Ειδικά κεφάλαια παραγωγής ενέργειας

Ενότητα 4(β): Anaerobic Digestion of Biomass

Αν. Καθηγητής Γεώργιος Μαρνέλλος
(Γραφείο 208)
Τηλ.: 24610 56690,
e-mail: gmarnellos@uowm.gr

Τμήμα Μηχανολόγων Μηχανικών

Άδειες Χρήσης

Χρηματοδότηση

- Το παρόν εκπαιδευτικό υλικό έχει αναπτυχθεί στα πλαίσια του εκπαιδευτικού έργου του διδάσκοντα.
- Το έργο «**Ανοικτά Ψηφιακά Μαθήματα στο Πανεπιστήμιο Δυτικής Μακεδονίας**» έχει χρηματοδοτήσει μόνο τη αναδιαμόρφωση του εκπαιδευτικού υλικού.
- Το έργο υλοποιείται στο πλαίσιο του Επιχειρησιακού Προγράμματος «Εκπαίδευση και Δια Βίου Μάθηση» και συγχρηματοδοτείται από την Ευρωπαϊκή Ένωση (Ευρωπαϊκό Κοινωνικό Ταμείο) και από εθνικούς πόρους.

Ευρωπαϊκή Ένωση
Ευρωπαϊκό Κοινωνικό Ταμείο

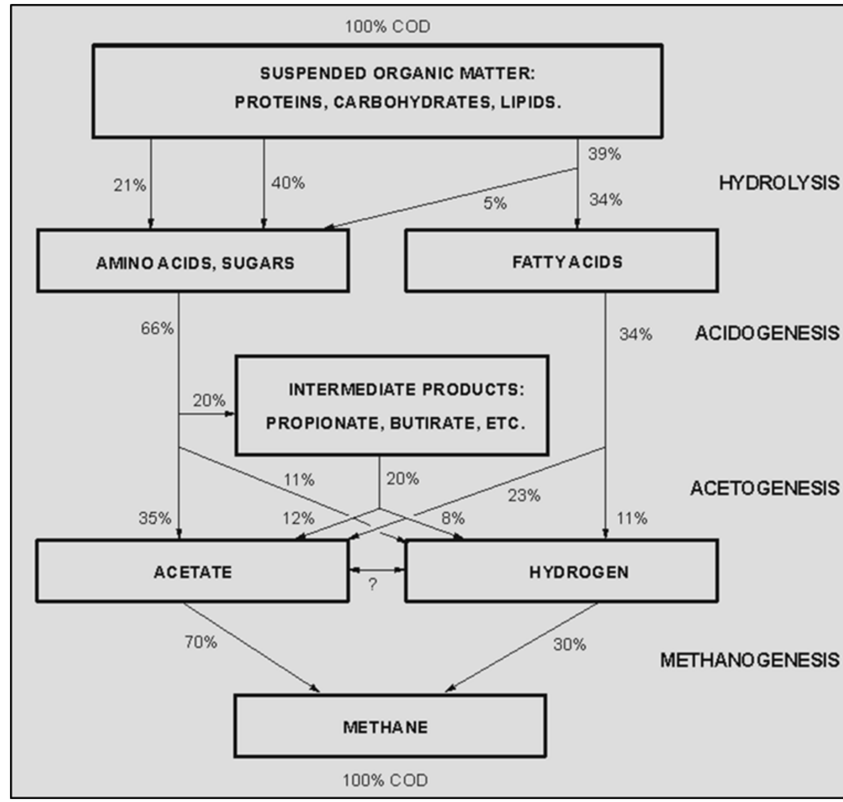
ΕΠΙΧΕΙΡΗΣΙΑΚΟ ΠΡΟΓΡΑΜΜΑ
ΕΚΠΑΙΔΕΥΣΗ ΚΑΙ ΔΙΑ ΒΙΟΥ ΜΑΘΗΣΗ
επένδυση στην κοινωνία της γνώσης
ΥΠΟΥΡΓΕΙΟ ΠΑΙΔΕΙΑΣ ΚΑΙ ΘΡΗΣΚΕΥΜΑΤΩΝ
ΕΙΔΙΚΗ ΥΠΗΡΕΣΙΑ ΔΙΑΧΕΙΡΙΣΗΣ

ΕΣΠΑ 2007-2013
πρόγραμμα για την ανάπτυξη
ΕΥΡΩΠΑΪΚΟ ΚΟΙΝΩΝΙΚΟ ΤΑΜΕΙΟ

Με τη συγχρηματοδότηση της Ελλάδας και της Ευρωπαϊκής Ένωσης

Anaerobic Digestion Mechanism (1/2)

- Anaerobic digestion (AD) is a set of biochemical reactions conducted by microorganisms that live or grow in the absence of oxygen, and are responsible for the conversion of complex organic biomass molecules into simpler chemical molecules (mainly organic acids) and finally to CH_4, CO_2, CO, NH_3, H_2S, H_2 etc.
- AD is a complex biochemical process which takes place in a sequence of steps which often interact between each other. Each step is carried out by a group of microorganisms which grow at different rates and displays different kind of sensitivity to environmental conditions (pH, hydrogen partial pressure, etc.).



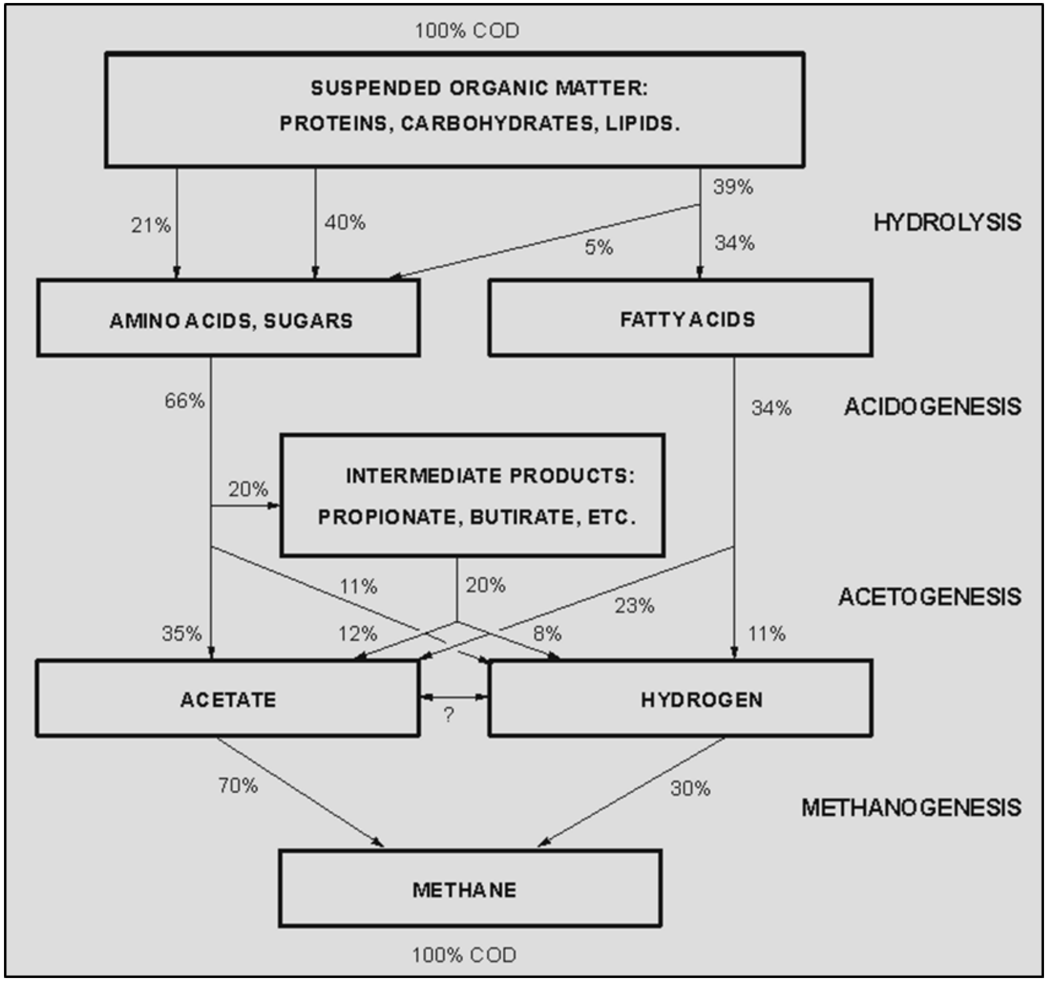
Anaerobic Digestion Mechanism (Various Steps) (1/2)

- **Decomposition:** the composite particulate material of biomass decomposes to the organic polymers that it consists of (carbohydrates, proteins, lipids).
- **Hydrolysis:** the organic polymers are hydrolyzed (depolymerized) by extracellular enzymes to their respective monomers (sugars, amino acids, lipids), which may be retained by the microorganisms for further degradation.
- **Acidogenesis**: simple monomers are converted to a mixture of volatile fatty acids (valeric, butyric, propionic, acetic, etc.), alcohols and other simpler organic compounds and gas products (carbon dioxide and hydrogen).

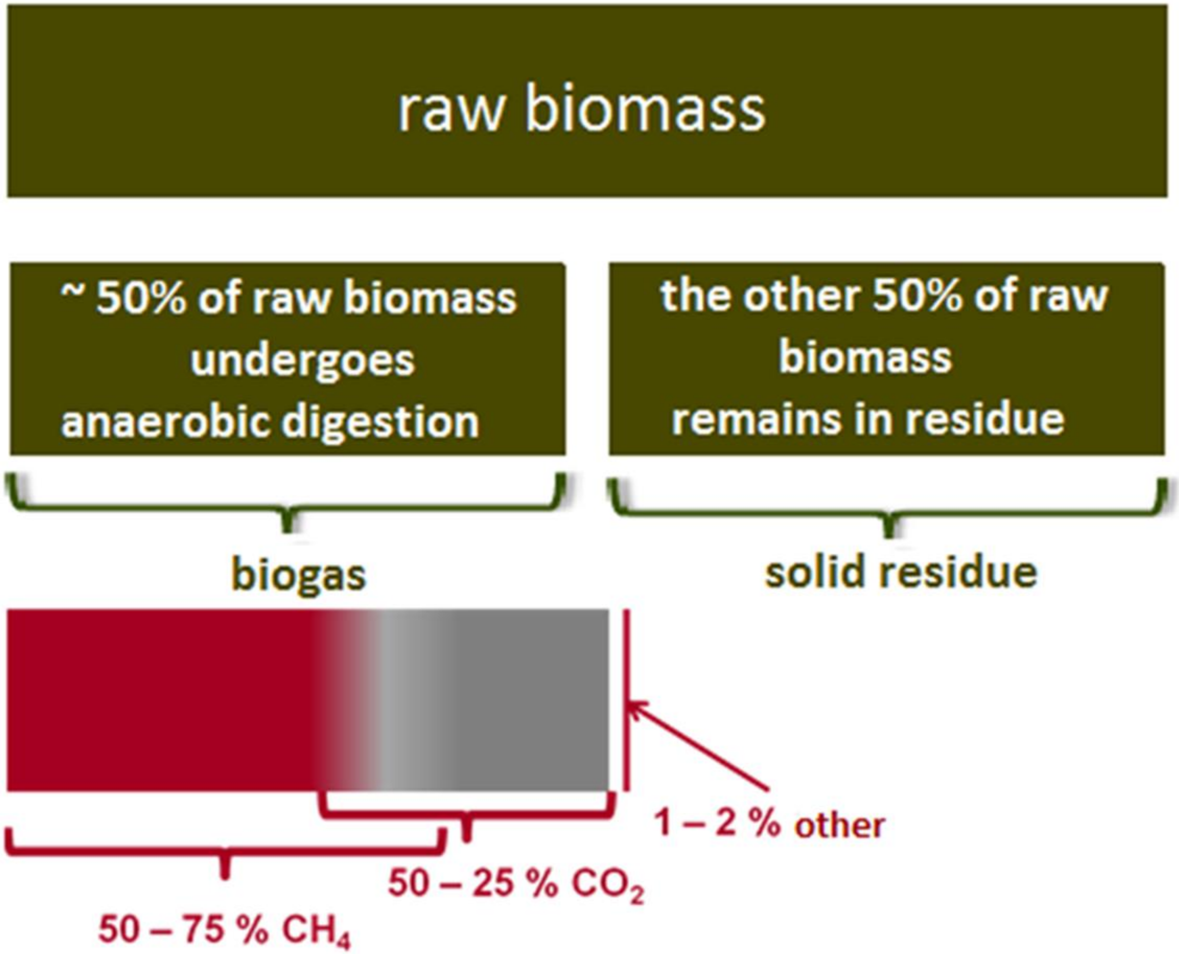
Anaerobic Digestion Mechanism (Various Steps) (2/2)

- **Acetogenesis**: volatile fatty acids with a longer chain than that of acetic acid (valeric, butyric, propionic, etc.) and other organic molecules produced in the process of acidogenesis are transformed into acetic acid, carbon dioxide and hydrogen from acetogenic bacteria.
- **Methanogenesis**: the production of methane is achieved by two separate groups of microorganisms: (a) methanogenic acetogens developed with acetic acid and produce almost 70% of the biogas and (b) hydrogen-consuming methanogens which consume hydrogen and carbon dioxide.

Anaerobic Digestion Mechanism (2/2)



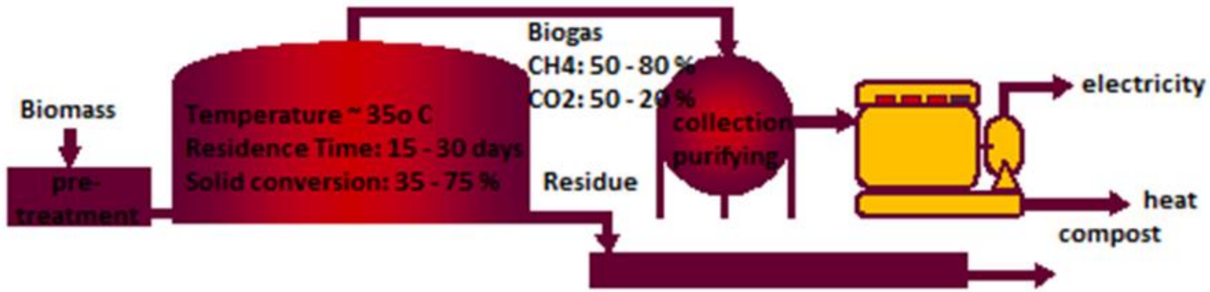
Composition of Biogas (1/2)



Composition of Biogas (2/2)

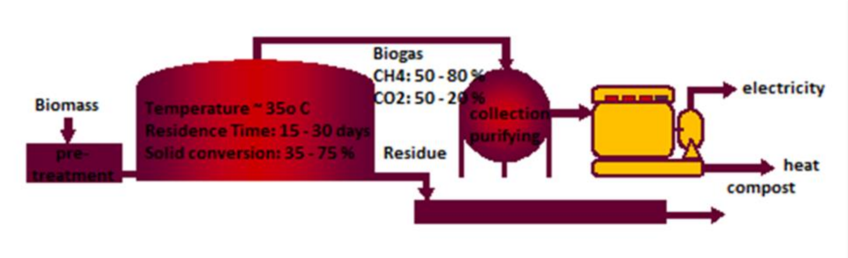
- The biogas consists of 98-99% of CH_4 and CO_2 and 1-2% of CO, NH_3, H_2S and traces of other gases.
- The CH_4/CO_2 ratio ranges from 1/1 to 3/1.
- The solid residue (solid + liquid, the first is in the form of sludge and the second one in the form of a suspension of particles in wastewater with increased COD), displays high concentration of metal salts (from the inorganic part of biomass), and it can be used as a fertilizer.
- Generally, any type of biomass can undergo AD to produce biogas, but because of the **slow metabolism of crude lignin**, woody biomass is avoided. In addition because of the fact that **the process takes place in the liquid phase and in large excess amount of water** (total solids concentration ranges from 0.5-25% wt.):
  - ✓ Fresh agricultural residues.
  - ✓ Fresh biomass of herbaceous energy crops.
  - ✓ Animal wastes.
  - ✓ Food industry wastes.
  - ✓ Organic fraction of urban wastes.
  - ✓ Activated sludge from wastewater treatment plants.

Description of AD process (1/2)



- **Biomass pretreatment**: Depending on raw material type may include storage (agricultural wastes), grinding (plant biomass), sanitation when it stays at temperatures higher than 70°C for the period required to destroy any pathogens (animal waste), initial extracellular hydrolysis, mixing of various raw materials, dilution or condensing of solids, pH regulation, preheating etc.
- **Anaerobic Digestion Tank (Digester)**: AD takes place under special conditions of temperature and residence time in the digester. Biogas that comes out from the top of the reactor moves to power generator, while solid residue is discharged from the bottom to the drying tanks.

Description of AD process (2/2)



Purification and Collection of Biogas: To balance the cogeneration system supply, also includes a water sprinkler system that removes ammonia and H_2S.
Co-generation Unit: A series of biogas internal combustion engines and heat exchangers for industrial and household heat production.
Digestate Drying Tanks: The residue solid material is fed into sequential drying tanks, from where it can be taken either in liquid form (for direct use in rural areas) or packed in dry form and sold as fertilizer.

Efficiency of Anaerobic Digestion (1/4)

The general reaction that describes AD is:

$$C_aH_bO_cN_d + [(4a-b-2c+3d)/4]H_2O \rightarrow [(4a+b-2c-3d)/8]CH_4 + [(4a-b+2c+3d)/8]CO_2 + dNH_3.$$

However, it consists of a large number of intermediate enzymatic reactions which are performed by a variety of microbial populations and are divided into categories:

1. Enzymatic Acidogenesis Reactions:

- **Extracellular Enzymatic Hydrolysis Reactions**: Microorganisms release enzymes from the degradation of the biomass macromolecules (polysaccharides, proteins, fats, etc.) into smaller molecules which can be consumed as food by themselves and,
- **Intracellular Enzymatic Acidogenesis Reactions**: Smaller molecules are consumed by microorganisms and are released from their digestive system as volatile organic (fatty) acids (mainly propionic, butyric, valeric and small amounts of acetic acid) and smaller quantities of alcohols and amines.

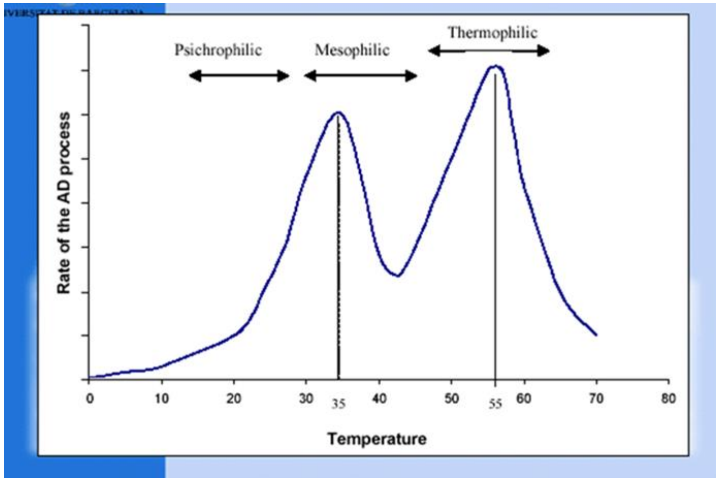
Efficiency of Anaerobic Digestion (2/4)

2. Enzymatic Acetogenesis Reactions: The acids are transformed, during their digestion by other groups of microorganisms, into acetic acid (hydrogen is released).

3. Enzymatic Methanogenesis Reactions: A third group of microorganisms consume acetic acid (but also alcohols and amines) and with the help of hydrogen and carbon dioxide, they produce methane.

Efficiency of Anaerobic Digestion (3/4)

- AD has two rate peaks in two temperature regions and based on this criterion AD processes are divided into:
  - **mesophilic**, taking place in the region of 35^oC and,
  - **thermophilic**, taking place in the region of 55^oC.
- Thermophilic processes are relatively faster than Mesophilic and achieve higher conversions of solids, for the same **Hydraulic Retention Time** (higher conversion and higher biogas production for the same volume of digester).
- Their advantage, is balanced by the increased energy costs of the process and the higher capital cost for the thermal insulation of tanks.



Efficiency of Anaerobic Digestion (4/4)

- Three different operational parameters are associated with the solids content of the feedstock to the digesters:

low solid	**solid concentration by weight**	**<10%.**
semi-dried solid	**>>**	**10 - 25%.**
high solid	**>>**	**>25%.**

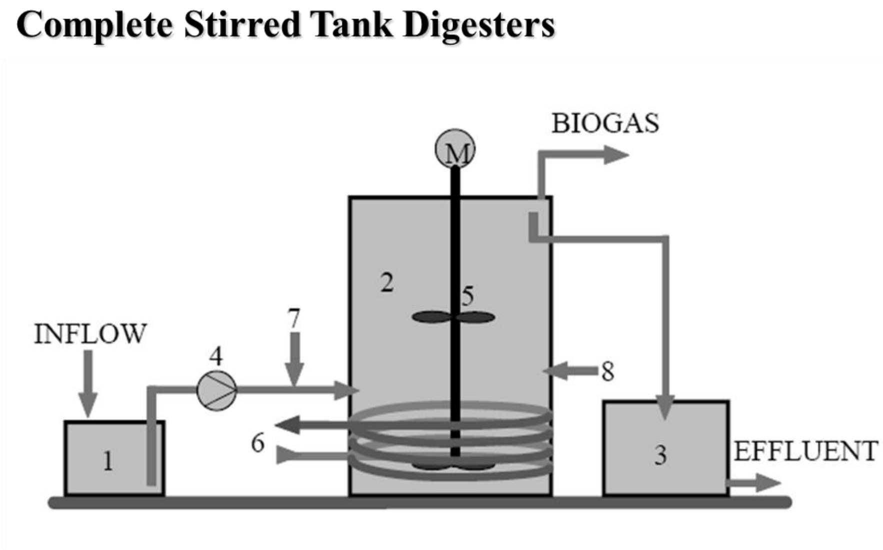
- With usual applications on the order of 3 to 8% by weight of solid concentrations.
- The optimal solid concentrations fed to the anaerobic digester, are determined by its technology (continuous flow stirred tank reactor, plug flow, with filling material, one or multi-stage, etc.), the type of raw material and the physical condition of biomass (liquid streams of high organic load, particle size, etc.) and adequate mixing.
- Solid raw materials are divided into the fraction which can be converted into biogas and are called **volatile solids** (volatile solids - VS) and the fraction that cannot be converted during the process (inorganic, lignin, large particles). For common types of biomass the volatile solids fraction is about 90%.

Types of Digesters (1/3)

Covered Lagoons

- Up to 2 % solids.
- High feed rates, in order to have adequate substrates.
- Low VS conversions.
- Applied at warm areas.
- Economical viable.
- 1/3 of digesters worldwide, at China, India, South US.

Types of Digesters (2/3)



- 2 – 10 % solids.
- Insulated and stirred tank digesters.
- High VS conversions.
- Energy consumption due to mixing: 40 – 50 watt / m^3.
- High cost.
- 1/3 of digesters worldwide, mainly in Europe.

Types of Digesters (3/3)

Plug Flow Digesters

- 10 – 15 % solids.
- Insulated and elongated tanks.
- High VS conversions.
- More than 1/3 of digesters worldwide, mainly in Europe.

Efficiency of Anaerobic Digestion (1-2)

- The **hydraulic Retention Time** (HRT) determines the overall conversion of volatile solids into biogas and is determined by a variety of factors such as the type of biomass, the process temperature, the time of reproduction of microorganisms, etc.
- Assuming there are two phases in the digester, a solid and a liquid, there are two values of retention times, Ti and Ts, which tend to be equal in the presence of a homogeneous feedstock, without recycling of sludge and with good stirring.

Efficiency of Anaerobic Digestion (2-2)

- The conversion of VS, to the HRT for low solids processes is given by:

mesophilic process: % conversion VS = 17.9 x lnHRT – 3.9.

thermophilic process: % conversion VS = 19.8 x lnHRT + 14.9.

- The HRT determines the anaerobic digester's volume for a given volumetric flow of the biomass/water mixture: $\mathbf{V_{digester} = Q \times HRT}$.
- For standard feedstock HRT varies from 5-30 days (usually 10-20).
- The digester contains apart from the liquid phase an additional volume for the release of biogas. In practical applications, $\mathbf{V_{digester} = 4/3\ V_{liquid\ phase}}$.

Example for Anaerobic Digestion

Calculate the digester's volume required to achieve 50% conversion of total solid biomass with typical composition, in a mesophilic process with load of total solid 5% by weight. Calculate also the annual biogas production and its specific calorific value. The available amount of biomass for anaerobic digestion is 40.000 ton/year and the volatile part of it (dry biomass minus inorganic part minus fixed carbon) corresponds to 80% by weight of total solids.

Considering typical composition of biomass:

- moisture 10%
- ash 5%
- carbon 43%
- oxygen 37%
- hydrogen 5%

Crucial Parameters of the AD process

Organic Loading Rate, OLR:

$OLR = (Q \times S)/V = S/HRT$ [kg of solids / m^3 digester / d],

where Q inlet volumetric flow rate, m^3/d,

S Volatile Solids concentration, kg/m^3,

V digester volume, m^3,

HRT hydraulic retention time, d.

Specific Gas Production, SGP:

$SGP = Q_{gas}/(Q \times S)$ [m^3 biogas / kg of solids],

where Q_{gas} biogas volumetric production, m^3/d .

Gas Production Rate, GPR:

$GPR = Q_{gas}/V$ [m^3 biogas / m^3 digester / d].

OLR, SGP and GPR are related as follows: $GPR = SGP \times OLR$.

Anaerobic Digestion Process

Anaerobic Digestion:

single stage TS 3 – 8 %
single stage semi-dried solids TS 15 – 23 %
single stage high solids TS > 25 %

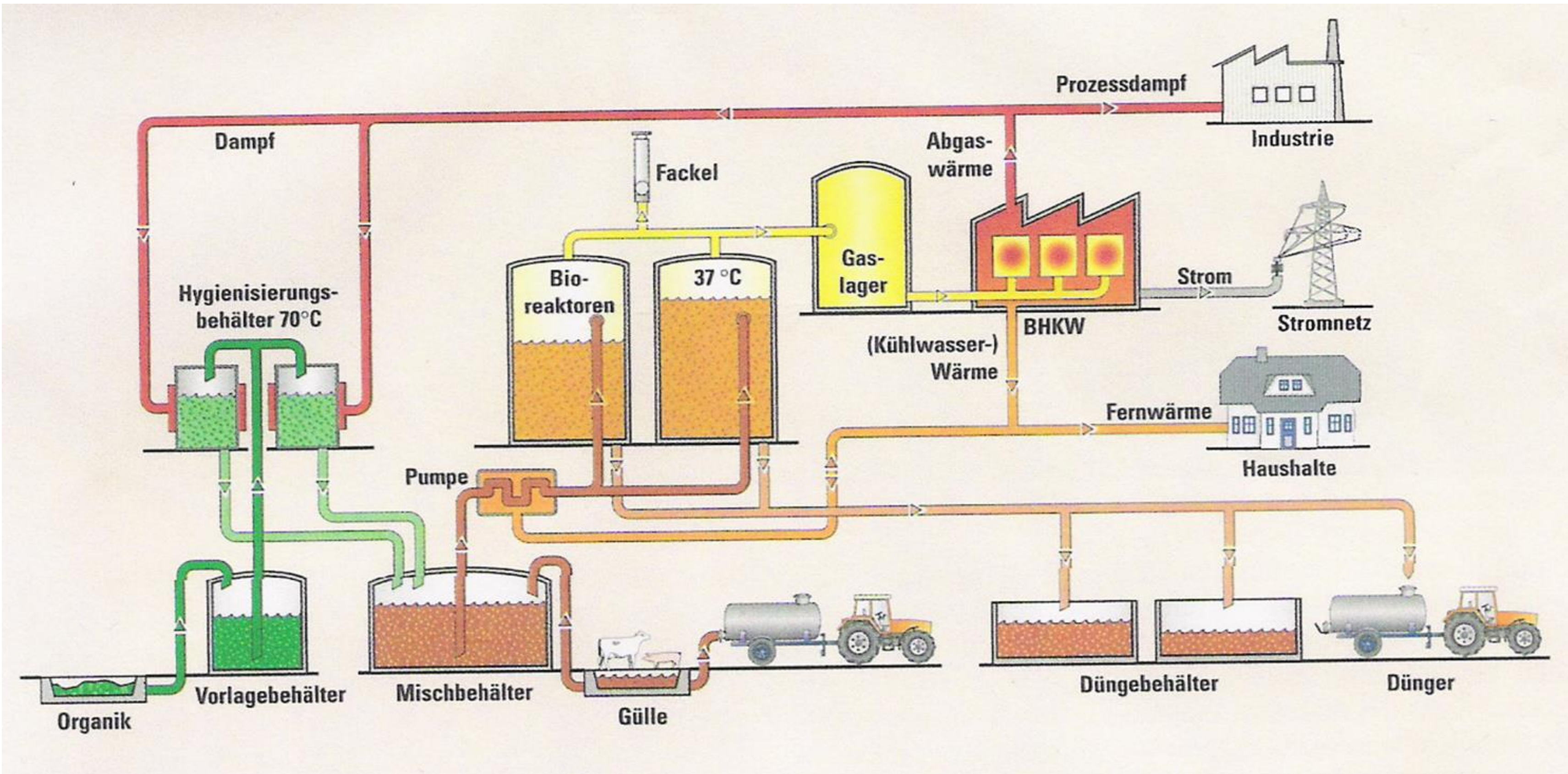
psichrophilic T < 20 °C
mesophilic 30 °C < T < 40 °C
thermophilic 50 °C < T < 70 °C

T,°C residence	volatile time, days	CH_4 solids, kg/m^3	solids m^3/kg	conversion, %	
Municipal Wastes	35-40	15-27	1-14	0.19-0.43	25-75
Fruit and Vegetable Wastes 28-39	8-59	1-9	0.09-0.53	34-99	
“Green” matter	33-56	5-30	1-3	0.11-0.42	35-95
Woody Biomass	25-55	5-55	1-5	0.09-0.32	25-65

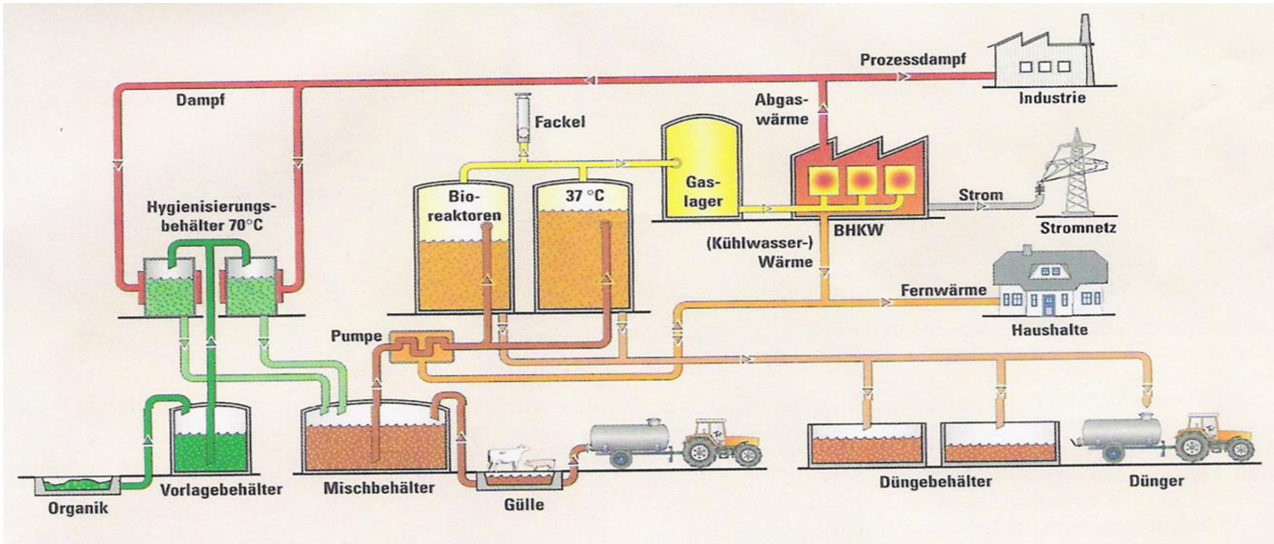
Calculations

	Pigs	Cattles
Weight, kg	60	350 – 650
Waste (solids + liquids), lt/d	5	25 – 50
Solids (initial), %	10	15
Solids (after dillution), %	7	8
Wastes (after dillution), lt/d	7 – 8	45 – 90
Volatile Solids, kg/d	0.45	2 - 5
Digester Volume, m^3/animal	0.14	0.5 – 1.3
Loading, kg VS / m^3 digester	3	4
Residence Time, d	20	13 – 15
VS conversion, %	50	35 – 45
Biogas Yield, m^3/m^3 digester m^3/animal/d	1 0.1	1 0.8 – 1.3

Anaerobic Digestion Flowchart



1 MW(el) Anaerobic Digestion Plant (1/2)



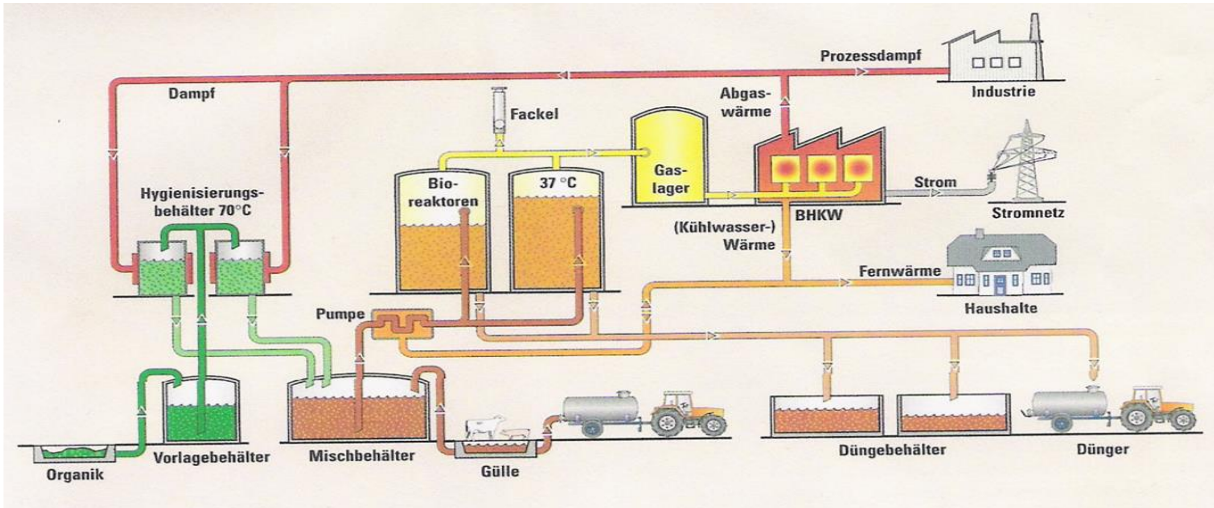
Area 8 – 10 str. **Agro-residue storage tank: 5.000 m^3 .**

animal waste storage tank: 5.000 m^3 .

Pasteurization tank: **70 ^oC, 2 x 5.000 m^3 .**

Anaerobic Digesters : **Temperature between 30 – 40 ^oC**
Residence Time 15 - 30 days,
Volume 2 x 8.000 m^3.

1 MW(el) Anaerobic Digestion Plant (2/2)



- **Cogeneration unit:** Biogas ICE (for the generation of electric power) and heat exchangers for the production of heat.
- Drying tanks for the produced solid residue for the production of high quality fertilizer.

Biogas Characteristics

Biogas is mainly consisted (99 %) of CH_4 and CO_2.

H_2S is the main byproduct, which is corrosive and has to be removed.

Raw Material	solids, 2 gr/lt			solids, 3.5 gr/lt.		
	CH_4	CO_2	H_2S	CH_4	CO_2	H_2S
Rape seed	53	46	0.10	55	44	0.80
Cardoon	51	48	0.00	51	48	0.08
Sunflower	58	41	0.02	40	59	0.10
Wheat	53	46	0.01	52	47	0.03
Rice	53	46	0.00	52	47	0.01
Maize	53	46	0.00	53	46	0.00

Biogas Heating Value

Heating Value of Methane:

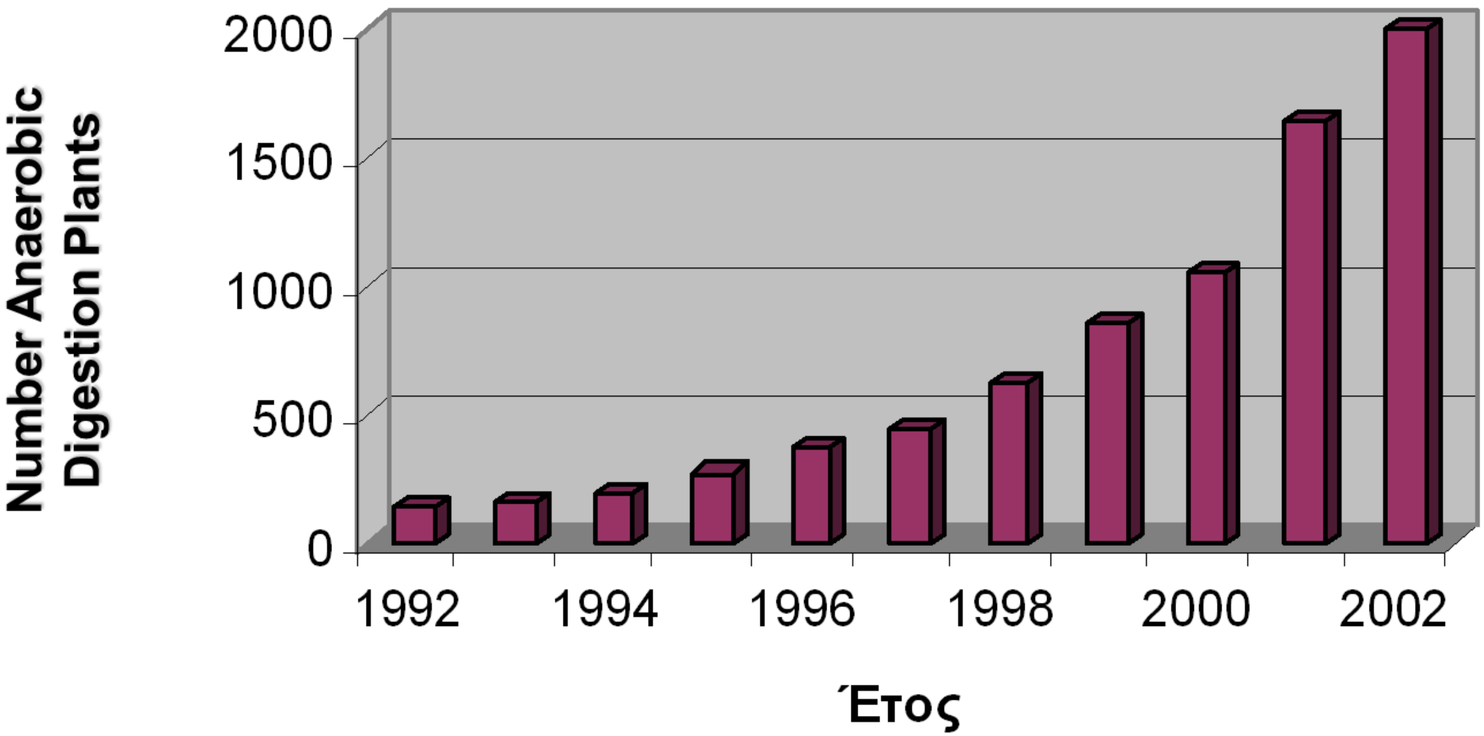
$$CH_4 + O_2 = CO_2 + 2\ H_2O + 876\ kJ$$

876 kJ/mol = 876 kJ/22.4 lt = 39.1 kJ/lt.
Natural Gas Heating Value.

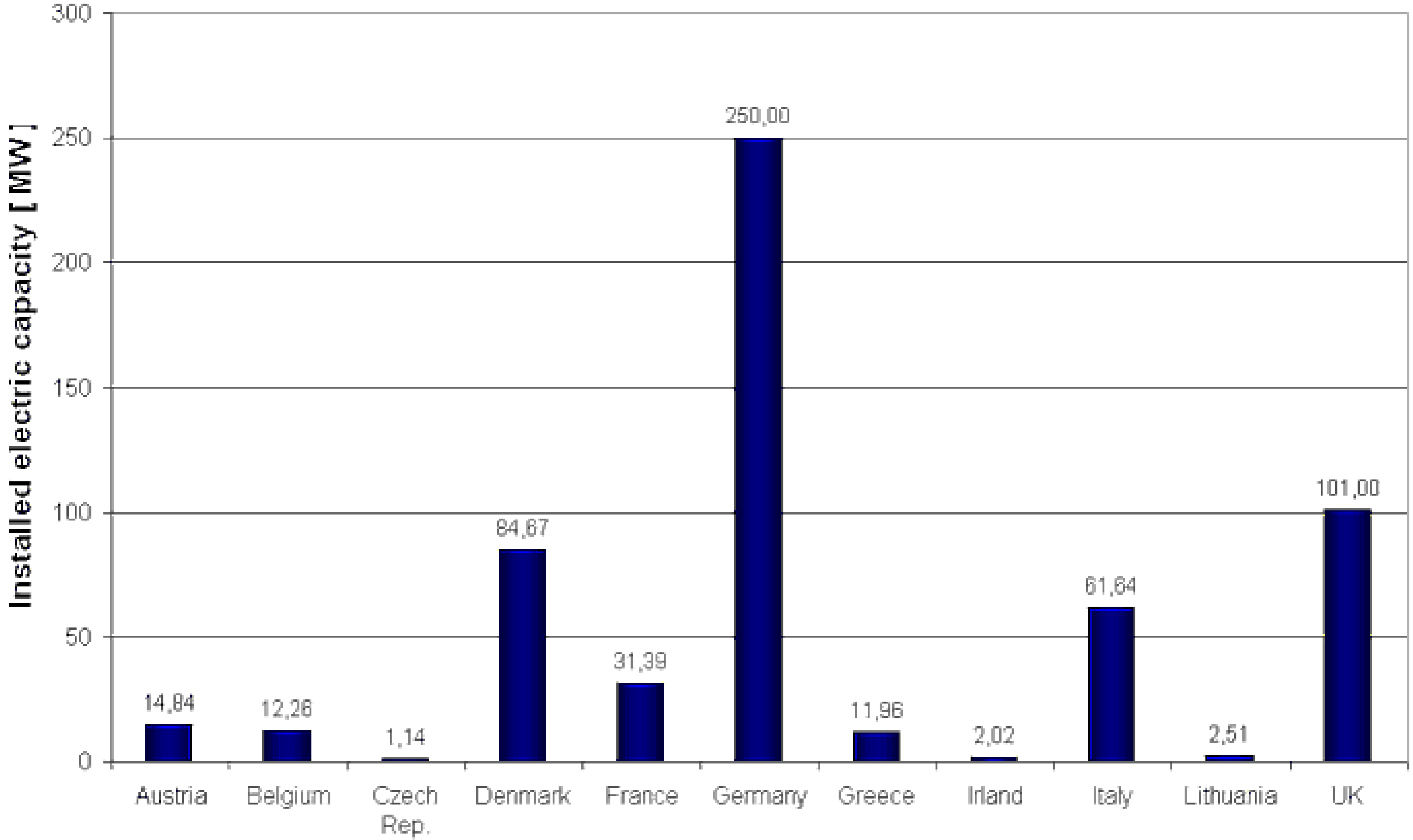
60 – 95 % CH_4: 526 – 788 kJ/22.4 lt = 23 – 35 kJ/lt.
Biogas Heating Value.

50 – 80 % CH_4: 438 – 700 kJ/22.4 lt = 19 – 31 kJ/lt.

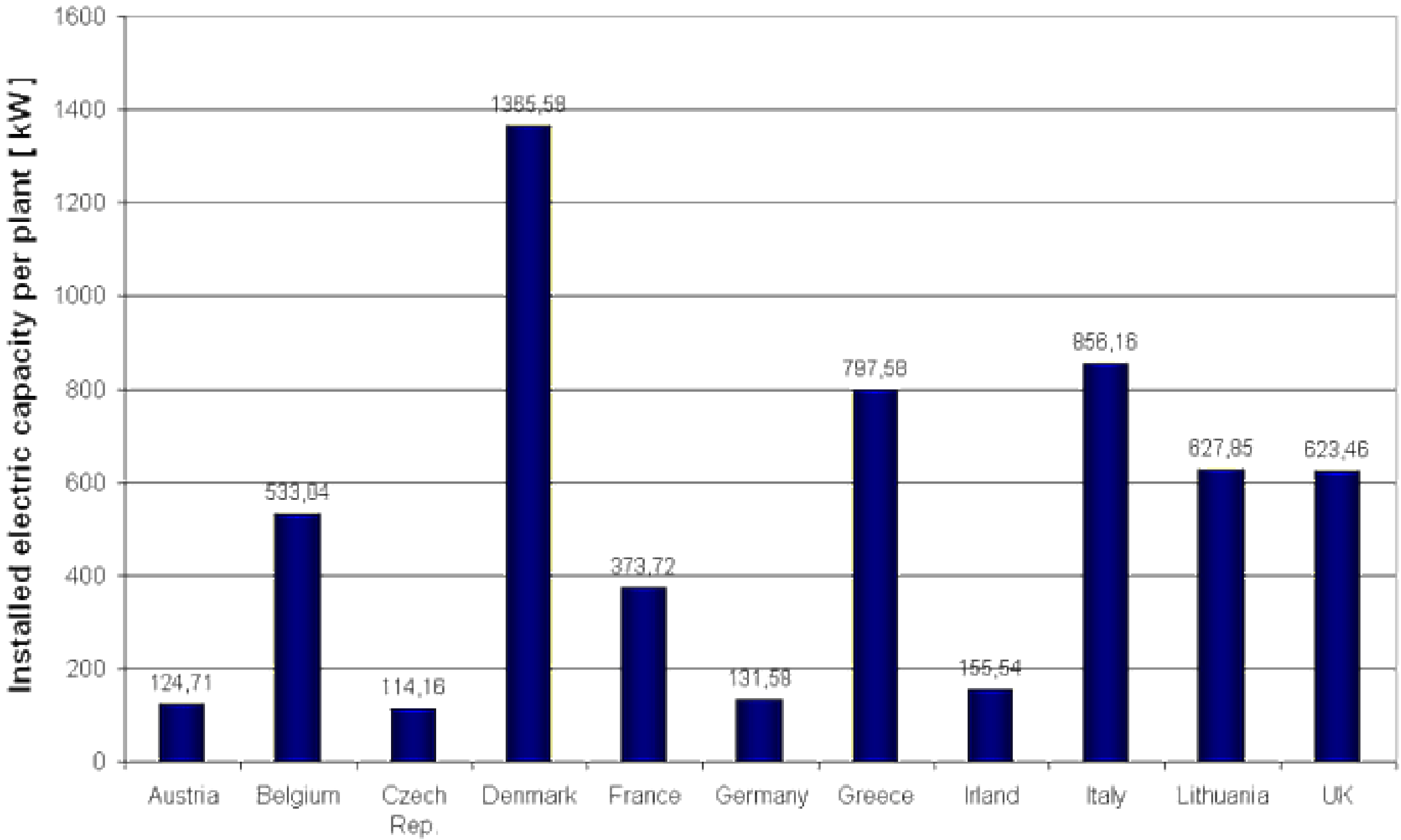
Anaerobic Digestion in Europe (1/3)



Anaerobic Digestion in Europe (2/3)



Anaerobic Digestion in Europe (3/3)



Biomass Energy Conversion Technologies

Anaerobic Digestion

AD/CHP Plant in Germany, 8.4 MW

AD Reactors
2 X 3.000 m^3,
AD/CHP Plant
2.6 MW
Germany

CHP Biogas ICE - 600 kW

AD/CHP Plant, in Denmark

Energy and Economic efficiencies in real AD Plants Anaerobic Digestion in Europe (1/3)

	Cattles			Pigs		
	min	med	max	min	med	max
Capital cost per animal € / animal	144	470	733	47	62	80
Energy per animal kWh / yr / animal	400	1.240	2.058	60	75	80
Capital cost/annual energy production €/MWh/yr	269	409	818	707	800	1.000
Profits per animal € / animal /yr	27	83	138	4	4,7	5
Profits per capital costs € / 1.000 €	82	180	249	67	85	95

Energy and Economic efficiencies in real AD Plants Anaerobic Digestion in Europe (2/3)

	Pigs	Cattles (dairy)	Cattles (broiler)	Chickens
Animal Weight (kg)	70	680	390	2.0
Solid/Liquid wastes (m^3/d)	0.0058	0.050	0.025	0.00013
Volatile Solids (kg/d)	0.56	6.56	3.28	0.0204
Solids conversion (%)	55	55	55	65
Biogas Production (m^3/animal/d)	0.154	2.471	1.388	0.0100
Energy Content (kWh / m^3)	5.965	6.257		6.543
Energy Production (kWh/animal/d)	0.918	15.46	8.685	0.065
Net Energy Production (kWh/animal/d)	0.689	11.60	6.514	0.049
Electric Energy kWh/animal/yr	74.41	1253	703.5	5.292
Profits (€/animal/d)	4.5	75.2	42.2	0.3

Energy and Economic efficiencies in real AD Plants Anaerobic Digestion in Europe (3/3)

	Nr. Animals	MWh /yr	Capital Cost €	An. Revenues €	An. Costs €	An. Profits €	Payback Time Yr
Dairy Cattles							
Best Scenario	3.000	3.600	1.080.000	216.000	72.000	144.000	7,5
Average Scenario	3.000	2.100	840.000	126.000	63.000	63.000	13,3
Worst Scenario	3.000	1.200	960.000	72.000	48.000	24.000	40,0
Broiler Cattles							
Best Scenario	3.000	2.100	630.000	126.000	42.000	84.000	7,5
Average Scenario	3.000	1.350	540.000	81.000	40.500	40.500	13,3
Worst Scenario	3.000	750	600.000	45.000	30.000	15.000	40,0
Pigs							
Best Scenario	30.000	2.100	1.470.000	126.000	42.000	84.000	17,5
Average Scenario	30.000	1.500	1.200.000	90.000	45.000	45.000	26,7
Worst Scenario	30.000	1.050	1.050.000	63.000	42.000	21.000	50,0
Chicken							
Best Scenario	1.000.000	5.300	1.325.000	318.000	106.000	212.000	6,3
Average Scenario	1.000.000	3.700	1.480.000	222.000	111.000	111.000	13,3
Worst Scenario	1.000.000	2.500	2.000.000	150.000	100.000	50.000	40,0

Anaerobic Digestion

A 1 MW(el) AD can generate annual revenues of 1200000 €:

Electric Power: 1 MW × 7500 hr/yr × 0.06 €/kWh ≈ 450000 €.

Thermal Power: 1.5 MW × 7500 hr/yr × 0.03 €/kWh ≈ 350000 €.

Fertilizer: 4000 – 5000 tn/yr × 100 €/tn > 400000 € .

Capital cost per electricity power generation:

Electricity Power	Digester Volume	Cost
10 kW	150 m^3	20 – 45000 €.
1 MW	10.000 m^3	2 – 4 M€.

Energy Efficiency of an Anaerobic Digestion Plant (1/5)

Feed Energy Content

$E_{FEED}=(V_R/\Theta)*t_Y*\rho*S*HHV_{VS}$ [kWh/y]

where	V_R	digester volume, m^3	
	Θ	hydraulic residence time, d	(usually 10 - 30 d)
	t_Y	annual operating time, d/y	(usually 365 d/y)
	ρ	feed density, Kg/m^3	(usually 1000 Kg/m^3) S
	Feed VS concentration, Kg/m^3		(usually 2 – 30 d/y)
	HHV_{VS}	VS Higher Heating Value, kWh/Kg	(3 – 4 kWh/Kg)

Energy Consumption - Pasteurization

$E_{PAS}=(V_P/\Theta_P)*t_Y*\rho*C_P*(T_P - T_A)$ [kWh/y]

Where	V_p	Pasteurization Tank Volume, m^3	
	Θ_P	Desired residence time, d	(usually 1 - 2 d)
	t_Y	Annual operating time, d/y	(usually 365 d/y)
	ρ	Feed density, Kg/m^3	(usually 1000 Kg/m^3)
	C_P	Feed Specific heat, kWh/kg*K	(0.0012 kWh/Kg)
	T_P	Pasteurization temperature, °C	(usually 70 – 90 ^oC)
	T_A	Mean feed temperature, °C	(usually 10 – 20 ^oC)

Energy Efficiency of an Anaerobic Digestion Plant (2/5)

Thermal losses of Pasteurization

$$E_{losses\ Pas} = t_y * 24 * V_P * K_{V,P} * (T_P - T_Y) \quad [kWh/y]$$

where	V_p	Pasteurization tank volume, m^3	
	$K_{V,P}$	Coefficient of volumetric losses in the pasteurization tank, kW/m^3K	(0.002 kW/m^3K)
	t_Y	Annual operating time, d/y	(usually 365 d/y)
	T_P	Pasteurization Temperature, °C	(usually 70 – 90 ^oC)
	T_A	Mean feed temperature, °C	(usually 10 – 20 ^oC)

Feed Heating

$$E_{HEATING} = (V_R/\Theta) * t_Y * \rho * C_P * (T_R - T_A) - E_{PAST} \quad [kWh/y]$$

where	V_R	Digester volume, m^3	
	Θ	Hydraulic residence time, d	(usually 10 - 30 d)
	t_Y	Annual Operating Time, d/y	(usually 365 d/y)
	ρ	Feed Density, Kg/m^3	(usually 1000 Kg/m^3)
	C_P	Feed specific heat, kWh/kg*K	(0.0012 kWh/Kg)
	T_R	Digestion temperature, °C	(usually 35 – 60 ^oC)
	T_A	Mean Feed Temperature, °C	(usually 10 – 20 ^oC)

Energy Efficiency of an Anaerobic Digestion Plant (3/5)

Thermal losses of the digester

$$E_{losses,\ DIG} = t_y * 24 * V_R * K_{V,R} * (T_R - T_A) \qquad [kWh/y]$$

where	V_R	Digester volume, m^3	
	$K_{V,R}$	Coefficient of volumetric losses in the digester tank, kW/m^3K	($0.002\ kW/m^3K$)
	t_Y	Annual operating time, d/y	(usually 365 d/y)
	T_R	Digestion Temperature, °C	(usually 35 – 60 ^oC)
	T_A	Mean Feed Temperature, °C	(usually 10 – 20 ^oC)

Energy requirements for mixing

$$E_{MIX} = 24 * t_Y * V_R * W_{A,R} \qquad [kWh/y]$$

where	$W_{A,R}$	Power per digester volume, kW/m^3	($0.03 – 0.04\ kW/m^3$)

Energy Efficiency of an Anaerobic Digestion Plant (4/5)

Energy Content of Biogas

$$E_{biogas} = (V_R/\Theta)*t_Y*\rho*S*d_{VS}*n_{MET}*HHV_{MET}*Bo \qquad [kWh/y]$$

where

V_R	Digester volume, m^3	
Θ	Hydraulic residence time, d	(usually 10 - 30 d)
t_Y	Annual Operating Time, d/y	(usually 365 d/y)
ρ	Feed Density, Kg/m^3	(usually 1000 Kg/m^3)
S	VS concentration in the Feed, Kg/m^3	(usually 2 – 30 d/y)
Bo	Maximum Methane Production, m^3_{CH4}/Kg_{VS}	(0.2 – 0.4 m^3_{CH4}/Kg_{VS})
$d_{VS\ \eta}$	VS conversion, %	(usually 40 – 70 %)
n_{MET}	Methane yield, % Bo	(usually 70 – 90 %)
HHV_{MET}	Methane higher heating value, kWh/Kg	(10.8 kWh/ m^3_{CH4})

Total Thermal Requirements

$$K_{TH} = E_{PAS} + E_{LOSSES,PAS} + E_{DIGEST} + E_{LOSSES,DIGEST} \qquad [kWh/y]$$

Total Electric Consumption

$$K_{EL} = E_{MIX} \qquad [kWh/y]$$

Energy Efficiency of an Anaerobic Digestion Plant (5/5)

Net Electricity Production

$$E_{EL} = n_{EL} * E_{BIOGAS} - K_{EL} \quad [kWh/y]$$

where n_{EL} Electric Efficiency Coefficient of biogas CHP generators, % (usually 25 - 35 %)

Net Thermal Production

$$E_{TH} = n_{TH} * E_{BIOGAS} - K_{TH} \quad [kWh/y]$$

where n_{TH} Thermal Efficiency Coefficient of biogas CHP generators, % (usually 45 - 60 %)

AD Electric Efficiency

$$N_{EL} = 100 * E_{EL} / E_{FEED} \quad [\%]$$

where E_{EL} Net electricity production, kWh/y

AD Thermal Efficiency

$$N_{TH} = 100 * E_{TH} / E_{FEED} \quad [\%]$$

where E_{TH} Net thermal production, kWh/y

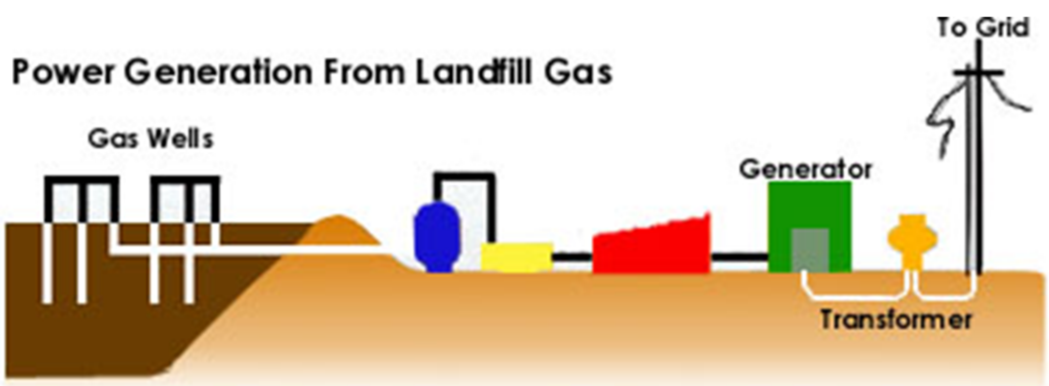
Biomass Energy Conversion Technologies (1/2)

Municipal Wastes Fermentation

Conversion of biodegradable wastes to biogas (mix of methane – carbon dioxide 50 / 50)

	Overall Efficiency
biogas	**Electrical Efficiency of ICE**

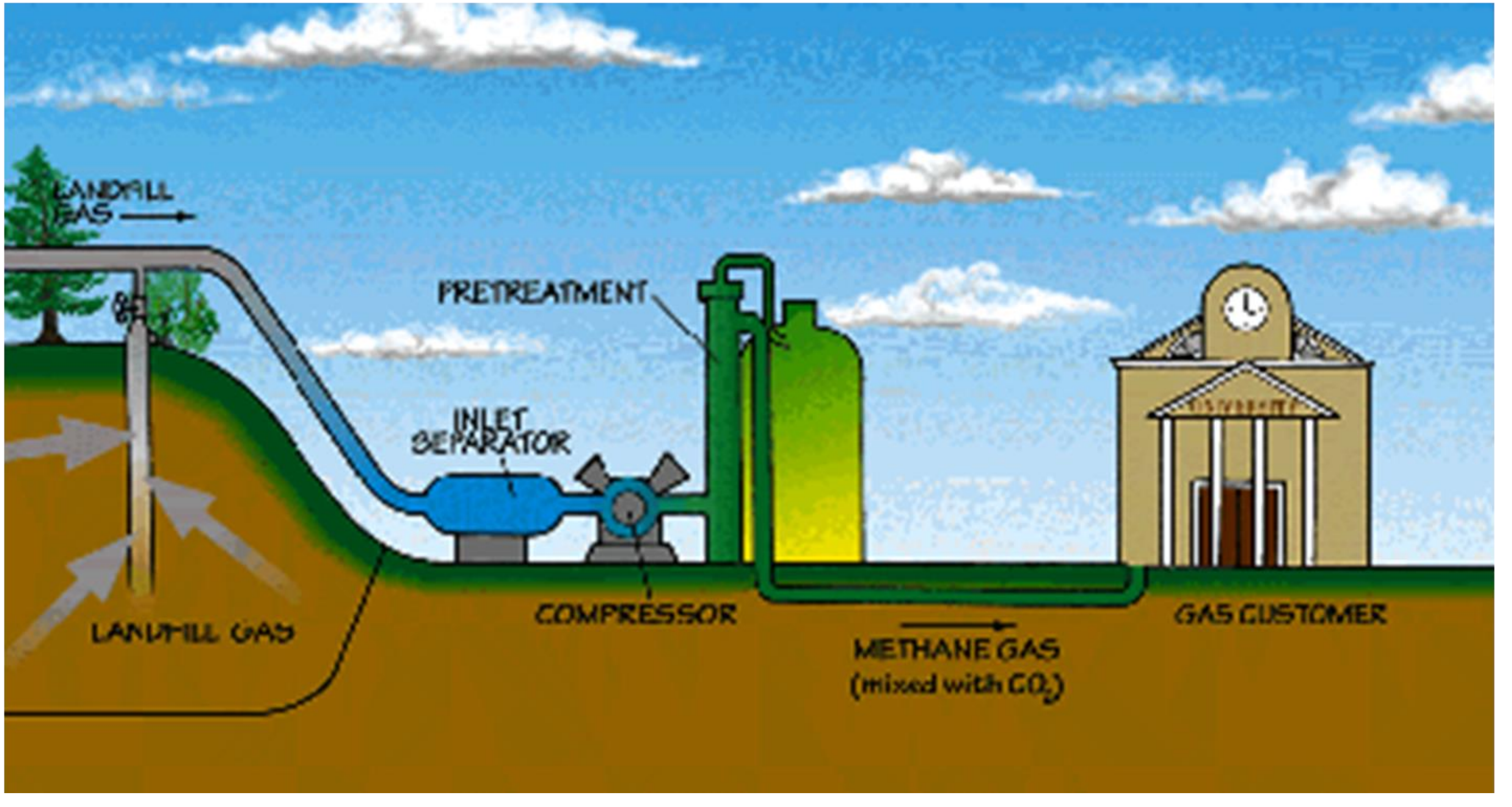
A mature and promising technology in EU.
This treatment is mandatory in most EU countries for energy as well as safety purposes.



Operation concept of biogas Capture and use

Biomass Energy Conversion Technologies (2/2)

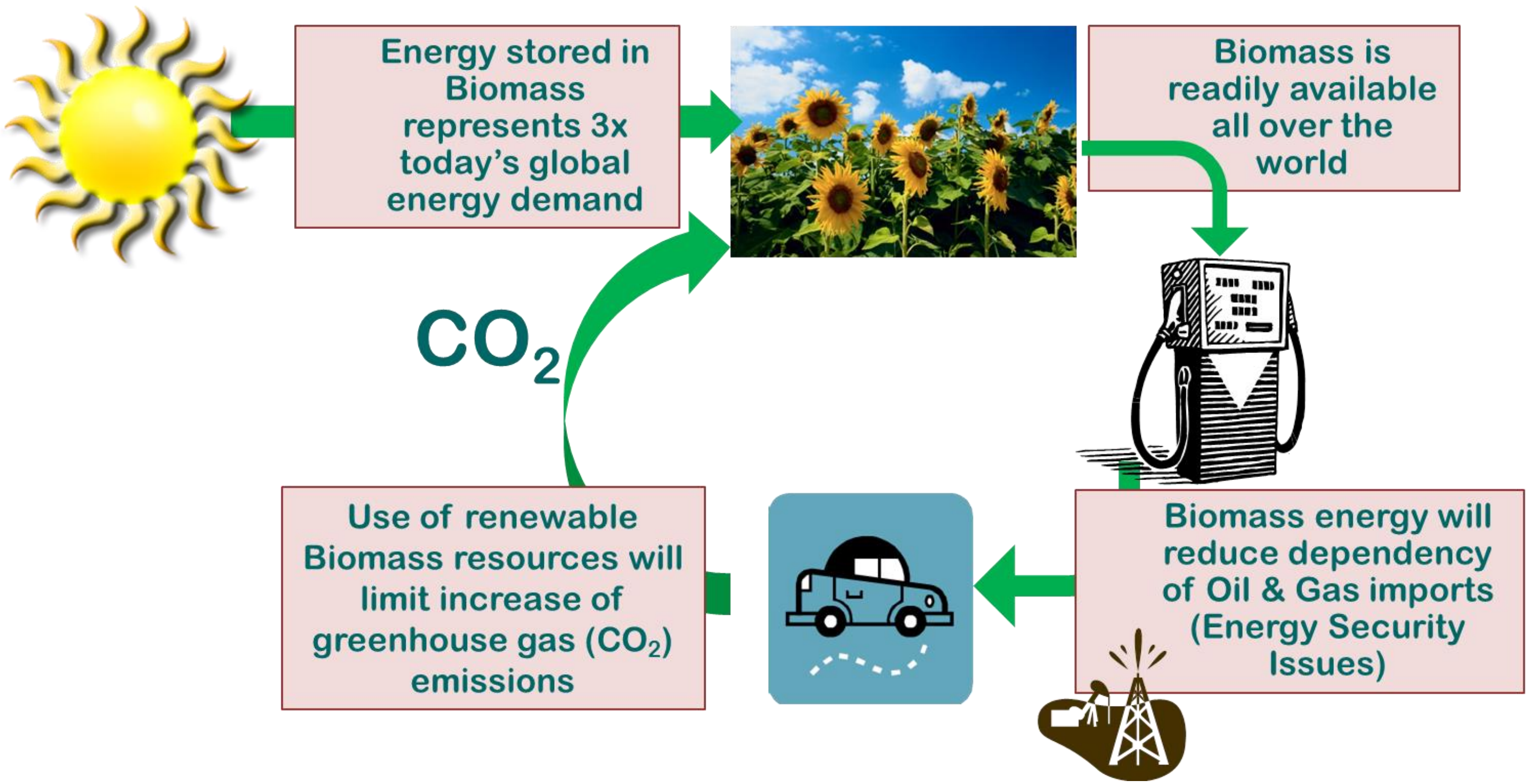
Landfill Gas



BioFuels

Biomass conversion:

A big entry in energy generation the next years



1st and 2nd Generation Biofuels

1st Generation:

- Bio-diesel: methyl-esters of fatty acids produced from vegetable or animal oil.
- Bioethanol: ethanol produced from sugars and starch crops.

Potential problem with the use of 1st generation biofuels:

Cultivation of energy crops become antagonistic to food crops:

Decrease of availability and increase of price of food products.

2nd Generation: *use of residues and by-products*:

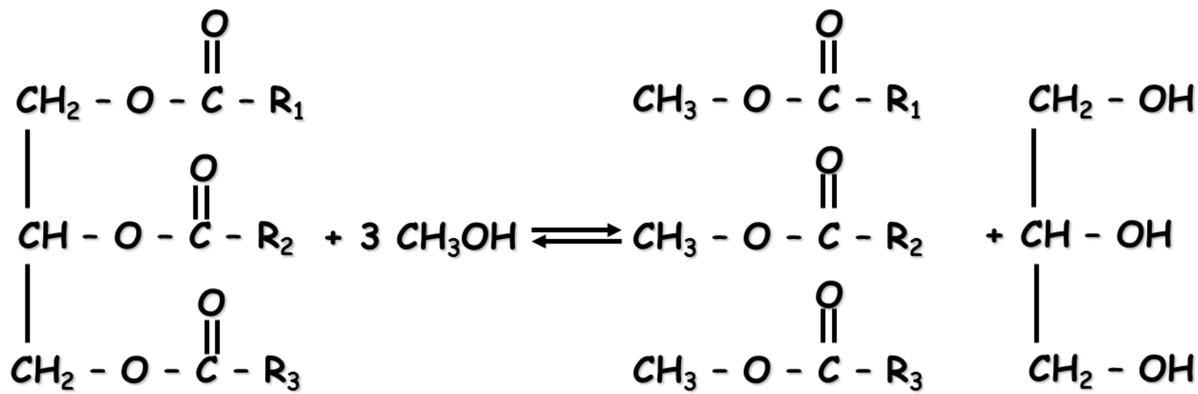
- **Biofuels derived from lignocellulosic biomass:**
  - Ethanol (from cellulose), Diesel or gasoline (BtL – Biomass to Liquid).
  - Pyrolysis bio-oil, Hydrogen, Methane – Synthetic natural gas.

Biomass sources: *agricultural residues, wood, forestry residues and biodegradable fraction of municipal solid waste and perennial annual crops.*

Biomass Energy Conversion Technologies (1/10)

Biodiesel

Esterification of vegetable oils to methyl esters of fatty acids

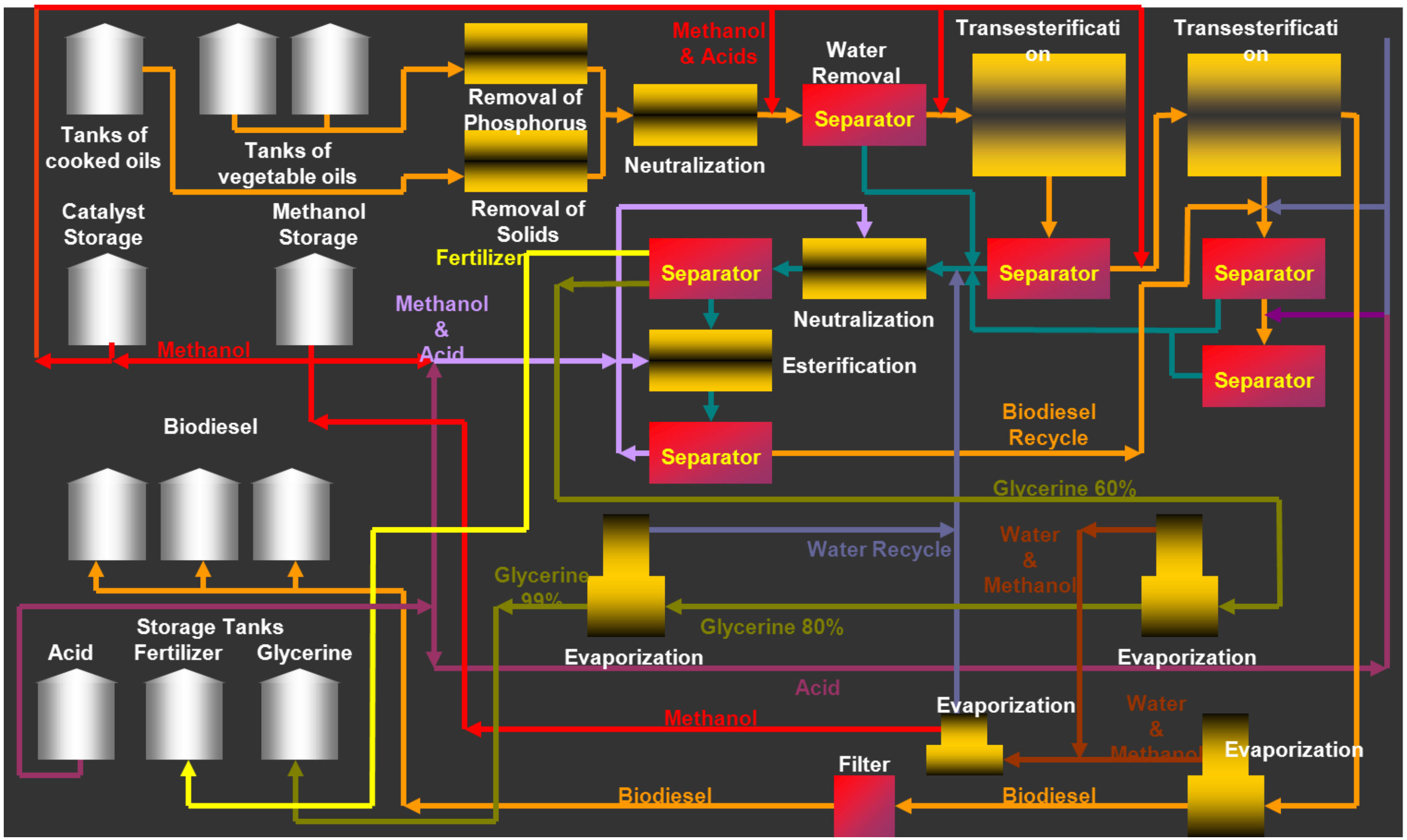


1 kg vegetable oils ⇌ 1 kg biodiesel

	vegetable oils	biodiesel
LHV (MJ/kg)	39,7	40,5
Density (kg/lt)	0,91	0,88
HV (MJ/lt)	36,1	35,6
ketane Number	37,6	51,0
Flash point (^oC)	246	120
Viscosity (mm^2/s)	37,0	3,9

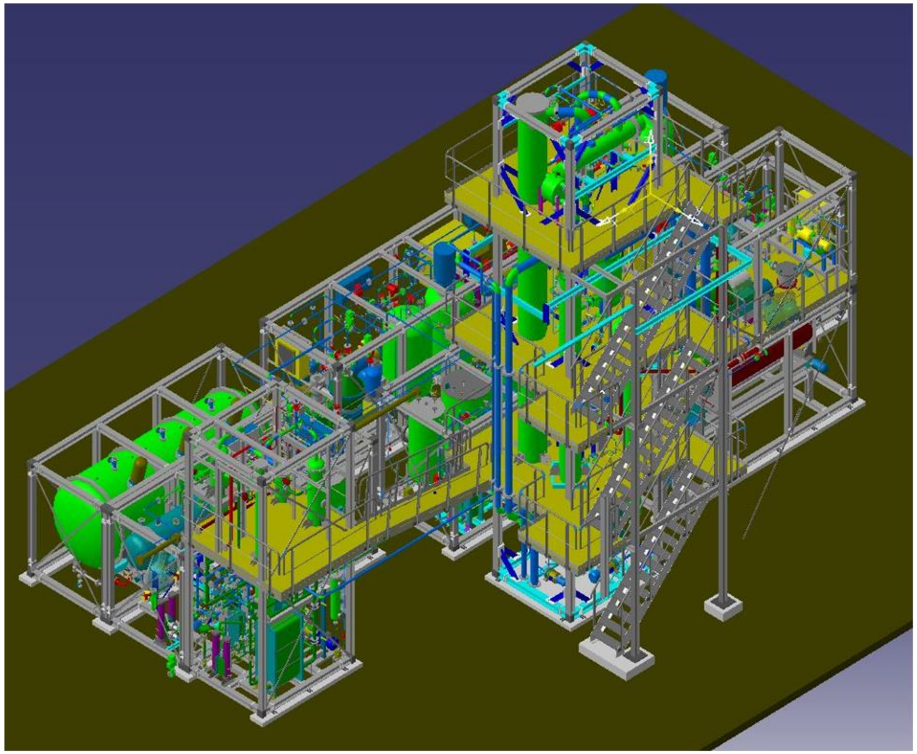
Biomass Energy Conversion Technologies (2/10)

Biodiesel



Biomass Energy Conversion Technologies (3/10)

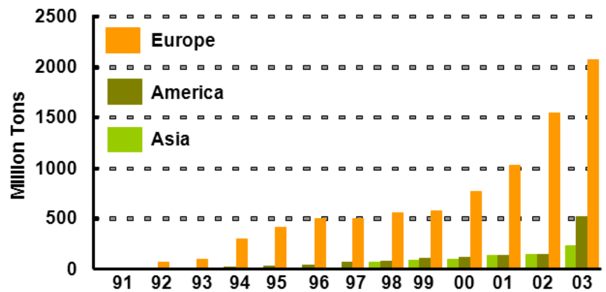
Biodiesel



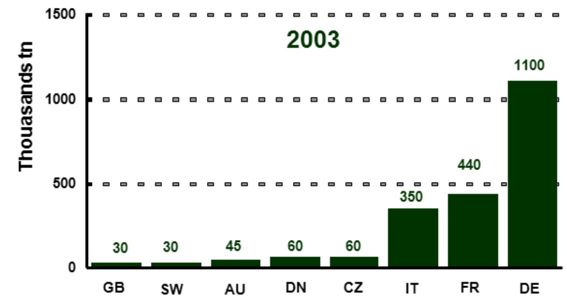
BIODIESEL PRODUCTION PLANT

Biomass Energy Conversion Technologies (4/10)

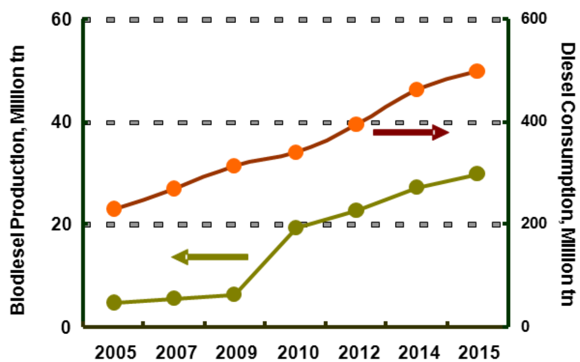
BioDiesel



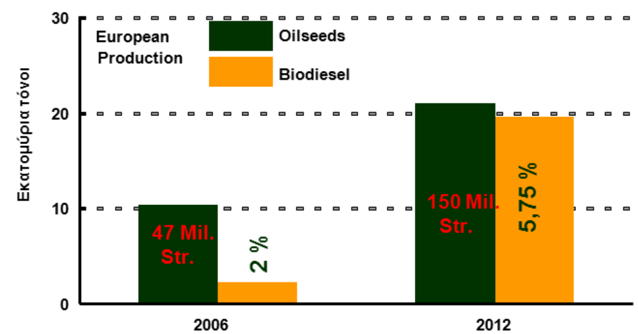
World Biodiesel Production



European Biodiesel Production



Projection



Projections on oilseed crops

Biomass Energy Conversion Technologies (5/10)

Biodiesel

Biodiesel Production Plant, 40000 tn/y

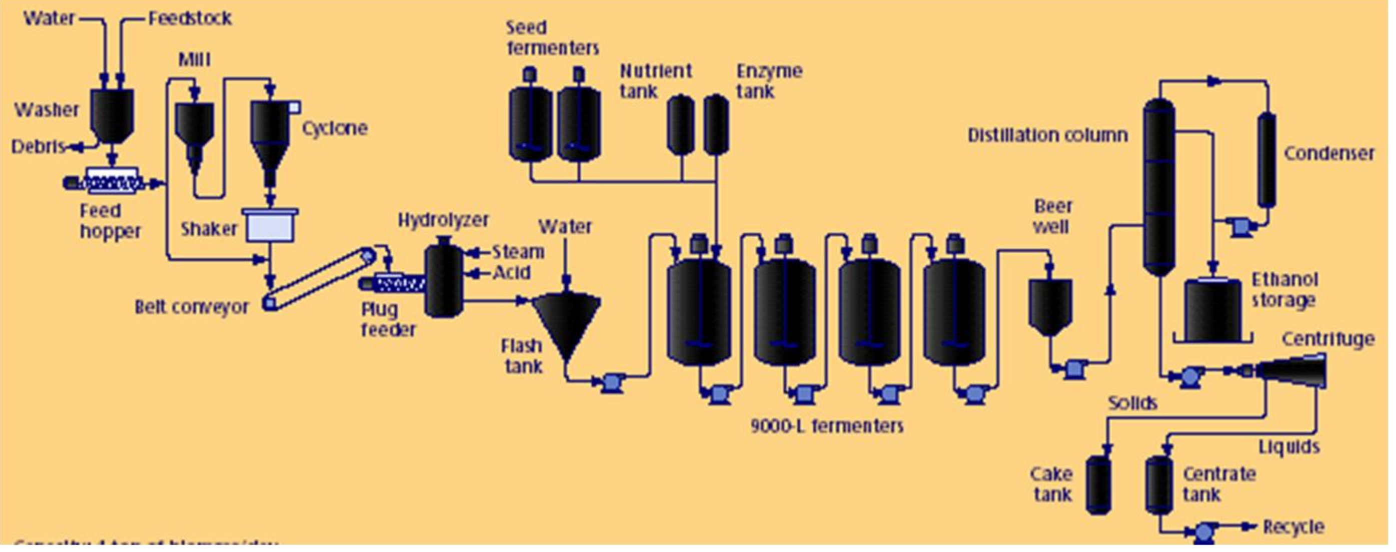
250000 tn/yr

Biomass Energy Conversion Technologies (6/10)

Bioethanol

Cellulosic hydrolysis to sugars
Fermentation to ethanol

It is ad-mixed with gasoline at low contents without any engine modifications



Process Flowchart

Biomass Energy Conversion Technologies (7/10)

Bioethanol

	Bioethanol	Gasoline
Specific density (kg/lt)	790	690
Vapor Pressure (mmHg)	50	398
LHV (MJ/kg)	26.1	46.0
LHV (MJ/lt)	20.6	31.7
Ignition Temperature (^oC)	425.0	280

BIOETHANOL WORLD MARKET (year 2002)

Trading volume ~ 2 million m^3/y

Production Cost from Sugar Cane (Brazil) ~ 160 €/m^3

Price of anhydrous ETOH (Brazil) ~ 220 €/m^3

Dewatering Cost (depending on capacity) ~ 30/60 €/m^3

Production Cost of anhydrous ETOH (USA) ~ 250 €/m^3

Production Cost of anhydrous ETOH from CB real (EU) ~ 380/480 €/m^3

EU import duty: 190 €/m^3

Biomass Energy Conversion Technologies (8/10)

Bioethanol

Production of Bioethanol at Brazil

Bioethanol at US

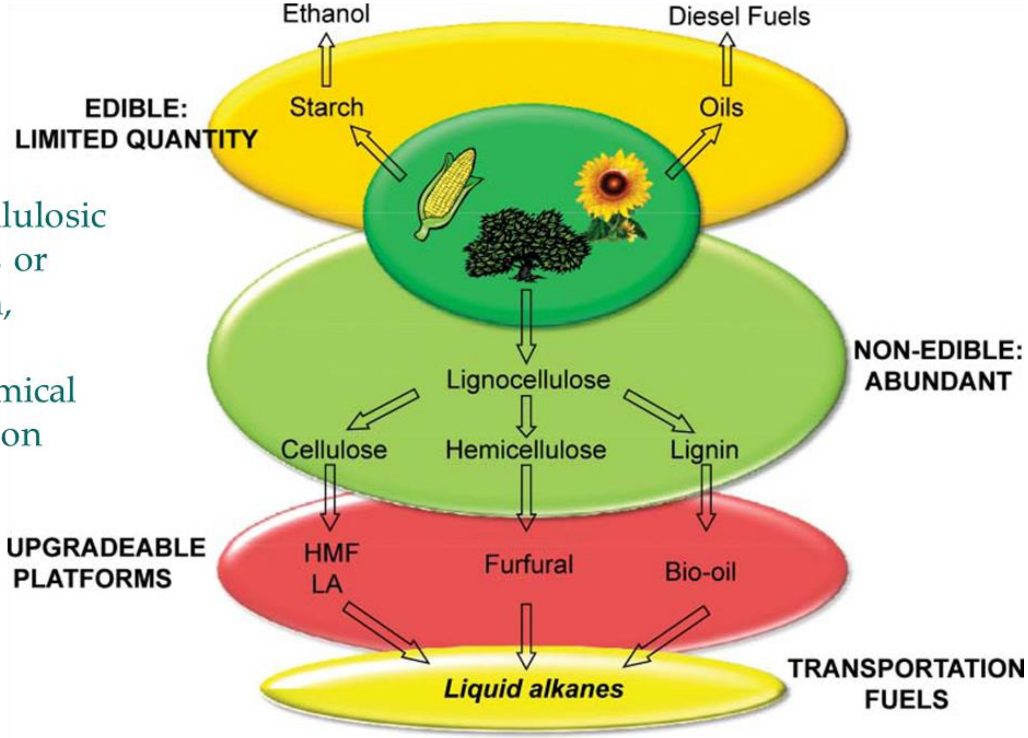
Biomass Energy Conversion Technologies (9/10)

Fuels production from biomass - Overall strategy

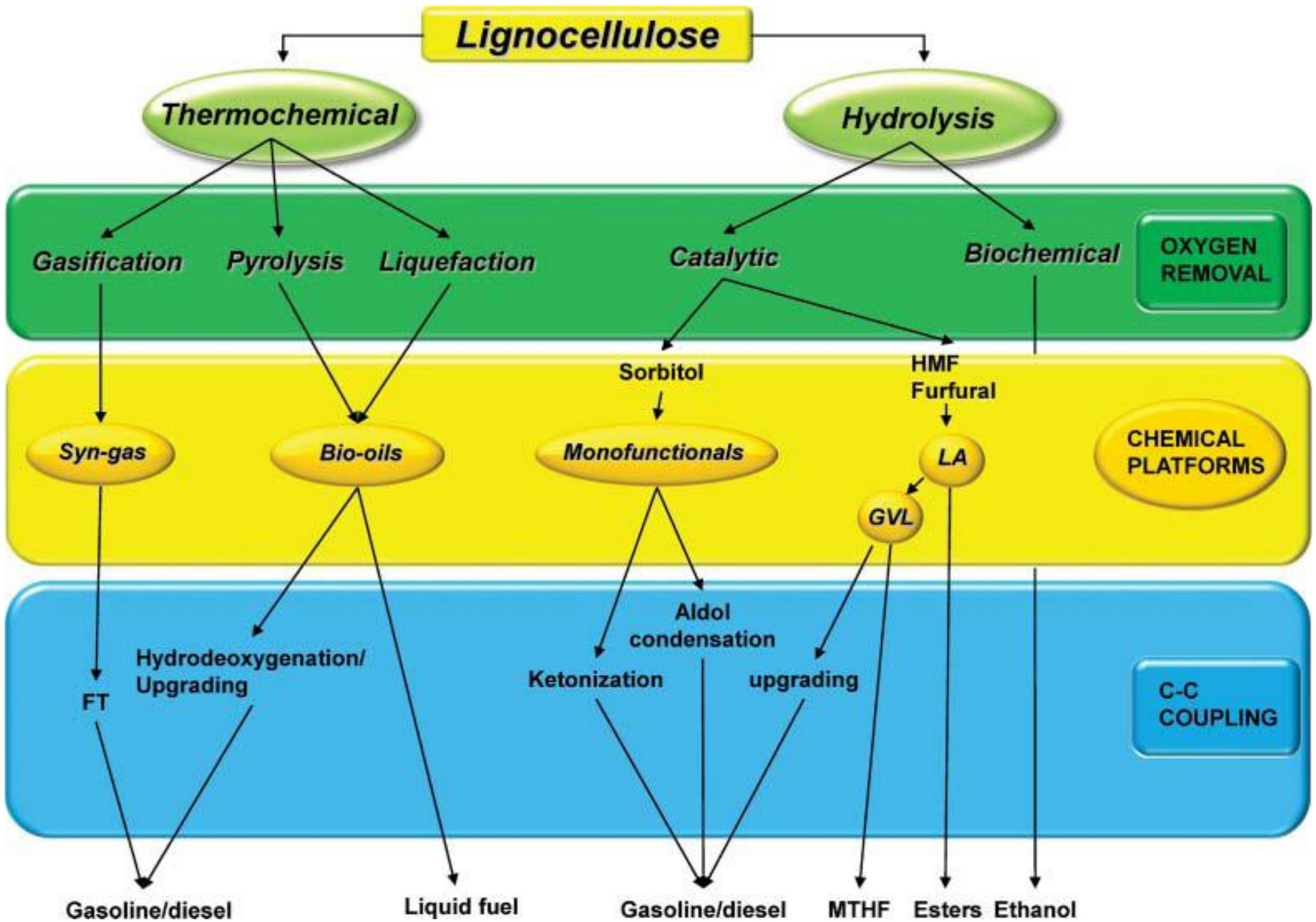
(i) reduce oxygen content to improve energy density
(ii) create C–C bonds between biomass-derived intermediates to increase MW of the final HCs
(iii) requiring the least amount of H_2 from an external source

Goal approach

(i) conversion of the solid lignocellulosic biomass feedstock to a gaseous or liquid phase chemical platform, involving partial O_2 removal
(ii) catalytic upgrading of this chemical platform to the final hydrocarbon fuel



Exploitation of Lignocellulosic Biomass



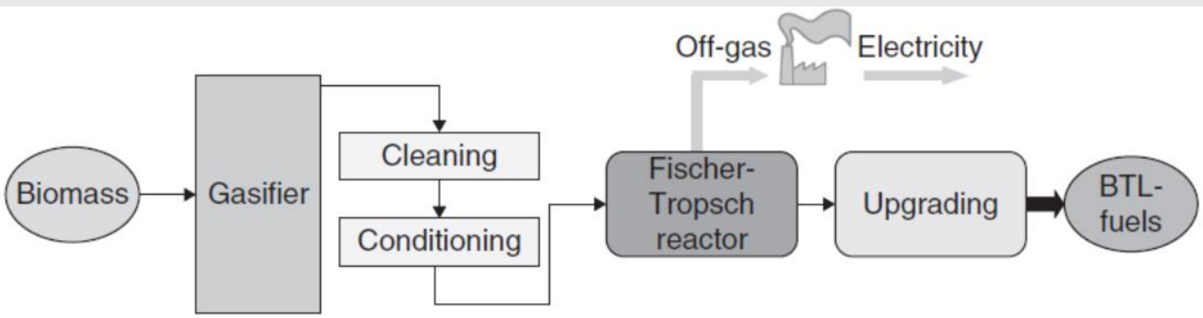
BTL process (1/6)

Thermochemical conversion of biomass to liquid fuels: (BtL process):

- Gasification of biomass for the production of syngas ($CO + H_2$): & gas cleaning.
- Conversion of syngas via Fischer Tropsch synthesis to middle distillates:

$$CO + 2\,H_2 \rightarrow \text{“-CH2-”} + H_2O.$$

- “-CH2-” represents a product consisting mainly of paraffinic hydrocarbons of variable chain length hydrogenation reaction mainly catalyzed by Fe and Co catalysts.
- Upgrading to high-quality fuel products (i.e. biodiesel or lighter fuels: gasoline, additives) via “conventional” (hydro)cracking processes.

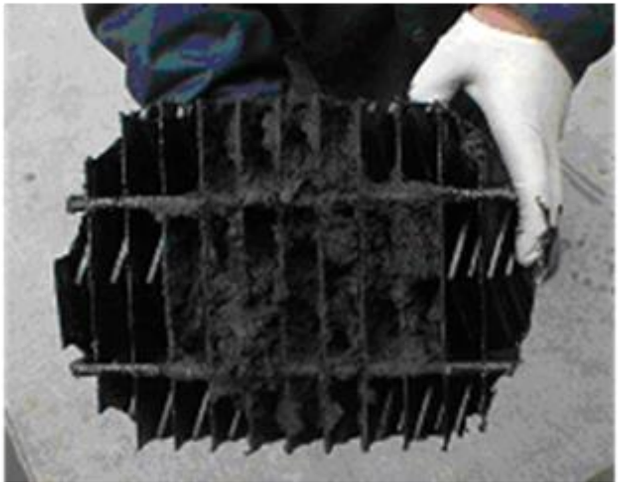


BTL process (2/6)

Maximum allowable concentration of impurities in syngas

Impurity	Specification
$H_2S + COS + CS_2$	< 1 ppmv
$NH_3 + HCN$	< 1 ppmv
$HCl + HBr + HF$	< 10 ppbv
Alkali metals (Na + K)	< 10 ppbv
Particles (soot, ash)	'almost completely removed'
Hetero-organic components (incl. S, N, O)	< 1 ppmv

Fouling of equipment



Syngas cleaning:

- Syngas purification step is the most expensive part of an FT complex.
- Different kinds of contaminants:

particulates, condensable tars, BTX (benzene, toluene and xylenes), alkali compounds, H_2S, HCl, NH_3, HCN.

F-T catalysts employed for the synthesis of the liquid fuels are notoriously sensitive to such impurities, especially sulphur and nitrogen compounds ⇨ irreversibly poison of F-T catalysts.

- Catalytic cracking/reforming of tars in the presence of dolomite/olivine, nickel-based catalysts or alkalis overcomes thermal cracking limitations.

low thermal efficiency, expensive materials required, large amounts of soot produced.

BTL process (3/6)

Sythesis of Biofuels via Fisher-Tropsch – Catalysts:

- Main requirement for a good F-T catalyst .

⇨ **high hydrogenation activity .**

to catalyze hydrogenation of CO to higher hydrocarbons.

Metals with sufficiently high hydrogenation activity:

Fe, Co, Ni and Ru (transition metals of the VIII group).

Ru

Exhibits the highest hydrogenation activity,
buts its extremely high price and low availability
render it unsuitable for large-scale FT process.

Essentially a methanation catalyst,
⇨ leading to the undesired production
of large amounts of methane.

Ni

BTL process (4/6)

Sythesis of Biofuels via Fisher-Tropsch – Catalysts:

Fe

Co

the only industrially relevant catalysts currently commercially used in F-T.

Catalyst choice depends on FT operating mode:

- Fe-based catalysts are suitable for the *high temperature Fischer-Tropsch (HTFT)* operating mode: 300–350°C temperature range used for the production of gasoline and linear low molecular mass olefins.
- Both Fe & Co catalysts used for the *low temperature Fischer-Tropsch (LTFT)* operating mode: 200–240°C range used for the production of high molecular mass linear waxes.

BTL process (5/6)

Reactors & Process conditions:

- The heterogeneously catalyzed FT reaction is highly exothermic (heat released per reacted C atom ~ 146 kJ, an order of magnitude higher than heat released in oil industry processes).

Rapid removal of heat is of major consideration in the design of F-T reactors:

✓ quickly extract heat from catalyst particles to avoid catalyst overheating & deactivation and ,

✓ simultaneously maintain good temperature control .

Reaction usually takes place in a three-phase system:

- gas (CO, H_2, steam and gaseous HCs), liquid HCs and solid catalysts imposing great demands on the effectiveness of interfacial mass transfer.
- F-T process is a capital-intensive process, thus for both economic & logistic reasons, it is only economically favourable on a very large scale ➔ Easy reactor scale-up is a third important requirement!

BTL process (6/6)

F-T Summarizing:

Two available catalyst systems for large-scale commercials plants: Co & Fe -based **.**

Two operating modes of the FT process: low and high temperature .

In the high-T range: Fe catalyst produces gaseous and gasoline range .
products, usually in fluid catalyst bed reactors.

In the low-T: both Fe and Co catalysts produce a large amount .
of high boiling, waxy products and straight-run diesel and naphtha.

Wax is *upgraded* to lower .
boiling range products &
normally distilled to yield .
- highly paraffinic,
- zero sulphur &
- zero aromatic .

middle distillate diesel fuels,
with naphtha as a co-product .

Typical carbon number distribution of HTFT and LTFT products

Description	HTFT (Synthol)	LTFT (Arge)
Carbon number distribution (mass %)	–	–
C_3–C_4, LPG	30	10
C_5–C_{10}, naphtha	40	19
C_{11}–C_{22}, distillate	16	22
C_{22} and heavier	6	46
Aqueous products	8	3
Compound classes	–	–
Paraffins	> 10%	Major product
Olefins	Major product	> 10%
Aromatics	5–10%	< 1%
Oxygenates	5–15 %	5–15%
S- and N-species	None	None
Water	Major by-product	Major by-product

H_2 production processes from biomass (1/5)

- **CO_2 neutral H_2 production:**
  - Biomass gasification.
  - Pyrolysis of bio-oils.
  - Steam reforming of biomass derived higher alkanes & alcohols.
  - Aqueous phase reforming of oxygenated hydrocarbons.

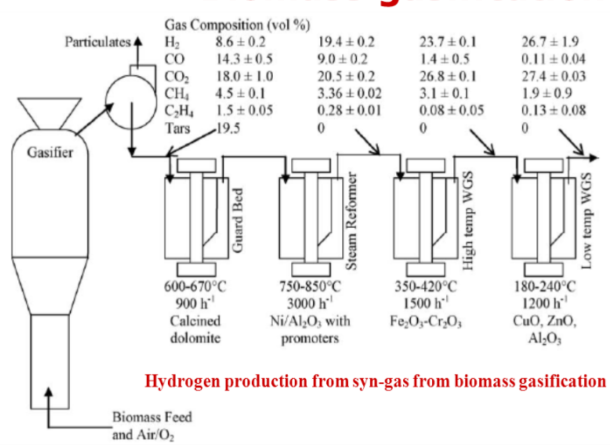
H_2 production processes from biomass (2/5)

- **Relatively pure H_2 by steam reforming followed by a WGS reactor.**
- **WGS reaction:** $CO + H_2O \rightarrow CO_2 + H_2$ **carried out at two temperature ranges.**
  - **High temperature WGS:** 350-500°C .
  - **Low temperature WGS:** 200-250°C .
- **Low temperature WGS catalysts:** Cu–Zn oxide catalysts & metals on partially reducible metal oxides, *e.g. transition metals & Au on* Al_2O_3, CeO_2, CeO_2–ZrO_2.
- **High temperature WGS catalysts:** Fe and Cr oxides.

H_2 production processes from biomass (3/5)

- Gasified biomass stream filtered in a heated particulate filter & purified to remove tars in a guard bed dolomite reactor at 600°C.
- Syn-gas (may contain unreacted light HCs & tar traces) converted to H_2 and CO by steam reforming reaction (supported Ni catalyst at 750–850°C.
- Remaining CO from steam reforming is converted by sequentially high temperature and low temperature WGS to increase the H_2 yield.

Biomass gasification



Steam reforming

$$CxHyOz + H_2O \rightarrow xCO + yH_2$$
$$CxHyOz + nH_2O \rightarrow aCO + (x\text{-}a)CO_2 + yH_2$$
$$CxHyOz + (2x\text{-}z)H_2O \rightarrow xCO_2 + (2n + (y/2) - z)H_2$$

H_2 production processes from biomass (4/5)

H_2 production from fast pyrolysis and bio-oils:

- **Gaseous products can be obtained from fast pyrolysis of biomass increasing T :**

as T ↑ from 500 to 750°C, char and liquids ↓ while gaseous yield ↑

gaseous yield at 750°C ~45–50% compared to 30–35% at 500°C.

H_2 content in gaseous yield is also increased BUT STILL TOO LOW!

Hydrogen from the fast pyrolysis bio-oil products using steam reforming.

- **investigating bio-oil model compounds suggests:**

steam reforming competes with the gas phase thermal decomposition of the bio-oils.

➔ coke formation ➔ reactor plugging & catalyst deactivation.

➔ a special reactor design configuration.

- **ADDITIONAL PROBLEM: very high steam/carbon ratio used to avoid coke deposition:**

➔ Increases the energy demand of the plant in order to produce the excess steam.

Autothermal reforming (ATR) is an attractive alternative to steam reforming.
ATR is a combination of steam reforming & partial oxidation of HCs to CO, CO_2 & H_2.
$CxHyOz + aO_2 + bH_2O \rightarrow cCO + dH_2 + eCO_2$.

H_2 production processes from biomass (5/5)

H_2 production from catalytic aqueous phase reforming (APR):

- converts biomass-derived oxygenated hydrocarbons with C:O ratio of 1:1, e.g. methanol, ethylene glycol, glycerol, glucose & sorbitol. to H_2, CO, CO_2 and gaseous alkanes using supported metal catalysts. APR carried out at 200–250°C and 10–50 bar to maintain the liquid phase.

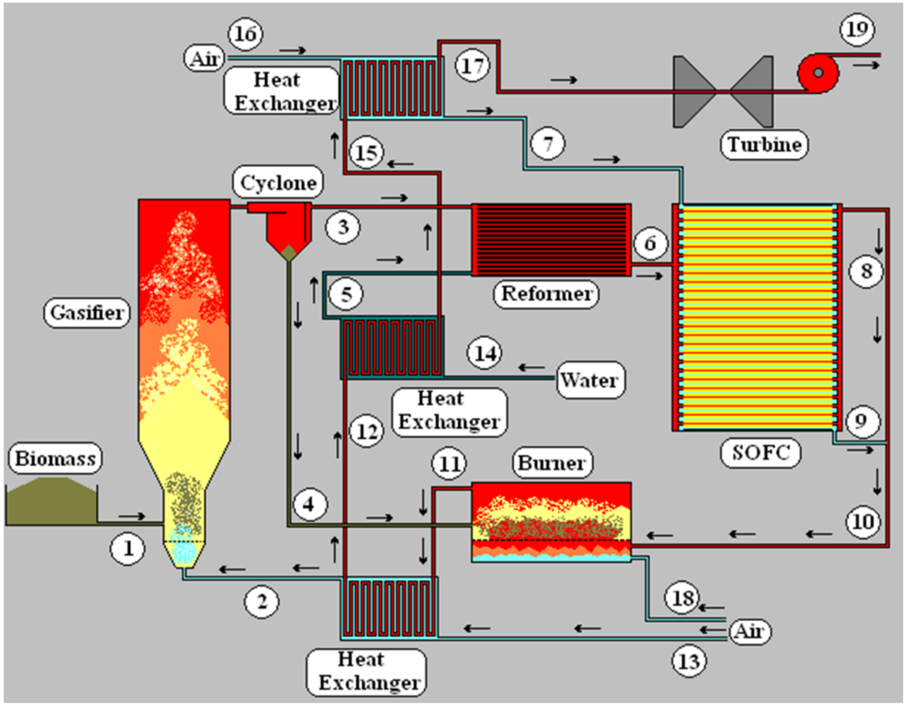
Method advantages:

- ❖ moderate reaction T and P favoring WGS reaction in the same reactor.
- ❖ low CO level in the gas stream (100–1000 ppm)➔ ideal for fuel cell application.
- ❖ oxygenated hydrocarbon feed & water are in the liquid phase.
  ➔ Lower energy requirement compared to steam reforming.
- ❖ the feedstock is non-hazardous ➔ relatively easier storage.

Pt was found to be the most suitable catalyst for the APR reactions but its cost prohibits large-scale applications.

Biomass Energy Conversion Technologies (10/10)

Bio-Hydrogen Production



Gasification – Reforming – Fuel Cell

Τέλος Ενότητας