Crops for AD
Types - ensiling - pre-treatment

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ENERGY CROPS
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
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
Jyväskylä Summerschool 2013

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.

\[
\text{storage losses} = \text{energy losses}
\]

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
- Conditioning
- Harvest
- Filling the silo
- Compaction and Sealing

Accurate time with respect to content of energy, fibre and WSC

Wilting, maceration, etc.

Chopping, pick-up wagon, treatment with additives

Bunker silo: thin layers, compaction with heavy machines, covering and sealing with plastic wrapping

Big bale silage: pressing of bales, wrapping

Bunker silo: thin layers, compaction with heavy machines, covering and sealing with plastic wrapping

Big bale silage: pressing of bales, wrapping
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.)

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, CO₂ 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.
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.

<table>
<thead>
<tr>
<th>Process</th>
<th>Classification</th>
<th>Approximate loss (%)</th>
<th>Causative factors</th>
</tr>
</thead>
<tbody>
<tr>
<td>Residual respiration Fermentation</td>
<td>unavoidable</td>
<td>1–2</td>
<td>Plant enzymes</td>
</tr>
<tr>
<td>Effluent or Field losses by wilting</td>
<td>unavoidable</td>
<td>2–4</td>
<td>Microorganisms</td>
</tr>
<tr>
<td>Secondary fermentation</td>
<td>mutually</td>
<td>5– &gt;7 or 2– &gt;5</td>
<td>DM content, Weather, technique, management, crop</td>
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<tr>
<td></td>
<td>unavoidable</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aerobic deterioration during storage</td>
<td>avoidable</td>
<td>0– &gt;5</td>
<td>Crop suitability, environment in silo, DM content</td>
</tr>
<tr>
<td>Aerobic deterioration after unloading</td>
<td>avoidable</td>
<td>0– &gt;10</td>
<td>Filling time, density, silo, sealing, crop suitability</td>
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<td></td>
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<tr>
<td>Total</td>
<td></td>
<td>7– &gt;40</td>
<td></td>
</tr>
</tbody>
</table>

Ensiling losses

[McDonald et al., 1991]
Factors with negative influences 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

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

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 knives => 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 pretreatment

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 used 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