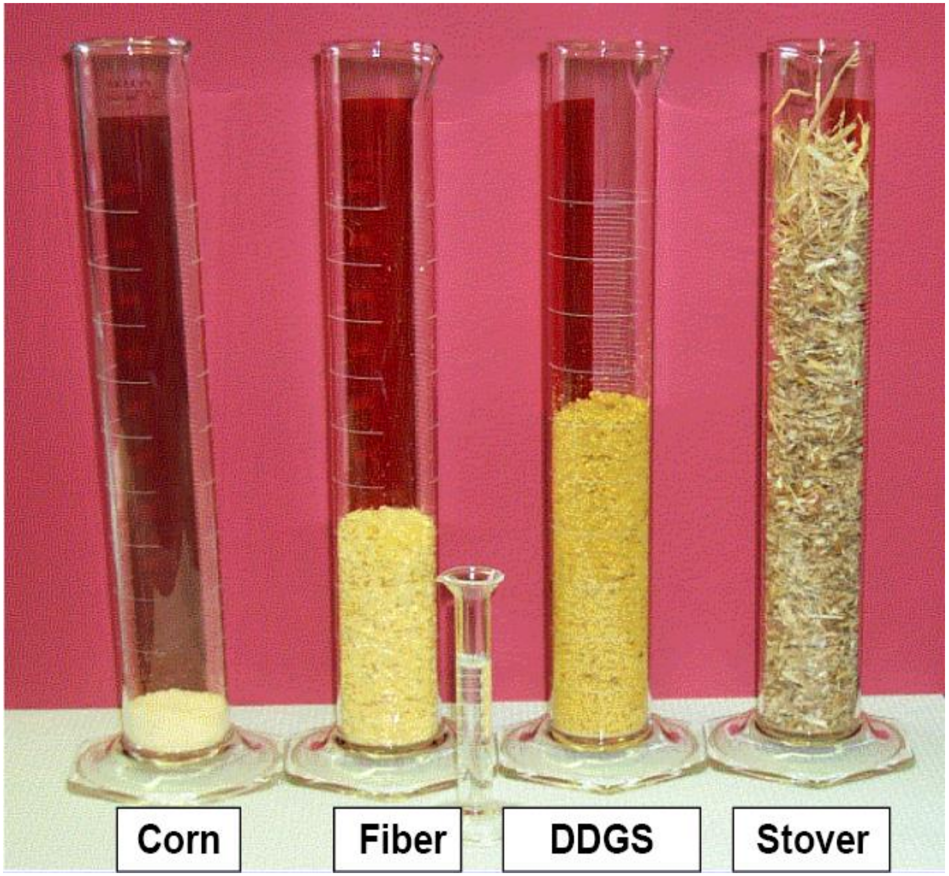
	Wet Milling	Dry Milling	Mean weight
Electricity & Fuel	$0.112	$0.131	$1.118
Labor cost, Repair and Maintenance	$0.124	$0.109	
Yeast, Enzymes, Chemicals and other	$0.114	$0.090	
Administration, Insurance and Taxes	$0.038	$0.037	
All Other Costs	$0.072	$0.051	
Total Cash Costs	$0.46	$0.42	
Combined with “NET” cost of wealth	$0.48	$0.53	$0.94
Depreciation (imp./ Eq.)	$0.10-$0.20	$0.10-$0.20	
Notice: Investment costs of ethanol production are estimated between $1.07 per gallon and $2.39 per gallon, depending on type, dimension and technology plant.			

Source: Encyclopedia of Energy (Ethanol Fuels , Charlie Wyman)

Cellulosic Ethanol - Feedstock Bulk Density.

Raw material for cellulose:

- Low density feedstock
- Costly pre-treatment
- Sophisticated enzymes
- New biocatalysts needed
- Low co-product value
- Product recovery.



Amounts of feedstock needed to produce 11,00 ml ethanol.

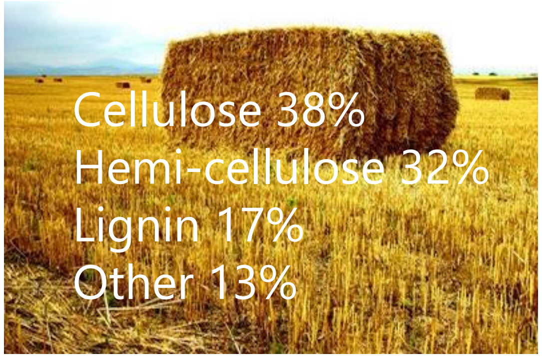
Process Design and Economics for Biochemical Conversion of Lignocellulose Biomass to Ethanol.

Dilute-Acid Pretreatment and Enzymatic Hydrolysis of Corn Stover.

Technical Report
NREL/TP-5100-47764
May 2011

Fiber Depolymerization Issues.

- Cereal fibers contain more components:
  - Cellulose which can be degraded to glucose (via dextrin)
  - Hemi-cellulose which can be degraded to a so called pentose (xylose, arabinose)
  - Lignin
- Yeasts can ferment glucose to ethanol, and more or less completely pentoses
- Productive efforts are addressed to :
  - Pre-treatments – opening of structure – different technologies (acids, enzymes, steam explosion)
  - *Degradation of Cellulose via Cellulase Enzymes*
  - Use of hemi-cellulose via *hemicellulases* genetically modified to ferment pentoses



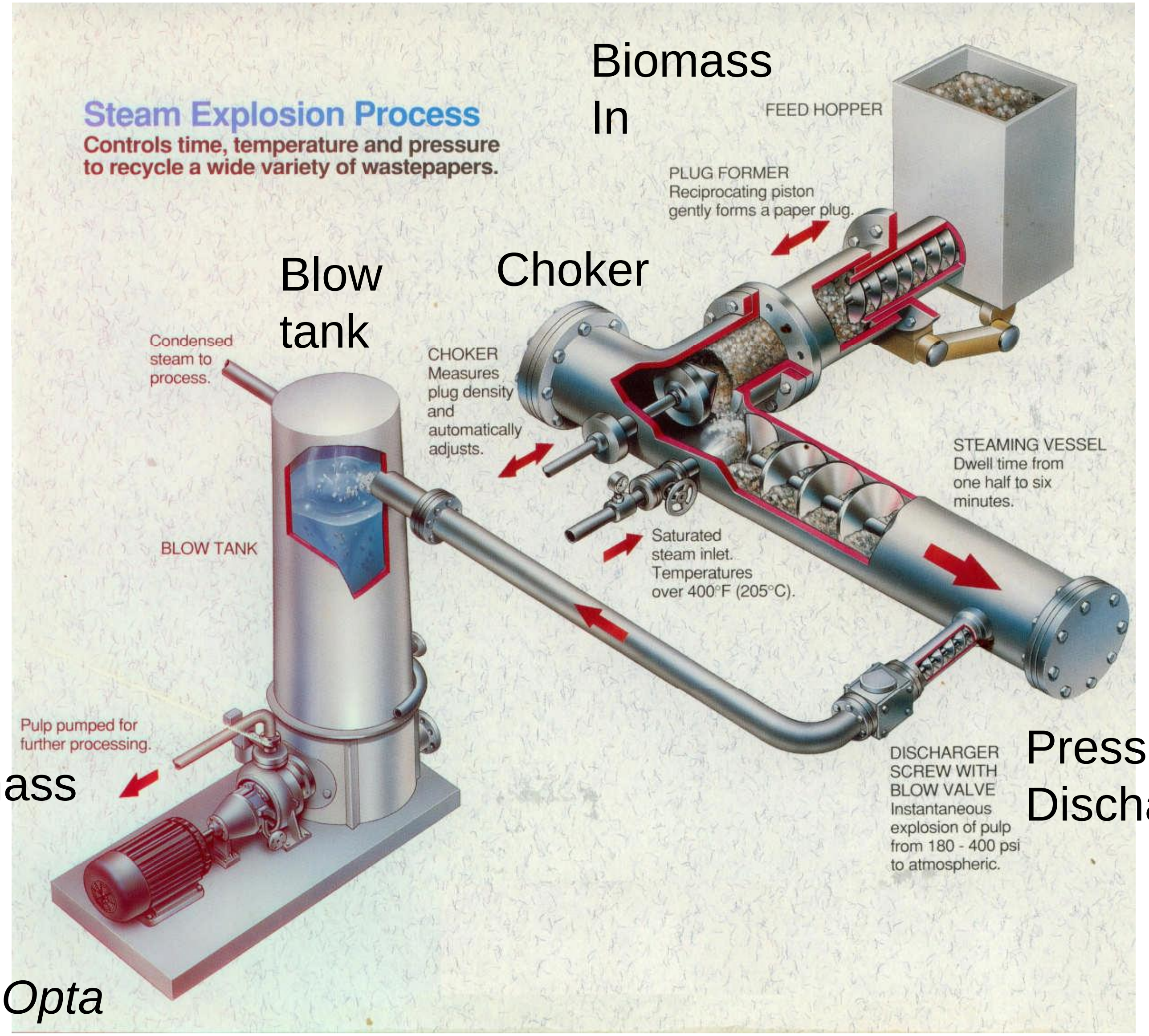
Agricultural Residues

Acid

Pretreatment	Pentoses	Inhibitors
Strong Acid	+	++
Dilute Acid	+	++
Hot water	-	+
AFEX	-	-
Alkaline peroxide	-	-
NH_3	-	+

Base

Diagram of Steam Explosion Reactor.



Biomass In

Blow tank

Choker

Reactor 0.5-6 min R.T.

Pressure Discharge

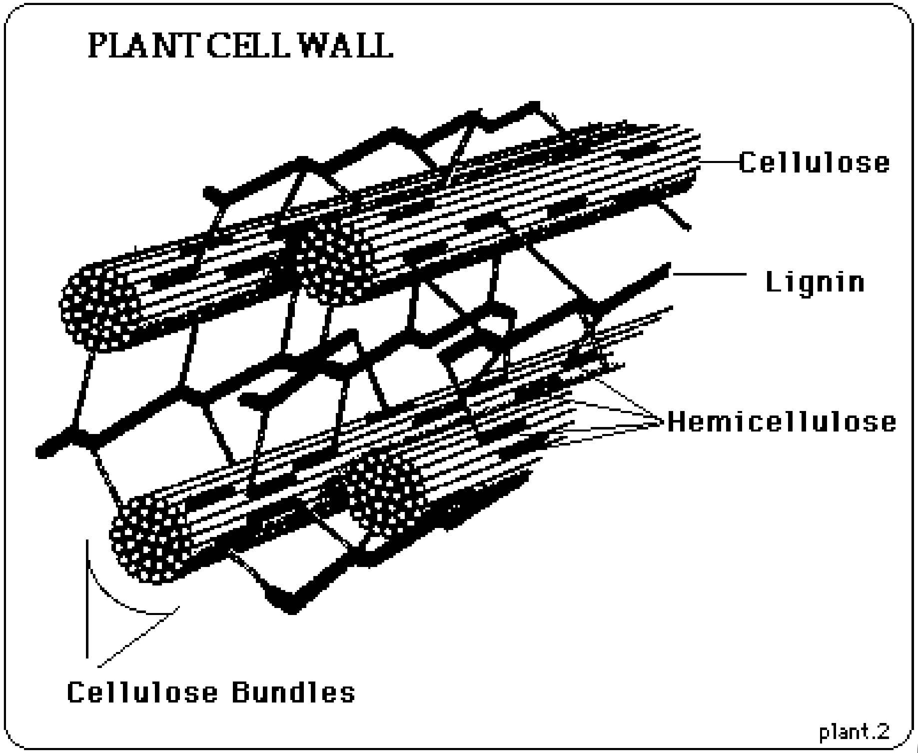
Biomass out

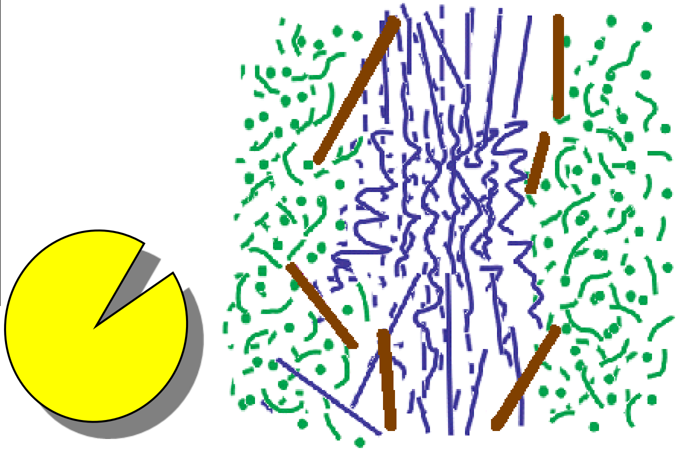
SunOpta

Pretreatment Expected Results.

Allow cellulase access to cellulose polymers by disrupting cell wall structure.

- ✓ Dissolve Hemicellulose
- ✓ Displace Lignin
- ✓ Swell Cellulose Bundles





The Biomass Saccharification Process.

Mineral acid gives good hemicellulose sugar yields and high cellulose digestibility.

H_2SO_4 usual choice because of low cost.

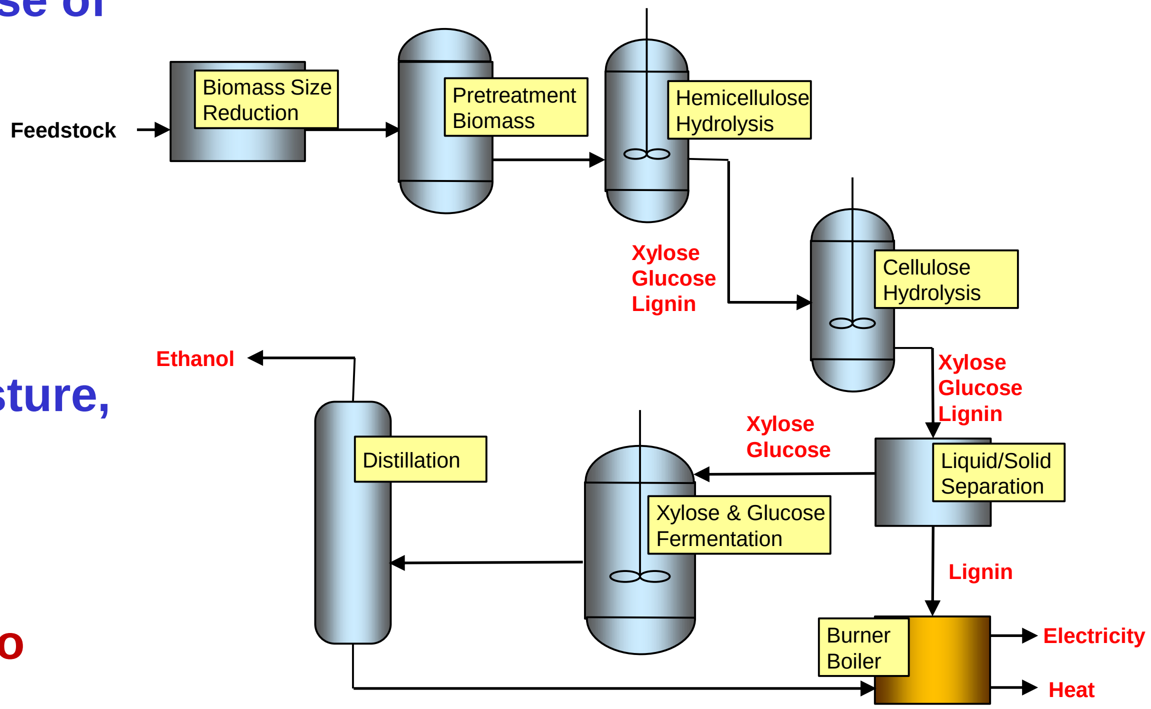
Requires downstream neutralization and conditioning.

***Typical conditions*:**

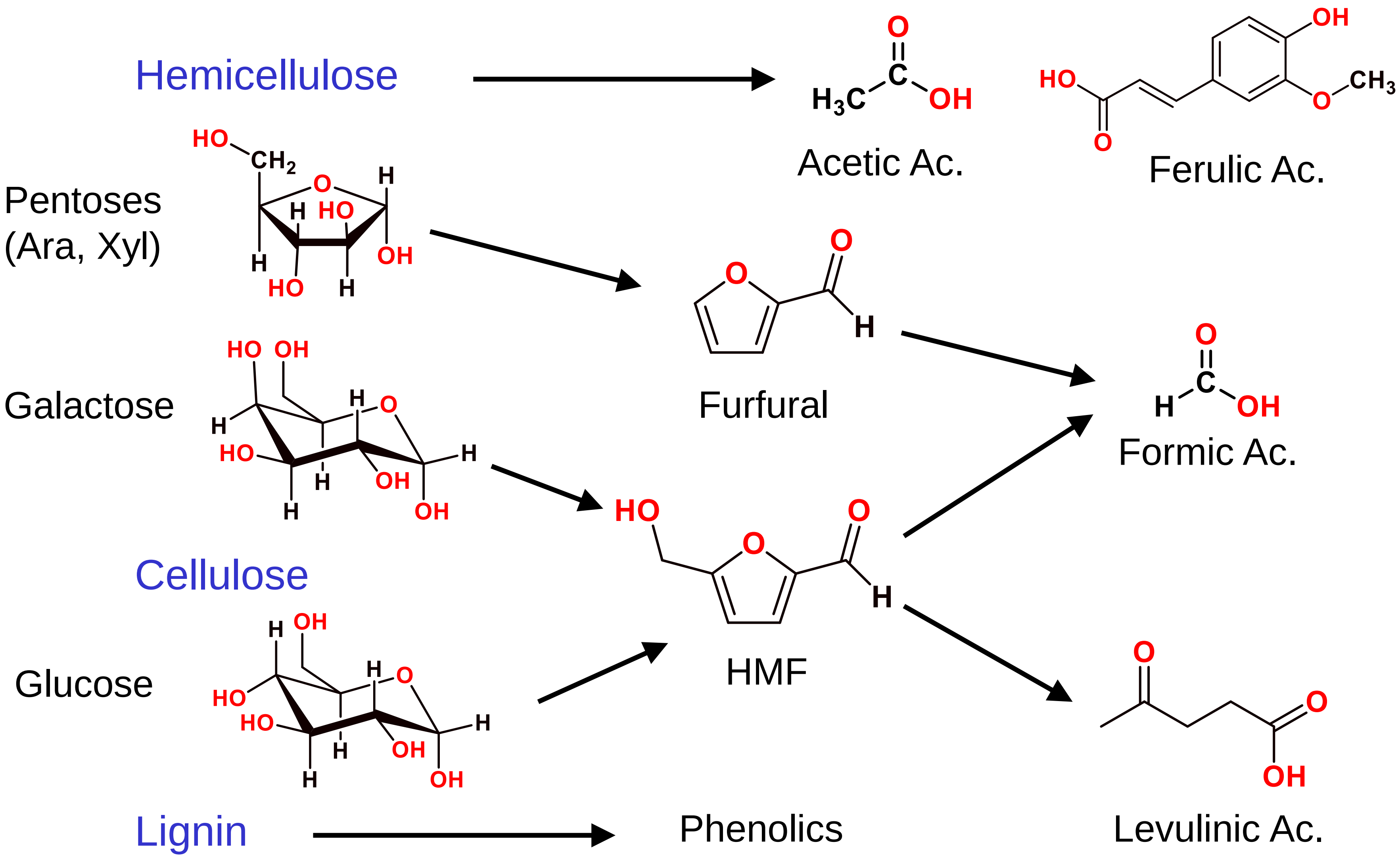
100-200°C, 50 to 95% moisture, 0-1% H_2SO_4.

Some degradation of hemicellulose sugars.

Cellulase enzymes are also used to release glucose, cellobiose, and other sugars (mainly xylose).



Inhibitors Formed During Hydrolysis.



Detoxification.

Several alternatives were proposed:

- **Chemical:**

option 1: precipitation changing the pH by $Ca(OH)_2$ and H_2SO_4:

- Step 1: pH 9-10, at 50-60 °C
- Step 2: pH 6, at 30 °C
- Step 3: filtration at 0.2 μm

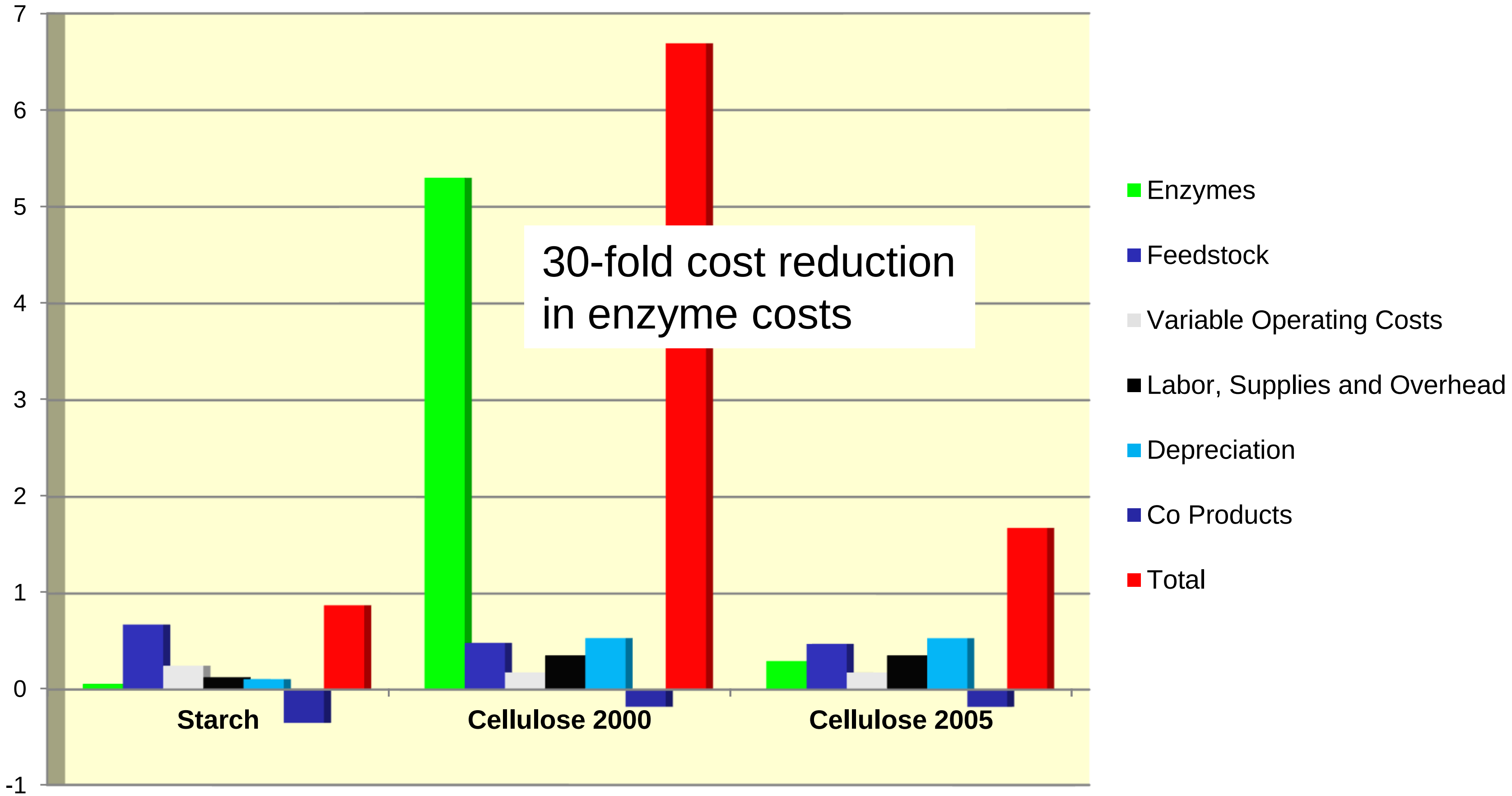
option 2: adsorption on active carbon, diatomaceous earth or ion exchange resins

- **Physical:** separation by vacuum evaporation inhibitors (acetic acid, furfural)

- **Enzymatic**: laccase and peroxidase enzymes, active on phenolic compounds

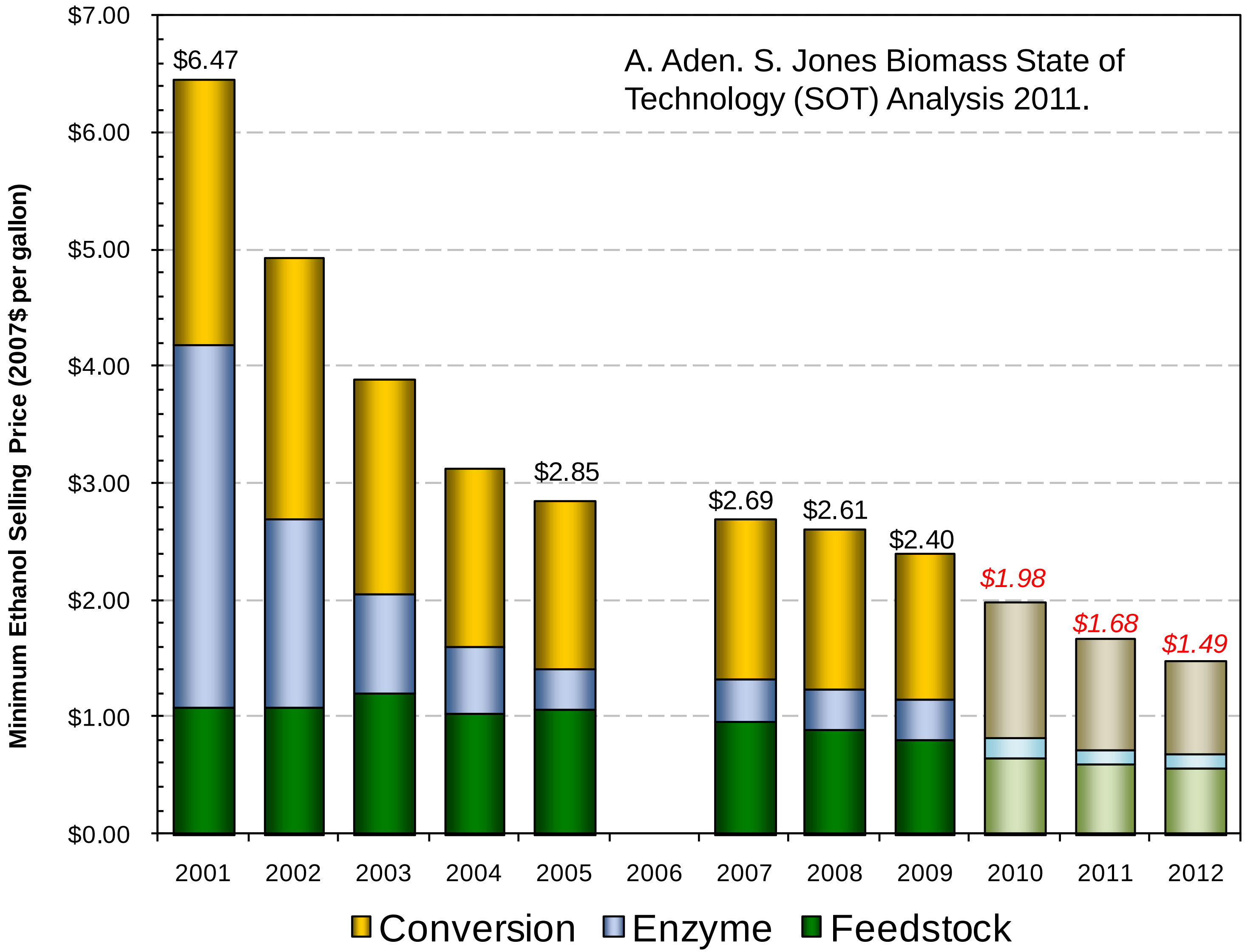
- **Microbiological**: degradation by *Saccharomyces cerevisiae*, quite active toward acetic acid..

Cost Comparison: Grain vs. Biomass in USD per gallon Ethanol.



Currently the cost has been reduced twelve-fold to approx. $0.50 per gallon. However, combining the recent enzyme improvement with new pretreatment technologies, the cost is expected to be further reduced.

Lignocellulose Bioethanol Process: Demonstrated Cost Reductions from R&D.



Corn Grain vs. Biomass: Why the Difference in Enzyme Cost?

Corn

72% Starch
10% Cellulose/Hemicellulose
9% Protein
4% Oil
4% Other

Yield = 114 gallons ethanol per dry ton = 18 lbs. corn grain per gallon
Enzyme usage ~ **0.26 g protein·L^{-1}**

Corn stover

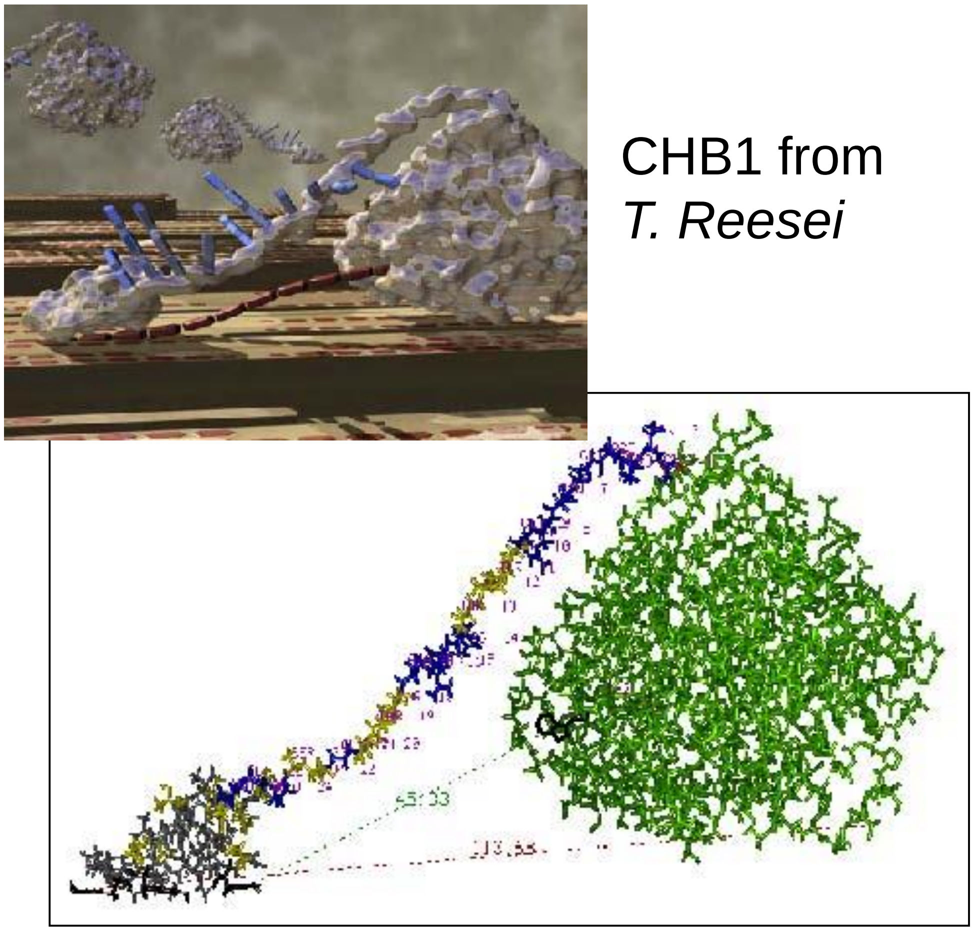
38% Cellulose
32% Hemicellulose
17% Lignin
13% Other

C5 sugars

Acid pretreated corn stover
56% Cellulose
5% Hemicellulose
28% Lignin
13% Other

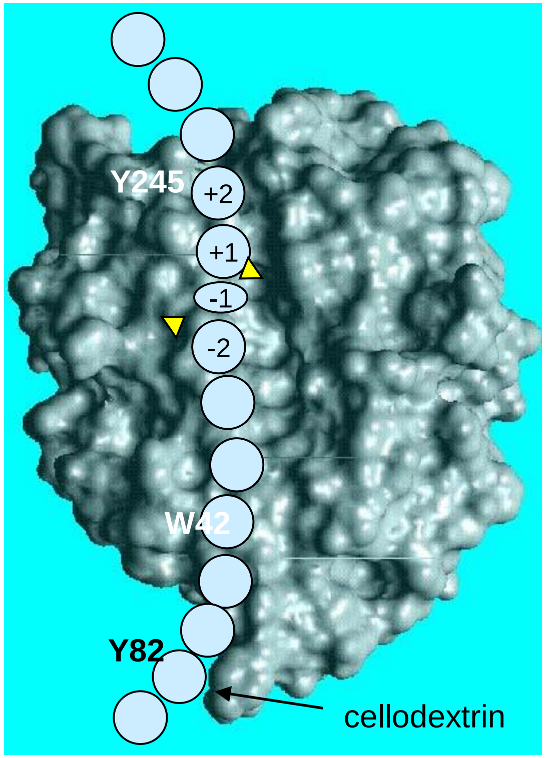
Yield = 72 gallons ethanol/dry ton = 30 lbs. corn stover per gallon
Enzyme **usage ~26 g protein·L^{-1}**

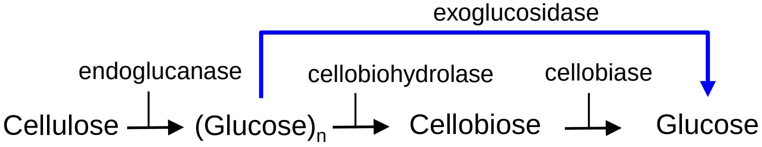
Cellulase - cellulose surface interaction



CHB1 from
T. Reesei

E1 from *A. Cellulotiticus*

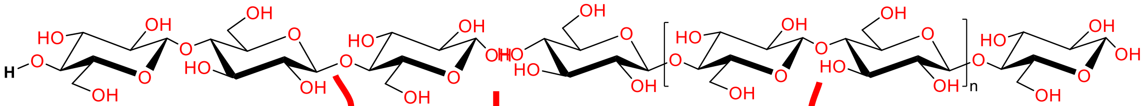




Cellulose Hydrolysis by Cellulase Enzymes.

Cellulases

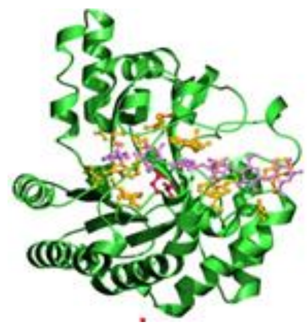
Exo *Endo* *Exo*



Cellobiohydrolase

Acting from non reducing end

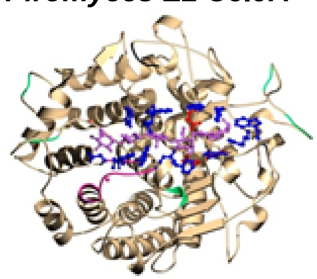
***E. g. Piromyces* sp. E2 Cel6A**



Endoglucanase

Acting from the middle

***E. g. Piromyces* E2 Cel9A**

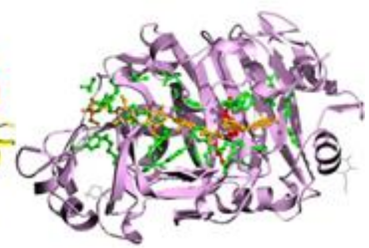


Cellobiohydrolase

Acting from reducing end

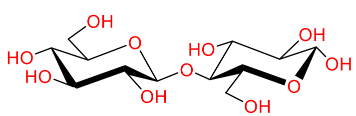
***E. g. Phanerochaete* Cel7s**

Pc_Cel7A

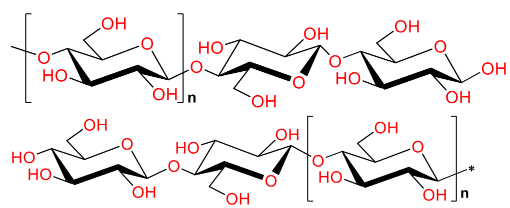


Pc_Cel7D

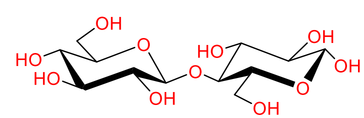
Product - cellobiose



Product – oligosaccharides of different sizes



Product - cellobiose



Complex Mixture of Enzymes Needed to Degrade Arabinoxylan.

Xylanase

..Xß1-4Xß1-4Xß1-4Xß1-4Xß1-4Xß1-4Xß1-4X…..

I 3 I α I Af I 5 I Fer I Fer-O-Fer- I 5I Af I α I 3 I

I 3 I Af

Arabinofuranosidase

Feruloyl esterase

4Xß1-4X

2X

ß-xilosidase

α-Glucuronidase

Lignin

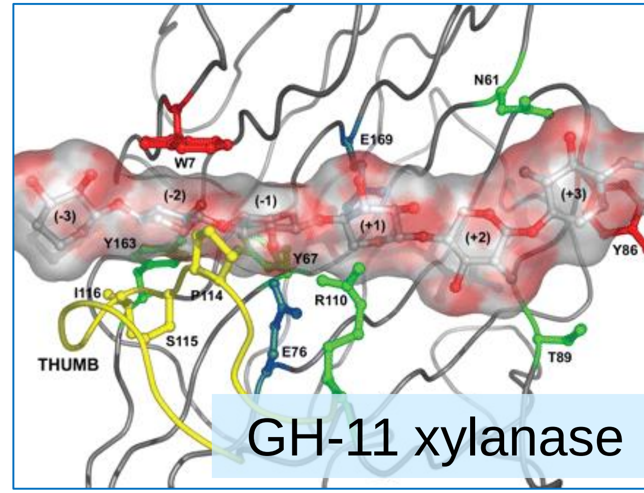
mGu I 1 I 2 I

Af I 3 I

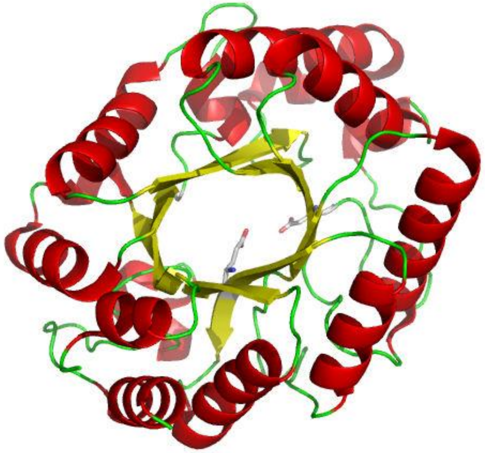
Acetylxylan esterase

……Xß1-4Xß1-4Xß1-4Xß1-4Xß1-4Xß1-4Xß1-4X…

Selinger et al., 1996



GH-11 xylanase



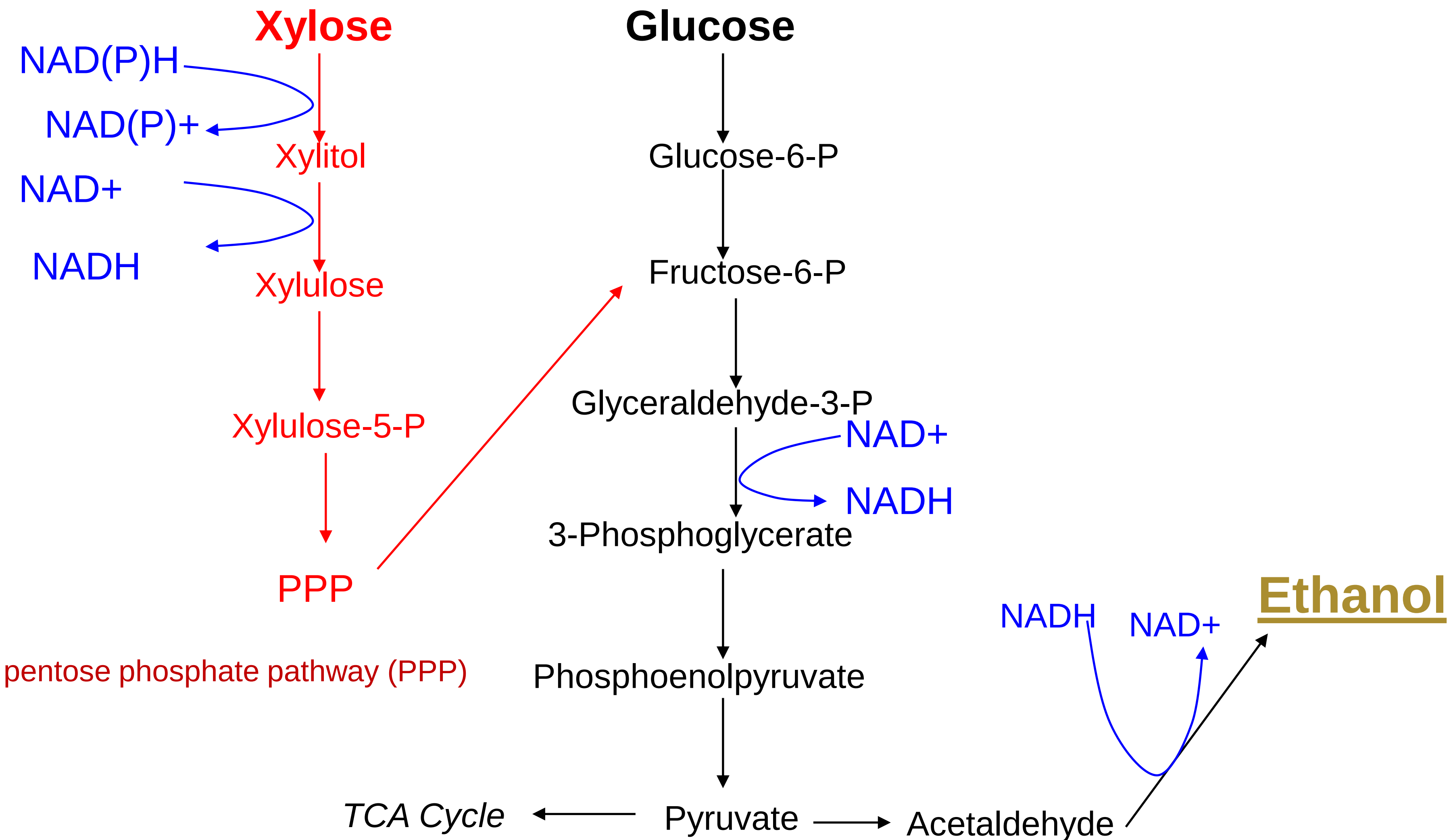
Enzymatic Depolymerization.

1. Cellulose
   - Cellulases
   - Optimize with the Biocatalyst
2. Xylose
   - Xylanases, Xylosidases
3. Glucuronoxylan
   - α-Glucuronidase; Xylosidase
4. Acid Hydrolysis

Biocatalyst

1. High Growth Rate
2. High Cell Yield
3. High Product Yield
   - Volumetric Productivity
   - Specific Productivity
4. Purity of the Product
   - Optical
   - Chemical
5. Minimal Growth Requirements
6. Metabolic Versatility
7. Co-utilization of Various Sugars
8. Tolerate High Sugar Concentration
9. Resistance to Inhibitors
10. Insensitive to Product Inhibition
11. High-value Co-products
12. Amenable to Genetic Engineering
13. Robust
14. Cellulases
15. Xylan degradation

Yeast Metabolism: Pentose Fermentation.



Ho et al

Activity Comparison for Xylanases of Various Sources.

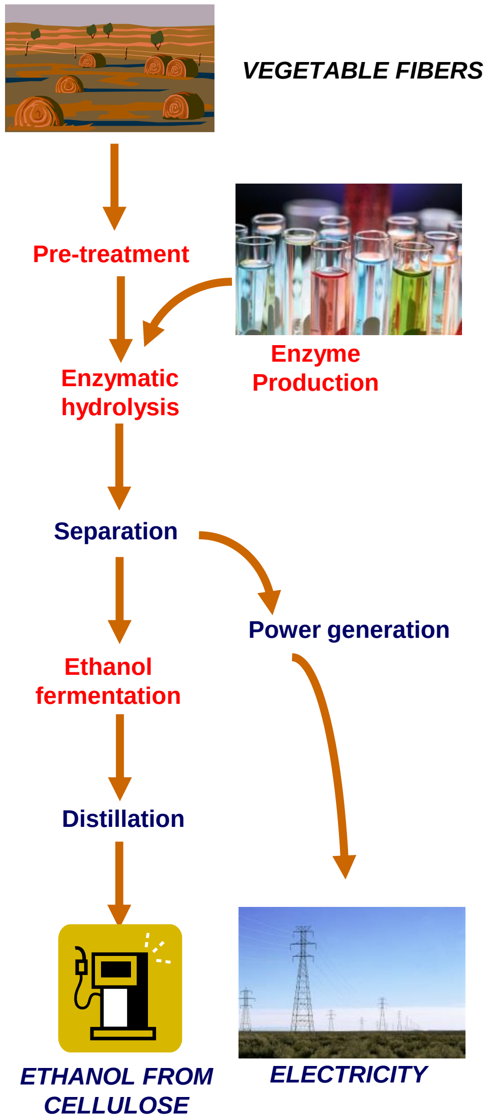
Organism	Specific Activity* (mmol/min/mg)	Reference
Orpinomices XynA	4500	X. Li 2005
Bacillus sp. strain T-6	288	Khasin et al. 1993
Clostridium sp. Strain SAIV	36	Muity, Chandra 1992
Fibrobacter succinogenes S85	34	Muity, Forsberg 1992
Trichoderma longibrachiatum	130	Roger, Nakas 1991
Aspergillus syndowii	204	Ghoh, Nanda 1994
Aspergillus ficheri	588	Raj, Chandra 1996

* All specific activities were compared on purified enzyme basis. The temperatures for assaying the enzymes were in the range of 40 to 50°C.

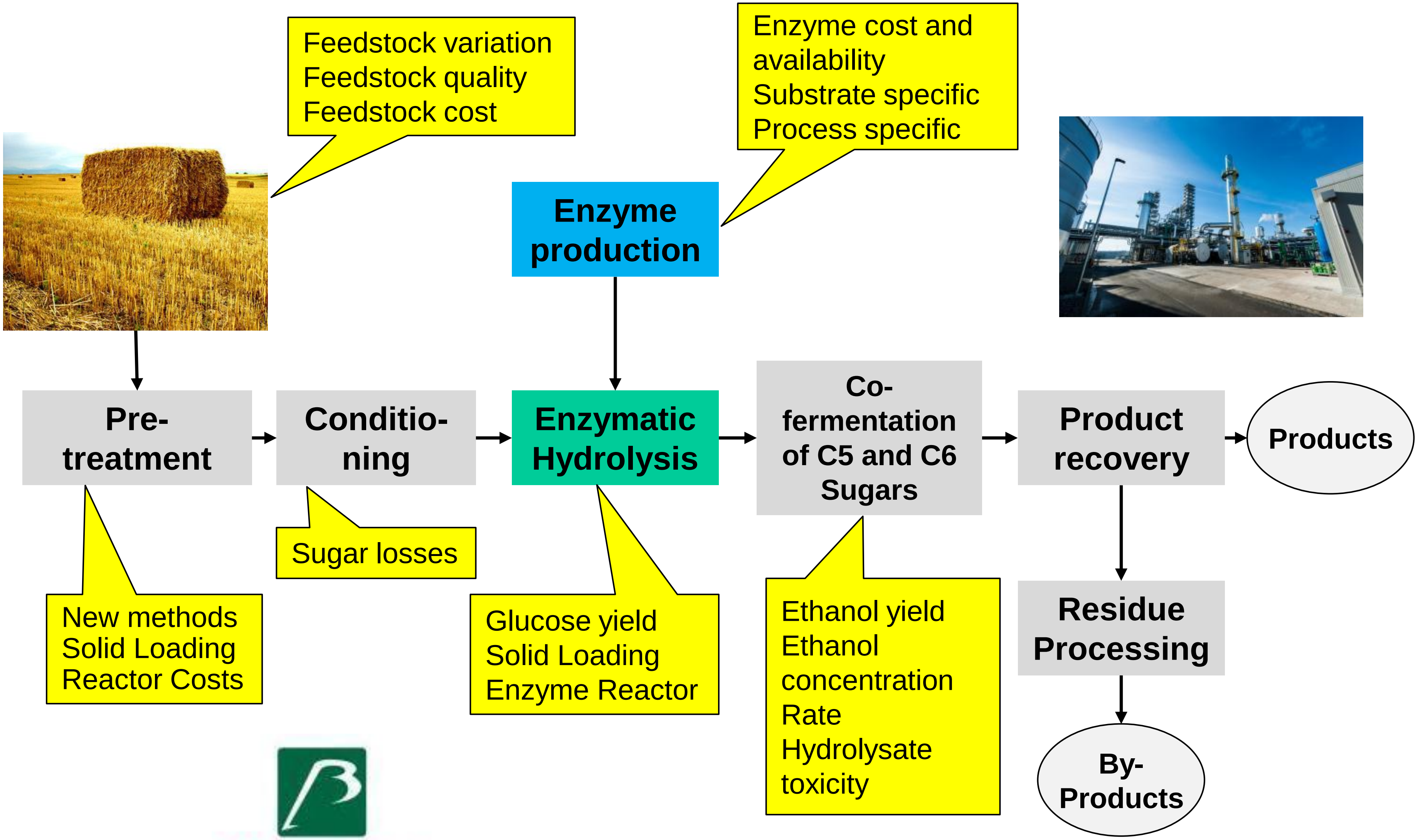
State of Cellulose Fuel.

- Technologies for converting Cellulose are presently widely investigated on industrial scale and are economically available.
  - For long time, the main variable for industry was the cost to produce most efficient enzymes to convert cellulose into alcohol.
- Two other significant variables for a valued industry of biofuels from cellulose are:
  - availability of feedstock (i.e. tonnage composition)
  - production logistics, harvesting, storage and transport of cellulose biomasses.

In 2012 the Italian firm Biochemtex started the first plant in EU of bioethanol from lignocellulosic feedstock at 40000 ton·year^{-1}.

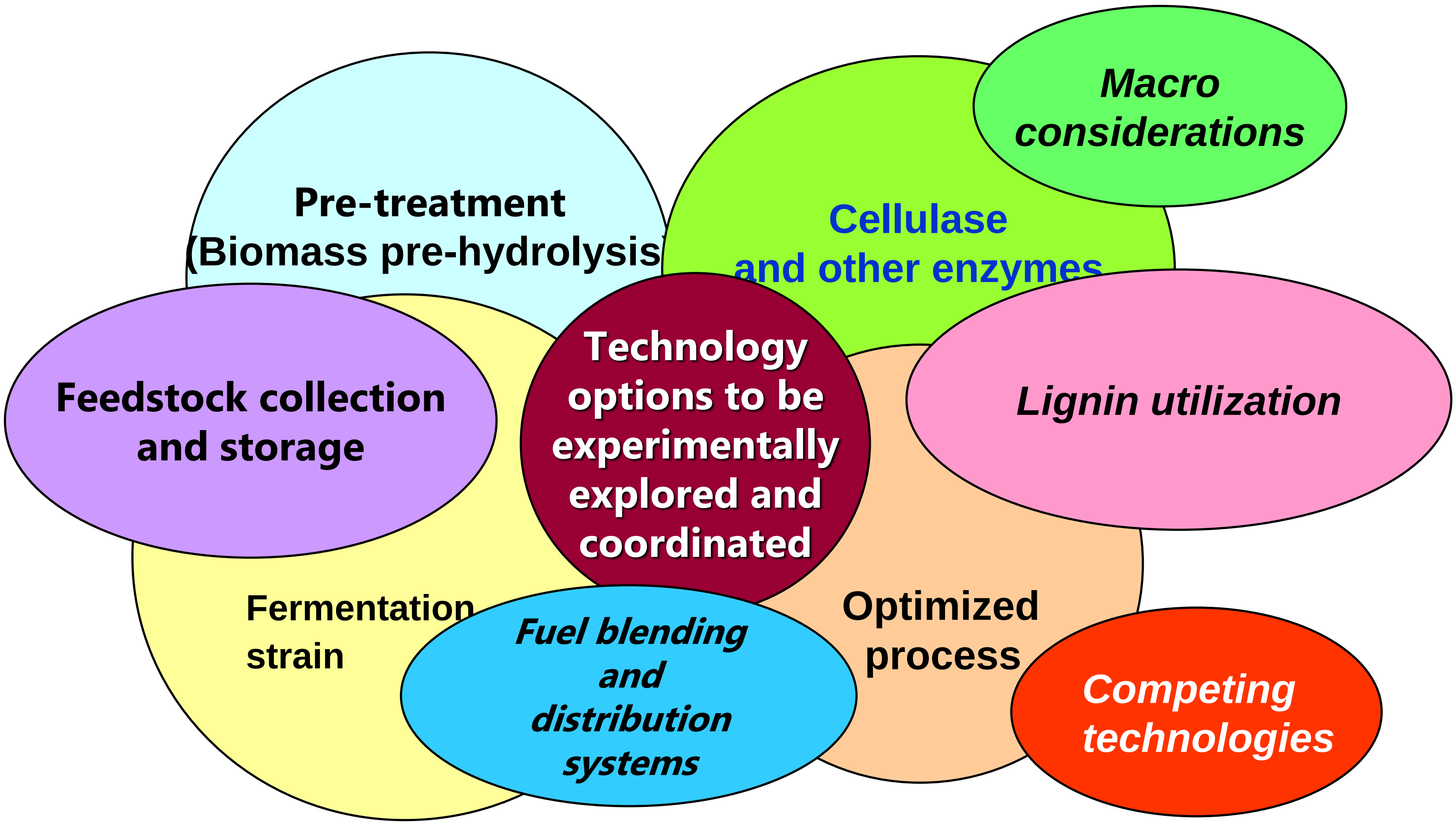


Technical Barriers to II Generation Ethanol.

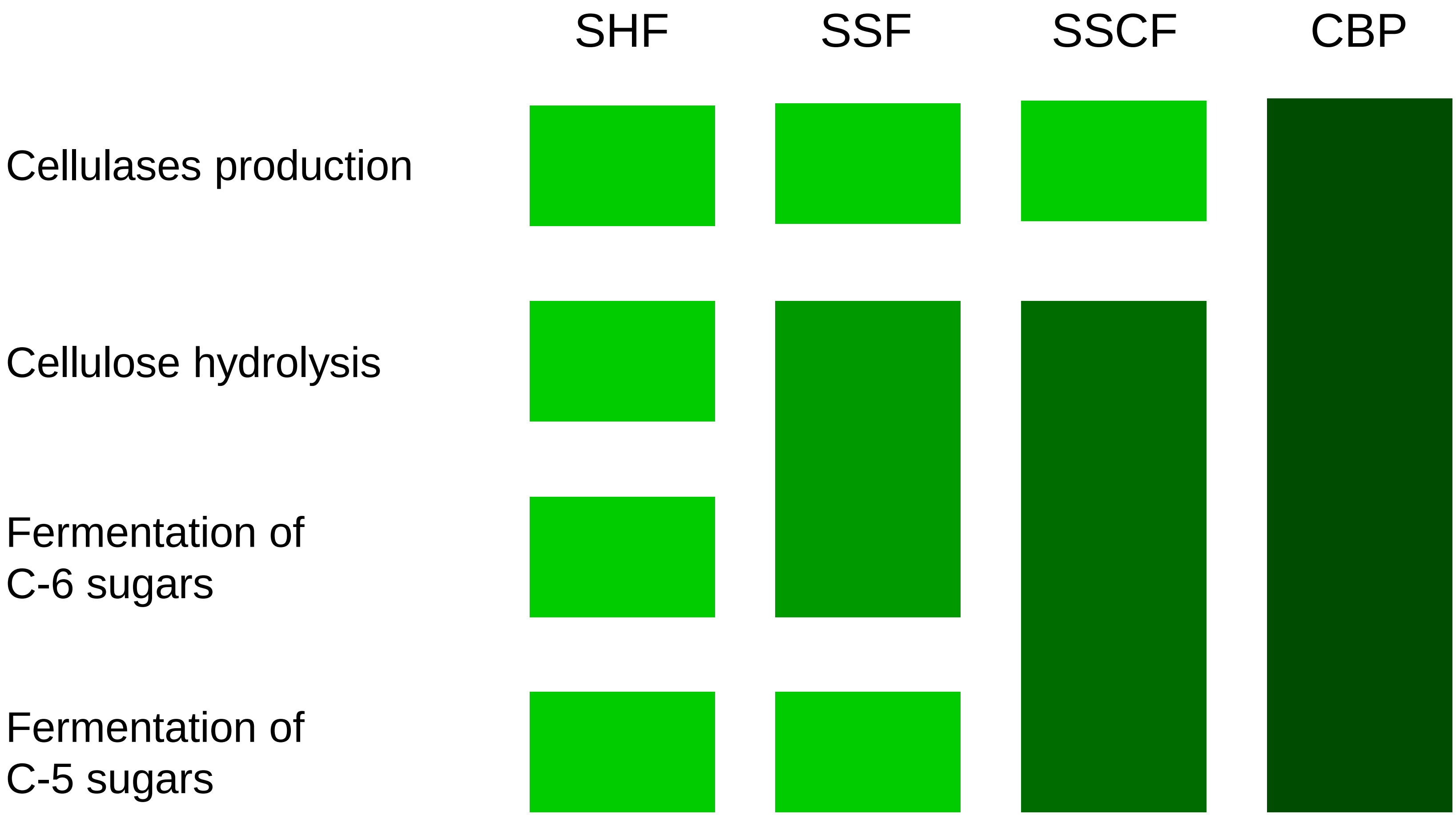


BETARENEWABLES

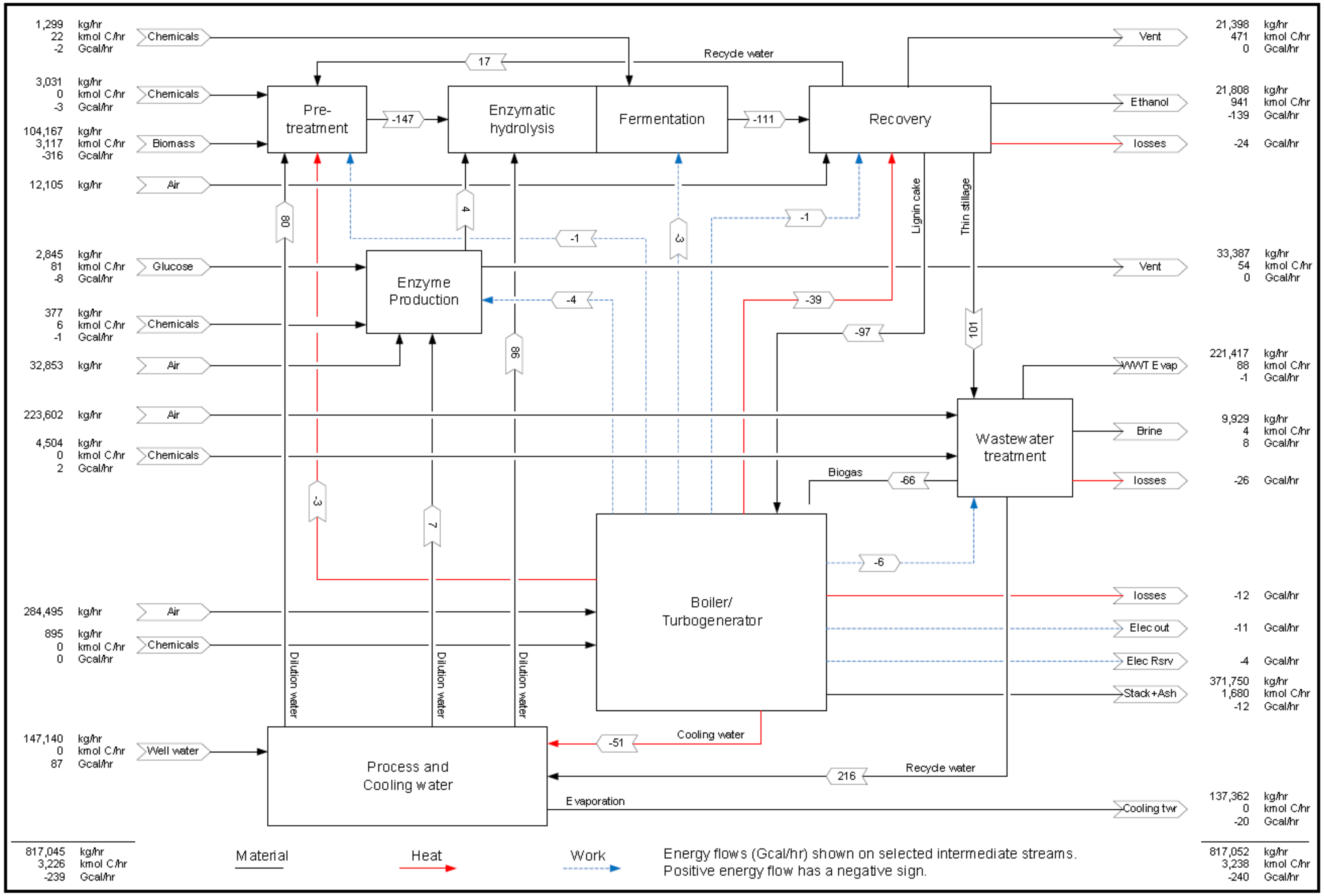
Technology Development Needs.



Strategie di Processo per l'Etanolo da Biomasse Lignocellulosiche.

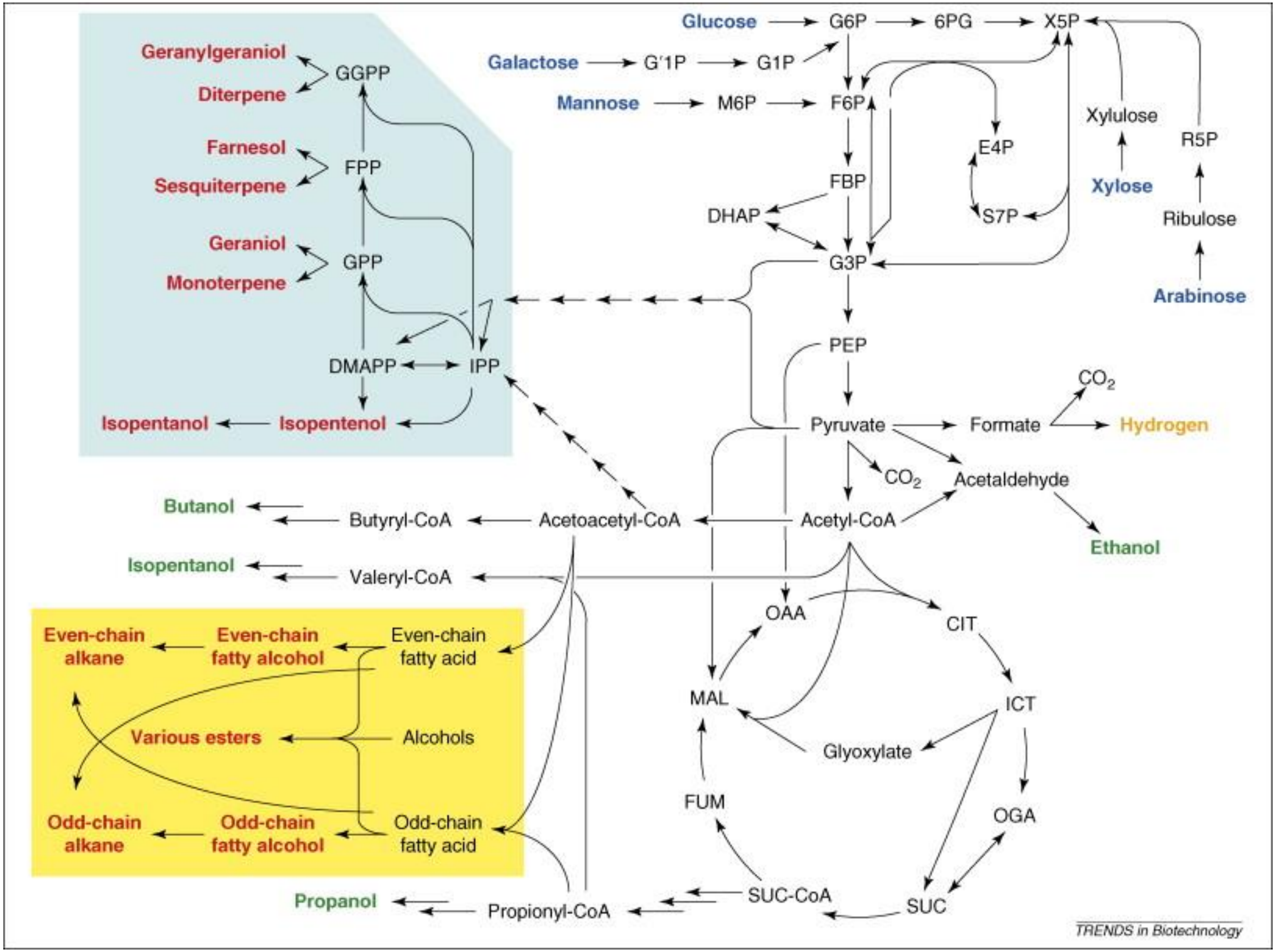


Mass, carbon, and energy balance diagram for the overall Bioethanol process from Corn Stover.



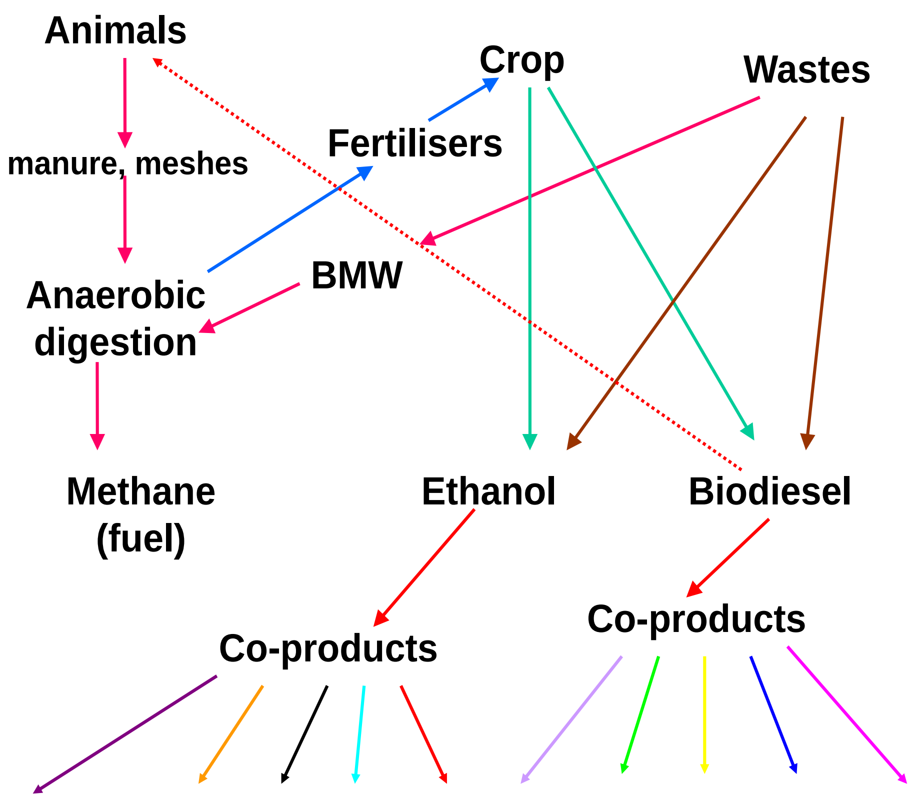
Humbird, D. ; Davis, R. ; Tao, L. ; Kinchin, C. ; Hsu, D. ; Aden, A. ; Schoen, P. ; Lukas, J. ; Olthof, B. ; Worley, M. ; Sexton, D. ; Dudgeon, D. Process Design and Economics for Biochemical Conversion of Lignocellulosic Biomass to Ethanol: Dilute-Acid Pretreatment and Enzymatic Hydrolysis of Corn Stover, NREL/TP-5100-47764 (2011)

Biofuel Alternatives to Ethanol: the Microbial Hydrocarbon Derivatives.

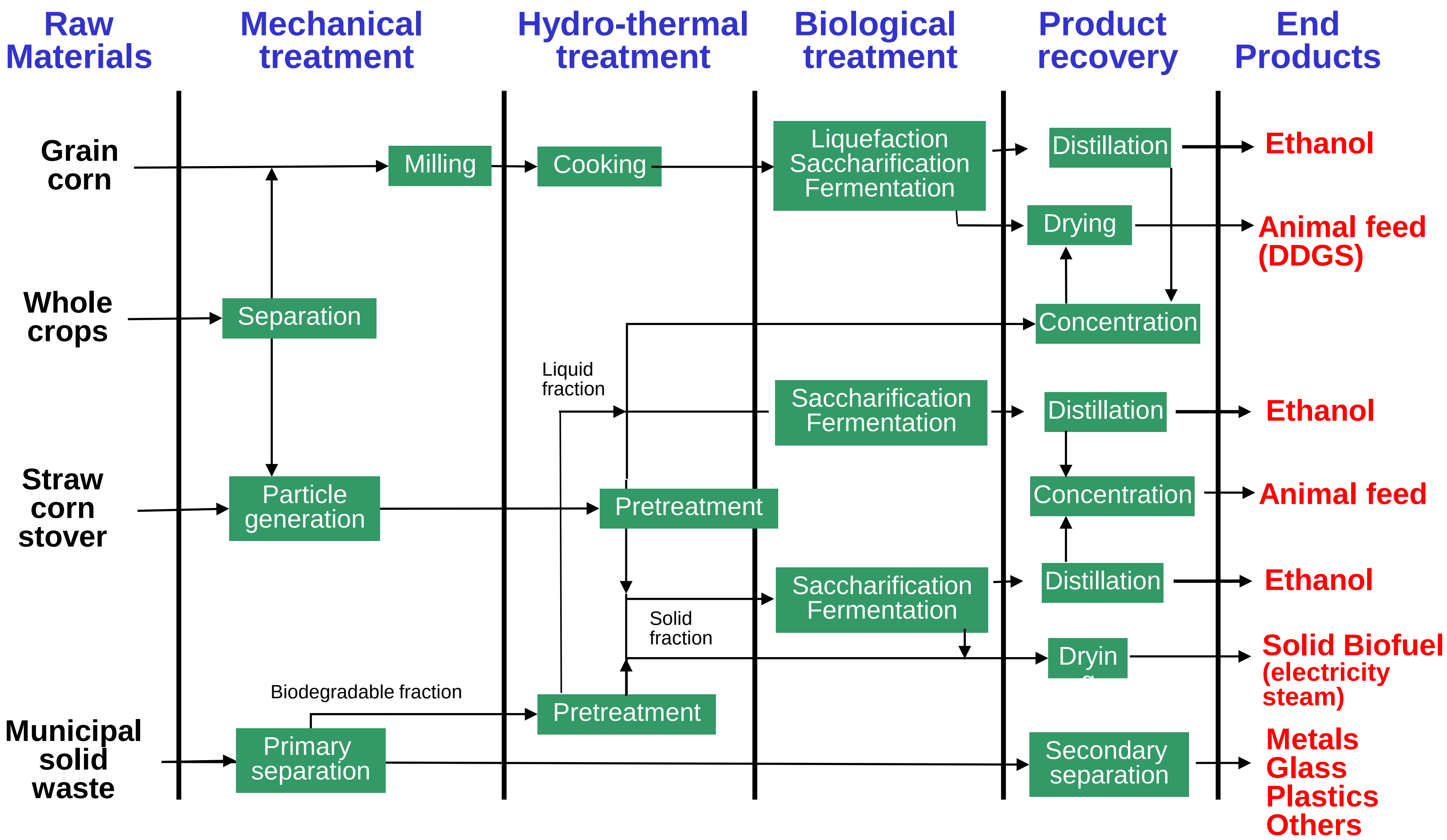


An Integrated Approach (Bio-refinery).

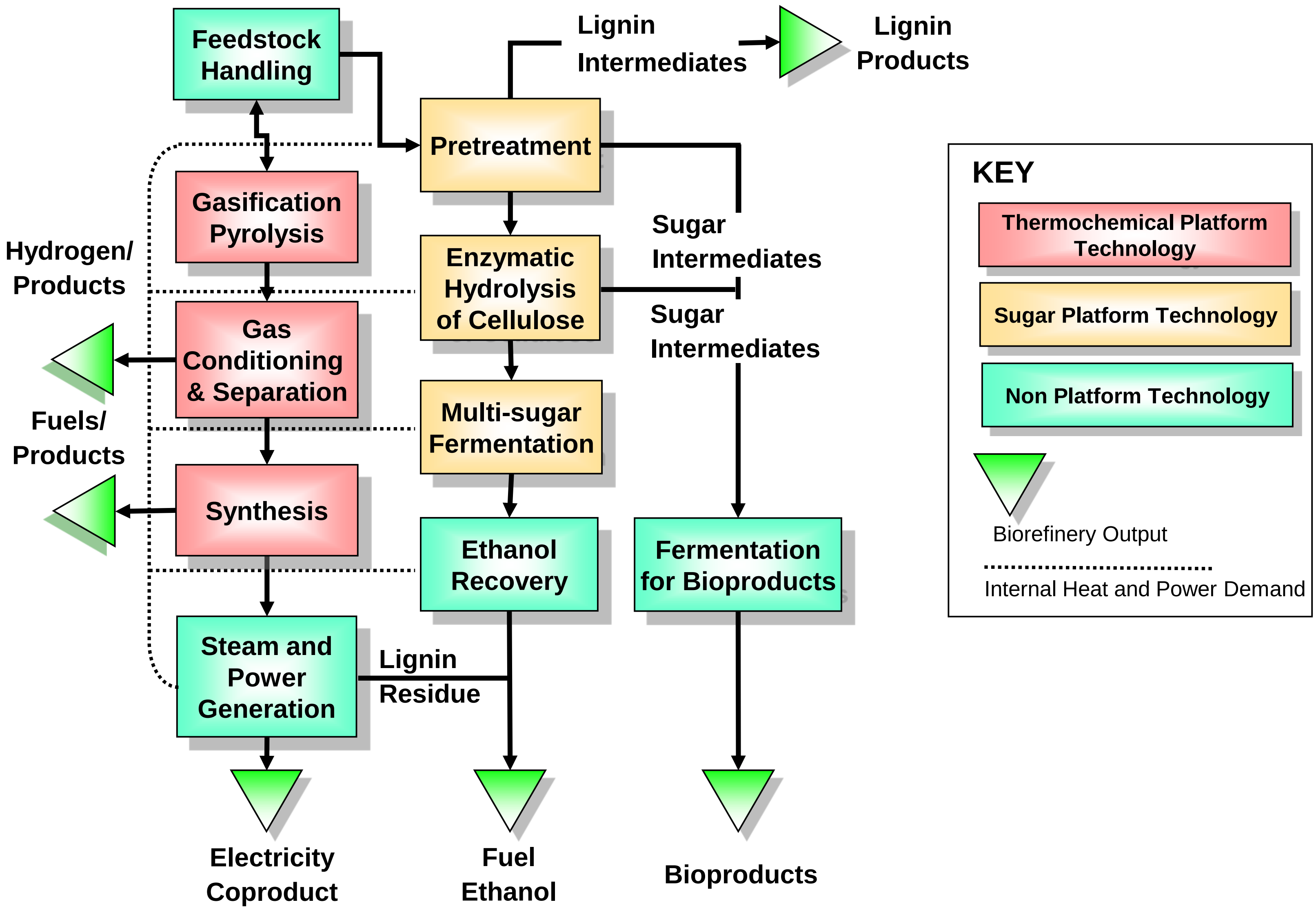
- Using feedstock from agriculture, forestry and organic wastes we can obtain:
- Fuels, fertilizers and animal feed
- Thousand of potential co-products (furfural, xylitol, carbon dioxide, lactic acid, glycerol, …..)
- Create a Bio-refinery
- An holistic view will be necessary.



Integrated Biomass Utilization System.



Schematic of an Integrated Bio-refinery.



Directions in Plant and Agricultural Biotechnology for II/III/IV Generation Biofuels.

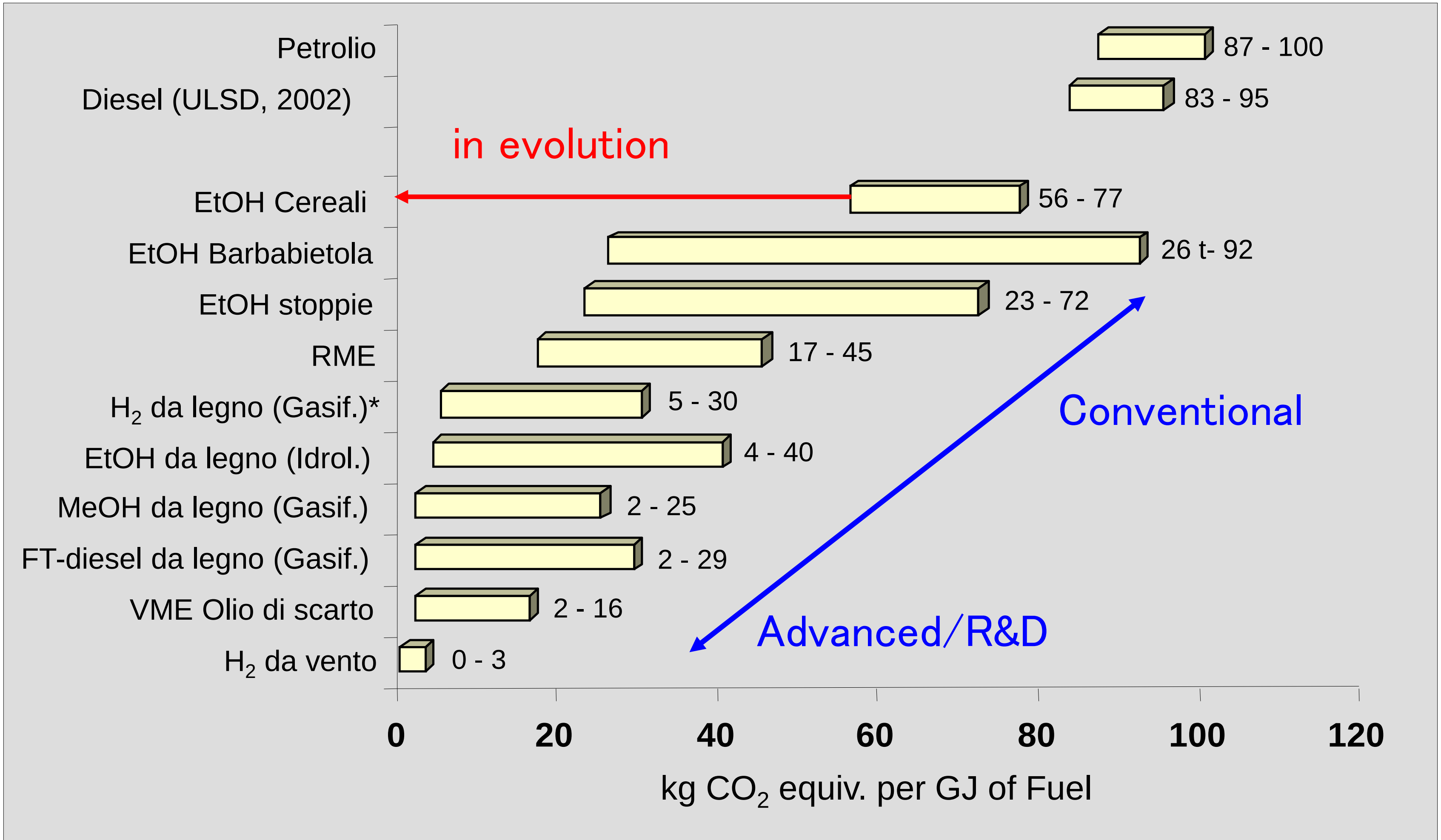
- **Generate treatment friendly biomass**
  - *Changes in cellulose-lignin-hemicellulose structure*
  - *Decrease lignin content/Increase cellulose content*

- **Co-production of enzymes like cellulases**
  e.g. INPLANT technology at QUT, Australia

- **High yield, drought/pest resistant, low-input biomass**
  - *Increase solar efficiency from <1 w/m^2 to >5 W/m^2*
  - *Increase yield to average 100 ton/ha*
  - *To grow on marginal non-agricultural land*
  - *High yield Perennial grasses !*
  - *More efficient CO_2 fixing varieties*

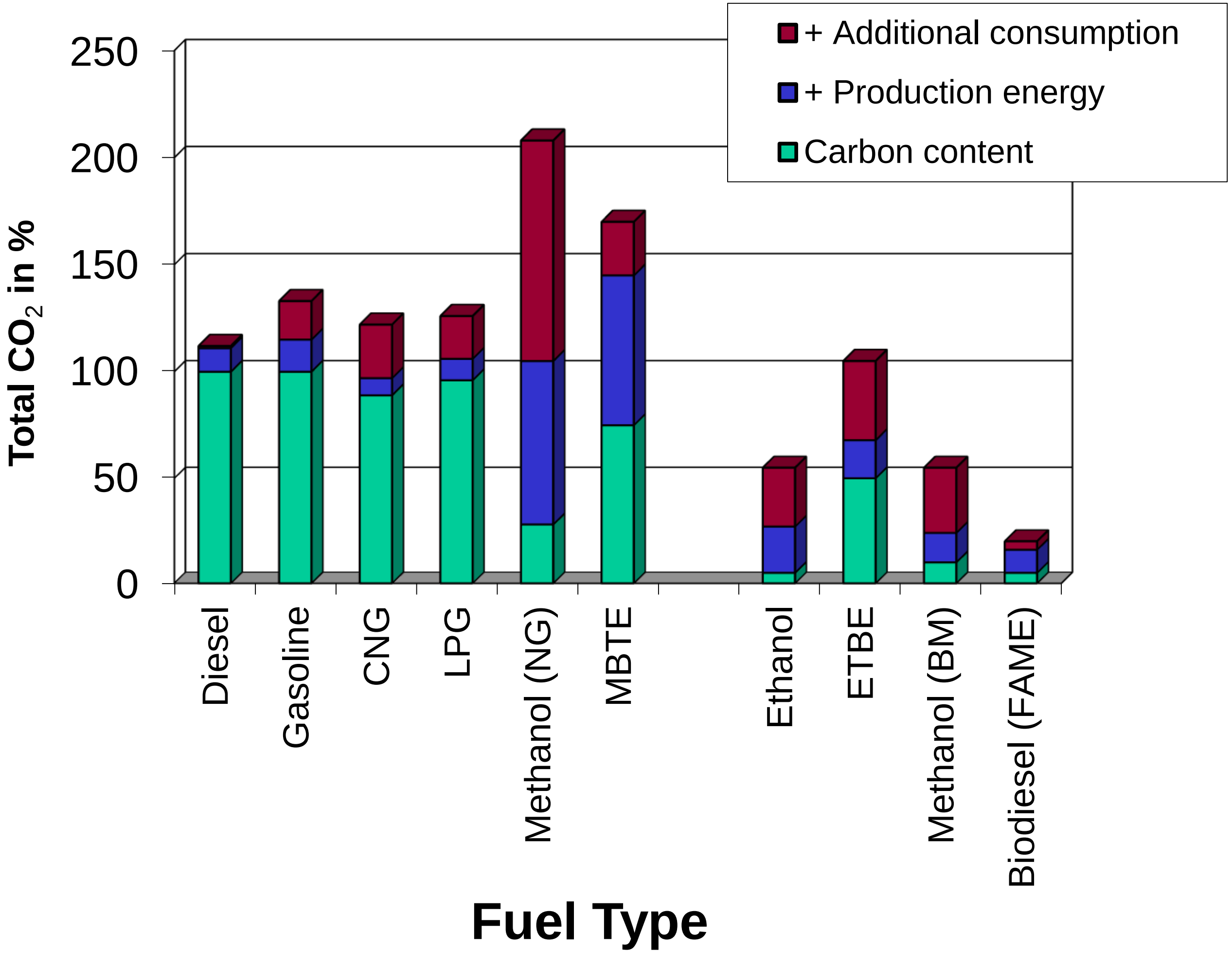
- **Technologies to replenish soil micronutrients**
  - *Synergic crops*
  - *Development of micro-floral species e.g. N-fixing microbes.*

GHG Emissions from Biofuels and Conventional Fuels.



* The range in emissions arises from different modes of hydrogen transport.

Global CO_2 Development - Different Fuels.



Algal Oil or Oilgae and Algal Biomass

Growth of microscopic plants in water medium permits better use of sunlight and nutrient Carbon Dioxide.

Strains of micro-algae and other algae can produce (vegetable) oil or biodiesel (*up to 50% of biomass*).

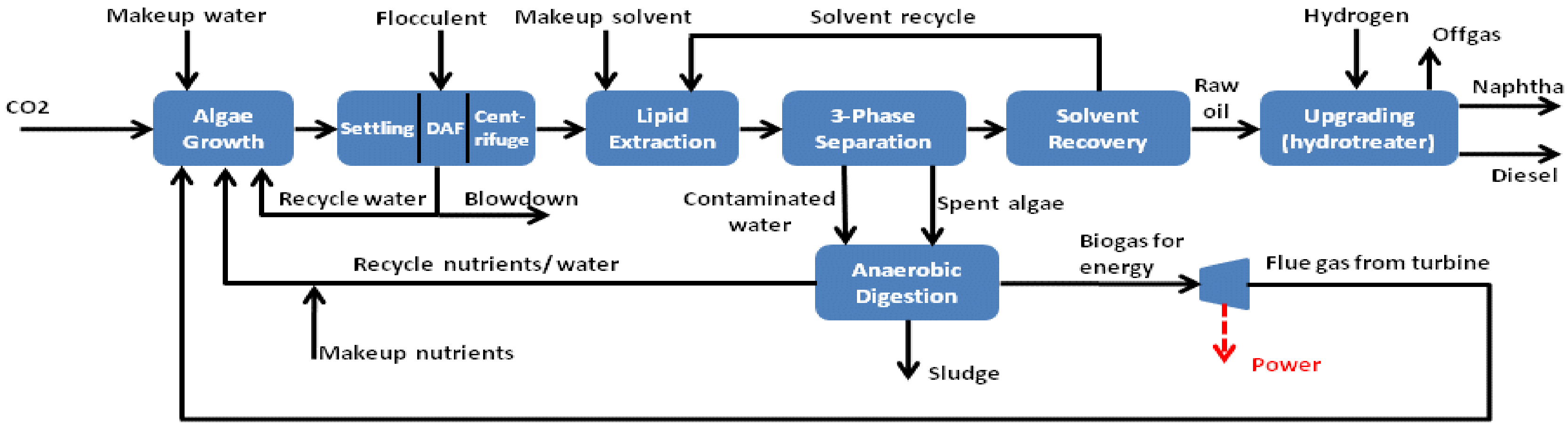
Comparison of Crop Biomass vs. Algal Biomass:

1 hectare → 100 ton max biomass → 25 ton ethanol
→ 5-15 ton oil → 5 -15 ton biodiesel

against algal case which gives (*in best cases!*)

→ 100 ton algal oil → 100 ton biodiesel
→ 1000 ton biomass → 250 ton ethanol

Biofuels from Algae.



Algal Biomass

Solid Cell Component

- Sugar 1 → Bio-Alcohols
- Sugar 2 → Bio-Alcohols; Other valued products e.g. mannitol
- Oil → Direct fuel or after cracking and refining

Biodegradable part

- Biogas or recycled nutrients

UE Forecast for Least 20 Years.

Only three options seem to have a potential volume of more than 5% of fuel consumes. If it will be decided to promote them with an **active policy**, an **optimistic** development will be (% fuel consumption):

	Biofuels	Natural Gas	Hydrogen	Total
2005	2*			2
2010	5*	2		8
2015	(7)**	5	2	14
2020	(8)**	10	5	(23)

*Just ruled in UE following the Kyoto protocol
**Foreseen by UE

European Directives.

- **European Directive 98/70/EC**: only a 5% biodiesel blend is authorized. If it is higher, the customer must be informed.
- **European Directive 2003/30/CE**: 2 and 5.75 % of the gasoline and diesel used in the transport sector should be obtained from biofuels within respectively 2005 and 2010.
- **European Directive 2003/96/EC**: the Member States are allowed to totally or partially exempt biofuels from excise tax. Taxation on biofuels is established by each Member State.
- **European Directive 2009/28/EC**: Biofuels use was extended to replace 10% of transport and residential fuels.

Communications:

- **Biomass Action Plan** (December 2005)
- **An EU Strategy for Biofuels** (February 2006)

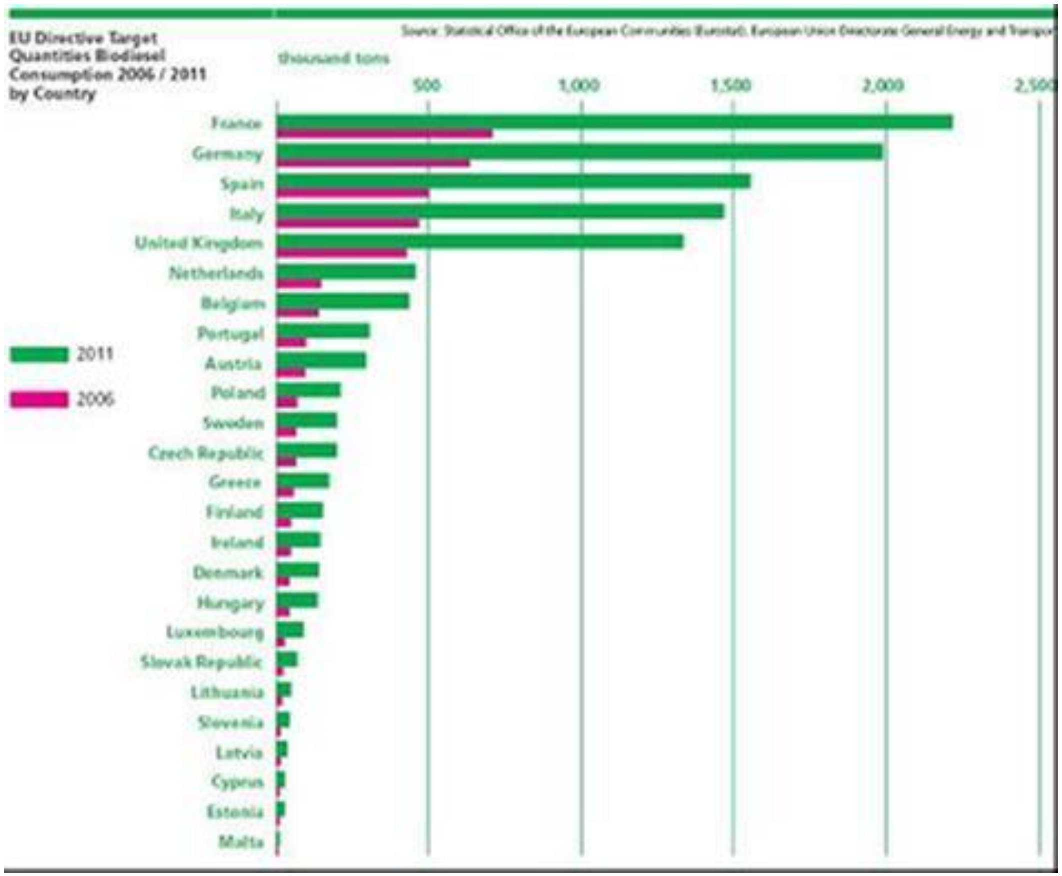
Objectives:

- ✓ To promote large-scale biofuel production, both in Europe and in Southern countries
- ✓ To promote energy farming in Southern countries, especially the ones affected by the sugar reform

The Council Decision.

European Council of 23-24th March 2006:

- Renewable energy: **15%** of the total energy use by 2015
- Biofuels: **8%** of the energy use for transport by 2015

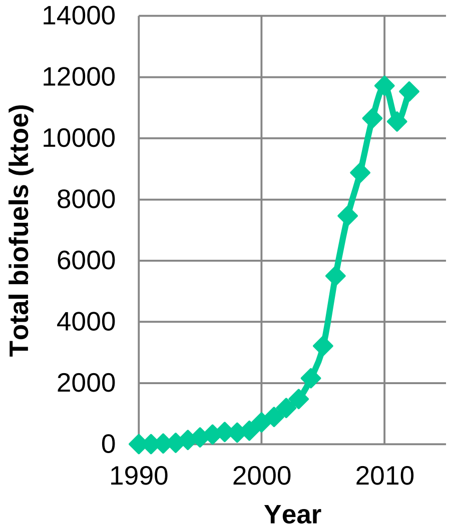


(among the renewable sources a quantitative target is established only for biofuels)

European Directive Objective for Biofuels consumption.

Production and Share of Biofuels in EU-27 (1990-2012).

	Production			Share in Transport Fuels		
	Total Biofuels	Biodiesel	Biogasoline	Total Biofuels	of Biogasoline in Motor Gasoline%	of Biodiesel in Gas/Diesel Oil
	ktoe			%		
1990	6	6	0	0,00%	0,00%	0,00%
1991	7	7	0	0,00%	0,00%	0,00%
1992	20	16	2	0,00%	0,00%	0,00%
1993	48	25	18	0,00%	0,00%	0,00%
1994	135	95	25	0,00%	0,00%	0,10%
1995	222	188	24	0,10%	0,00%	0,20%
1996	313	268	39	0,10%	0,00%	0,20%
1997	401	338	53	0,10%	0,00%	0,30%
1998	383	310	63	0,10%	0,00%	0,20%
1999	441	369	58	0,10%	0,00%	0,30%
2000	709	634	59	0,20%	0,00%	0,40%
2001	886	789	70	0,20%	0,00%	0,50%
2002	1186	997	159	0,30%	0,10%	0,60%
2003	1472	1183	239	0,40%	0,20%	0,70%
2004	2155	1780	266	0,50%	0,30%	0,90%
2005	3211	2365	452	0,80%	0,50%	1,20%
2006	5497	3683	742	1,50%	0,80%	2,00%
2007	7462	5302	1032	2,10%	1,10%	2,90%
2008	8878	6613	1384	2,70%	1,70%	3,80%
2009	10646	7941	1706	3,30%	2,30%	4,60%
2010	11717	8915	1980	3,70%	3,00%	5,00%
2011	10541	8465	1743	3,90%	3,20%	5,20%
2012	11532	9188	2036	4,20%	3,30%	5,80%



Next EU Use of Bioethanol and Biodiesel

Ethanol. In the EU, ethanol production for fuel (mainly from wheat, coarse grains and sugar beet) is projected to reach a maximum of 9.7 Bln L in 2020 when the RED target is assumed to be met and then to decrease to 9.3 Bln L by 2025 because of assumptions of decreasing gasoline use. Ligno-cellulosic biomass based ethanol should remain marginal over the period 2015-2025.

Biodiesel. Global biodiesel production is expected to reach 41.4 Bln L by 2025 corresponding to a 33% increase from the 2015 level. The EU is expected to be the major producer of biodiesel. Policy rather than market forces will continue to influence production patterns in almost all countries. In the EU, biodiesel production is projected to reach its maximum in 2020 when the RED target is met with 12.6 Bln L. A significant amount of this increase should be met by biodiesel produced from waste oil and tallow.

School of Industrial and Information Engineering

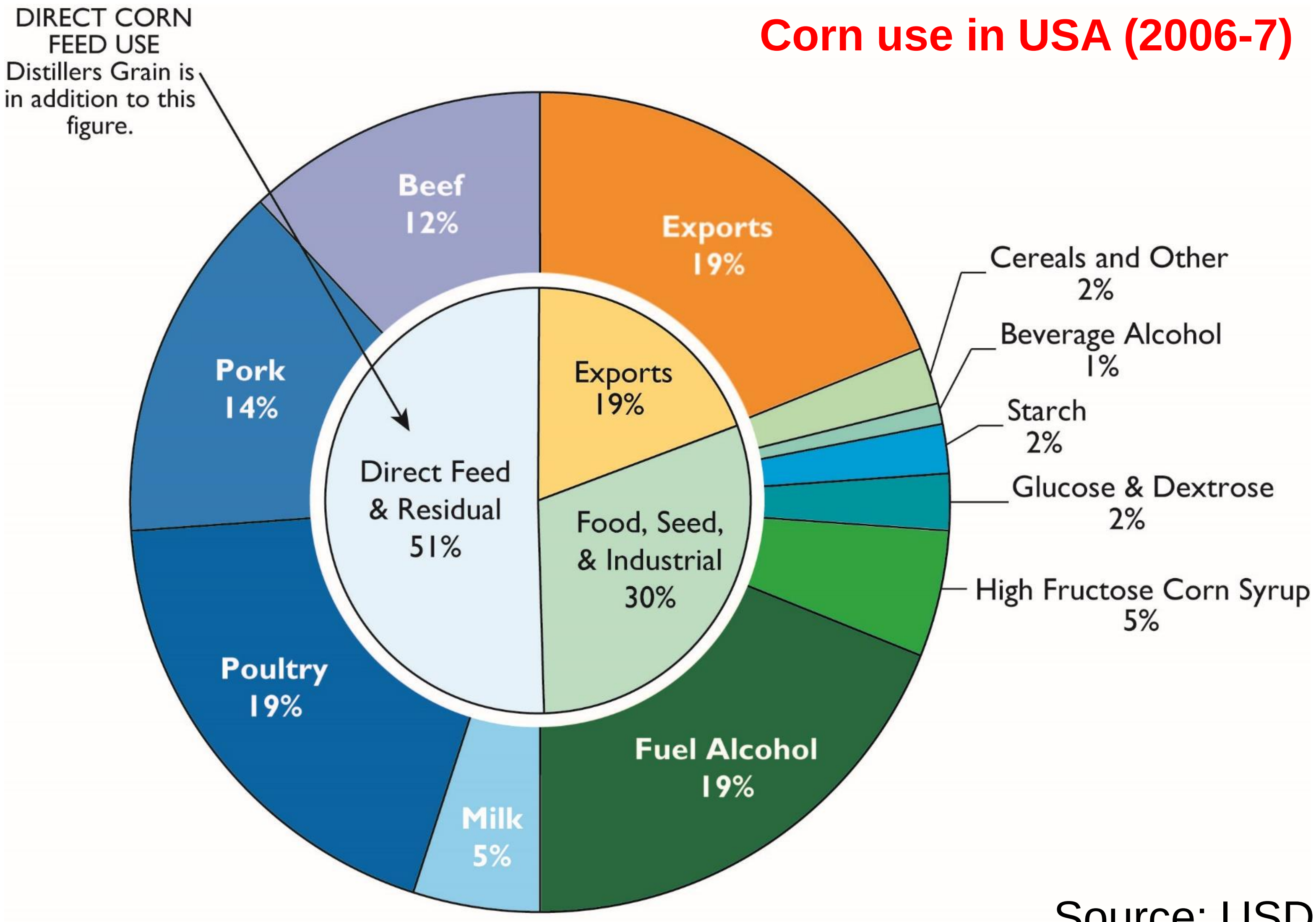
Course 096125 (095857)

Introduction to Green and Sustainable Chemistry

POLITECNICO DI MILANO

Life Cycle Analysis of Biofuels.

Ethical Reservation.

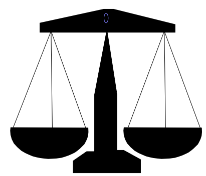


Source: USDA

Why LCA for Biofuels.

Environmental advantages and disadvantages

+



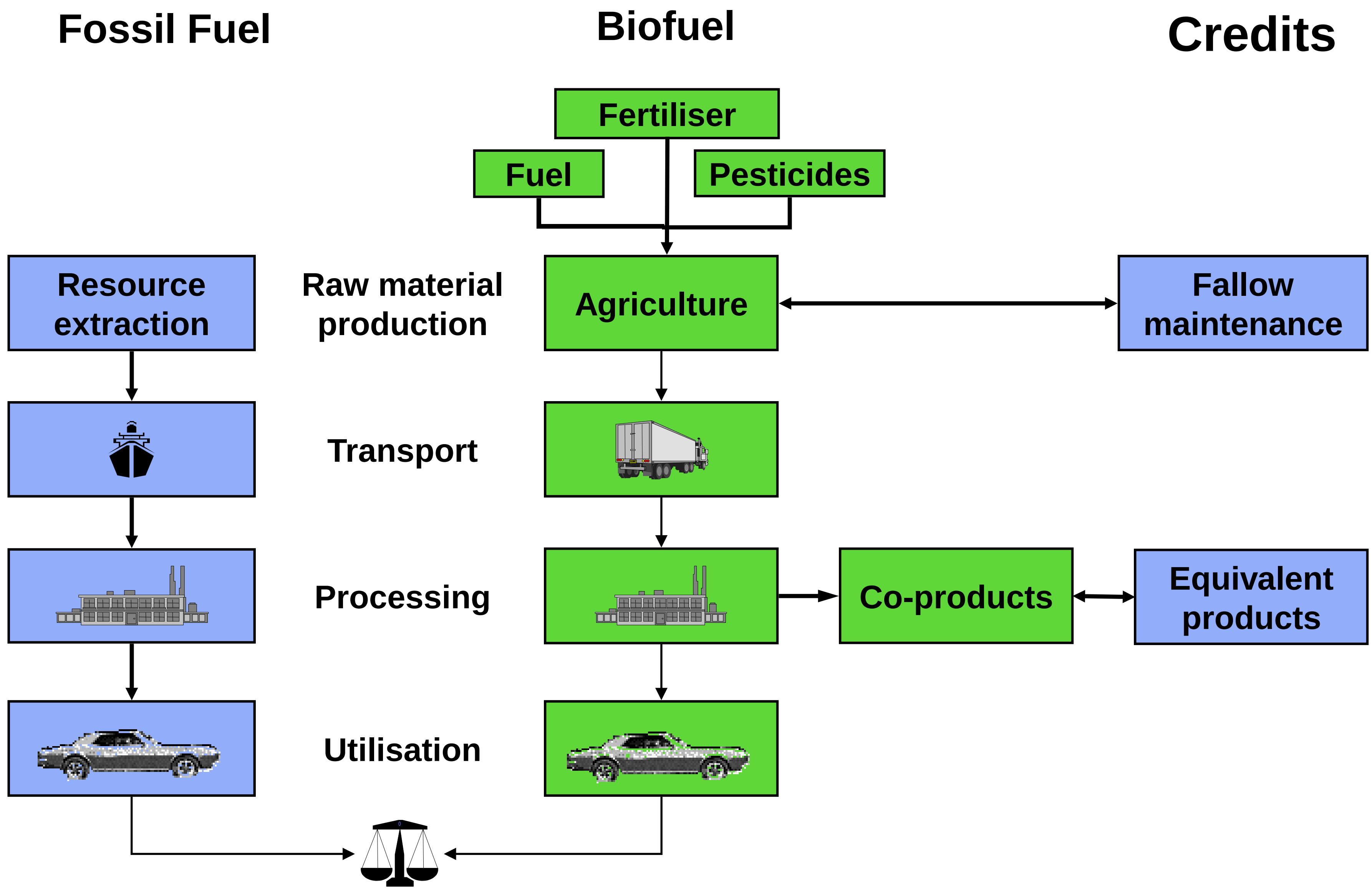
–

CO_2 neutral (?)
Energy source saving
Organic wastes reduction
Less transport
etc.

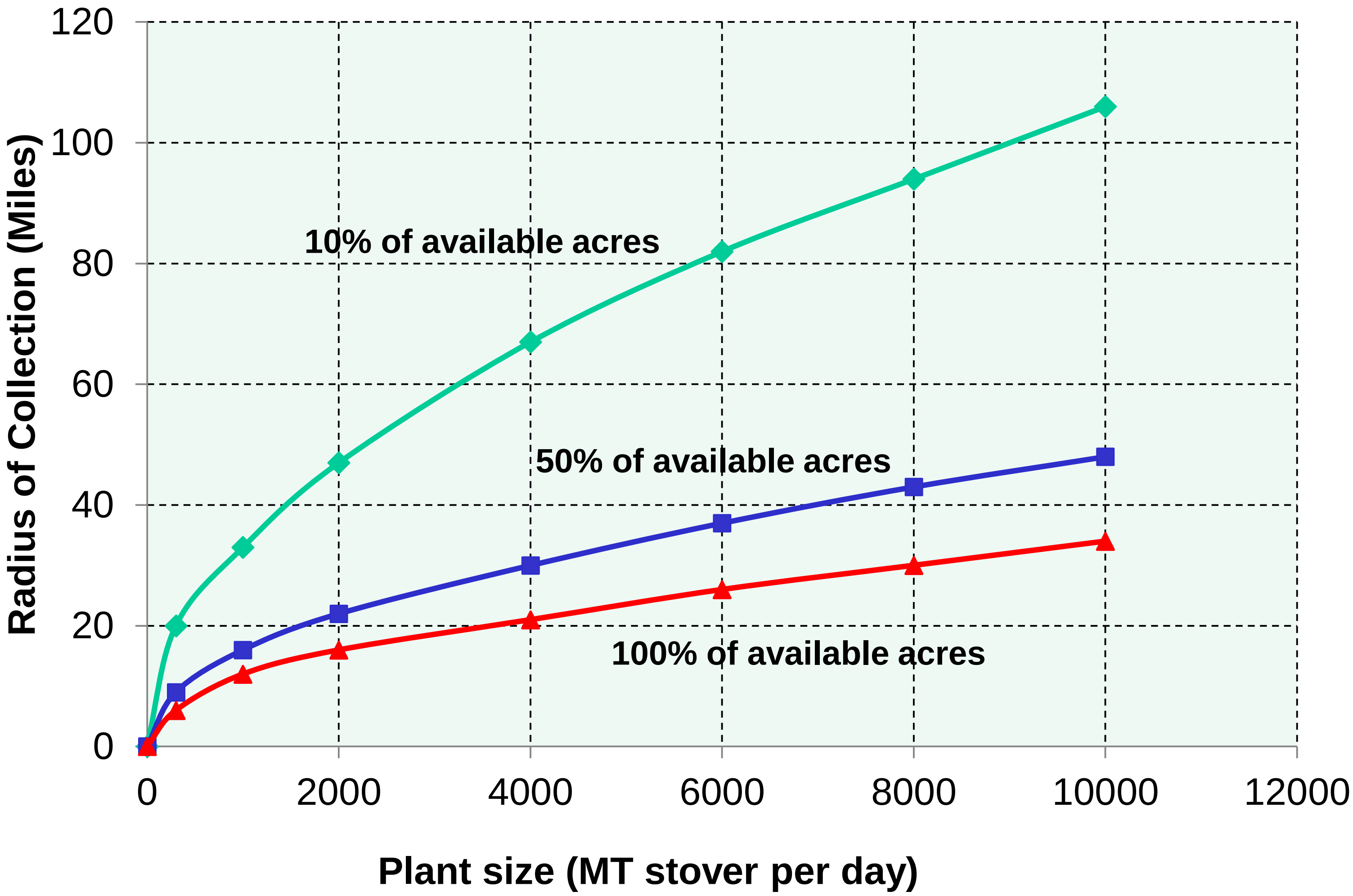
Use of land
Surface water eutrophication
Pesticides water pollution
Intensive production of energy
etc.

Total:
positive or negative impact
?

Life Cycle Comparison.



Corn Stover Collection.



Mass and Energy Balance.

When producing fuels by energy cropping the knowledge of the necessary inputs and the produced energy output is very important to achieve a good result. There are usually two ways to do it:

a) Calculating the relationship between output and input energies and

b) Obtaining the difference between output and input energies, that is called "net energy gain".

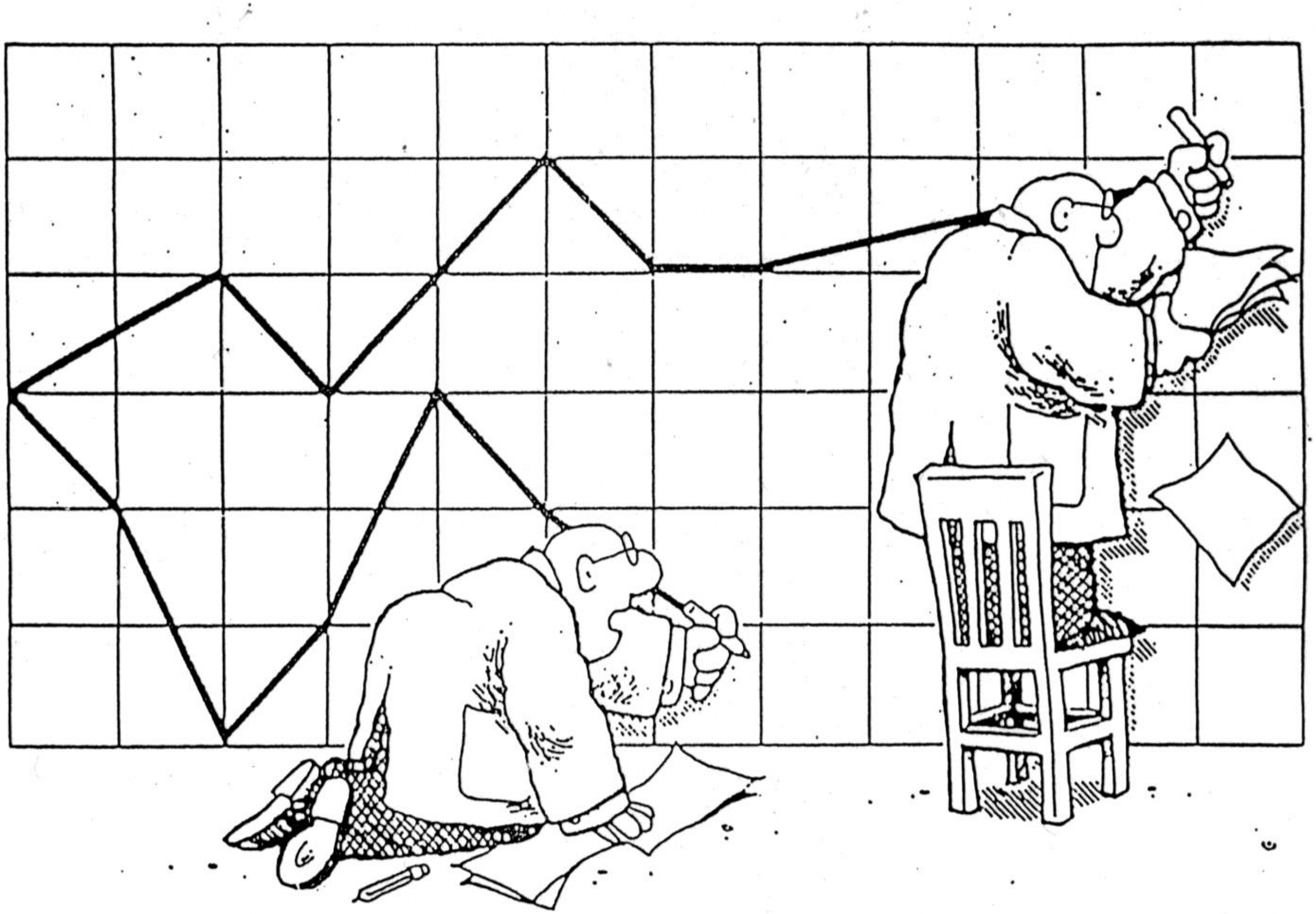
In the following example, are presented the average values obtained for sunflower and rapeseed oils compared to ethanol obtained from sugar beet, maize and wheat for Austrian conditions (2003).

The overall energy balance for the vegetable oils and their methyl esters including agricultural production and conversion is a very positive one, with a final energy ratio ranging between 2:1 to 3:1, considerably higher than for alcohol. This ratio proves that energy supplied by oils from vegetable origin is higher than the sum of the energies used for its production during agricultural processing, seed crushing, vegetable oil refining and its transesterification.

Energetic Balance for Same Crops.

Crop product	Yield primary product ($kg \cdot ha^{-1}$)	Energy ratio output/input	Net energy gain output/input ($GJ \cdot ha^{-1}$)
Sunflower oil	2600	2.8	43.3
Rapeseed oil	2700	2.8	43.4
Ethanol from Sugar beat	60000	1.3	39.2
Maize	7700	1.3	18.4
Wheat	4400	1.1	5.2

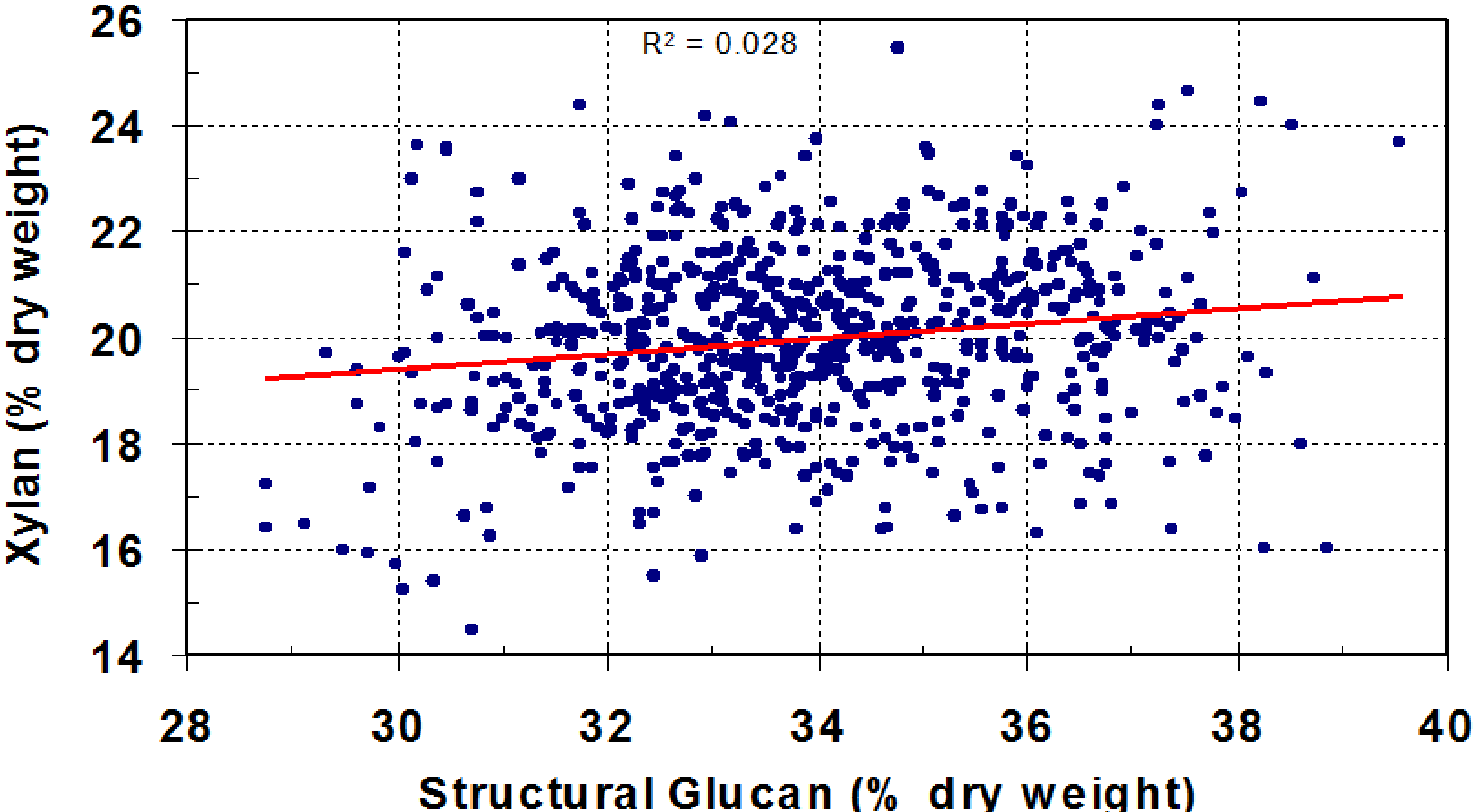
Data Reliability.



"HEY, I THOUGHT WE WERE WORKING WITH THE SAME DATA..."

Feedstock Variability.

731 corn stover samples from the 2001 harvest



J.D. McMillan, NREL

Energy Equivalents of the Input in Rape Seed Production.

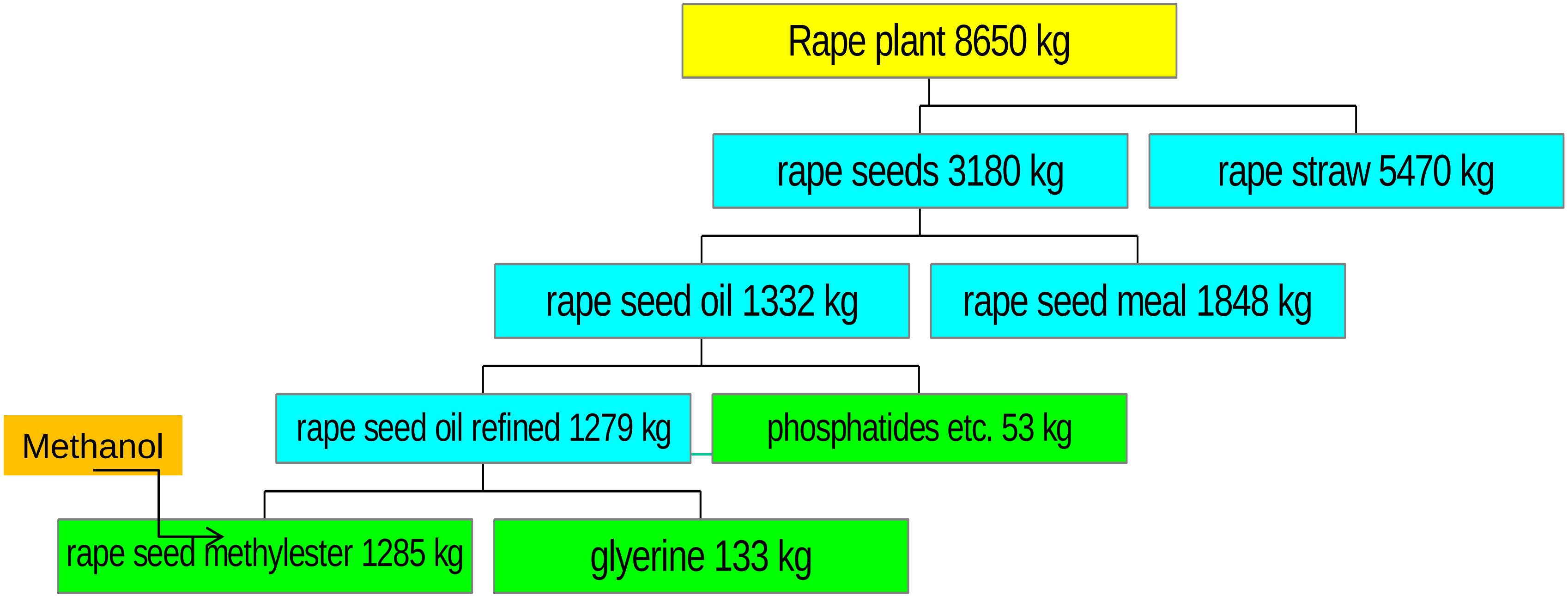
Fertilizer	Amount ($kg \cdot ha^{-1}$)	Energy Equivalents ($GJ \cdot ha^{-1}$)
N	140	8.40
P_2O_5	60	0.84
K_2O	120	0.72
CaO + MgO	300	0.45
		10.41
Seeds	10	0.24
Plant protection (3 treatments each with 1 kg/ha active ingredients; Energy (all included))	0.79	
Fuel consumption (seed bed preparation, harvesting, handing, drying, cleaning, prim. tillage	4.0	
Machinery, building	2.0	
Total energy for technical equivalent in 496 $L \cdot ha^{-1}$ Diesel	**17.44**	

Composition and Specific Energy of Rape Seed and Rape Straw.

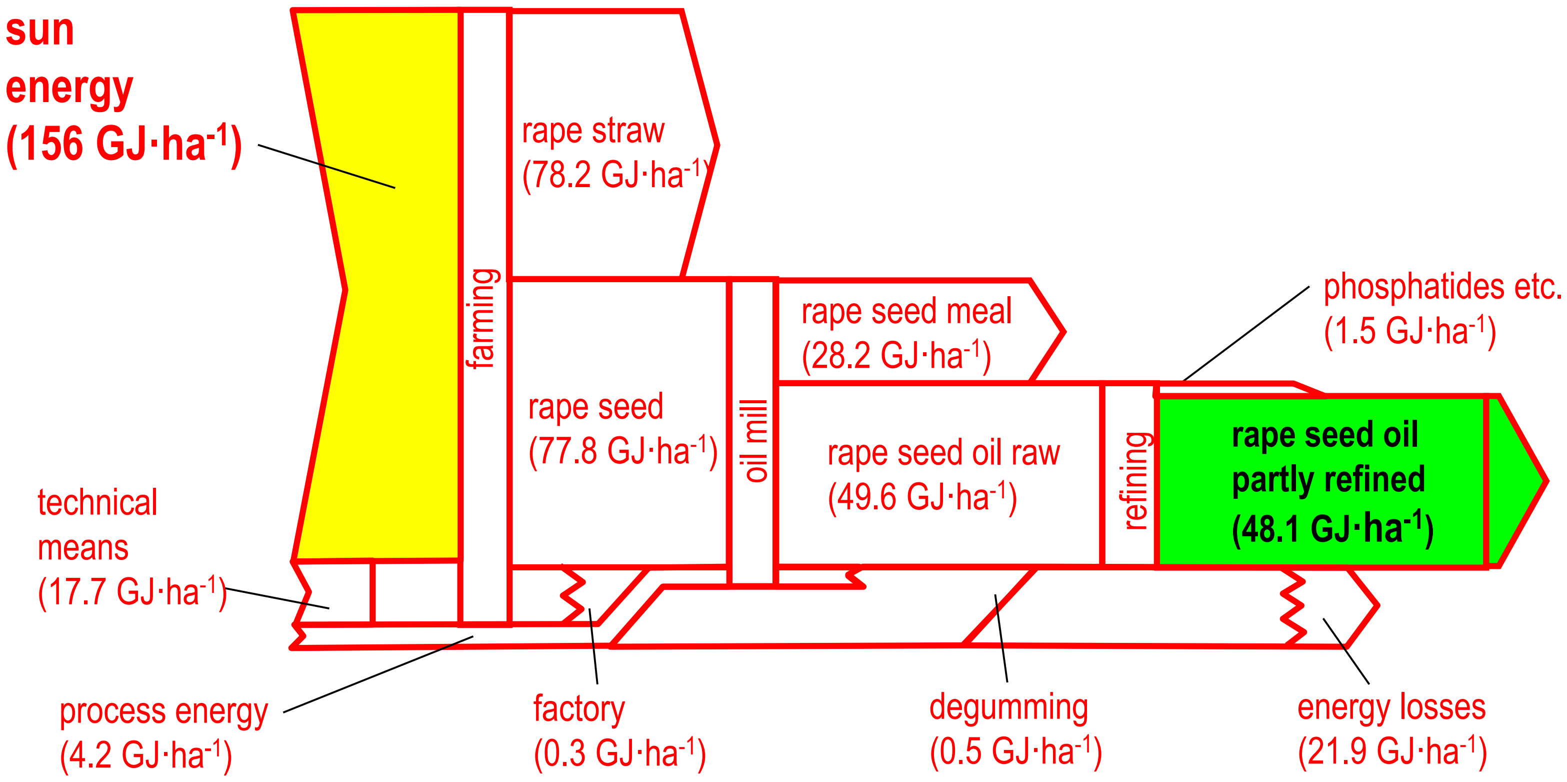
Rape seeds	mass (%)	specific energy ($MJ \cdot kg^{-1}$)	product mass % x specific energy ($GJ \cdot ha^{-1}$)
Fat	42.2	37.21	15700
Crude protein	20.6	22.44	4623
Fiber	5.8	18.71	1065
N-free substances	19.0	16.06	3061
Sp. energy of rape seed			24.462 $MJ \cdot kg^{-1}$
Rape straw			
Fat	1.2	37.21	0.447
Crude protein	2.5	22.44	0.561
Fiber	37.8	18.71	7.072
N-free substances	38.7	16.06	5.213
Sp. energy of rape seed			14. 296 $MJ \cdot kg^{-1}$

TOTAL equivalent to 4431 $L \cdot ha^{-1}$ Diesel-fuel 155.98 $GJ \cdot ha^{-1}$

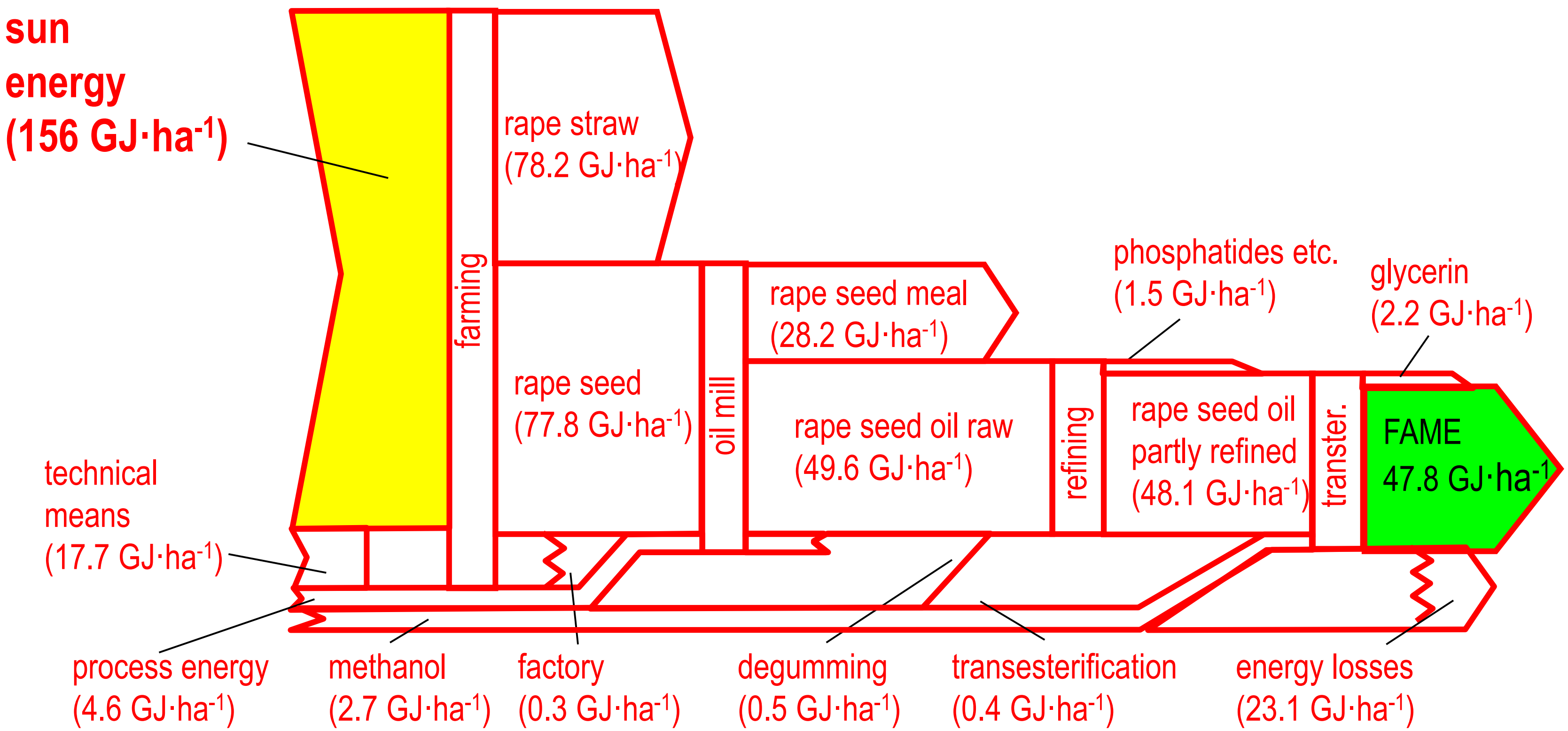
Mass Flow Diagram for the Production of Rape Seed Oil and FAME for 1 Hectare.



Energy Flow Diagram for the Production of Partially Purified Rape Seed Oil.

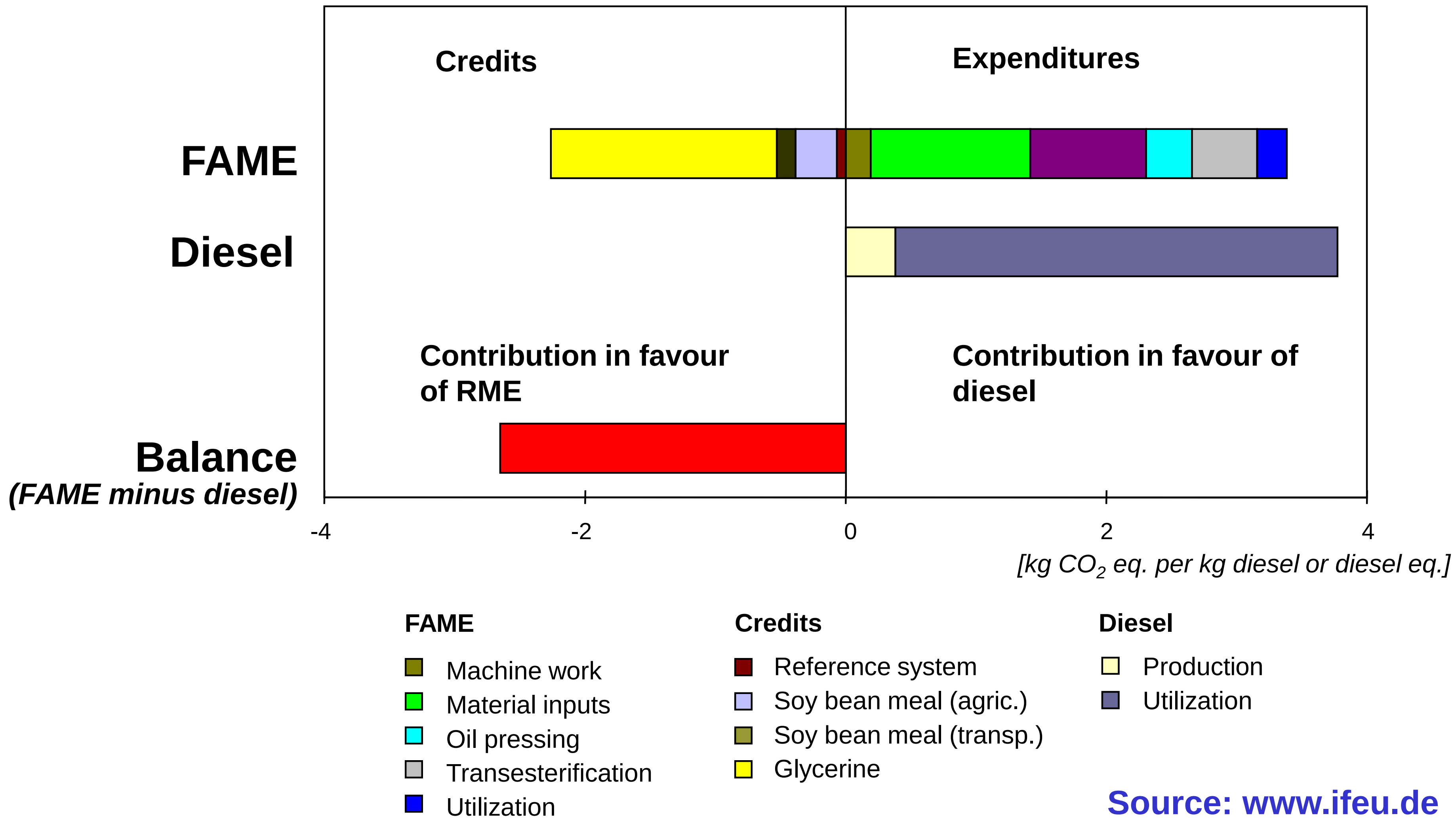


Energy Flow Diagram for the Production of Rape Oil Methyl Esters.



Biodiesel (FAME) vs. Diesel.

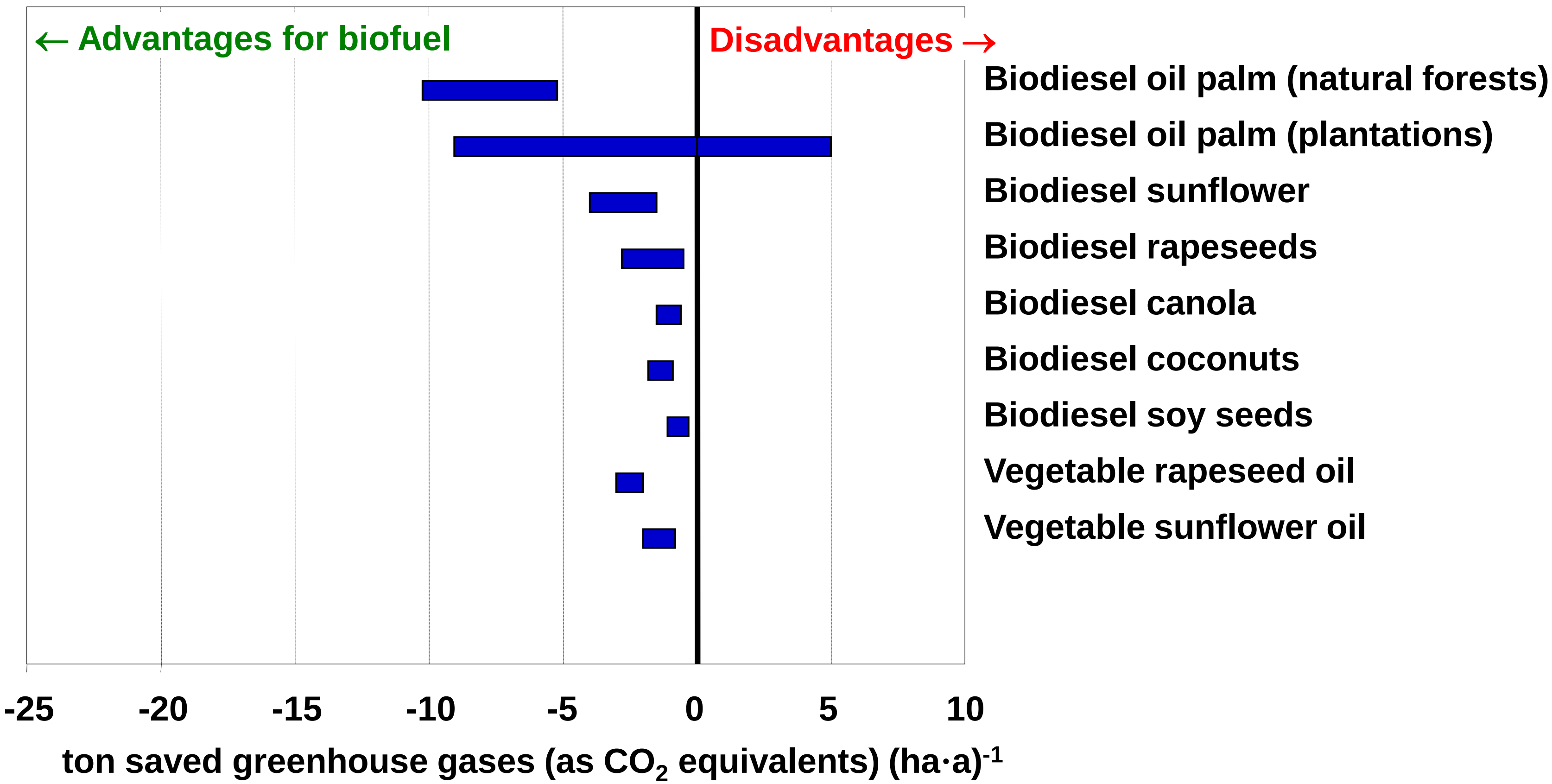
Greenhouse effects



Source: www.ifeu.de

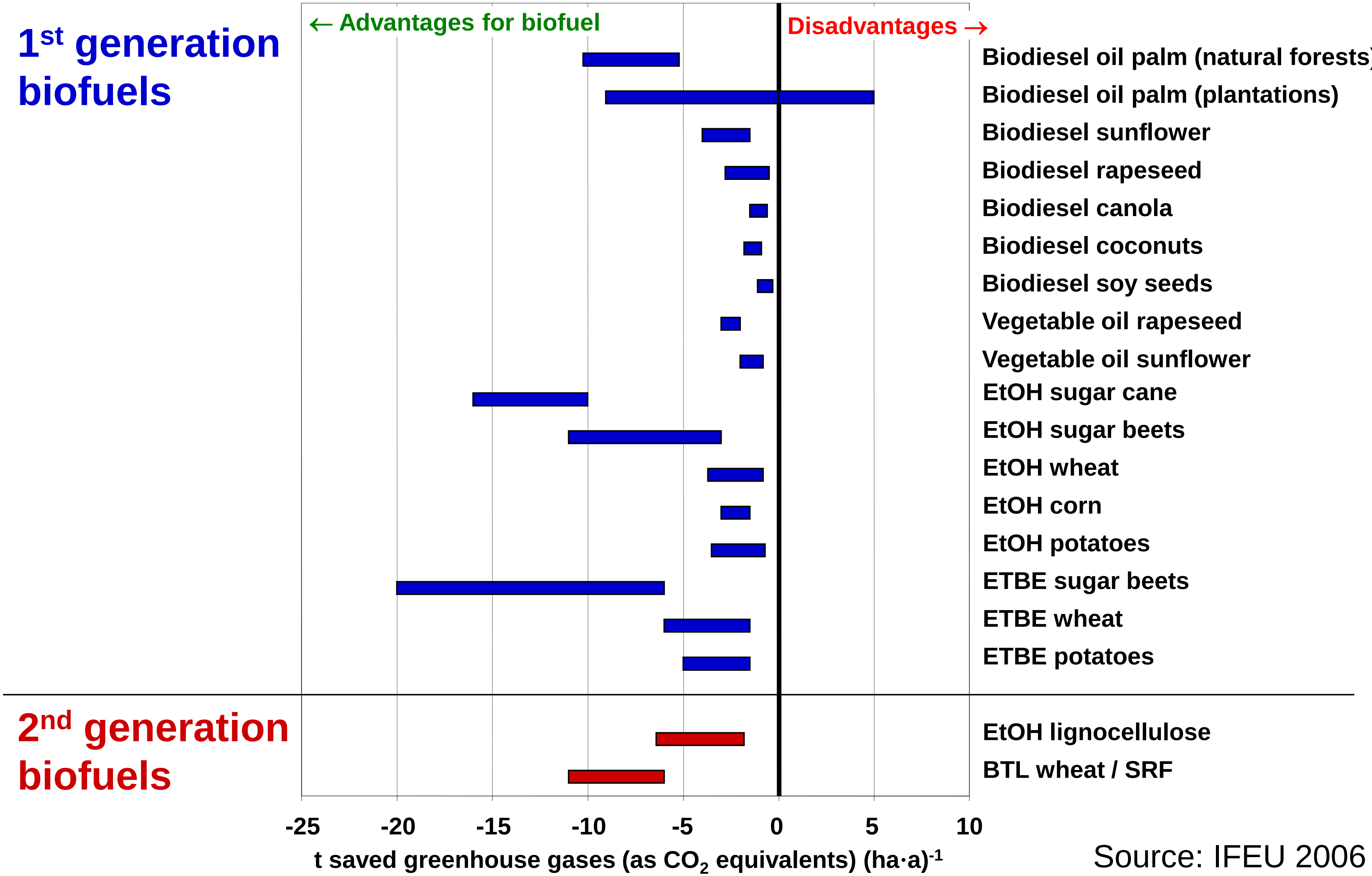
CO_2 Balance of Biofuels.

1st generation biofuels



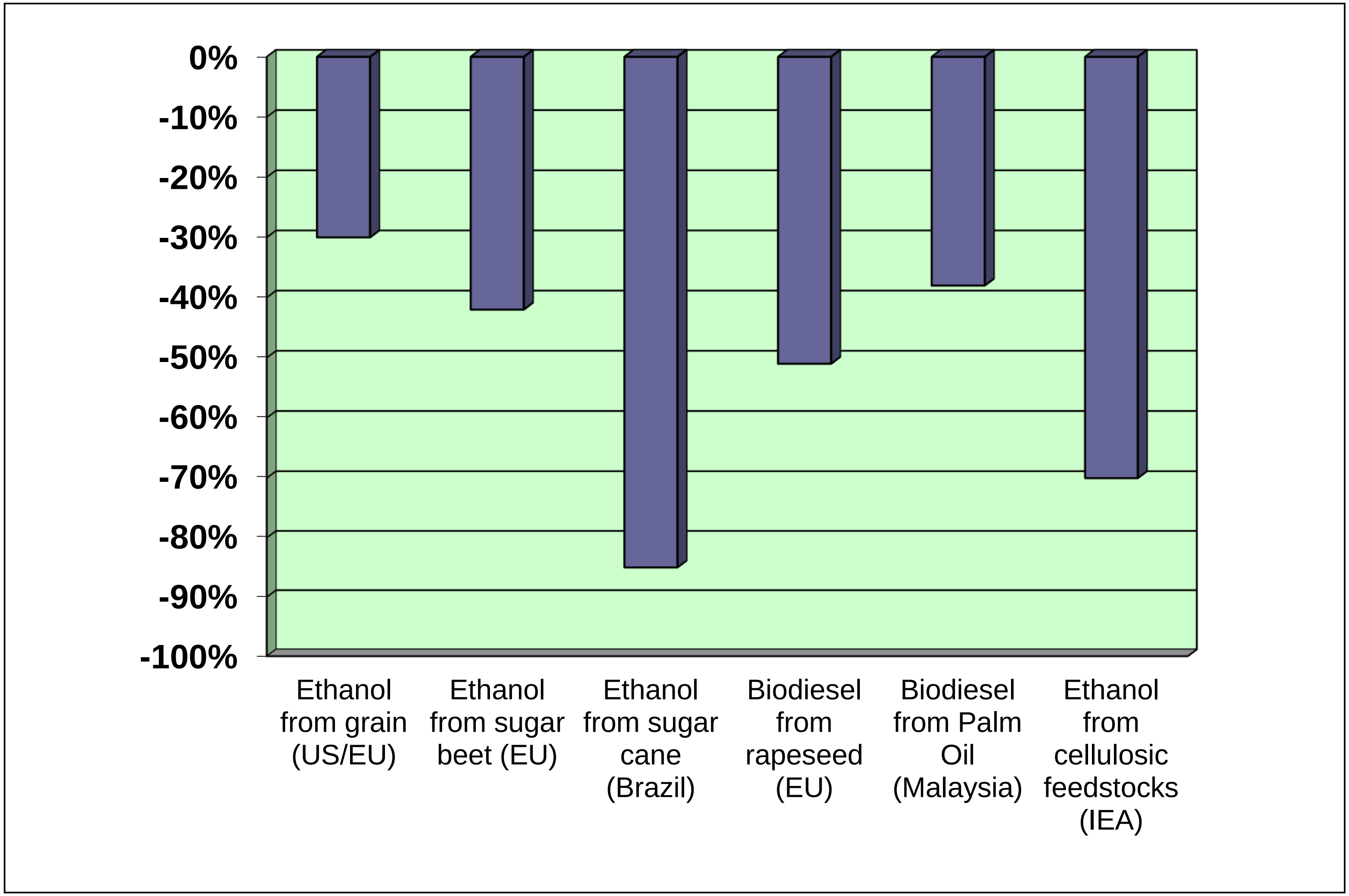
Fonte: www.ifeu.de

CO_2 Balance of Biofuels (2).



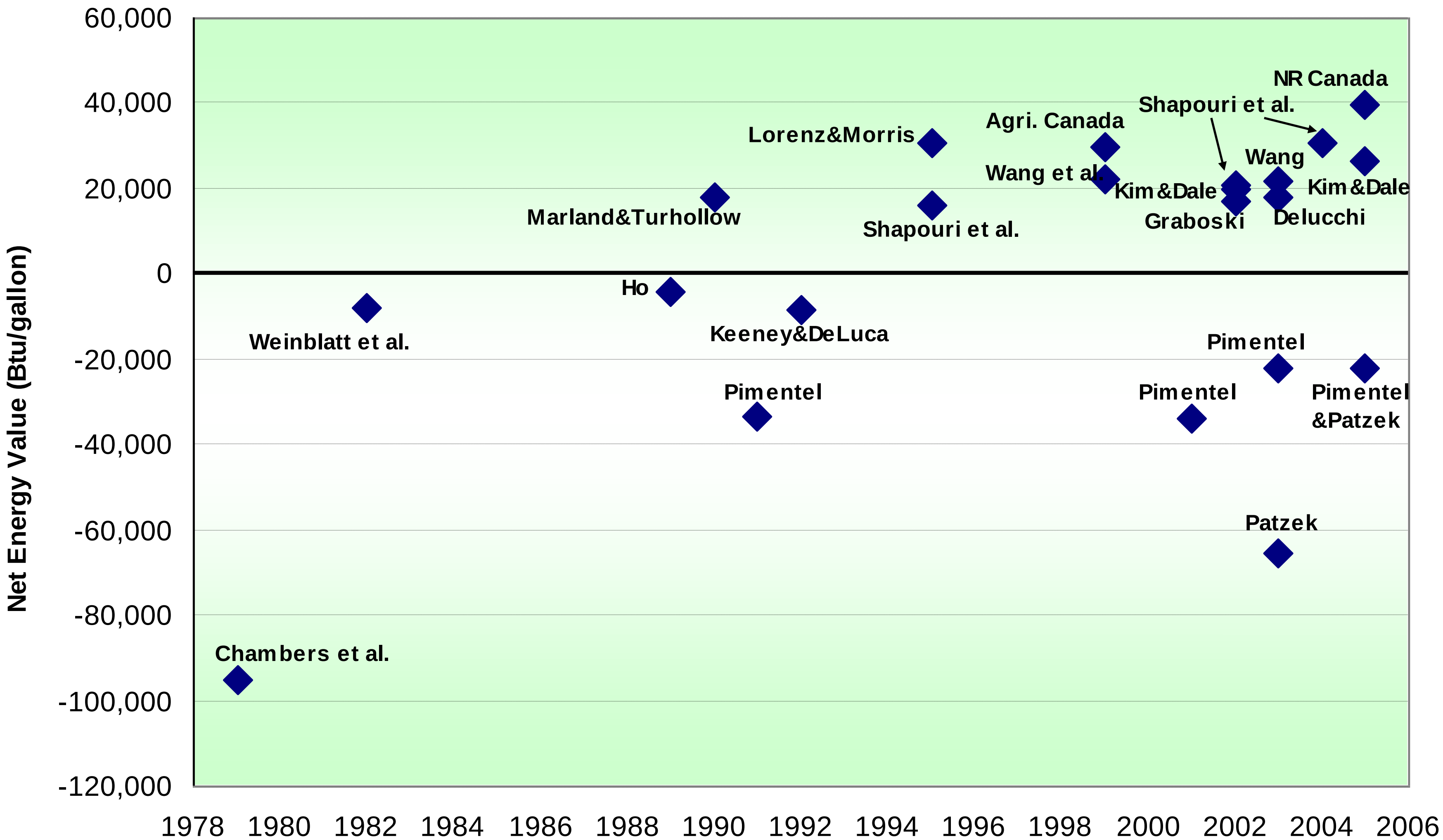
Source: IFEU 2006

Emissions Reductions from Biofuel Production and Use.



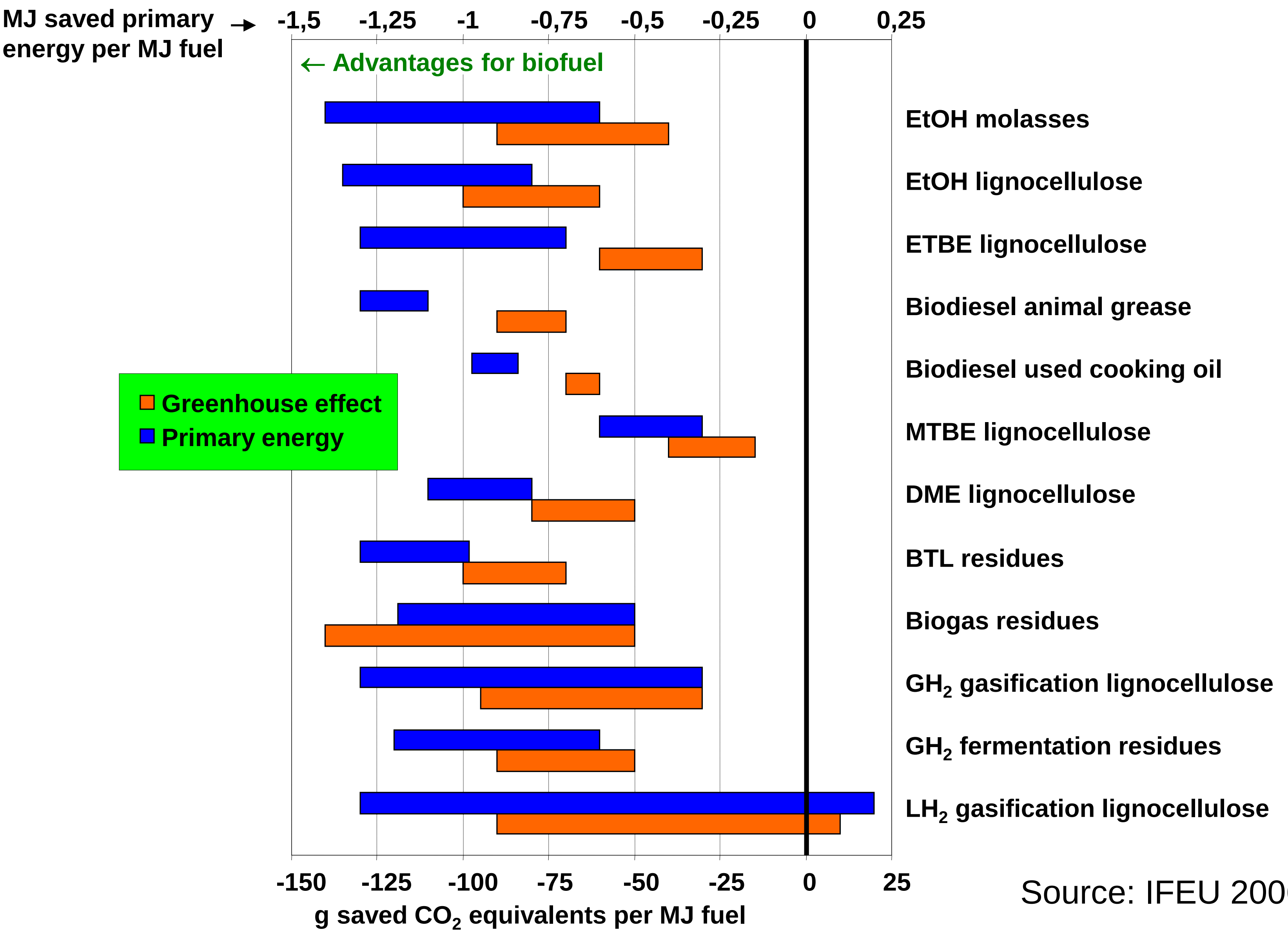
Source: IEA, 2005 and EMPA (biodiesel from palm oil). Note: Reduction in well-to-wheels CO_2-equivalent GHG emissions per kilometer

Net Energy Balance of Ethanol Biofuel (comparative studies).



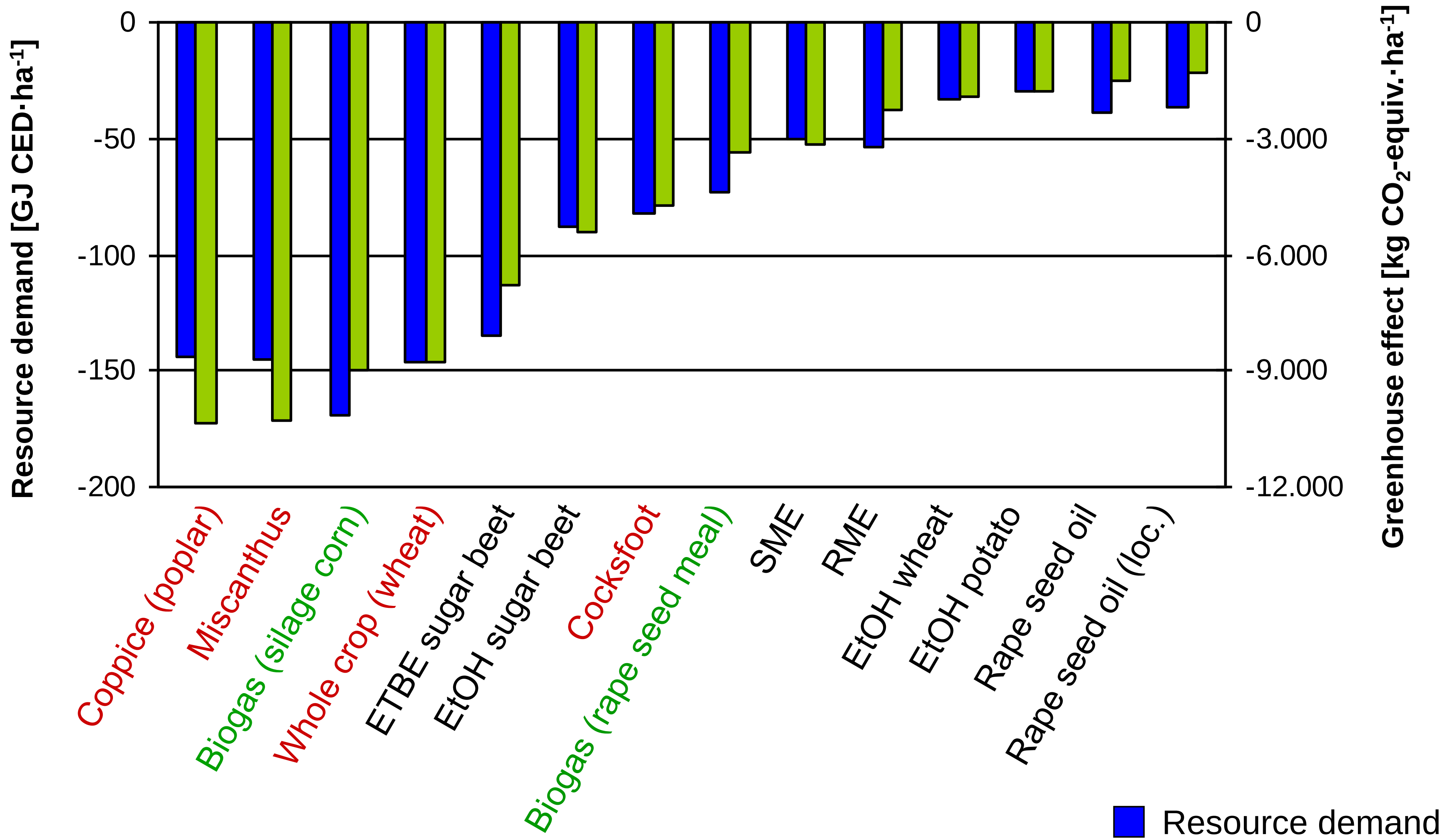
Michael Wang, Argonne National Laboratory,
http://www.anl.gov/Media_Center/News/2005/NCGA_Ethanol_Meeting_050823.ppt#1

Biofuels from Residues.



Source: IFEU 2006

Results: Biofuels versus Biofuels.



Source: IFEU 2006

Evaluation of Alternative Fuels (2010).

	EURO 4	Unreg. Emiss.	Degrad. + Toxic.	Engine wear	Costs + Availab.	LCA-CO_2
CNG	✳	●	●	✖	✳	✕✕
LPG	✳	●	✖	✖	✳	✕
Methanol (NG)	✳	●	✖	✖	✳	✕✕✕
BIODIESEL	✳	✳	✳	✳	●	✳✳
Biofuel (B5D)	●/✳	●	✖	✳	✳	●
Biofuel (E15D)	●/✳	●	✖	●	✳	●
Biofuel (E85G)	●/✳	●/✳	●	✖	●	✳
ETBE/Gasoline	●/✳	●/✳	✖	✖	✳	●

✖ PROBLEMATIC ● PROMISING ✳ VERY PROMISING

LCA – Some Conclusions.

Environmental assessment

- **In general, biofuels save fossil energy and GHG compared to conventional energy supply. Exemptions exist and explanations can be given.**
- **Solid biofuels usually perform better than liquid biofuels from energy crops.**
- **Biogas options based on energy crops lie within the range of liquid and solid biofuels. Detailed analyses are necessary to determine their impacts. Some biogas options have quite a high potential to save GHG.**

Sustainable potentials

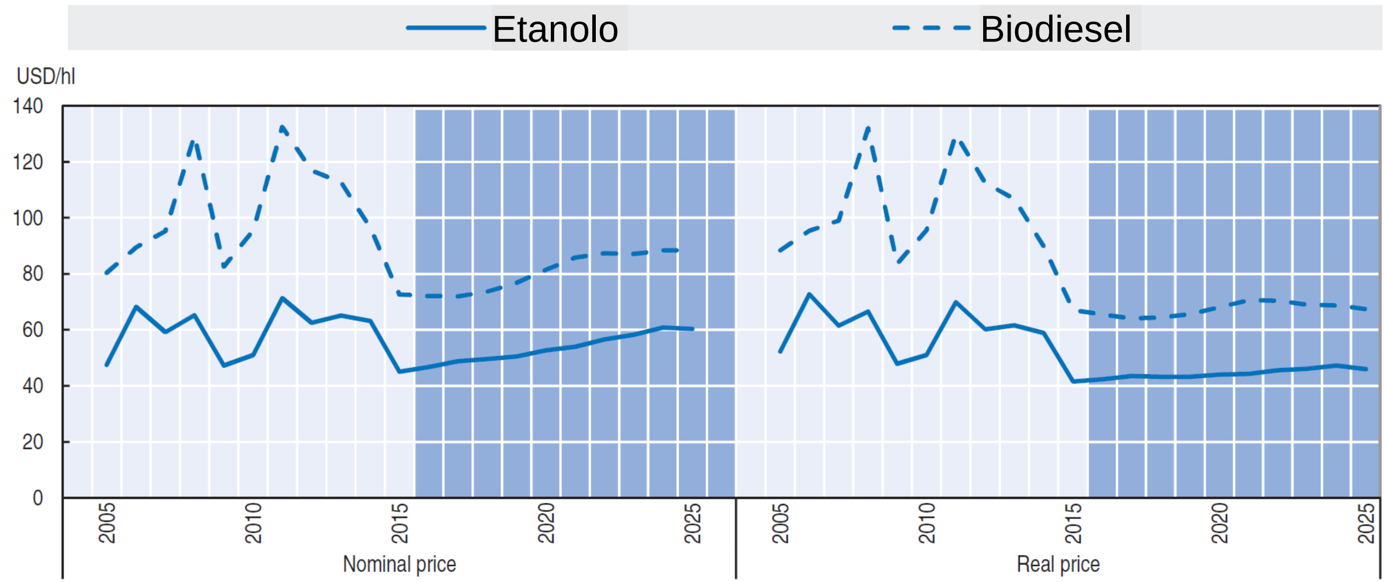
- **Because of competition for land and competition in the usage of biomass the potentials for energy crops are limited.**
- **If energy crops are used for biofuels, biggest greenhouse gas savings are associated with high yield crops like SRF, sugar beet or wheat.**
- **Lignocellulose has by far the biggest sustainable mass potential (energy crops and residues). This comes along with very effective greenhouse gas savings.**

Costi dei Biocombustibili.

Production costs	Eur/toe	Production costs	Eur/toe
Biodiesel	720	Ethanol from sugar beet	716
BTL from straw	1008	Ethanol from wheat	649
BTL from farmed wood	1147	Cellulosic ethanol from straw	957
Diesel (da petrolio)	550	(Anno 2010)	

'BTL' = 'Biomass to Liquid', biodiesel di 2° generazione

1 TOE = 41.87 GJ = 11.63 MWh



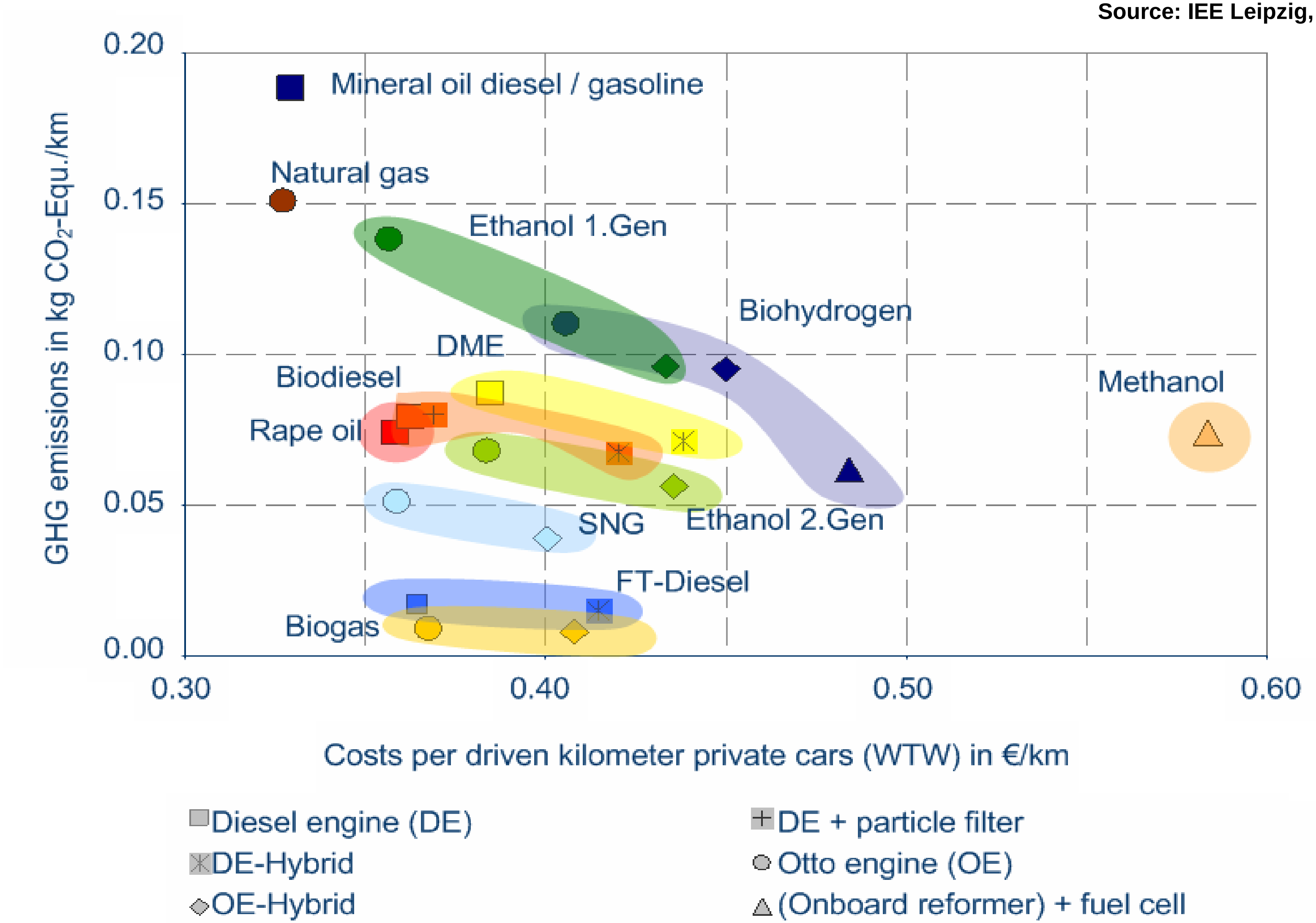
Note: Ethanol: wholesale price, US, Omaha; Biodiesel: Producer price, Germany, net of biodiesel tariff and energy tax.
Source: OECD/FAO (2016), "OECD-FAO Agricultural Outlook", *OECD Agriculture statistics* (database), *http://dx.doi.org/10.1787/agr-data-en.*
StatLink *http://dx.doi.org/10.1787/888933381654*

2014 – Actual Fuel Cost in EU-28.

En/In EURO						
	Euro-super 95 (I)	Automotive gas oil (I)	Gasoil Heating gas oil (II)	Fuel oil - (III) Sulfur ≤ 1%	Fuel oil - (III) Sulfur > 1%	
	1000L	1000L	1000L	t	t	
Austria	1.386,00	1.316,00	901,66	547,70		
Belgium	1.617,10	1.401,90	802,60	455,90		
Bulgaria	1.303,81	1.329,38	821,56			
Croatia	1.412,20	1.340,16	859,32	690,16		
Cyprus	1.420,87	1.430,83	1.017,90	746,08		
Czech Republic	1.337,36	1.332,17	880,63	409,01		
Denmark	1.665,73	1.454,82	1.505,20	1.067,81		
Estonia	1.280,00	1.260,00	945,00			
Finland	1.620,00	1.457,00	1.046,00			
France	1.500,00	1.299,40	872,30	525,48		
Germany	1.571,00	1.374,00	832,33			
Greece	1.670,00	1.358,00	1.246,30	575,65		
Hungary	1.342,74	1.353,44	1.353,44	662,69		
Ireland	1.573,00	1.479,00	1.038,23	807,43		
Italy	1.734,90	1.615,28	1.390,44	548,70		
Latvia	1.289,00	1.257,50	864,63			
Lithuania	1.337,61	1.276,52	771,26		519,40	
Luxembourg	1.335,24	1.186,82	738,56			
Malta	1.440,00	1.360,00	1.050,00			
Netherlands	1.735,00	1.416,00	1.029,00	501,00		
Poland	1.263,38	1.233,44	874,50	566,14	495,02	
Portugal	1.550,00	1.312,00	1.265,00	690,27		
Romania	1.393,73	1.413,16	1.106,47	561,03		
Slovakia	1.466,00	1.342,00		614,60	607,96	
Slovenia	1.441,00	1.355,00	1.019,00	667,08		
Spain	1.415,68	1.326,62	869,41	536,89		
Sweden	1.577,40	1.532,78	1.295,37	977,70		
United Kingdom	1.615,61	1.674,71	773,87			
CE/EC/EG EUR 28 (IV) Weighted average	1.558,44	1.408,04	906,58	608,43	509,66	
CE/EC/EG Euro Area 18 (€) V) Weighted average €	1.586,04	1.384,57	897,51	565,08	607,96	

Comparison of Technologies
Economic versus Environmental Aspects.

Source: IEE Leipzig, 2007



Costs: Longer-term Prospects.

Costs:

- 1st generation: 80% of production costs is cost of oil seed feedstock
- 2nd generation: potentially cheaper feedstock; higher capital costs for production method
- Lowered by using crops with higher yields (e.g. *jatropha*; palm, *miscanthus*) and mass production of biofuels
- Costs of 2nd generation likely to be less volatile, whereas costs of conventional diesel to become more volatile?

Prices:

- Affected by national taxes and subsidies
- Price of other fuels

Costs for Biofuel Production (High Yield).

Cash Price for Breakeven Return over Variable Costs - North RRV, N.D. **Base Crop is** **Corn**

Enter the futures price for	Corn	$3.60
Enter your expected local basis		$0.60
Expected local cash price for	Corn	$3.00

Base crop = 1	1	0	0						
	Corn	Soybean	Wheat	Barley	Drybeans	Oil Snflr	Conf Snflr	Canola	Flax
Yield	101	31	42	57	14.7	13.7	12.5	13.2	23
Price	$3.00	$6.94	$5.90	$3.98	$18.07	$17.21	$20.58	$19.17	$9.30
Income	$303.00	$215.28	$247.64	$226.67	$265.70	$235.84	$257.19	$253.03	$213.98
Variable costs:									
seed	$38.36	$32.59	$13.80	$11.00	$31.00	$16.32	$23.60	$18.15	$6.40
herbicide	8.00	8.00	14.20	12.50	24.00	15.50	15.50	17.50	14.71
fungicide			5.00	1.25					
insecticide						5.00	11.00	7.00	
fertilizer	43.25	0.10	33.93	25.61	21.09	17.32	14.54	31.76	17.10
crop insurance	17.70	8.30	10.30	4.91	15.30	7.52	12.35	10.90	5.55
fuel & lube	19.74	11.88	14.27	15.46	15.87	15.21	15.69	12.35	14.78
repairs	15.46	10.43	11.42	12.03	13.02	11.96	12.15	10.44	12.01
drying	13.64					2.74	2.52		
misc.	1.00	1.50	1.00	1.00	1.00	1.00	5.75	1.00	1.00
operating int.	6.29	2.91	4.16	3.35	4.85	3.70	4.52	4.36	2.86
Total var.costs	$163.44	$75.71	$108.08	$87.11	$126.13	$96.27	$117.62	$113.46	$74.41
Return over variable costs	$139.56	$139.56	$139.56	$139.56	$139.56	$139.56	$139.56	$139.56	$139.56

Note: - Only variable costs are considered in this comparison. You can include an amount under "misc." to account for any differences between crops in fixed costs, labor, management and risk.

Costs for Biofuel Production (Low Yield).

Cash Price for Breakeven Return over Variable Costs - North West N.D. **Base Crop is** **Corn**

Enter the futures price for	Corn	$3.60
Enter your expected local basis		$0.60
Expected local cash price for	Corn	$3.00

Base crop = 1	1	0	0								
	Corn	S. Wht	Durum	Barley	Oats	Oil Snflr	Field Pea	Canola	Flax	W. Wht	Lentils
Yield	63	28	29	47	58	12.1	31	13.7	19	32	13.5
Price	$3.00	$5.27	$5.19	$3.09	$2.43	$14.00	$4.76	$13.86	$7.44	$4.40	$10.93
Income	$189.00	$147.63	$150.62	$145.09	$141.05	$169.34	$147.50	$189.82	$141.42	$140.82	$147.57
Variable costs:											
seed	$26.03	$8.63	$10.50	$6.25	$7.50	$15.98	$19.20	$18.15	$4.80	$6.00	$13.30
herbicide	11.00	14.30	14.30	13.80	4.88	23.65	20.00	20.50	20.71	8.15	23.50
fungicide		1.50	1.50	1.25							
insecticide						5.00		7.00			
fertilizer	26.01	21.00	22.16	22.54	24.48	16.86	6.47	37.63	14.50	25.66	4.70
crop insurance	15.00	6.50	7.10	3.89	6.44	8.44	3.81	8.50	5.50	6.50	7.71
fuel & lube	11.73	8.77	8.80	10.37	10.75	9.36	10.97	9.64	9.21	8.84	10.96
repairs	11.68	9.48	8.70	9.64	9.80	9.35	10.61	9.33	9.49	8.48	10.95
drying	8.51					2.42					
misc.	5.00	5.00	5.00	5.00	5.00	5.00	4.00	5.00	5.00	5.00	4.00
operating int.	4.60	3.01	3.12	2.91	2.75	3.84	3.00	4.63	2.77	2.75	3.00
Total var.costs	$119.56	$78.19	$81.18	$75.65	$71.60	$99.90	$78.06	$120.38	$71.98	$71.38	$78.12
Return over variable costs	$69.44	$69.44	$69.44	$69.44	$69.44	$69.44	$69.44	$69.44	$69.44	$69.44	$69.44

Note: - Only variable costs are considered in this comparison. You can include an amount under "misc." to account for any differences between crops in fixed costs, labor, management and risk.
- Crop insurance for corn is only available by written agreement. An estimate is used.

Sustainability Concerns.

- **Concerns over potential impacts of growing crops for biofuels on:**
  - **Competition with food**
  - **Biodiversity (e.g. forest clearance)**
  - **Water and soil resources**
  - **Greenhouse gas balance**

- **No useable, common sustainability standards or certification for biofuels**
  - "*A misjudged push for the wrong kinds of 'green' fuels could damage the climate and destroy the world's last remaining rain forests*"

Environmental NGOs (inc. WWF, Greenpeace and Friends of the Earth) May 2007

Link to Biomass.

- Alternative Fuels Data Center
  www.eere.energy.gov/afdc/
- Biomass Energy Foundation
  www.woodgas.com
- Canadian Renewable Fuels Association
  www.greenfuels.org
- European biomass association
  www.ecop.ucl.ac.be/aebiom
- Federazione di Produttori di Energia Rinnovabili – Fiper
  www.fiper.it
- Istituto di Ricerche sulla Combustione-CNR
  www.irc.na.cnr.it
- Italian Biomass Association
  www.itabia.it
- The Anaerobic Digestion Network
  http://mara.jrc.it/adnett.html

References on Alternative Fuels.

http://www.eere.energy.gov/afdc/index.html

http://www.energyinstitution.org/Alt%20Fuels%20Index%20free%20request.htm

http://www.soygrowers.com/

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