Crops for AD
Types - ensiling - pre-treatment

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ENERGY CROPS

Jyväskylä Summerschool 2013

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Energy crops for AD

Question: Food or Fuel ?

- First Food and then Fuel if it is:
- Really Renewable
  - Good carbon input to output ratio
- Sustainable
  - Can produce the same or more energy each year without harm to the environment

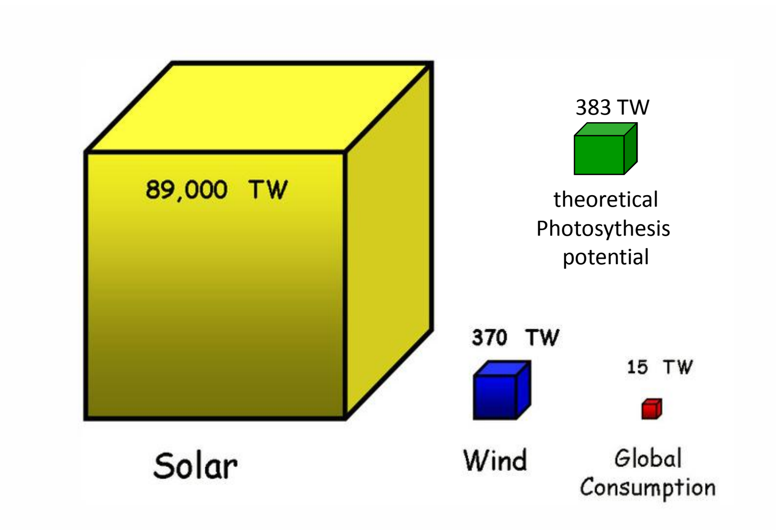
Energy input to output ratio for bioenergy

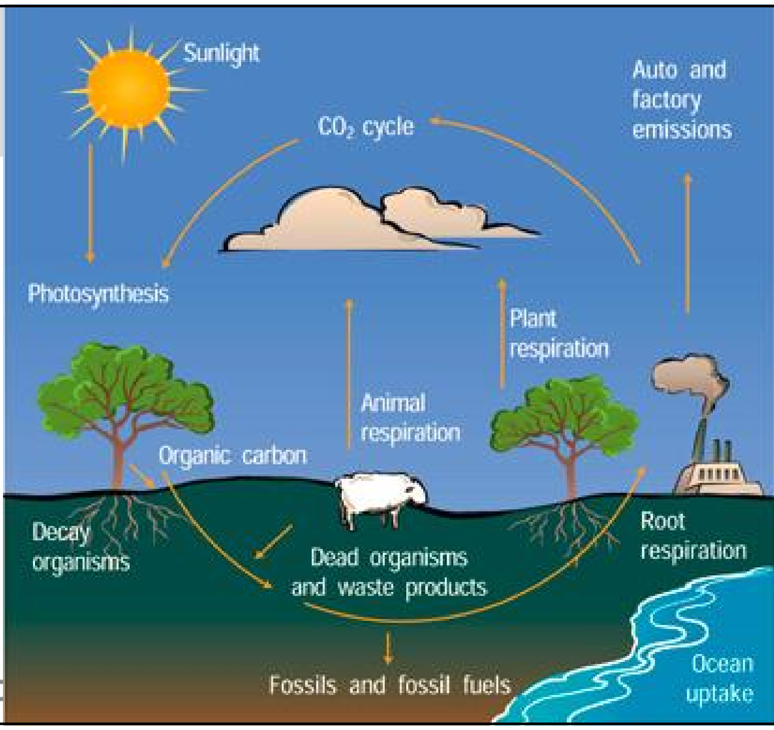
- Ethanol (corn, wheat, sugar beet)	1,2 – 1,4
- Ethanol (sugar cane)	~ 9
- Biodiesel	2,2 – 3,4
- Biogas waste	up to 28
- Biogas energy crops	2,5 – 5,6

Energy from the sun

- 61541 GJ solar energy per ha at 40°latitude (Mediterranean area)
- 43% of total solar energy available for photosynthesis (wave spectrum)
- Photosynthesis – efficiency less than 1%
- Plants fix 200 billion tons of carbon per year
- Theoretical limit of crop production = 250 tons of dry matter per hectare
- Cannot be maintained throughout the year – climate, vegetative cycles, growing seasons, mutual shading, unfavorable soil water content, low and high temperatures

Energy from the sun





What are crops?

- Definition

- A crop is a non-animal species or variety that is grown to be harvested as food, livestock fodder, fuel or for any other economic purpose.

- 250,000 species of higher plants in the world
- 1000 species comprise the world's crop crops

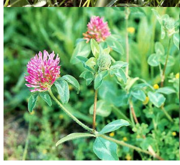
- 80% of edible plant material comes from 11 species (of which two-thirds are cereals)

Typical energy crops in Europe

- Maize
  Whole crop or grain only

- Grass

- Clover



Typical energy crops in Europe

- Cereals
  Whole crop or grain only

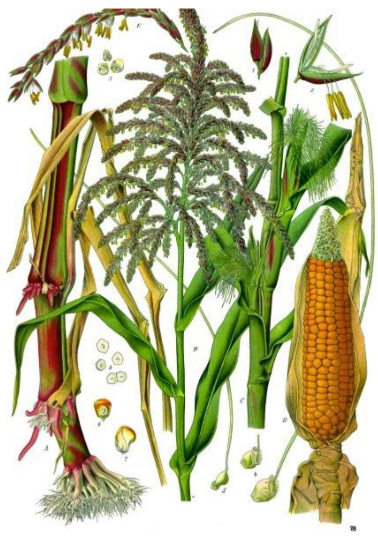
- Sunflower

- Others: sugar beet, sorghum, …

Factors for the selection of the optimum energy crop

- Soil properties
- Climatic conditions
- Water availability
- Seeding period
- Nutrient demands
- Possibility of secondary crop
- Crop rotation
- Harvesting period
- Estimated yields
- Mechanized production

Energy crops



STORAGE AND ENSILING OF ENERGY CROPS

Storage of energy crops

Why is it necessary to store energy crops?

- Fresh energy crops are available only during a short period (after harvest)
- Continuous supply with substrate is required for the continuous generation of bioenergy

Storage of energy crops

How can energy crops be stored?

- Pile up at the facility with no further treatment (not recommended)
- Drying
- Wet storage at anaerobic conditions (= silage)

- Storage should always include the preservation of the crops.

storage losses = energy losses

Ensiling of energy crops

Advantages of ensiling:

- lower costs (compared with drying)
- lower losses of components and energy
- less dependent on weather

Silage

- Silage is:

- **fermented** organic material (grass, maize, cereals, legumes, ...)
- with **high moisture content** (usually >50%)

Silage is used for:

- animal feed
- energy production from renewable resources („energy crops")

Ensiling process

- Storage at **anaerobic conditions** - exclusion of air:
  - Compaction of the material
  - Seal air-tight with plastic foil
    Weight the top with sandbags, tyres, etc.
- **Lactic acid** fermentation:
  - Conversion of water soluble carbohydrates by lactic acid bacteria
  - Low pH prevents spoilage (= growth of unwanted microorganisms)
  - Undissociated lactic acid is more effective against the growth of microorganisms

Ensiling process

The preservative effect of ensiling is based upon:

- the inhibition of **aerobic spoilage microorganisms** due to the **exclusion of air**

and:

- the inhibition of **anaerobic spoilage microorganisms** because of the rapid **decline in pH** due to lactic acid formation

Plants for ensiling

- low dry matter content (<50%, ideally 20-30%)
- water soluble carbohydrates as substrate for lactic acid fermentation

  - Grasses
  - Cereals grains or whole crop
  - Legumes
    (clover, lucerne, alfalfa, ...)
  - Sunflower
  - Sugar beet tops
  - Fibrous residues
    (residues from sugar beet extraction, brewer grains, ...)

Ensiling technique

Cutting	Accurate time with respect to content of energy, fibre and WSC
↓ Conditioning	Wilting, maceration, etc.
↓ Harvest	Chopping, pick-up wagon, treatment with additives
↓ Filling the silo	Bunker silo: thin layers, compaction with heavy machines, covering and sealing with plastic wrapping
↓ Compaction and Sealing	Big bale silage: pressing of bales, wrapping


CLAAS
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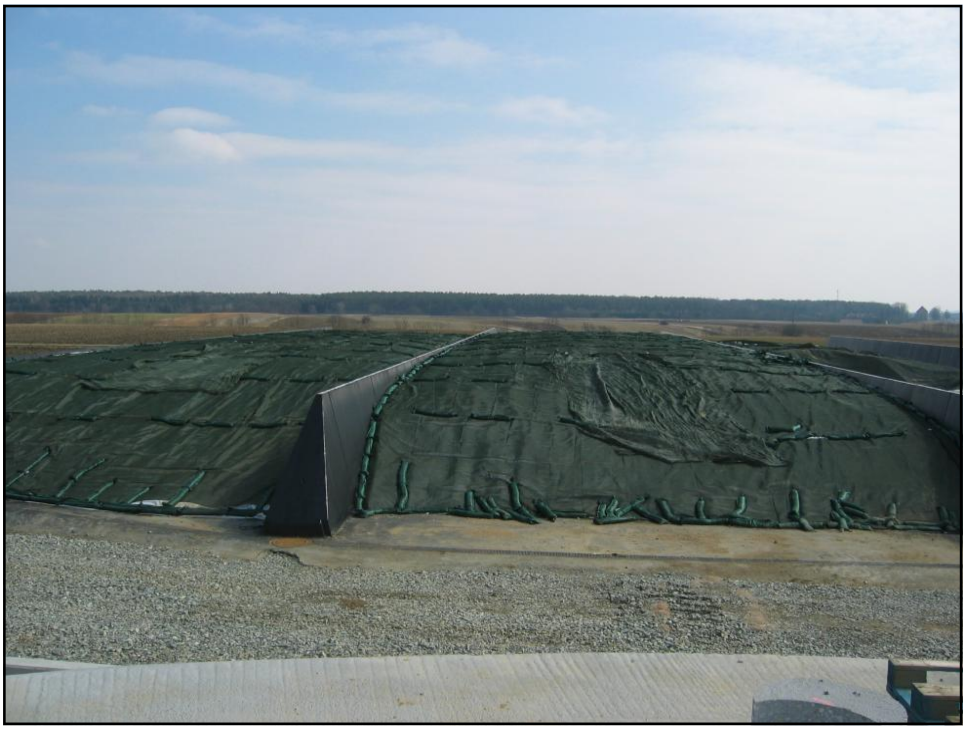


Silos

- Stack or clamp silo without retaining walls
- Tower silo
- Surface-walled clamp or bunker silo
- Flexible-walled silo
- Vacuum silo
- Plastic sausage silo
- Big bale

4 phases of ensiling

- Aerobic phase
- Fermentation
- Stabilisation
- Unloading

4 phases of ensiling

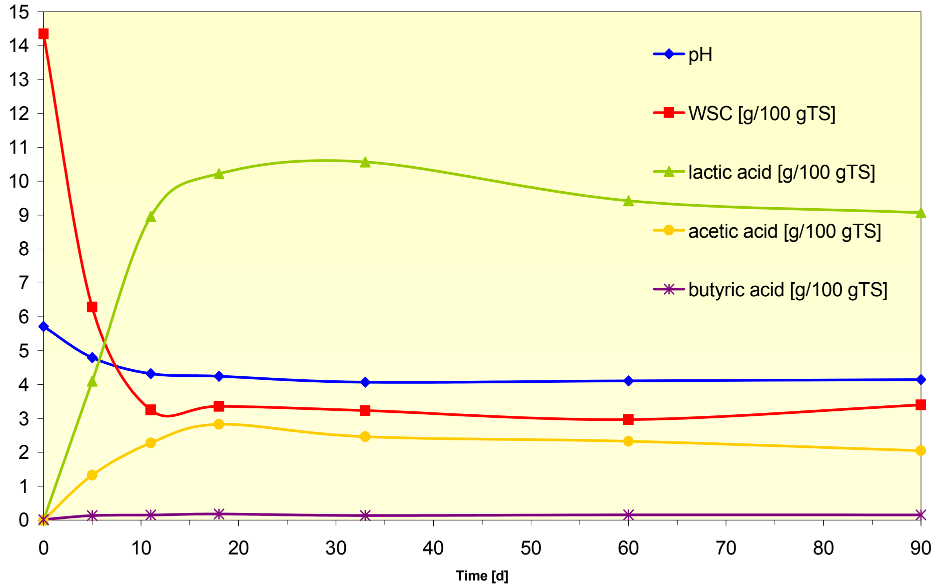
1. **Aerobic phase** (beginning of ensiling process)

- Residual oxygen is used up
  - Plant material (respiration)
    plant enzymes are still active
  - Aerobic microorganisms (Yeasts, Fungi, *Bacillus* sp., Enterobacteriaceae, etc.)

4 phases of ensiling

2. Lactic acid fermentation

- Conversion of water soluble carbohydrates (5-20% of TS) to lactic acid.
  - **Homofermentative lactic acid bacteria:**
    lactic acid is the only fermentation product
    Lactobacillus plantarum, Lactococcus lactis, Pediococcus pentosaceus, ...
  - **Heterofermentative lactic acid bacteria:**
    lactic acid, acetic acid, ethanol, CO_2 as fermentation products
    L. buchneri, L.brevis, Leuconostoc mesenteroides, ...



4 phases of ensiling

3. Stabilisation

- No more growth of microorganisms because of low pH (below 4.5)
  - Some heterofermentative LABs (*L. buchneri*) can convert lactic acid to acetic acid
    important for Aerobic Stability
  - If the silage is not stable, „secondary fermentation“ (anaerobic spoilage) can occur:
    Clostridia convert lactic acid into butyric acid and/or acetic acid.

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4 phases of ensiling

4. Unloading

- For unloading the silo must be opened and is exposed to air!
  - „Aerobic instability“
    - warming of the silage and increased losses
    - aerobic microorganisms (yeasts, moulds) are able to grow!
    - health problems can occur when silage is used as animal feed.

Ensiling losses

Process	Classification	Approximate loss (%)	Causative factors
Residual respiration	unavoidable	1–2	Plant enzymes
Fermentation	unavoidable	2–4	Microorganisms
Effluent or Field losses by wilting	mutually unavoidable	5– >7 or 2– >5	DM content Weather, technique, management, crop
Secondary fermentation	avoidable	0– >5	Crop suitability, environment in silo, DM content
Aerobic deterioration during storage	avoidable	0– >10	Filling time, density, silo, sealing, crop suitability
Aerobic deterioration after unloading	avoidable	0– >15	As above, DM content, silage, unloading techique, season
Total		7– >40	

[McDonald et al., 1991]

Factors with negative influens on silage quality

High amounts of:

- Crude protein
- Water (TS <25%)
- Crude ash
- Microbial count

Low amounts of:

- Fermentable carbohydrates (<1.5-2% of TS)

Silage additives

- Fermentation inhibitors
  - Acids
    - formic acid, propionic acid, benzoic acid
    - mineral acids
  - Salts
    - formiate, benzoate, nitrate, nitrite
- Stimulants
  - Fermentable carbohydrates (molasses, whey, etc.)
  - Enzymes
  - Bacterial additives

Microbial silage additives

- Homofermentative lactic acid bacteria
  - Rapid degradation of carbohydrates
  - Produce large amounts of lactic acid in a short time
  - Rapid decline of pH (below 4)
- Heterofermentative lactic acid bacteria
  - pH goes down slowly
  - Lactic and acetic acid as products

  - Acetic acid:
    - inhibits growth of yeasts and moulds at aerobic conditions
    - improves aerobic stability of silages

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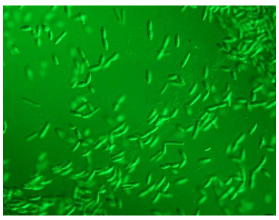
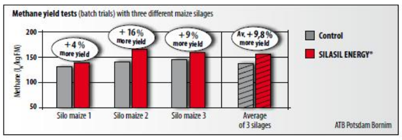
Microbial silage additives

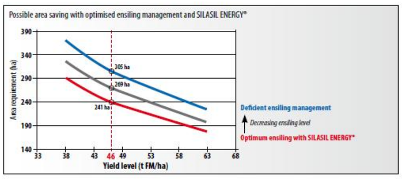
- Liquid or powder
- Cost: 1-2 Euro/t FM



Economic efficiency

Using SILASIL ENERGY® increases the area efficiency of the biogas plant. Because of the energy conservation and increased bioavailability of the substrate, the area requirement can be reduced with correct ensiling techniques and product metering.





Example of a biogas plant with 500 kW_{el} installed capacity

	Yield level		
	low	average	high
Yields per hectare t FM/ha	38	46	62
Area requirement [ha] 1,300 kWel. /t DM (minimum losses with SILASIL ENERGY®)	292	241	177
Area requirement [ha] with defective ensiling management (15% losses)	326	269	198
Area saving [ha] Losses cut from 15% to 5%	34,3	28	20,8

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Ensiling of energy crops

Aims:

- Storage
- Preservation
  - Minimising losses during storage
  - Minimising energy losses
- Hydrolysis of biopolymers
  - Starch, fructans, hemicelluloses?, (celluloses ???)

PRE-TREATMENT OF ENERGY CROPS

Pretreatment of energy crops

Why pre-treatment?

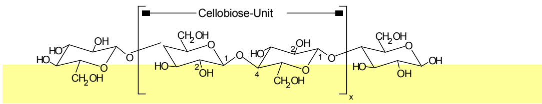
- Energy crops contain compounds that are difficult to degrade.
- If the availability of these compounds for microorganisms can be improved, the whole process can become more economic
  - better utilisation of the substrate
  - lower retention times required

Pretreatment methods

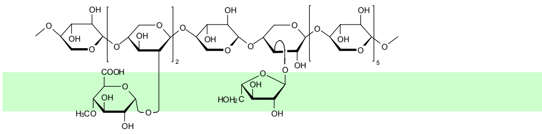
- Physical methods:
  - Particle size reduction (milling)
  - Thermal pre-treatment (pressure cooking, steam explosion…)
  - Ultrasonication, Radiation
- Chemical methods:
  - Dilute and concentrated acids
  - Alkali
  - Oxidising agents
  - Solvents
- Biological methods

Aim of pretreatment for AD

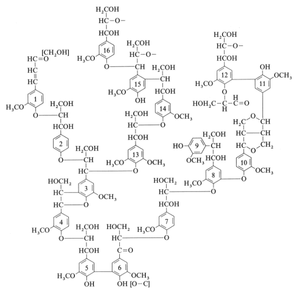
- In the cell wall of plants cellulose and hemicelluloses are incrusted with lignin.
- Those compounds are very difficult to be degraded by enzymes



Cellulose



Hemicellulose (Arabino-4-O-methyl-glucuronoxylan)



Lignin (Lin und Lin, 1989)

Pretreatment

Fundamentals:

- Particle size reduction enlarges the surface which enzymes may effect
- Chemical or thermal pre-treatment helps to disintegrate the recalcitrant complex between cellulose, hemicelluloses and lignin. Afterwards the compounds are better available for enzymatic degradation.
- High temperatures and long reaction times (eventually combined with low pH) lead to the release of mono- and disaccharides and subsequently to the formation of sugar degradation products.

Thermal pretreatment

Thermo-pressure-hydrolysis
- 180 – 230°C
- 20 – 30 bars

- Steam explosion
  - 160 – 220°C
  - 20 – 30 bars
  - Sudden pressure release

Thermo-chemical-hydrolysis
- 95 – 180°C
- Acidic
- Alkaline

Thermal pretreatment

- Such processes are suggested as pre-treatment for the enzymatic saccharification of lignocellulose (wood, straw, etc.) in bioethanol production.
- Expectations:
  - Fast and complete enzymatic degradation of cellulose and hemicelluloses
  - Rapid and increased methane formation in the anaerobic digestion process.

Thermal by-products

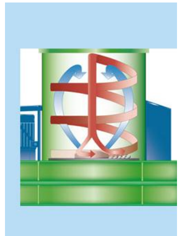
- Not only celluloses, hemi-celluloses and lignin are degraded to smaller size molecules but also other (unwanted) compounds are formed
- Temperatures higher than 160°C promote the solubilization of lignin but cause the formation of toxic compounds
  - phenols
  - fufural
  - hydroxy-methyl-furfural

Mechanical pretreatment (particle size reduction)

- Milling (Hammer mill, ball mill, …)
  - Provides advantages for process technology (mixing, pumping)
  - Size reduction often not sufficient enough or increasing methane yield (example cracking hulls, grains, …)
  - High energy demand and Expensive equipment
- Extruder
  - Compressing and shear forces reduce particle size
  - Feedstock is heated up
- Ultra sonication
  - Cell walls are disintegrated (active biomass made accessible)

Cross flow chipper

- Crushing of substrate with chains
- Chains accelerate substrate inside the machine
- No cutting knifes => less maintenance
- Chains are quite cheap spare parts
- High energy demand

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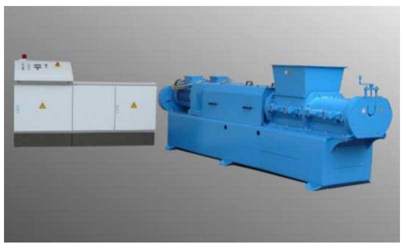
Bio-extrusion

- Bio-extrusion tears apart particles
- Very small particle sizes achievable
- Substrate is heated up during compression
- High energy demand
- High abrasion => high operation costs



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Chemical pretretment

Chemical reaction break down the high molecular structures

Alkaline
- Addition of caustic chemicals (sodium hydroxide, potassium hydroxide)
- pH 12 and higher

Acidic
- Addition of acids (sulfuric acid, phosphoric acids, …)
- pH 2 or lower

Biological pretreatment

- Microbes and microbial enzymes are use to degrade the large molecules to lower sugars and organic acids
- Pre Acidification / Biological hydrolysis
  - Takes place in special fermenters
  - Specific conditions for hydrolytic microbes (low pH, high temperatures)
- Addition of hydrolytic enzymes (microorganisms) to the anaerobic digester
  - Externally produces microbes or enzymes are fed to the digester

Conclusion pre-treatment

- Technologies for pretreatment of AD feedstock require
  - Precise process control (temperature, thermal by-products, …)
  - Energy (thermal or electrical)
  - Equipment (machinery, vessels, …)
  - Demand on chemicals / biological additive (acids, caustic solutions, enzymes, bacteria, …)

=> Good pre assessments and economic calculations necessary

Conclusion

- During the production of biogas from energy crops losses can occur due to:
  - inappropriate storage
  - incomplete utilisation of the substrate
- Improvements are possible by:
  - good agricultural practice during ensiling of the crops
  - pre-treatment methods
- Thermal pre-treatment is not suitable for all substrates
  - fibrous substrates: positive effects can be expected
  - substrates rich in sugars and starch: negative effects are possible

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from waste to value

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