Renewable chemistry from biogas: \( \text{CH}_4 \) and \( \text{CO}_2 \) as feedstock

Dr. Fabrizio Sibilla, CIB & Krajete GmbH
Trieste 17.05.2017
Fabrizio Sibilla

- Born & grew up in Metanopoli, MI, (Methane city)
- MSc. In Food Technology at Milano University
- Fellowship in Trieste University (Biocatalysis in organic solvents)
- PhD Student in the Graduated School „BioNoCo“, RWTH-Aachen (Biocatalysis in non conventional media, Enzyme Promiscuity & Metagenomics)
- Post-Doc at RWTH-Aachen in the TMFB Project (Taylor Made Fuels from Biomass, Directed evolution)
- Business Development Manager at Krajete GmbH (A)
- Scientific advisor for the Italian Biogas Council
- Business Development Manager at BSE Engineering Leipzig GmbH (DE)
Krajete GmbH Company Facts

• Established 2012 as “Krajete GmbH” (“Limited Liability Company”)
• Slogan “Learning From Nature.”
• Private owned; > 1 million EUR spent on overall development (funds, own, earned)
• 4 employees (3 PhDs, 1 Dipl.-Ing)
• 2 PhD topics funded, 3 diploma thesis (TU Vienna - biology, JKU Linz - chemistry)
• 6 patents applications (2011 – 2015), new field with almost no prior art
• Assets: 2 benchscale reactors (1 L, 10 L) in Vienna, in steady operation since 2009
  + gas bottle fleet (15 x 50 l) and mobile compressor for sampling of industrial gases,

Customer pool diversified: car producers, power producers, international gas
organizations, steel companies, biogas companies, machine producers
Why gases fermenting?

Gases are available all year round as black or green

Methane:
• available all year round from biogas upgrade
• available from Power to Gas plants
• available fossil

Syngas:
• available from various biomasses all year round
• available from steel gases, MSW gasification, fossils

CO2:
• available from biogas upgrade & ethanol fermentation
• available fossil
Gases or sugars?

Microorganisms need carbon sources

1 ton glucose $\rightarrow$ 40% C; 53% O; 7% H; it costs 350 €/ton $\rightarrow$ Carbon atom costs 0,875 €/kg

1 ton CH4 $\rightarrow$ 75% C; 25% H; it costs 350 €/ton $\rightarrow$ Carbon atom costs 0,466 €/kg (circa 2 times less than glucose)

1 ton CO2 $\rightarrow$ 27% C; 73% O; it costs 50 €/ton $\rightarrow$ Carbon atom costs 0,185 €/kg (circa 5 times less than glucose)
Best source of green gases for fermentation? Biogas! (at least in EU)

• AD is Multifeedstock:

  – It can use any organic substance available on any agro-ecological distribution area, to convert 70-80% of carbon fixed in chlorophyll photosynthesis into gas

  – Avoid MONO-CULTURES that, even though “no-food crops”, are displacing food crops

  – Biogas crops can improve farm land rotation and crop diversity
Best source of green gases for fermentation? Biogas! (at least in EU)

- AD is converting biomass to energy in an efficient way on small scale (>500,000 litre diesel equivalent), therefore:

  - Applicable to any sized professional farm

  - It can use any biomass and avoid transporting watered (95-70%) biomasses over long distances

- Nutrients cycling:

  - By means of the digestate, the undigested carbon and all nutrients (N-P-K micronutrients) may be re-employed on site, sustainably and efficiently, restoring organic fertilization in areas where there is no more breeding and improving efficacy

- With biogas we can dramatically reduce the modern agricultural pollution in the fields and in the stables
To summarize some prices of commodities for fermentation.
SWOT Analysis Biogas in EU

**Strength**
- Improves economic of farms
- Protect from price volatilities
- Generates constant and foreseeable cash flow
- Allows the farmer to produce his fertilizers and fuel

**Opportunities**
- Environmental regulations
- "Renewable fertilizers" Trademark
- Lowers GHGs emissions from agriculture

**Internal**

**External**

**Weakness**
- Access to Credit
- Learning of new business models
- Not in every countries possible 2nd or 3rd harvest

**Threats**
- Fossil fertilizers price lowers
- Natural gas price lowers
- Subsidies fully lifted
Scenario di sviluppo del biometano e previsioni di evoluzione della *land efficiency* del biogas italiano al 2030 grazie all’adozione del modello Biogasfattobene®

Estimation methodology and data analysis according to the Italian Biogas Consortium position paper

<table>
<thead>
<tr>
<th></th>
<th>2010</th>
<th>2015</th>
<th>2020</th>
<th>2025</th>
<th>2030</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Total Biomethane</strong> (Gm³/year)</td>
<td>0,7</td>
<td>2,2</td>
<td>4,2</td>
<td>5,5</td>
<td>8</td>
</tr>
<tr>
<td><strong>UAA Monocrop</strong> (ha)</td>
<td>85.000</td>
<td>200.000</td>
<td>250.000</td>
<td>300.000</td>
<td>400.000</td>
</tr>
<tr>
<td><strong>UAA Monocrop</strong> (ha/Mm³ bioCH₄)</td>
<td>121</td>
<td>91</td>
<td>60</td>
<td>55</td>
<td>50</td>
</tr>
<tr>
<td><strong>BioCH4 yield Monocrop</strong> (m³/ha bioCH₄)</td>
<td>6720</td>
<td>6720</td>
<td>6720</td>
<td>6720</td>
<td>6720</td>
</tr>
<tr>
<td><strong>LAND EFFICIENCY</strong> (m³/ha bioCH₄)</td>
<td>8.235</td>
<td>11.000</td>
<td>16.800</td>
<td>18.333</td>
<td>20.000</td>
</tr>
<tr>
<td><strong>BioCH4 from Monocrop</strong> (Gm³/year)</td>
<td>0,57</td>
<td>1,34</td>
<td>1,68</td>
<td>2,02</td>
<td>2,69</td>
</tr>
<tr>
<td><strong>BioCH4 from integration biomasses</strong> (Gm³/year)</td>
<td>0,13</td>
<td>0,86</td>
<td>2,52</td>
<td>3,48</td>
<td>5,31</td>
</tr>
<tr>
<td><strong>BioCH4 from integration biomasses</strong> %</td>
<td>18</td>
<td>39</td>
<td>60</td>
<td>63</td>
<td>66</td>
</tr>
</tbody>
</table>

**2030** 8 billion Nm³ biomethane equivalent (12% natural gas consumption)
(1) It is possible to produce food AND energy (and biobased materials) via biogas done right «integration biomasses»

The biogas done right integration biomasses

- Double crops before and after a cash crop
- Perennial crops where C3 or C4 aren’t deployed
- Livestock effluents
- Agricultural and agroindustrial by products
- (OMW)

### The biogas land efficiency

<table>
<thead>
<tr>
<th></th>
<th>Etanolo da Mais granella</th>
<th>Biodiesel da Colza</th>
<th>Etanolo da Arundo donax</th>
<th>Biogas da monoculture</th>
<th>Biogas done right**</th>
</tr>
</thead>
<tbody>
<tr>
<td>N. impianti</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>27</td>
<td>27</td>
</tr>
<tr>
<td>produzione etanolo ton./anni</td>
<td>80.000</td>
<td>80.000</td>
<td>59.200.000</td>
<td>59.200.000</td>
<td>586.667</td>
</tr>
<tr>
<td>MWh th./anni</td>
<td>586.667</td>
<td>586.667</td>
<td>586.667</td>
<td>586.667</td>
<td>586.667</td>
</tr>
<tr>
<td>ton biomassa</td>
<td>239.232</td>
<td>123.333</td>
<td>380.992</td>
<td>538.182</td>
<td>720.000</td>
</tr>
<tr>
<td>fCLR ** ha</td>
<td>22.688</td>
<td>35.088</td>
<td>15.238</td>
<td>10.764</td>
<td>2.960</td>
</tr>
<tr>
<td>Land efficiency (ha prima raccolto/10GWh th)</td>
<td>383</td>
<td>593</td>
<td>257</td>
<td>182</td>
<td>50</td>
</tr>
<tr>
<td>Moltiplicatore fabbisogno di terra arable rispetto biogas done right</td>
<td>8</td>
<td>12</td>
<td>5</td>
<td>4</td>
<td>1</td>
</tr>
<tr>
<td>Arco agricolo (ha) interessato considerando rotazioni e % seminativi</td>
<td>54.019</td>
<td>292.398</td>
<td>25.397</td>
<td>59.798</td>
<td>7.048</td>
</tr>
</tbody>
</table>

*Area interessata Ha sottratta alle produzioni food/feed*

**nel fabbisogno di terreno di prima raccolto (fCLR) andrebbero tali i crediti derivanti dalla produzione di biomassa o piane per l'alimentazione zootecnica

*impianti da 1,0 MWe ad 90%*  
**30 ha/1 MWe Nett*
(1) Italian biomethane road map

Italian road map

Table 1 – Development scenario for bioCH4 and evolution forecasts for italian bioCH4 production and land efficiency di evoluzione della land efficiency until 2030

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<tbody>
<tr>
<td>(A) Biometano totale</td>
<td>0,70</td>
<td>2,20</td>
<td>4,20</td>
<td>5,50</td>
<td>8</td>
</tr>
<tr>
<td>(FCLR) - SAU primo raccolto</td>
<td>85.000</td>
<td>200.000</td>
<td>250.000</td>
<td>300.000</td>
<td>400.000</td>
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<tr>
<td>(C x P) - Resa primo raccolto</td>
<td>121</td>
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<td>18</td>
<td>39</td>
<td>60</td>
<td>63</td>
<td>66</td>
</tr>
</tbody>
</table>

The integration biomass

Obiettivo 2030 (m3/anno) 8.000.000.000
- CH4 da primo raccolto (m3/ anno) 2.664.000.000
- SAU ha FCLR (ha) 400.000
- Mais - resa CH4 (m3/ha) 6660
- CH4 da Biomasse di integrazione (m3/anno) 5.336.000.000
  - di cui da colture (m3/anno) 2.668.000.000
  - di cui da sottoprodotti (m3/anno) 2.668.000.000

SAU ha 2030 400.000

CIB Team, 2016 – «Considerations about italian «biogasdoneright» potential from agriculture». Methodology, data gathering and analysis in the Italian Biogas Consortium 2016 position paper
(2) Not only is possible but is desirable doesn’t make sense to produce bioenergy with the current agricultural practices biogas done right practices help to decarbonize agriculture

**Biogas done right farming practices**

- the organic fertilization, with soil nutrient balance and new machinery avoiding nutrients losses and soil compaction
- the mitigation of emissions from livestock effluents,
- keeping the soil covered the whole year applying new and improved crop rotations with a larger fraction of nitrogen fixing crops,
- the shift from deep plowing to precision farming and minimum tillage agriculture,
- increased share of renewable energy in agriculture
- Etc. etc.
(3) Biogas done right carbon efficiency

Valli and others, “Greenhouse gas emissions of electricity and biomethane produced using the Biogasdoneright™ system: four case studies from Italy”, submitted
(4) BIOGAS TRAJECTORY COST

Cost of Advanced Biofuels compared to current price of key transportation fuels on energy cost basis.

- Production cost of the “lowest hanging fruits” is about 50% higher than today’s price of gasoline and diesel.

Source: Mainly EGFTF report 2015.
THE BIOGAS REFINERY AS A BIOMASS DENSIFICATION CENTER

BIOGAS REFINERY SCHEME: ON SITE AND CENTRALIZED PRODUCTION SCHEME VIA NG GRID

- **Biomass input**
- **AD plant**
- **Waste heat**
- **Fuel cell**
- **Electricity grid**
- **Off grid**
- **ELECTROLYZER**
  - **H₂**
  - **O₂**
- **Power to CH₄**
  - **CH₄ >98%**
- **Upgrading**
  - **CH₄ >98%**
- **LNG**
  - **Natural gas grid**
  - **Combined cycle power generation**
- **On site production**
  - **Steam reforming or biotech conversion**
- **Methanol**
- **Fuel blend**
- **DME (diesel like)**
- **Centralized production**
  - **Methanol**
  - **Methanol to olefins (plastic)**
  - **Combined cycle power generation**
- **Solid fertilizer**
- **Liquid fertilizer**
- **Solid fertilizer**
- **Liquid fertilizer**
- **Raw biogas**
The future carbon sources for the Chemical Industry: CH$_4$, CO$_2$, and Biomass – together integrate and complement each other

CH$_4$ and CO$_2$ utilization overcome the dogma, that biomass is the only renewable carbon feedstock und it’s reducing the pressure on biomass and land substantially

*) Crude oil based: molecules from Fischer Tropsch can be better derived via CH$_4$ and CO$_2$ incl. bitumen and asphalt.
Methane

- Well known energy source
- Well known feedstock in industrial chemistry
- Best fossil fuel ever (120 octane number vs 98 of gasoline)
- Does not leave pollution in case of spillage
- 44 times less soluble than CO2 in water
- 4400 less soluble than glucose at 100 g/l
Syngas

What is syngas?
• It is a blend of CO, H2 and CO2 in various ratios
• It can be produced from the gasification of coal or biomass and CH4 steam reforming
• It is used for power generation
• It is used for Fischer-Tropsch synthesis (Gas to Liquids)
CO₂

- Well known "pollutant"
- Carbon source for life on earth through photosynthesis
- Feedstock in many industrial chemistry process
- Many applications in the food industry
- Since 1912 people think on how to use CO₂ as feedstock in industrial chemistry¹
- 70 times less soluble than glucose at 100 g/l

Methane conversion via Biotechnology

- Methane to Polyhydroxyalkanoate (PHA) is already a pre-commercial reality (TRL 6-7)

- Methane to Polylactic acid is currently at R&D stage. The company NatureWorks in US is actively following this route (TRL 3-4)

- Methane to ethanol is already at pre-commercial stage (TRL 7-8 via syngas). From ethanol is easy to go to ethylene and then different options are available for ethylene based plastics

- Very likely in the next years new polymers from biotech use of methane will arise, due to the increased abundance of methane
Multiple options for the conversion of methane via chemistry are already available:

- Through syngas and then methanol, ethylene, propylene and butylene can be produced. Critical is here the number of steps required (more steps implies higher costs).
- Methane to ethylene in a single step with catalysis is very near to market. This route will open the path from biogas to ethylene based plastics (PE, PET, PP, PVC) as will make ethylene from methane cheaper than with today syngas route.
Syngas conversion options

Syngas can be converted:

• to ethanol and 2,3 butanediol via fermentation and then ethanol can be then dehydrated to ethylene and open the path to ethylene based plastics
  butanediol can be converted to butadiene and then to synthetic rubbers

• To methanol via chemistry and then Methanol can be converted to olefins (ethylene, propylene and butylene)
Syngas: a versatile intermediate from multiple sources

Syngas can be produced from:

- Biomass
- Municipal solid waste
- Coal
- Natural gas
- Shale gas
- Recycled paper

Syngas can be then converted to many useful chemicals
CO2 can be converted:

• to polyurethanes, from the company Bayer AG with a process that is already commercial

• to PPC and PEC by Novomer, SK Innovation and other players with processes that is already commercial

• to PHA, by Newlight Technologies with a process that is already commercial

• to all the polymers that are methane or methanol derived, once CO2 is re-upgraded to these two molecules with H2 and renewable energy

• to now polymers that are likely to come as more and more researchers and company are targeting CO2 as feedstock for polymers and plastics
Lanzatech syngas fermentation

Accessible Feedstock Pool

- Pet Coke: ~90M MTA
- Flue Gases
- Municipal Waste: >2B MTA
- Natural Gas: 3300B M³
- Biomass: >1B MTA US Alone
<table>
<thead>
<tr>
<th>Country</th>
<th>Potential Ethanol Production Capacity (MMGPY)</th>
</tr>
</thead>
<tbody>
<tr>
<td>USA</td>
<td>925</td>
</tr>
<tr>
<td>Brazil</td>
<td>955</td>
</tr>
<tr>
<td>W. Europe</td>
<td>4,870</td>
</tr>
<tr>
<td>E. Europe</td>
<td>1,300</td>
</tr>
<tr>
<td>India</td>
<td>1,315</td>
</tr>
<tr>
<td>China</td>
<td>10,800</td>
</tr>
<tr>
<td>Russia</td>
<td>1,830</td>
</tr>
<tr>
<td>Japan</td>
<td>3,750</td>
</tr>
<tr>
<td>South Korea</td>
<td>1,270</td>
</tr>
<tr>
<td>E. Europe</td>
<td>1,300</td>
</tr>
<tr>
<td>Total</td>
<td>27,015 MMGPY</td>
</tr>
</tbody>
</table>
Metabolic Engineering for Fuels/Chemicals

Pyruvate → Fatty Acids, Terpenoids → Isoprene
CO/H₂ → Fatty Acids
Acetyl-CoA → Isobutylene, 1-Butanol, 2-Butanol, Succinate, MEK, 2,3-Butanediol

Genetic Tools in place
- Efficient transformation protocol
- Knock-Out/Integration tools
- Vector and promoter library
- Proprietary non-antibiotic growth associated markers
2,3 BDO: A Route to Platform Chemicals

- LanzaTech is the first company to demonstrate 2,3-butanediol (2,3-BDO) production by gas fermentation
- **Process Control**: Ethanol:BDO ratios of 30:1–4:1 demonstrated
- PNNL has demonstrated conversion of 2,3-BDO to chemicals

![Chemical Structures]

**Preliminary Screening Demonstrates Technical Feasibility**

- 2,3-BDO: 
  - ~11M MPA >$20B
- Butenes: 
  - 1-Butylene: ~19.5M MPA >$21-28B
  - 2-Butylene: ~19.5M MPA >$21-28B
  - Isobutylene: ~19.5M MPA >$21-28B
- Methyl Ethyl Ketone: ~1.5M MPA >$2.3B
Using $\text{CO}_2$ as a Carbon Source

$\text{CO}_2$ uptake and capture demonstrated in a continuous fermentation

- $\text{CO}_2$ is the carbon source, $\text{H}_2$ is the energy source for product synthesis
Power to Gas at Krajete GmbH: The Origin – Motivation CO₂ Conversion

Today’s problems

- human made (= anthropogenic)

--> CO₂ & Energy Supply

New Approach = “Biomimicry”

- “Biomimicry is the examination of nature to take inspiration from it in order to solve human problems”
Bio Building Block of “Power to Gas”

\[
\text{CO}_2 + 4 \text{H}_2 \rightarrow \text{CH}_4 + 2 \text{H}_2\text{O} - 130 \text{kJ/mol}
\]

\[4 \times 3,54 \text{ kWh} \quad 11,06 \text{ kWh} \quad \text{efficiency, 78\% max.}\]

**Catalyst**  
“Archaea”

**Process**  
“Methanogenesis (“Biological Methanation”)

\[\text{CO}_2 / \text{water} \quad \text{light} \quad 1\text{st} \quad 2\text{nd} \quad 3\text{rd} \quad 0.1 \text{ kg/m}^3 \times \text{h} \quad \rightarrow \quad \text{CH}_4\]

+ \text{H}_2 \quad \text{reduction agent !}

“Photosynthetic Bypass”

4th Generation Biofuels  
(> 15 kg/m\(^3\) x h)
Krajete GmbH Setup

I. GASES
- > 95 vol. % CH₄
- H₂
- CO₂

II. LIQUIDS
- A
- B
- C

III. SOLIDS
- “Slurry” (water, biomass)
- biomass
- waste water

1 bioreactor (dominating element)
2, 3, 4 auxiliary feed (“media”, liquid salt solutions)
5, 6, 7 pumps
8 harvest pump
9 vessel
10 separator
11 drying unit (condenser)
12 desulfurization unit (optional)
One Step Synthesis = our Route

DVGW spec. is 95 vol. % methane
Proof through Gas Sampling & Feasibility
– Automobile/Power/Biogas Industry

Example Biogas: 3 bottles with 70 - 100 bars were sampled and transported to Vienna

sampled on Aug. 30, 2013
From Biogas to DVGW conform Gas

CO₂ Biogas

F6_GT_Bgas2
Fermenter 6 02-09-2013 14:36:21
Challenge - Intermittency
How would an ideal Response look?

Ideally, methane (energy storage) follows instantly surplus electricity.
4. Can we make Natural Gas under “intermittent” Conditions in 1 Step for longer Time?

1. Fast response to natural gas & reproducible in 1 step!
2. Transitions - complete shutdown!

2 Days
Almost Ideal
Can we make Natural Gas under “intermittent” Conditions in 1 Step with frequent Changes?

1. Fast response to natural gas & reproducible in 1 step!
2. Transitions - complete shutdown, no energy losses
Is Biology fast?

Conversion = “MER” = “methane evolution rate”

\[ \text{m}^3 \text{CH}_4/\text{m}^3 \text{suspension x hour} \]

Volumetric production: >25 m\(^3\) CH\(_4\)/m\(^3\) susp. x hour
Specific production: >2 m\(^3\) CH\(_4\)/kg biocatalyst x hour

typical biomass concentrations: 5 – 10 g/Liter suspension volume
## Process Attributes in a Nutshell

<table>
<thead>
<tr>
<th>Asset</th>
<th>Parameter</th>
<th>Content</th>
<th>Economic Impact</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Energy input</td>
<td>low, mild conversion at low pressure (1 bar) &amp; low T (65 °C)</td>
<td>save compressor &amp; heating/cooling elements;</td>
</tr>
<tr>
<td>2</td>
<td>Selectivity &amp; impurity tolerance</td>
<td>high, microbes extract nutrients from complex mixtures, example black smoker (proof through real gas applications)</td>
<td>save upstream gas processing operating units (e.g. purifier, desulfurization, PSA, amine scrubber)</td>
</tr>
<tr>
<td>3</td>
<td>Stability , Adaptation &amp; Easy Process Control</td>
<td>high, suited for intermittency, fast response in both directions within 1-2 minutes; adjustment to feedstock, robustness</td>
<td>application feasible, “power to gas” potential, high operability</td>
</tr>
<tr>
<td>4</td>
<td>Conversion</td>
<td>22 m³ methane/m³ bioreactor x hour</td>
<td>lower CAPEX</td>
</tr>
<tr>
<td>5</td>
<td>Catalyst preparation &amp; Image</td>
<td>easy, from waste ingredients; REACH compliant, sustainable</td>
<td>cheap &amp; independent gas conversion</td>
</tr>
</tbody>
</table>

„Bioprocess is a) simple, b) robust, c) dynamic & d) fast!“
Essence in 2 Key Attributes!

“DVGW Methane in 1 Step”

also with Biogas!
Applications: Efficiency & Power Storage

Where is Your interest?

Waste or Renewable H₂

H₂

Bioreactor

CH₄

Zero emission mobility

Where is Your interest?

Combustion, Biogas or Waste CO₂

Example:
1 year / 1 MW electricity via PtG into 500 000 m³ nat. gas, sufficient for 1000 cars with 10 000 km/year
Example: early engineering for car manufacturers

- Study done in cooperation with us
- Inputs from the car manufacturer
- Krajete GmbH delivered 5 detailed reports
- 1 Report based on “Intermittent Power Storage”
- > 250 pages, with 2 concept studies (Pilot & Commercial plant)

- **Report 1** – Dimension of commercial plant
- **Report 2** – influence of different locations on the pilot and commercial plant
- **Report 3** – Intermittent Power Storage
- **Report 4** – Conceptual Engineering Pilot plant
- **Report 5** – Conceptual Engineering Commercial plant
Photofermentation
Coupling to cyanobacterial metabolism:

- **Brown, Pink**: Fuels
- **Blue, Green**: Chemicals
- **Green**: Carbon storage
Engineering with base-pair precision
Photanol (now acquired by Azko-Nobel)
Fourth generation type of process: 

**Cyanobacterial cell factories**

**Definition cell factory:**

\[ \text{CO}_2 \text{ partitioning } > 50 \% \]
Pilot plant: (@ Science Park)
Towards 2-Butanol production

Other products formed from CO₂ with cyanobacteria:

hydrogen, ethanol, ethylene, propanol, acetone, acetoine, meso-butanediol, S,S-butanediol, iso-butyraldehyde, n-butanol, iso-butanol, 2-methyl-1-butanol, L-lactic acid, D-lactic acid, glucose, sucrose, isoprene, long-chain alkanes, long-chain alkenes, long-chain fatty acids, long-chain fatty alcohols, etc., → ...
**Escherichia coli** as a cell factory

- **Glycolysis**
- **PP-pathway**
- **GAP**
- **Pyr**
- **Ac-CoA**
- **TCA cycle**
- **CO₂**
- **N₂**
- **NH₃**
- **Amino acids**
- **C,H,O-based monomers (e.g. succinate)**
- **Alcohols**
- **Alkenes**
- **Fatty acids**
- **‘other’ products**

**PluGbug for sugar**
Synechocystis: The new PluGbug: for CO₂

- **GAP**
- **pyr**
- **Ac-CoA**

**Calvin cycle**

- **CO₂**

**TCA cycle**

- **CO₂**
- **NH₃**
- **N₂**

**other products:** Isoprenoids, terpenes, etc.

**C,H,O-based monomers (e.g. succinate)**

- **alcohols**
- **alkenes**
- **fatty acids**

**Glycolysis**

**PP-pathway**

**sugars**
Beyond the 3D approach:

Assuming:
Efficiency of PV-cells: 50 %
Efficiency of LEDs: 70 %
Efficiency conversion 700 nm photons into fuel of 35 %

→ Overall efficiency = 10 %! => 0.1 MW/acre

In other words: A field full of solar panels on non-fertile soil would drive natural photosynthesis more efficiently than plant photosynthesis itself!
CO\textsubscript{2} photofermentation: also Phytonix

Production cost
\approx \$1.35/\text{gallon}

Wholesale Price
\approx \$6.00/\text{gallon}

High-Value, High-Margin Product
CO$_2$ photofermentation: also Phytonix

For every gallon of n-butanol produced
16.3 pounds (net) of carbon dioxide is consumed

- 151 lt water
- 8,1 kg CO$_2$
- natural sunlight
- 0,8 kg CO$_2$
- 3,78 lt n-Butanol
- 8 kg O$_2$ as by product
- >95% water
- <5% water
**CO$_2$ photofermentation: also Phytonix**

<table>
<thead>
<tr>
<th></th>
<th>Small Size Phytonix Plant</th>
<th>Medium Size Phytonix Plant</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>CAPEX</strong></td>
<td>$14 million</td>
<td>$70 million</td>
</tr>
<tr>
<td><strong>Butanol production</strong></td>
<td>2.5 million gal/yr.</td>
<td>25 million gal/yr.</td>
</tr>
<tr>
<td><strong>CO$_2$ feedstock</strong></td>
<td>20,000 tons/yr.</td>
<td>200,000 tons/yr.</td>
</tr>
<tr>
<td><strong>Revenue: Butanol @ $6.25/gallon</strong></td>
<td>$15 million/year</td>
<td>$155 million/year</td>
</tr>
<tr>
<td><strong>EBITDA</strong></td>
<td>$11 million/year</td>
<td>$115 million/year</td>
</tr>
<tr>
<td><strong>EBITDA Payback on Investment</strong></td>
<td>≈ 1.3 years</td>
<td>&lt; 1 year</td>
</tr>
</tbody>
</table>

**Phytonix plants are scalable and cost-effective at capacities ranging from 500,000 to 500,000,000 gallons/year of n-butanol.**
Methane: ideal carbon source

- Cheap
- Available
- Can be green or black
- Flexible
- No capital intensive for preparation
Methane fermentation

![Methane fermentation reaction](image)

<table>
<thead>
<tr>
<th>Metric</th>
<th>Algae (Open Ponds)</th>
<th>Methane Fermentation</th>
<th>Biomass Fermentation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Capital Investment</td>
<td>Low</td>
<td>High</td>
<td>High</td>
</tr>
<tr>
<td>Ease of scale-up</td>
<td>Requires land use</td>
<td>Good</td>
<td>Good</td>
</tr>
<tr>
<td>Feedstock availability</td>
<td>Mod. (year-round sun)</td>
<td>Good (nat. gas / biogas)</td>
<td>Low (food competition)</td>
</tr>
<tr>
<td>Feedstock sensitivity</td>
<td>Low</td>
<td>Low</td>
<td>High (inhibitors)</td>
</tr>
<tr>
<td>Feedstock processing cost</td>
<td>Low</td>
<td>Low</td>
<td>High (release sugars)</td>
</tr>
<tr>
<td>Downstream processing cost</td>
<td>High (dilute culture)</td>
<td>Low (dense culture)</td>
<td>Low (dense culture)</td>
</tr>
<tr>
<td>Flexibility to strain selection</td>
<td>Low (open system)</td>
<td>High (closed system)</td>
<td>High (closed system)</td>
</tr>
<tr>
<td>Water use</td>
<td>High (evaporation)</td>
<td>Low</td>
<td>Low</td>
</tr>
</tbody>
</table>
Il Biogas può essere fermentato come fonte di C invece che il Glucosio
What does Calysta do?

Methane

Oxygen

Ammonia

Minerals
Salt, calcium, magnesium, etc.

Methanotrophs

CALYSTA Technology

Protein
Carbohydrates
Fatty acids
Vitamins/ImmunoStims
Lactic Acid
Butanediol
Fatty alcohols
Isoprene
N-Butanol
Succinic Acid
and more...

CHEMICALS/ENERGY

NUTRITION
Newlight technologies: biogas to PHA

• PHAs are a family of polymers, all with their own specific characteristics, both, related to their molecular structure and to their thermal, optical and mechanical properties.
• The simplest PHA, called P3HB or sometimes just PHB appears in nature for more than 3 billion years already, but was first isolated and characterized by Lemoigne in 1925
• PHA technology holds great promises, since the potential design space for PHA is very large.
Performance

Airflex™

various grades

- Tensile Strength: No break
- Flexibility: 648%
- Color / Clarity / Odor: Clear Film
- Thermal & Age Stability: Good
- Molecular Weight: Controlled
Pellets per fish farming?

BioProtein, Norway

BioProtein AS

Bioprotein - a healthy protein source

Bioprotein is a new, healthy source of proteins in a world facing a nutrition crisis.

The protein is produced from natural gas which is cheap and available worldwide.

The proteins is competitive to fish meal which is a common animal feed.
DME: diesel like fuel with LPG tank

Courtesy of: http://oberonfuels.com/technology/oberon-process/
DOE awards Microvi grant for innovative biogas conversion technology

October 16, 2016 | Jim Lane

In California, Microvi has been awarded a grant from the US Department of Energy for a new groundbreaking biocatalytic technology that converts methane and carbon dioxide in biogas into valuable liquid chemicals, the company announced today. The new technology, based on Microvi’s MicroNiche Engineering Platform Technology, can convert biogas that is created at facilities like landfills and wastewater treatment plants into important energy chemicals such as biobutanol.
Biogas to Liquids

Table 8. Comparison of the techno-economic analysis of BgTL and other related processes

<table>
<thead>
<tr>
<th>Feedstock</th>
<th>BgTL Model</th>
<th>Bechtel,\textsuperscript{13}</th>
<th>Timmesen \textit{et al.},\textsuperscript{10}</th>
<th>Hamelinck \textit{et al.},\textsuperscript{40}</th>
<th>Larson \textit{et al.},\textsuperscript{20}</th>
<th>Swason \textit{et al.},\textsuperscript{21}</th>
<th>Bao \textit{et al.},\textsuperscript{8}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Biogas</td>
<td>4 ($/GJ)</td>
<td>N/A</td>
<td>33</td>
<td>38</td>
<td>46</td>
<td>75</td>
<td>44\textsuperscript{a}</td>
</tr>
<tr>
<td>Natural Gas</td>
<td>8,391</td>
<td>1,741</td>
<td>400 MW\textsubscript{th}</td>
<td>4,536</td>
<td>2,000</td>
<td>21,800</td>
<td></td>
</tr>
<tr>
<td>Plant size (dry tonne/day)</td>
<td>57</td>
<td>3,912</td>
<td>4,000</td>
<td>4,536</td>
<td>2,000</td>
<td>21,800</td>
<td></td>
</tr>
<tr>
<td>Product</td>
<td>FT liquids</td>
<td>FT liquids</td>
<td>FT liquids</td>
<td>FT diesel</td>
<td>Diesel, gasoline</td>
<td>FT liquids</td>
<td>Synfuels</td>
</tr>
<tr>
<td>Capital investment (million $)</td>
<td>$90.5</td>
<td>$1842.5</td>
<td>$339</td>
<td>$303.5</td>
<td>$541\textsuperscript{b}</td>
<td>$610\textsuperscript{c}</td>
<td>10,800</td>
</tr>
<tr>
<td>Product value ($/GGE)</td>
<td>$5.29</td>
<td>N/A</td>
<td>$2.00</td>
<td>$1.22</td>
<td>$1.85</td>
<td>$4.30</td>
<td>$1.41\textsuperscript{d}</td>
</tr>
<tr>
<td>Product value ($/GGE) 2015</td>
<td>$5.29</td>
<td>N/A</td>
<td>$2.86</td>
<td>$2.73</td>
<td>$2.59</td>
<td>$4.81</td>
<td>$1.44\textsuperscript{d}</td>
</tr>
</tbody>
</table>

Note:
\textsuperscript{a} = calculated based on $3/1000 SCF natural gas price with a density of 0.8 kg/m\textsuperscript{3}  
\textsuperscript{b} = without spare scenario  
\textsuperscript{c} = high temperature scenario  
\textsuperscript{d} = reported in $/bbl which was converted to $/gal

Figure 1. A schematic of a biogas to liquid fuels production technology.
Conclusions

• Is it possible to ferment gases instead of sugar? Yes
• Are gaseous carbon sources cheaper than sugars? Yes
• Are gaseous carbon sources „simpler“ than sugars for their supply chain? Yes
• Is it possible to earn money using gaseous carbon sources or is it an academic curiosity? Yes, it is possible
• Are gaseous carbon sources „easier“ to ferment than sugars? No

• What is needed to enlarge gaseous carbon sources usage in IB? Better mass transfer → Revolutionary reactor design
  Broader products range → higher chance to meet market needs
• Process efficiency simulation for key process parameters in biological methanogenesis  
  doi:10.3934/bioeng.2014.1.53#sthash.AvW4uNDv.dpuf

• Analysis of process related factors to increase volumetric productivity and quality of biomethane with Methanothermobacter marburgensis  
  DOI: 10.1016/j.apenergy.2014.07.002

• Quantitative analysis of media dilution rate effects on Methanothermobacter marburgensis grown in continuous culture on H_2 and CO_2  
  DOI: 10.1016/j.biombioe.2011.10.038

• The changing paradigm in CO2 utilization  
  DOI: 10.1016/j.jcou.2013.08.001

• Commercial Biomass Syngas Fermentation  
  doi:10.3990/en5125372

• Rethinking biological activation of methane and conversion to liquid fuels  
  doi:10.1038/nchembio.1509

• Techno-economic assessment of biogas to liquid fuels conversion technology via Fischer-Tropsch synthesis  
  doi: 10.1002/bbb.1758

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  • http://mangomaterials.com/  
  • http://phytonix.com/