Module 6: AD Feedstock

6.1: Organics & organic waste (or residuals)

6.2: The ideal AD feedstock?

6.3: Vermont: farm vs. off-farm feedstock materials

6.4: Feedstock values of manures

6.5: Off-farm feedstock energy values

6.6: Inhibitors: the dark side of feedstock

6.7: Predicting feedstock energy content from labels?

6.8: Goal: consistent diet and homeostasis

This curriculum is adapted from: eXtension Course 3: AD, University of Wisconsin

Organics & organic waste (aka residuals or resources)

What is 'feedstock'?

Organic materials that are fed to an anaerobic digester and are degraded by anaerobic digestion to methane.

Organic material is **carbon-based**. While natural biomolecules are most frequently thought of as biogas feedstock, many synthetic or man-made molecules can also be degraded by AD.

However, organic molecules that are bacteriocidal (toxic to bacteria) should not be included in AD feedstock. And bacteriocides can be either natural and synthetic.

Many types of organic material can be used as feedstock, but **typical feedstock materials** include:

- Manure
- Crop residues / energy crops
- Food processing residuals
- Food residuals

What's been used as AD feedstock?

Manure

(Energy) crops

Food waste, pre- & post-consumer (aka food scraps; food residuals)

Food processing residuals:

- Chicken processing
- Juice processing
- Brewing
- Dairy production
- Aquicultural wastewater
- Seafood processing waste

Municipal solid waste – organic fraction (must be separated from MSW)

- Paper & processing pulp
- Shredded cardboard

Yard waste (for dry AD)

Wastewater sludge, human (aka biosolids)

 Himansen (2011); Nakasaki (2009); Richards, 1994; Sezum (2011)

The danger of non-biodegradables?

Non-biodegradable materials fall into two classes:

1. Organic but **refractory**, like non-digestable fiber has organic origin & structure, but would require a much longer HRT or a different biological process for digestion. This material remains (somewhat) intact captured in separated solids

2. Non-organic / **non-biodegradable**

 Himansen (2011); Nakasaki (2009); Richards, 1994; Sezum (2011)

Feedstock selection may be regulated

Some states allow AD of animal mortalities or slaughterhouse waste but some don't. AD operators must check to be sure that they are complying with **federal and state regulations.**

Some states **regulate the amounts** of high-strength organics like ethanol syrup or FOG to a maximum amount.

Other cautions:

- Don't overload with **high-energy** feedstock like food waste.
- Don't feed **known toxins** like fossil fuel derivatives, ammonia or sulfides at high pH.
- **Recalcitrant** (or poorly degradable) material requires long retention times in order to degrade most of the VS.
- **Inert materials** yield headaches rather than biogas.

Tools to estimate biogas yield

These tools can be downloaded at no charge:

AgSTAR

- AgSTAR Handbook
- FarmWare

Unversity of Minnesota Extension

- Anaerobic Digester Economics Excel spreadsheet

This module will focus on using biogas yield values (energy values) and similar values to predict the biogas and energy yields of feedstock mixtures.

The ideal AD feedstock

The ideal feedstock?

Organic materials that are fed to an anaerobic digester and are degraded by anaerobic digestion to methane.

- **C:N ratio** of 20:1 to 30:1
- High energy content
  - High **volatile solids** (VS) content
  - High calorific content
- Largely degradable [Materials like lignin are refractory to AD.]
- Low sulfur / sulfate content
- Low toxins content

 (Maishanu et al., 1991)

Volatile solids (VS)

Volatile solids: solid material that can be 'volatilized' or combusted.
Only VS can be made into methane.
The best feedstock materials have high levels of volatile solids.

Test for VS by combusting total solids at high temperatures.

- The mass lost in combustion represents volatile solids
- The mass of ash that remains are the 'unvolatile' solids.

Not all volatile solids will be destroyed, or converted, to biogas. The extent of VS conversion depends on:

1. The nature of the feedstock; and
2. The efficiency & operation of the AD process.

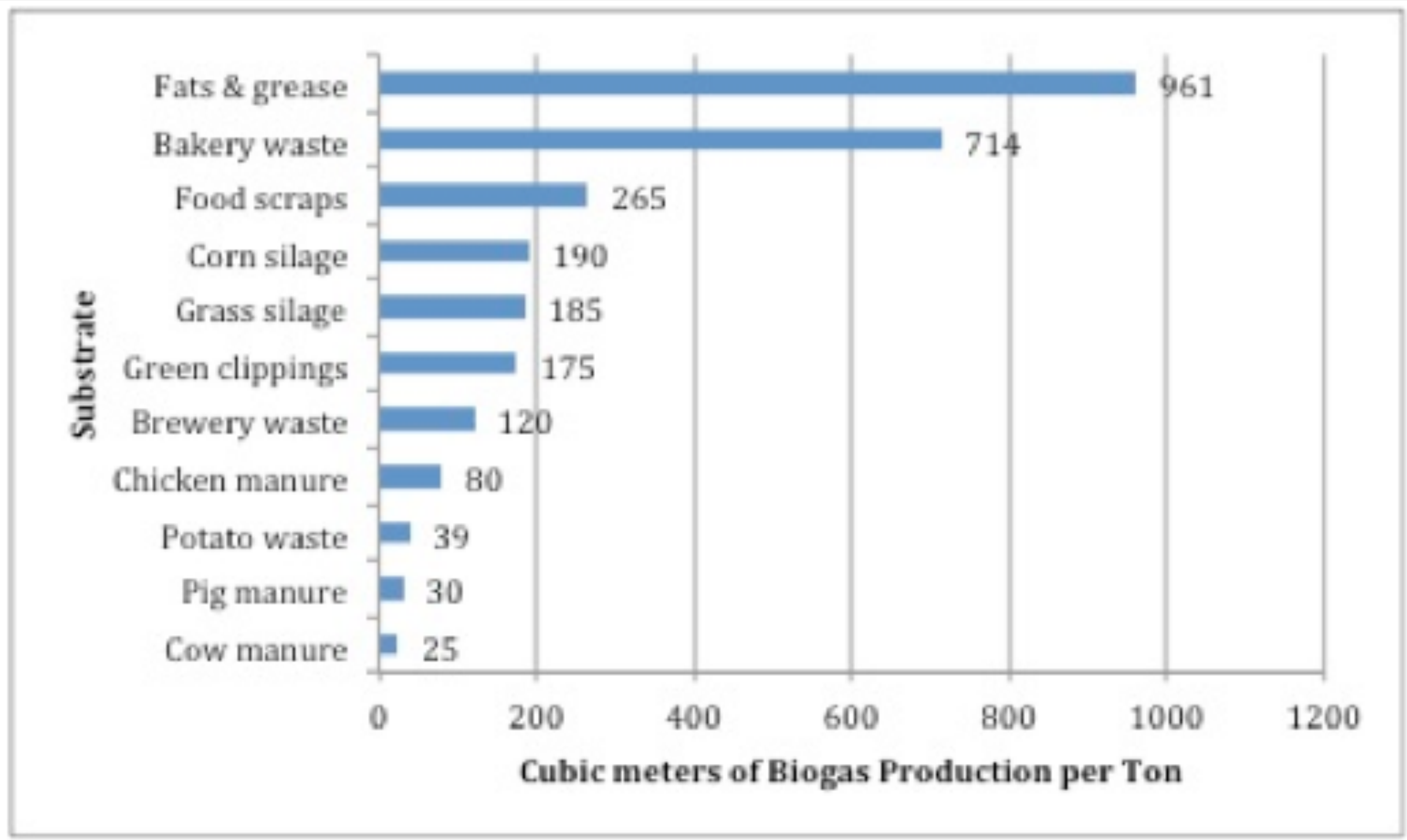
Typically, 10-40% of VS are not available to biological processes:

- Non-degradable fiber (NDF)
- Lignin

Biogas production can be estimated as **0.75 – 1.00 m^3 /kg VS destroyed**.

Volatile solids

Volatile solids are the organic compounds that can be made into methane. The best feedstock materials have high levels of volatile solids.



BOD & COD

BOD (biological oxygen demand): the amount of oxygen required for biological destruction of organic molecules

- Aka the amount of oxygen required by the bacteria that degrade organics
- Measured in a week-long assay (BOD_5 or BOD_7)
- [aka DR4 = dynamic respiration rate over 4 days]

COD (chemical oxygen demand): the amount of oxygen required for chemical destruction of organic molecules by oxidative reactions

- COD levels should be higher than BOD levels because material that cannot be degraded by bacteria can be chemically destroyed
  - Typically, COD = 1.5X BOD
- The COD assay is faster, requiring hours rather than days

BOD can underestimate the amount of destruction that occurs in anaerobic systems, so COD may be a more useful measure of the 'strength' of feedstock materials.

Volatile fatty acids are critical indicators

The most common VFAs are:

- Acetate (2 C) = 64% of methane
- Propionate (3 C) = 30% of methane
- Butyrate (4 C)

Acetate is converted directly to methane; concentration predicts success.

Propionate must be broken down by a specific population of bacteria that produce acetate & formic acid:

$$C_2H_5COO^{-1} + 3H_2O \rightarrow CH_3COO^{-1} + HCO_3^{-1} + 3H_2 + H^{+1}$$

$$\underset{\textit{propionate}}{C_2H_5COO^{-1}} + 2HCO_3^{-1} \rightarrow \underset{\textit{acetate}}{CH_3COO^{-1}} + \underset{\textit{formate}}{3HCOO^{-1}} + H^{+1}$$

Some methanogens can convert formate to methane. If this population is not robust and has sufficient trace minerals:

- formate accumulates
- high concentrations of formate inhibit propionate oxidizing bacteria

Banks & Zhang (2010); Batstone (2002); Jens & McCarty (1965); McCarty & Smith (1986)

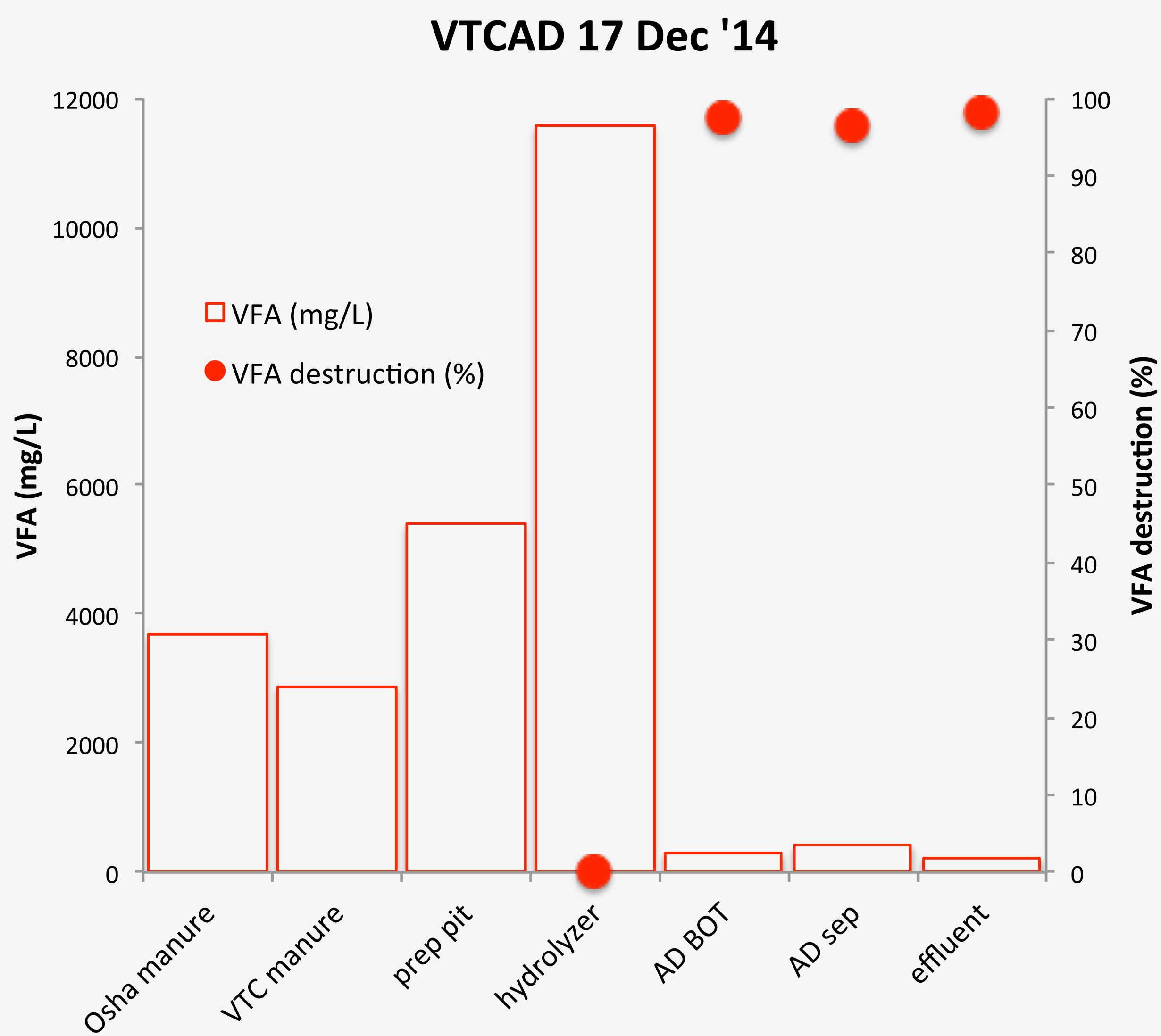
Production of volatile acids

In a stable AD system, VFAs are used by methanogens as quickly as they are made and the **concentration of acetic acid in the slurry should be 50 – 300 mg/L.**

If the loading rate is increased or feedstock rich in volatile solid is suddenly added, production of VFAs will surge and **pH will drop** because methane production won't be able to keep up. This is referred to as the AD going 'sour'.

- Sufficient buffering (alkalinity) will prevent this from happening.

Following VFA through the AD process



VFA:TA ratio

The ratio of volatile fatty acids : total alkalinity is a useful diagnostic test.

For manure, the VFA:TA should be no higher than 2:1

Since the ratio can reach 7.5:1 before pH changes, the Ripley ratio is a better predictor of AD stability than pH values.

AD systems with **low concentrations (< 3% TS)** are more sensitive to changes in acidity, so use lower VFA:TA ratios.

How important are trace elements?

A 2010 study tested a variety of feedstock mixtures in bench-scale digesters for nearly a year.

- Digesters were inoculated with sewage sludge but then feed other materials.
- After prolonged operation of nearly one year, digestion became unstable and failed.
- Failure was associated with increased concentrations of propionate.
- Further study found a drop of concentrations of **essential trace elements** had dropped below 1 mg/kg TS as the levels of propionate increased:
  - Cobalt
  - Selenium
  - Tungsten
- These trace elements are co-factors for enzymes, like formate dehydrogenase, required for conversion of propionate to methane.

Banks & Zhang (2010)

C:N ratio

Anaerobic bacteria use C for energy and N for building cells.

- Carbon is used 30-times faster than nitrogen so a **30:1 ratio** is optimal for AD.
- At higher C:N ratios the N is used up first & gas production then slows.
- At lower C:N ratios the C is used up and fermentation stops.
  - Lack of acetate then stops biogas production.
  - And excess N becomes excess ammonia.

C:N ratios (1)

Why do want want high levels of carbon?

- **Carbon** (C) is converted to methane by reduction (addition of H atoms).
- The AD process also converts carbon into CO_2.
- When CO_2 dissolves (partitions) into the digestate it reacts with water to form carbonic acid (H_2CO_3). Carbonic acid is unstable and immediately breaks down to release hydrogen ions (H^{+1}) and hydrogen carbonate ions (HCO_3^{-1}). Increased [H^{+1}] decreases the pH of the digestate.

And what's the problem with nitrogen?

- High levels of **nitrogen** (N) are problematic because protein nitrogen can be converted to ammonia (NH_3).
  - Ammonia is toxic to methanogens.
  - And ammonia absorbs H^{+1} to form ammonium ions (NH_4^{+1}), raising the pH of digestate.
- Feedstock with high TS tend to produce more ammonia, likely because of higher protein content.

Dioha et al., (2013)

C:N ratios (2)

C:N ratios are even more critical if AD is operated at thermophilic rather than mesophilic temperatures.

- Mesophilic = 30-40°C (usually 35-37°C)
- Thermophilic = 50-60°C (usually 55°C)

As temperature is increased ammonia production also increases.
While thermophilic temperatures often increase methane production, that increase won't be seen if ammonia levels rise and inhibit methanogenesis.

Fortunately, increasing C:N ratios reduce the risk of ammonia production.

Wang et al. (2014) showed that increasing C:N ratios could overcome ammonia inhibition when ratios were raised from:

- **15 to 25 for mesophilic temperatures**
- **20 to 30 for thermophilic temperatures**

Feedstock C:N ratios

Material	C:N
Dairy cow manure	**6:1 – 20:1**
Straw	90:1
Corn stalks	75:1
Leaves	30:1 – 80:1
Garden waste	30:1 – 150:1
Fruit waste	35:1
Weeds	30:1
Hay	25:1
Grass	12:1 – 25:1
Grass silage	10:1 – 25:1
Clover	23:1
Grass clippings	20:1
Alfalfa	12:1

Material	C:N
Cardboard	350:1
Newspaper	175:1
Vegetable scraps	25:1
Coffee grounds	20:1
Food waste	20:1
Grease trap waste	9:1 - 15:1
Brewery sludge/yeast	1.5 – 5:1
AD liquid effluent	*≤ 10:1*

Many use color to get a quick sense of nitrogen content in feedstock:

- Many high C materials are **brown**
- Many high-N materials are **green**

Biocycle (2006) 47(8): 27 / Steffen (1998) / Thomas (2006)

Estimating C:N of Mixtures

C:N ratios are actually a ratio of parts. Example: 20:1 C:N

- Consider a total of 21 parts:
  - 20 of those parts are C
  - 1 of those parts is N

It's useful to convert these ratios to percentages. Using the 20:1 example:

C = (20/21)(100) = 95.24%
N = (1/21)(100) = 4.76%

These values can then be used to calculate volume or mass of C & N in the dry weight of any feedstock and any mixture. The combined masses of C & N can then be used to calculate the overall C:N ration of an AD diet:

Optimal 20 - 30:1

feedstock	**literature value C:N**	**% C**	**% N**	**% DM**	**gallons feedstock**	**gallons DM**	**gallons C**	**gallons N**	**diet C/N**
manure	20:1	95.2	4.8	10%	7,000	700	667	33	20
GTW	12:1	92.3	7.7	50%	3,000	1,500	1,385	115	12
glycerol	100%	100.0	0.0	85%	500	425	425	-	
				Totals	10,000	2,625	2,476	149	**16.7**

Calculating C:N of Diet from Analysis

C:N ratios can also be estimated from some rudimentary biochemical data.

Volatile solids (VS; aka organic matter, OM) are that portion of feedstock that can be removed (volatilized) by combustion at high temperature. The amount of biogas that can be produced from feedstock is determined by its percent VS.

To estimate C:N ratios from VS (or OM) and total nitrogen (often TKN):

1. Divide mass (or %) of VS (OM) by 1.72 to estimate carbon content.
2. Then divide the amount of N into C content to estimate C:N, where N = 1.

Co-digestion of manure & food residuals

A 2010 study using a GHD plug-flow digester with 30-day HRT combined scraped dairy manure with 16% (v/v) food residuals:

	C:N	alkalinity CaCO3 g/L	pH	N:P:K	micro-nutrients
manure	11:1	9.63	6.94	6:1:6	Fe, Mn, S, Mg, Ca, Ni
residuals	56:1	3.39	5.19	10:1:1	Se, Ni
combination	28:1	8.96	6.87	8:1:4.5	sum

Biogas and methane production exceeded theoretical values calculated with Bushwell's equation by 33% suggesting that co-digestion of manure and food residuals had a **synergistic** effect.

	% destruction
TS	40.6
VS	55.3

	% destruction
COD	67.7
VFA	99.9

Frear et al. (2009)

Optimal AD conditions

Parameter	Optimal Range	Reference
C:N ratio	20:1 – 30:1	Liu et al. (2009)
C:N:P ratio	115:4:1	Liu et al. (2009)
Moisture content	*design dependent*	
TS	*design dependent*	
VS (organic loading rate)	0.0012 – 0.2248 kg/gallon	
pH	6.8 – 7.2	
alkalinity	2 – 5 g/L	Metcalf & Eddy (2003)
VFA/alkalinity (Ripley ratio)	0.2 – 0.4 (0.25 optimal)	Ripley et al. (1986)
TAN (total NH_3 nitrogen)	$\leq$ 1.7 g/L	Koster & Lettinga (1984)
effluent VFA	90% destruction	

Optimal HRT, %TS and temperature are dictated by AD design.

Feedstock loading

AD operators monitor and control AD feeding, **aka loading.**

Critical factors include:

- Concentration of feedstock (solids/volume)
- Volatile solids content of feedstock
- Inorganic (or inert) content of feedstock
- Volatile solids / AD volume
- Hydraulic retention time

Calculating the loading rate

Example: complete mixed AD (50′ dia x 20′ deep w/ 5′ cone depth)

- Fed 5,000 gallons manure/day @ 100F
- 6.5% TS, 69% VS, density =1

<u>Calculating manure volume</u>

cylinder = $(\pi)(r^2)(h) = (\pi)(25^2)(20) = 39{,}250\ ft^3$

cone = $(1/3)(r^2)(h) = (1/3)(25^2)(5) = 3{,}217\ ft^3$

total = $42{,}521\ ft^3$

<u>Calculating loading rate</u>

pounds TS/day = (gallons/day)(8.34 lb/gallon)(%TS)
= (5000)(8.34)(0.065) = 2,710 lb TS/day

pounds VS/day = (lb TS/day)(%VS) = (2,710 lb TS/day)(0.69) = 1,869 lb VS/day

loading rate = (lb VS/day) / volume of manure = 1,869 lb/day / 45,521 ft^3
= 0.04 lb / day / ft^3

Average loading rates are 0.02 – 0.37 lb VS / ft^3 volume

Vermont on-farm vs. off-farm feedstock

Vermont: farm vs. biomass AD

On-farm AD:

- Located on a farm.
- At least 51% of AD feedstock must come from the farm.
- SPEED contract electric revenue is around $0.014.

Biomass AD:

- Can be located anywhere.
- No restrictions on % of feedstock from a farm.
  - May use on-farm feedstock.
  - May not use any on-farm feedstock.
- SPEED contract electric revenue is around $0.021.

For VTCAD, this requirement is part of our SPEED contract and is mentioned in our Certificate of Public Good.

What's what?

On-farm AD:

- Manure
- Crops (fresh or ensiled)
- Crop waste
- Food processing residuals
- Effluent (?)

Biomass AD:

- Anything else that is permitted or regulated…
  - By ANR's Wastewater Division via an indirect discharge permit; or
  - By ANR's Solid Waste Division as the organic fraction of municipal solid waste.
- Of course, the material should be organic, biodegradable and energetic.

Feedstock value of manures

Manure: it's not the energy content

Manure: has low energy since the feed has already been digested.

But, manure has other properties that make it a valuable feedstock material.

- Manure has a neutral pH & high buffering capacity (alkalinity).
- Has all the microbes needed for AD.
- Has all the macro- & micronutrients needed for AD.
- Manure is abundant & pumpable.

Buffers

The stability of AD depends on pH, and pH is dependent on…

Buffering capacity: the ability of the slurry to resist changes of pH when chemical composition changes.

Alkaline buffers have two **sources**:

- Buffers present in feedstock (manure is a great buffer)
- Buffers created by methanogens: carbonates, bicarbonates, ammonia

Feedstock with low levels of alkalinity may need to be augmented with sodium bicarbonate (the 'Tums' for AD).

When pH begins to drop:

- The buffering capacity is nearly depleted.
- The rate of fermentation is greater than the rate of methanogenesis.
- Bacteria may be growing slowly or have been washed out.
- Toxins may be present.

Energy values (1)

All data approximately and can vary for exact data further samples are necessary	Dry solids (data can vary)	Organic dry solids (data can vary)	Specific gas-production per oDS (data can vary)	Gas-production per tonne fresh material (data can vary)	Produced kilowatt-hours per t FM (35 %electrical efficiency CHP, Heating value 21 MJ/m3, 55 % Methane content, 3.6 MJ/kWh)	Kilowatt per tonne fresh material and day
Unit	% of Fresh material	% of DS	m3 /t oDS	m3/t FM	kWh/t FM	kW/t FM d
Animal carcasses (homogenised	30.0	90	900	243.0	496.1	20.7
Animal fat*	90.0	90	850	688.5	1405.7	58.6
Beet top	12.0	70	420	35.3	72.0	3.0
Blood*	8.0	90	600	43.2	88.2	3.7
Canteen waste/food waste	20.0	85	700	110.0	224.6	9.4
Cattle-dung	25.0	80	300	60.0	122.5	5.1
Cattle-slurry	8.0	80	320	20.5	41.8	1.7
Cereal slop (alcohol production)	6.0	90	480.0	25.9	52.9	2.2
Cereals/grains	85.0	95	650	524.9	1071.6	44.7
Chaff	85.0	90	350	267.8	546.7	22.8
Chicken litter/dung	40.0	75	420	126.0	257.3	10.7
Chip fat	95.0	87	1000	826.5	1687.4	70.3
Clover	15.0	88	520	68.6	140.1	5.8
Concentrated whey	15.0	90	800	108.0	220.5	9.2
Corn Cob maize (CCM)	60.0	95	600	342.0	698.3	29.1
Draff from beer production	20.0	80	500	80.0	163.3	6.8
Fat	95.0	87	1000	826.5	1687.4	70.3
Fermentation slops	1.8	98	750	13.2	27.0	1.1
Food waste (disinfected)	20.0	85	700	110.0	224.6	9.4

Energy values (2)

Fruit Pomace	20.0	90	520	93.6	191.1	8.0
Fruit residuals	20.0	80	350	56.0	114.3	4.8
Fruit slop	2.0	95	450.0	8.6	17.5	0.7
Fruit wastes	15.0	90	550	74.3	151.6	6.3
Glycerine*	100.0	95	750	712.5	1454.7	60.6
Grass fresh	18.0	90	450	72.9	148.8	6.2
Grass silage	25.0	85	550	116.9	238.6	9.9
Grease trap	13.0	95	800	98.8	201.7	8.4
Gut and Stomach/Intestines content	15.0	80	400	48.0	98.0	4.1
Hemp cake	88.0	93	105	85.9	175.4	7.3
Horse manure	28.0	80	250	56.0	114.3	4.8
Maize silage	32.0	95	660	200.6	409.6	17.1
Municipal solid waste, MSW (brown bin)	35.0	50	580	101.5	207.2	8.6
Old bread	65.0	95	700	432.3	882.5	36.8
Pig slurry	4.5	80	320	11.5	23.5	1.0
Potato top	12.8	87	420	46.8	95.5	4.0
Potato pulp	15.0	95	650	92.6	189.1	7.9
Potatoes	25.0	92	680	156.4	319.3	13.3
Pure fat (rendering plants)*	99.0	100	750	742.5	1515.9	63.2
Rape seed-silage	16.0	80	500	64.0	130.7	5.4
Rapeseed cake	85.0	93	680	537.5	1097.5	45.7
Residuals from vegetables	20.0	80	450	72.0	147.0	6.1
Sewage sludge	12.0	80	490	47.0	96.0	4.0
Silage effluent*	1.4	95	800	10.6	21.7	0.9
Silage from grain (whole plant)	28.0	90	550	138.6	283.0	11.8
Sugar beet chopped	25.0	85	580	123.3	251.6	10.5
Sugar beet leaves siliert	22.0	75	450	74.3	151.6	6.3
Whey*	5.0	90	750	33.8	68.9	2.9

Sources: FNR (Biogashandreichung), KTBL-website, LfL-website, Big East Biogas handbook

Off-farm feedstock energy values

Off-farm feedstock adds energy

Off-farm feedstock materials have more energy content (thus energy value) than manures because they have not been digested.

- They add energy.
- The added energy boots biogas production and revenue.
- Off-farm feedstock also adds nutrients.

Disadvantages?

Off-farm materials will require: 1) more permitting; 2) communication & coordination; 3) attentive operation; and 4) may require storage.

- Permitting through Vermont Agency of Natural Resources.
- Communication & coordination with generators & haulers.
- Added nutrients must be properly managed.
- Large amounts of energetic off-farm feedstock may overload AD, causing chemical imbalance.
- High energy off-farm feedstock should be fed in small amounts.
    - So, either deliver frequently, or store on-site and pump in daily.

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Silage from grain (whole plant)	28.0	90	550	138.6	283.0	11.8
Sugar beet chopped	25.0	85	580	123.3	251.6	10.5
Sugar beet leaves siliert	22.0	75	450	74.3	151.6	6.3
Whey*	5.0	90	750	33.8	68.9	2.9
Sources: FNR (Biogashandreichung), KTBL-website, LfL-website, Big East Biogas handbook						

Searchable databases for energy values

There are a number of good sources for feedstock energy values and the most extensive are from Europe.

One of the best is from the Bayerische Landesanstalt für Landwirtschaft:
http://www.lfl-design3.bayern.de/ilb/technik/10225/?sel_list=14%2Cb&strsearch=sorghum&pos=left&button=Suchen

Landesanstalt für Landwirtschaft → Agrarökonomie → Ökonomik regenerative Energie

Biogasausbeuten verschiedener Substrate

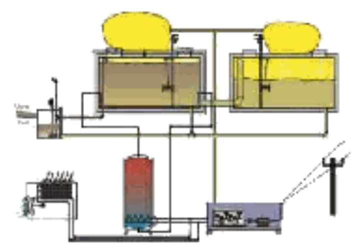
Die Gasausbeuten sind, soweit möglich, auf Basis durchschnittlicher Nährstoffgehalte (Fett, Eiweiß und Kohlenhydrate) und Verdauungsquotienten berechnet (siehe hierzu "Berechnung der Gasausbeute von Kosubstraten in Biogasanlagen").

Bitte Substrat wählen...

Grüngut: Gras
Grüngut: Klee/-gras
Grüngut: Leguminosen
Grüngut: Luzerne/Weidelgras
sonstiges Grüngut
Getreide/Mais grün
Grassilage
Silage: Klee/Kleegras

oder Suchbegriff eingeben:

sorghum
Suchtipps
Suchbegriff am
Wortanfang
irgendwo im Text
Suchen



1 Datensatz erfüllt Ihre Suchbedingungen!

Erläuterungen zu den Spaltenbezeichnungen

Substrat	TM [%]	oTM [%]	Nl/kg oTM	Nm^3/t FM	CH_4 [%]	Datenquelle
Sorghum-Zucker-Hirse	20,8	91,6	562,6	107,2	51,8	berechnet

Bitte haben Sie Verständnis, dass wir für die Richtigkeit der Gasausbeuten und deren Berechnung keine Haftung übernehmen können!

Other sources are linked in Module 5 materials at Richmond-hall.weebly.com

Inhibitors: the dark side of feedstock

Inhibitors

Challenge: critical elements & molecules are required for – and enhance – AD at optimal concentrations, but inhibit AD at non-optimal concentrations:

VFAs: high concentrations of VFAs cause pH to drop and inhibit AD

NH_3 from degradation of nitrogenous (protein-rich) feedstock

- Free NH_3 is more toxic than NH_4^{+1}
  - NH_3 toxic at levels > 150 mg/L
  - NH_4^{+1} toxic at levels > 3000 mg/L
- pH can shift the equilibrium and lower toxicity
  - At pH 7.2 NH_4^{+1} predominates

Metal ions from food feedstock or bases used to increase alkalinity

- Acclimatization is slow
- Heavy metals are more of a problem & must be avoided in feedstock

Sulfides are produced from the sulfur in protein-rich feedstock

- Precipitation of sulfides by iron prevents toxicity; only soluble S^{-2} is toxic

Toxins

Toxins (or toxicants): component of feedstock that causes an adverse effect on microbial metabolism.

- Fossil fuels and their derivatives
- High levels of ammonia
- Insecticides
- Fungicides
- Antibiotics (like ionophores)
- High levels of sulfides
- Copper sulfate

Treatment with buffers won't cure toxin problems.

Alkali & alkaline earth salt toxicity

These salts are needed for AD but are toxic at high levels. High soil levels will also inhibit crop growth.

cation (mg/L)	stimulatory	moderate Inhibition	strong inhibition
Na	100 - 200	3,500 – 5,550	8,000
K	200 - 400	2,500 – 4,500	12,000
Ca	100 – 200	2,500 – 4,500	8,000
Mg	75 - 150	1,000 – 1,500	3,000

Heavy metal toxicity

Like salts, trace amounts of heavy metals (particularly Cu, Zn, Ni) are needed for AD. But higher levels are toxic.

Addition of **sulfates or hydroxides** will precipitate many heavy metals at AD pH values.

Sulfide toxicity

Some soluble sulfides are needed for the growth of fermenting bacteria at levels of 50 – 100 mg / L. But **> 200 mg/L sulfides are toxic**.

- Sulfides are dervived from sulfates in the feedstock
- Or from proteins

Addition of iron salts can precipitate sulfides in the feedstock, preventing toxicity.

In the long run, diluting high-sulfur feedstock or reducing its use is a better solution to sulfide toxicity.

Ammonia toxicity

Livestock manures usually contain ammonium ion (NH_4^+) or proteins that can be degrade to ammonia. Ammonia easily accumulates to toxic levels within feedstock.

When AD pH is greater than 7.4, 1500 – 3000 mg/L of ammonia can inhibit AD. But, under these conditions acetogenesis will occur and will lower pH.

Treatment: hydrochloric acid (HCl) can be added to reduce pH to 7.0

When the concentration of ammonia rises **above 3000 mg/L it's toxic at any pH.** The best treatment is to withdraw high-nitrogen feedstock and switch to feedstock with lower ammonia potential.

Predicting energy from food labels?

Bushwell: theoretical methane yield

Bushwell's formula predicts the methane productivity of a feedstock material or mixture:

$$Bu = C_nH_aO_b + \left(n - \frac{a}{4} - \frac{b}{2}\right)H_2O \rightarrow \left(\frac{n}{2} - \frac{a}{8} + \frac{b}{4}\right)CO_2 + \left(\frac{n}{2} + \frac{a}{8} - \frac{b}{4}\right)CH_4$$

Bu is m^3 CH_4/kg $VS_{DESTROYED}$ at STP

Where:

$VS_{LIPID} = C_{57}H_{104}O_6$
$VS_{PROTEIN} = C_5H_7O_2N$
$VS_{CARBOHYDRATE} = C_6H_{10}O_5$
$VS_{VFA} = C_2H_4O_2$

Feedstock goal:
predictable homeostasis!

Homeostasis is the critical concept

Homeostasis: a stable state (aka steady-state) in which many biological and chemical processes are happening, but no change is apparent to the observer.

- Stability at chemical & biological levels

All biological systems strive to maintain homeostasis.

Example:
Our bodies strive to maintain a constant body temperature of 98.6°F.
Many chemical, biological and behavioral changes are used to maintain stable body temperature.

Homeostasis for AD?

In AD systems, homeostasis allows stable and predictable operation at high rates of energy production.

How do we get to homeostasis and stay there?

- **Find optimal operational parameters and maintain them.**
  - Temperature, feeding, mixing
- **Find optimal feedstock mixtures and maintain them.**
  - Make any changes slowly.
  - Changes must maintain consistent energy & biochemical inputs.
  - Monitor critical operational parameters like Ripley ratio, pH, C:N ratios.

Feedstock references:

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