Session on: Direct Conversion of Methane to Higher Value Products Using Biological Systems

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"Nature's first green is gold"

from: Nothing Gold Can Stay, Robert Frost

Started November 23, 2011

Portfolio company of Warburg Pincus

\$355 million, early-stage investment company

Focused on the carbon value-chain

Renewable carbon technology (green) Environmental/cleantech related to fossil carbon (black) Hybrid technologies (green-black)

North American focus

10 seed/early-stage deals, initial investments between \$500,000 and \$10 million

Ability to do large follow-on investments for capital intensive



The opportunity

Some challenges

A quick case study

"The best way to predict the future is to invent it." (Alan Kay, 1971 meeting at PARC, Palo Alto Research Center)

"Those who cannot remember the past are condemned to repeat it." George Santayana, 1924

Relative Cost Advantage of Natural Gas



Natural Gas

"Dry gas" is primarily methane

"Wet gas" contains a significant amount of "natural gas liquids"





Source: Energy Information Administration based on data from various published studies. Updated: March 10, 2010

Stranded, flared methane



Renewable sources of methane?

 $C_6H_{12}O_6 ---> 3 CH_4 + 3 CO_2$

Y = 0.27 pounds of product per pound of feedstock

Yield is low, but good waste feedstocks



Methane as a source of inexpensive energy

Methane as a source of H2 (reducing potential)

Methane as an indirect feedstock (for example, via syn gas)

Methane as a direct biological feedstock

"Those who cannot remember the past are condemned to repeat it."

THE ICI SINGLE CELL PROTEIN PROCESS

P. J. Senior * ICI Agricultural Division, Research & Development Department, P.O. Box 1, Billingham, Cleveland, TS23 1LD

and

J. Windass

ICI Corporate Research Laboratory, The Heath, Runcorn, Cheshire

Biotechnology Letters, May 1980, Volume 2, Issue 5, pp 205-210

From Senior and Windass article

Methane was cheap—North Sea

Limited methane solubility in water (so energy needed for mass transfer)

Yield of biomass from methane was poor

Massive oxygen requirements (more energy for mass transfer)

Massive cooling loads

Large capital costs and needs to protect against explosion

The key initial enzyme, methane mono-oxygenase, consumes reducing equivalents that could otherwise be used for energy and biosynthesis

Theoretical potential

CH₄ + ½ O2 ---> CH₃OH

But in biology, methane conversion is catalyzed by methane monoxygenase (MMO)

 $CH_4 + O_2 + 2[H] ---> CH_3OH + H_2O$

Need an external source of reducing potential

A brief "case study" of a bioproduct from 2 feedstocks



PHB from glucose

$$2 C_6 H_{12} O_6 + 6 [H] ---> 3 C_4 H_6 O_2 + 6 H_2 O_2$$

Get [H] from glucose $C_6H_{12}O_6 + 6H_2O ---> 6CO_2 + 24[H]$

Chemistry 101 balancing of equations: 9 $C_6H_{12}O_6 \longrightarrow 12 C_4H_6O_2 + 6CO_2 + 18 H_2O_2$

Y = 0.64 pound product per pound feedstockFor glucose at \$0.20/lb,\$0.31/lb for PBH (based on feedstock only)

Methane as sole feedstock

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4 CH<sub>4</sub> ---> C<sub>4</sub>H<sub>6</sub>O<sub>2</sub> + 14 [H]
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Need to use excess [H]
O_2 + 4 [H] ---> 2 H_2O
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Chemistry 101 balancing of equations

4 \text{ CH}_4 + 7/2 \text{ O}_2 \longrightarrow \text{ C}_4 \text{H}_6 \text{O}_2 + 5 \text{ H}_2 \text{O}
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Y = 1.34 pounds of product per pound of feedstock! CH₄ at \$4 mmBTU is approximately 0.10/pound, so

\$0.075/pound PHB (based on feedstock only) (recall was \$0.31/pound for glucose) A quick look at lactic acid

From glucose $C_6H_{12}O_6 \longrightarrow 2 C_3H_6O_3$

Y = 1.0 pounds of produce per pound feedstock

From methane 3 CH_4 + 3 H_2O ---> $C_3H_6O_3$ + 12 [H]

3 O₂ + 12 [H] ---> 6 H₂O

3 CH₄ + 3 O₂ ---> C₃H₆O₃ + 3H₂O

Y = 1.875 pounds of product per pound of feedstock! \$0.053/pound based on feedstock!



Thank you

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Glucose, with methane as a source of [H]

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2 C_6 H_{12} O_6 + 6 [H] ---> 3 C_4 H_6 O_2 + 6 H_2 O_2
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Methane as source of [H] $CH_4 + 2 H_2O ---> CO_2 + 8 [H]$

Chemistry 101 balancing of equations: 2 $C_6H_{12}O_6 + 0.75 CH_4 ---> 3 C_4H_6O_2 + 0.75 CO_2 + 4.5 H_2O$

Y = 0.72 pounds of product per pound of glucose feedstock

So need less sugar, at the expense of methane.