“Will alternative absorbent polymers ever be *Super* for use in hygiene?’

Ian Davenport

ian@davenport.com
www.davenportinternational.com
917-605-1174

PURPOSE

Overview of history, current status and future outlook for alternative (Super) absorbent polymers

AGENDA

- A confusing maze of definitions – designed to obfuscate?
- Some common misconceptions
- What is on offer?
- The impact of lower oil
- Will alternative polymers ever be competitive in hygiene applications?

Terminology

Renewable
Green
Biodegradability
Biocompatible
Super absorbent polymer

Biodegradable (Mirriam Webster)

adjective **bio·de·grad·able \-di-ˈgrā-də-bəl**
: capable of being slowly destroyed and broken down into very small parts by natural processes, bacteria, etc.

Simply: can be reduced to carbon dioxide, methane, & water

Renewable

adjective **re·new·able \-ˈnü-ə-bəl, -ˈnyü-**
: able to be extended for another time period
: able to be renewed
: restored or replaced by natural processes : able to be replaced by nature

Simply: made from a source that can be renewed in nature (plant etc.)

Candidates for review?

- Starch blends
- ‘Natural polymers’
- Sodium polyacrylate from renewable AA
- Other chemistries

Starch Blends:

LYSAC (ADM) – carboxyalkyl cellulose polymer and starch polymer blended in water

ADM/ LYSAC

- Canadian Groupe Lysac acquired 2006
- SNAP = Safe Natural Absorbent Polymer
- Patents covering “starch networks as superabsorbent materials and their preparation by extrusion”
- & “superabsorbent surface-treated carboxyalkylated polysaccharides and process for producing same”

- No recent data sheets available – last from 2009

LYSORB™
natural hypoallergenic absorbent

Lysorb® 220 for Hygiene Applications

- **Usage:** as additive with SAP in Baby Diapers and Adult Incontinence
- **Chemical basis:** cereal-based polysaccharides
- **Physical form:** non-abrasive, fine and odorless off-white powder
- **Storage:** more than 1 year under normal conditions without caking
- **Packaging:** 22.7 Kg bags or 850 Kg superbags

1. Particle size distribution (%)	**Typical results**	**Test method***
• Retain on 20 mesh (850 µm)	1.0 max	WSP 220.2-05A
• Retain on 30 mesh (600 µm)	30.0 max	
• Retain on 60 mesh (250 µm)	40.0 min	
• Retain on 100 mesh (150 µm)	45.0 max	
• Through 100 mesh (150 µm)	10.0 max	
2. Moisture content (%)	13.0 max	WSP 230.2-05A
3. Apparent bulk density (g/cm^3)	0.52 – 0.70	WSP 260.2-05WD
4. pH of hydrated solution	5.5 – 7.5	WSP 200.2-05A
5. Free swell absorption capacity (g/g)		
• 0.9 % NaCl aq	24.0 min	WSP 240.2-05A
• Tap water	49.0	
• Demineralized water	55.0	
6. Centrifuge retention capacity (g/g)		
• 0.9 % NaCl aq	17.0 min	WSP 241.2-05A
• Tap water	43.0	
• Demineralized water	44.0	
7. Absorption under load (g/g, 0.7PSI in 0.9 % NaCl aq)	6.4	WSP 220.2-05A
8. Residual monomer (ppm)	Not applicable	
9. Color	Off-white	

* WSP: World Strategic Partners (INDA & EDANA) - *Standard Test Methods for the Nonwovens Industry*, 2005
Ref.: http://www.inda.org/pubs/tests/WSPTableofContents.pdf

Results issued by	Nicole Lachapelle, R&D	February 25, 2009
Approved by	George Koutlakis, Product Development and Technical Services	February 25, 2009
Updated by	Daniela Kozubska, Sales	February 25, 2009

Archer Daniels Midland Co. • 995 Mill Street • Montreal • Quebec • Canada • H3C 1Y5 • Tel+1-514-937-9937

“Natural” polymers

- ADM/ Chemanex JV SL
- Tethis
- Vitallico
- Other

Chemcel Pvt Ltd. Sri Lanka

ADM/ Chemanex JV to produce BioSAP ™ for sale by ADM
Announced August 2013

Plant reported to be ready for operation

No products offered to the market as yet

TETHIS

Goal:

To create a bio-polymer based SAP that is adopted by the diaper industry

TETHIS

Initial Performance target:

CRC > 28 g/g

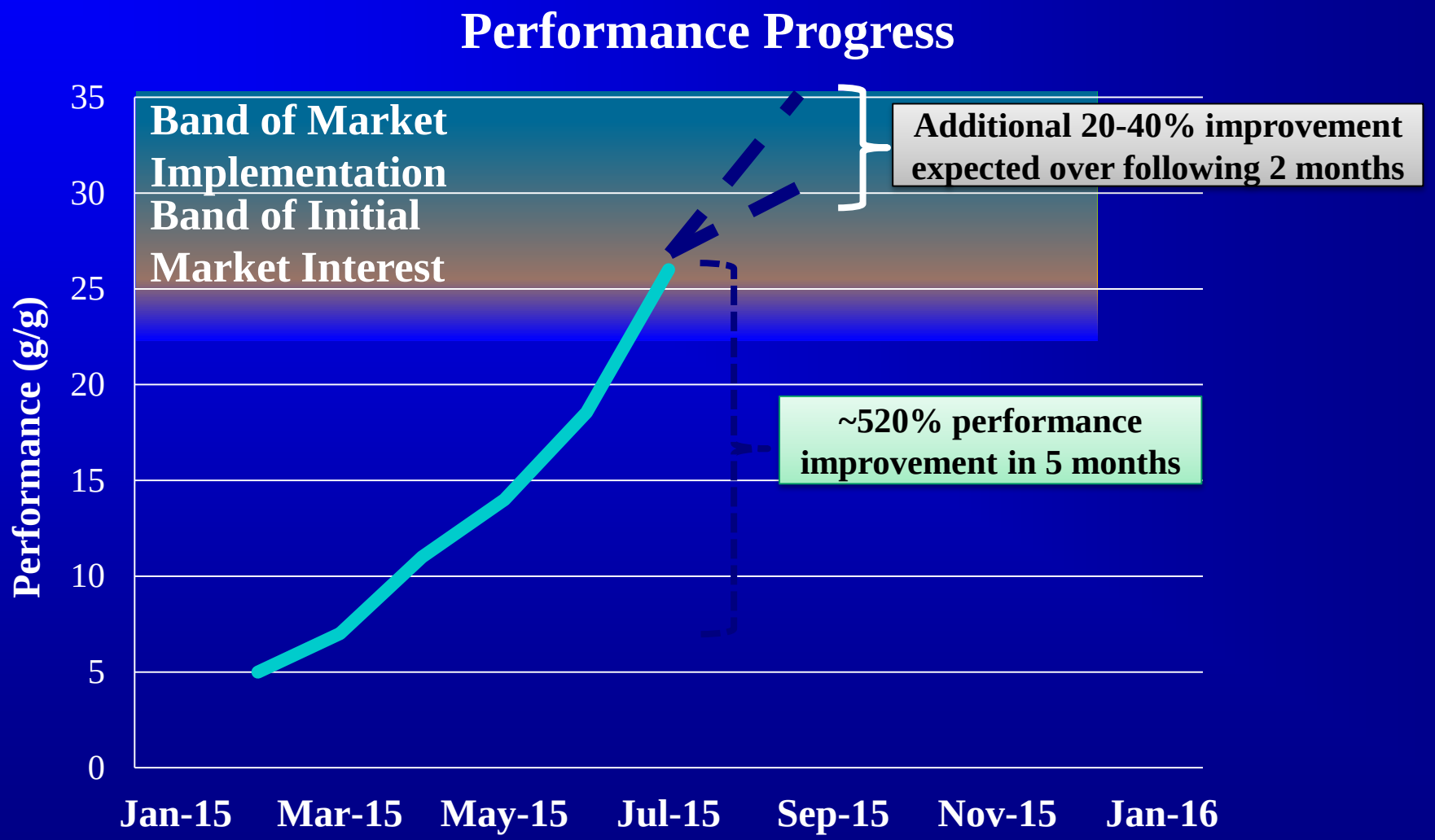
AUL (0.7 psi) > 15 g/g

Current values?

Long term target:

to achieve performance competitive with conventional SAP

Performance Momentum: CRC



TETHIS

	Initial Target g/g	Actual 31st Aug. 2015 g/g*
CRC	28	31.0
AUL 0.7 psi	15	13.6

*Tethis results

TETHIS

Moving fast, but a long way to go…still at small scale…

Will use toll manufacturing to scale up and prove the process

Extrusion process = possible fast scale up with known manufacturing technologies

TETHIS

Other benefits:

- Renewable raw materials
- Fast absorption
- High Ionic tolerance
- Biodegradable
- Novel forms possible (fiber, foam, films?)

VITALLICO

WO 2011/ 038374 Xiong et.al.
“Absorbent Composition & Methods Thereof”

Natural Hydrocolloids treated with porous Aluminum Silicate

VITALLICO

Approached Davenport 2 years ago, has since disappeared

OTHER CHEMISTRIES?

Variety of polymers promoted for Agriculture applications e.g.

Potassium Polyacrylate
PAM polymers
MCMC/HEC based polymers

What about Sodium Polyacrylate SAP from ‘renewable’ AA?

- Impurities may differ according to feedstock used
- Several projects

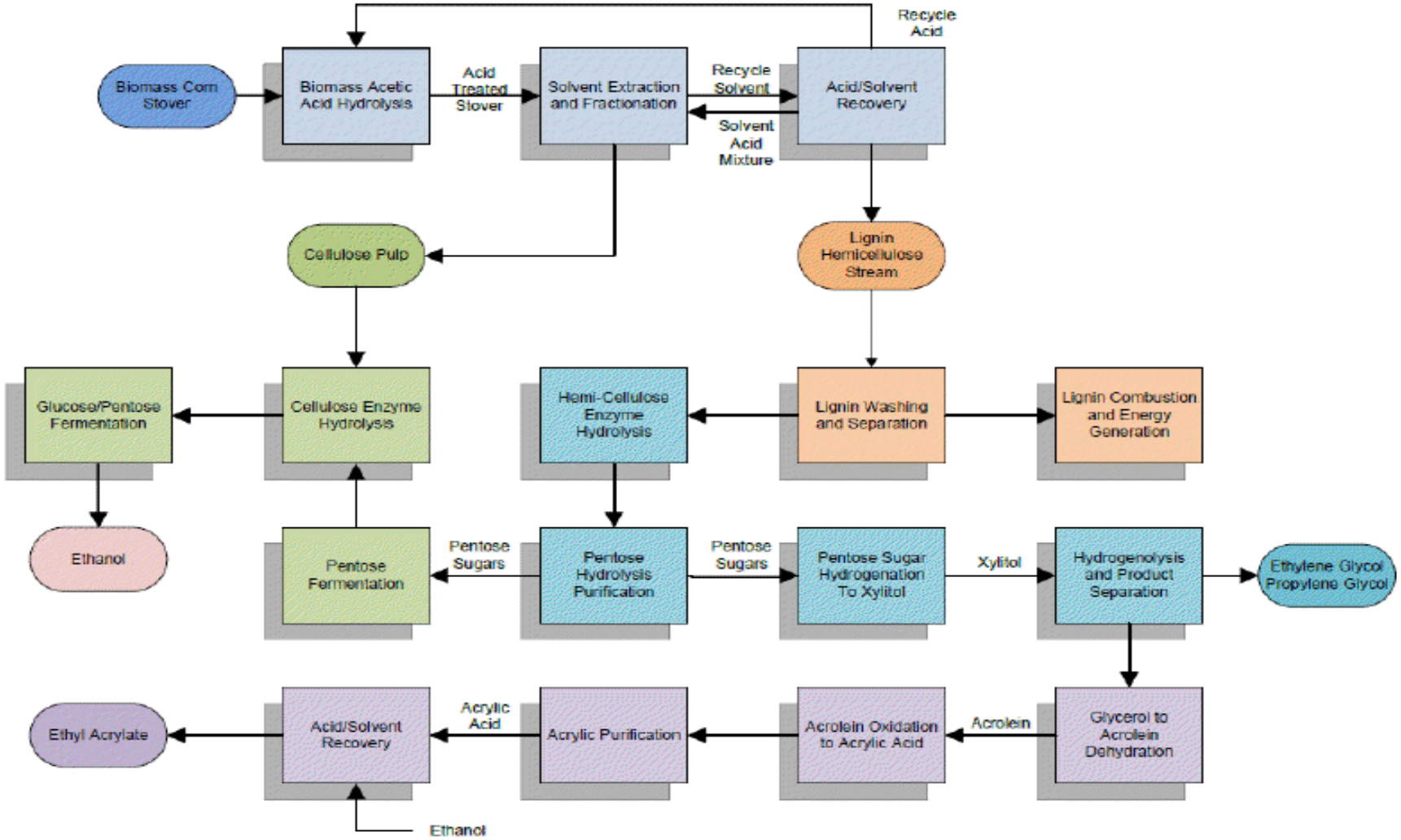
Sodium Polyacrylate from ‘renewable’ AA

- ADM
- Arkema
- Nippon Shokubai
- Cargill/ Novozyme
- Myriant
- Novomer

ADM : Direct Replacement of Chemicals

- **Successful Propylene Glycol Project running in Decatur since 2011**
- **Acrylic Acid - DOE grant $25 MM plus ADM investment**
- **Proprietary technology to separate cellulose, hemi-cellulose & lignin into individual components then utilized for fuel & chemical production**
- **ADM target is to produce cellulosic ethanol & acrylic acid/ esters**

Project Approach - Process



Source: DOE Feb 2011, Biomass Program Peer Review

ARKEMA

1) Glycerol to acrylic acid reported 2009 collaboration

2) Arkema & HTE (High throughput experimentation) Germany to screen catalysts

NIPPON SHOKUBAI

IHS PERP – Process Economics Report 2011 – also cites Nippon Shokubai work

Nippon Shokubai had project for AA in Indonesia based on Palm Oil

CARGILL

Aug. 2012:Cargill partnered with BASF/ Novozyme

July 2013: 3-hydroxypropionic acid (3-HP), one possible precursor to acrylic acid, made at pilot scale.

Sep 2014: successfully converted 3-HP to GAA and SAP

CARGILL

Jan 2015: BASF to exit 3-way partnership

Why?

We can speculate…

CARGILL

April 2015: acquires OPX Bio….

OPX BIO

Startup based Boulder, CO

OPXBIO ‘provides more sustainable value to customers by applying its proprietary EDGE ™ (Efficiency Directed Genome Engineering) technology to produce economic, bio-based chemicals that directly replace existing petroleum-based products’

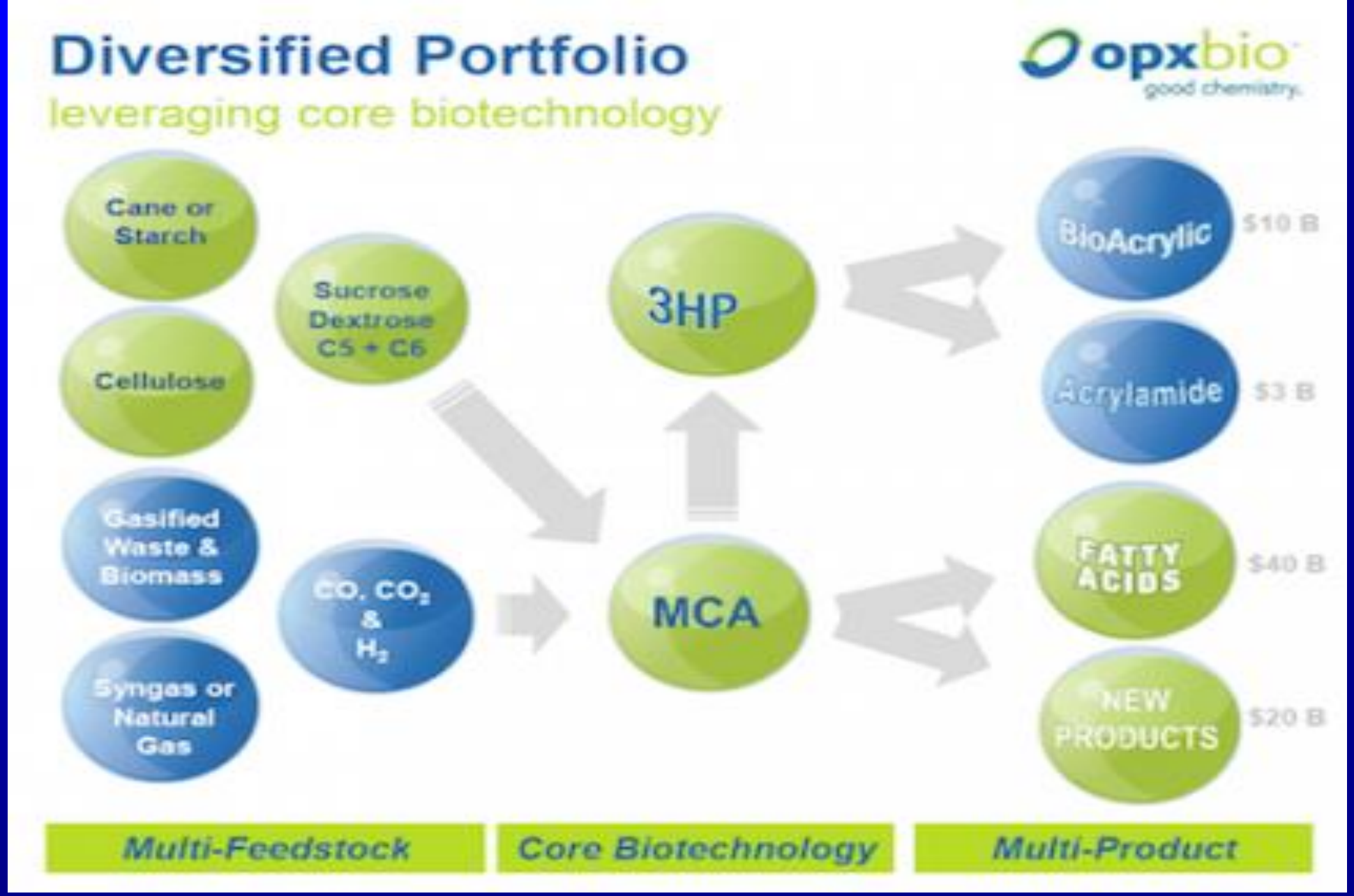
OPX BIO

April 2011: collaborate with Dow to ‘develop industrial scale process for the production of bio-based acrylic acid from renewable feedstocks.’

April 2013: collaborate with Evonik to ‘develop certain bio-based specialty chemicals.’

Sep 2014: cooperation with Dow ended

April 2015: acquired by Cargill



Source: Biofuels Digest April 2015

CARGILL

April 2015: acquires OPX Bio…

Why?

- **to give Cargill an option on a platform of chemical production technology & compete with ADM?**
- **Because BASF don't want to use renewable feedstock?**

What about other routes to ‘renewable’ AA?

- **Myriant**
- **Novomer**

Myriant

Chemicals from dextrose with Succinic Acid plant in Lake Providence, LA

Lactic acid to Acrylic acid route is progressing quickly in the product pipeline

Collaboration with Penn State University & MIT

Myriant – tech. claims 06/2015

At lab. scale achieved:

- **90% conversion of lactic acid**
- **> 80% selectivity for Acrylic acid**
- **1 easily separated and marketable by product**
- **Other by products at ppm level**
- **Stable catalyst performance**

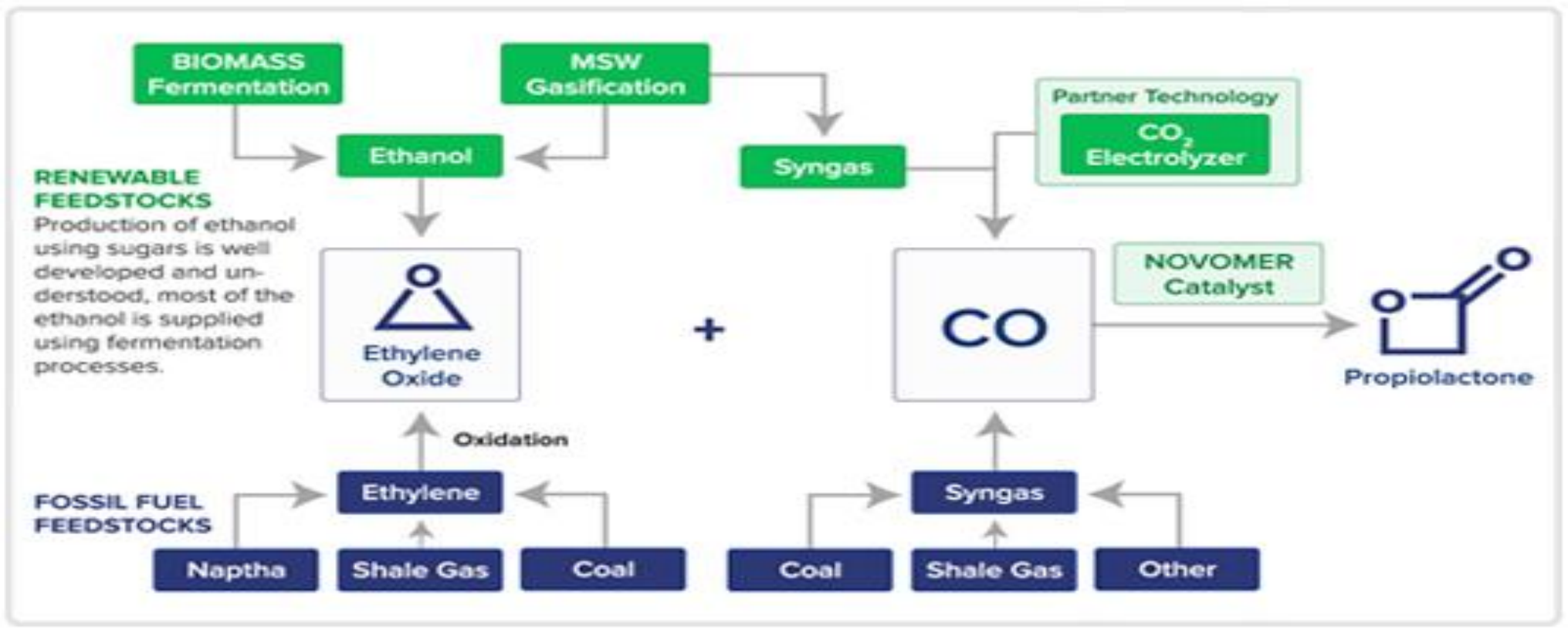
Myriant – status as of 06/2015

- **Funded to end 2015**
- **Well supported by PTTGC (Thailand)**
- **In discussions with potential partners based in EU & Asia**

Myriant – next steps

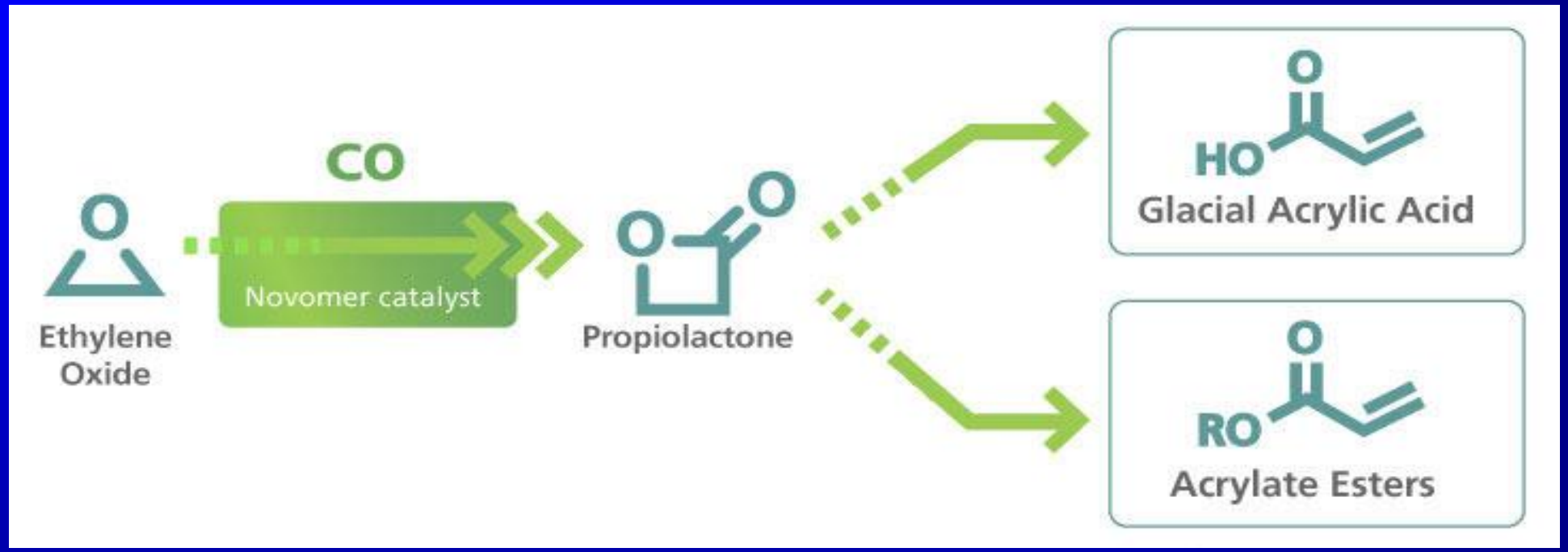
- Scale up reactor with technical support by PTTCG
- Produce samples for customer testing (1 & 2 levels of customer need to approve)
- Confirm catalyst life
- Find partner(s) for full scale manufacturing and/ or license agreements

Novomer AA via Propiolactone



Source: www.novomer.com

Novomer AA via Propiolactone



Claims:

- **Low capital processes**
- **Easy to ship Propiolactone**

Source: www.novomer.com

Novomer Latest:

The three co-founders of Novomer, a startup company based on Cornell research, have received the 2016 Kathryn C. Hach Award for Entrepreneurial Success from the American Chemical Society (ACS), the society has announced.

Sodium Polyacrylate from ‘renewable’ AA

a) Provided GAA is ‘drop in’ then SAP should meet all performance criteria

b) It will not be biodegradable SAP

c) What new impurities may be present?

Other chemistries

Exotech Bio Solutions

"Exotech manufactures biocompatible and biodegradable superabsorbent polymers (SAP) for use in the personal hygiene, pharmaceuticals, food, environmental and agriculture markets. ExoSAP has the same absorbent properties as the competition, yet has the advantage of being bio degradable as well as being cheaper to produce."

Zvika Meiri, CEO, Society of Plastics Engineers, Clean Technology Business Forum & Competition: GPEC® 2009

Exotech Bio Solutions

Variations on poly(styrene-co-maleic anhydride/acid) with patents 1970 – 2011 (not all related to SAP)

e.g. Biocompatible, Biodegradable, water-absorbent material and methods for its preparation
US 20020193516 (Dec.2002 Bucevski & Colt)

Exotech Bio Solutions

Independent test 2007

CRC	**34 g/g**
AUL 0.7 psi	**22 g/g**
PSD	**somewhat large (60% > 900 µ)**

University COIMBRA (Portugal) Biodegradation test OECD 310 positive results

So why no progress?

Exotech Bio Solutions

Chicken & Egg:

No investment = no larger scale production

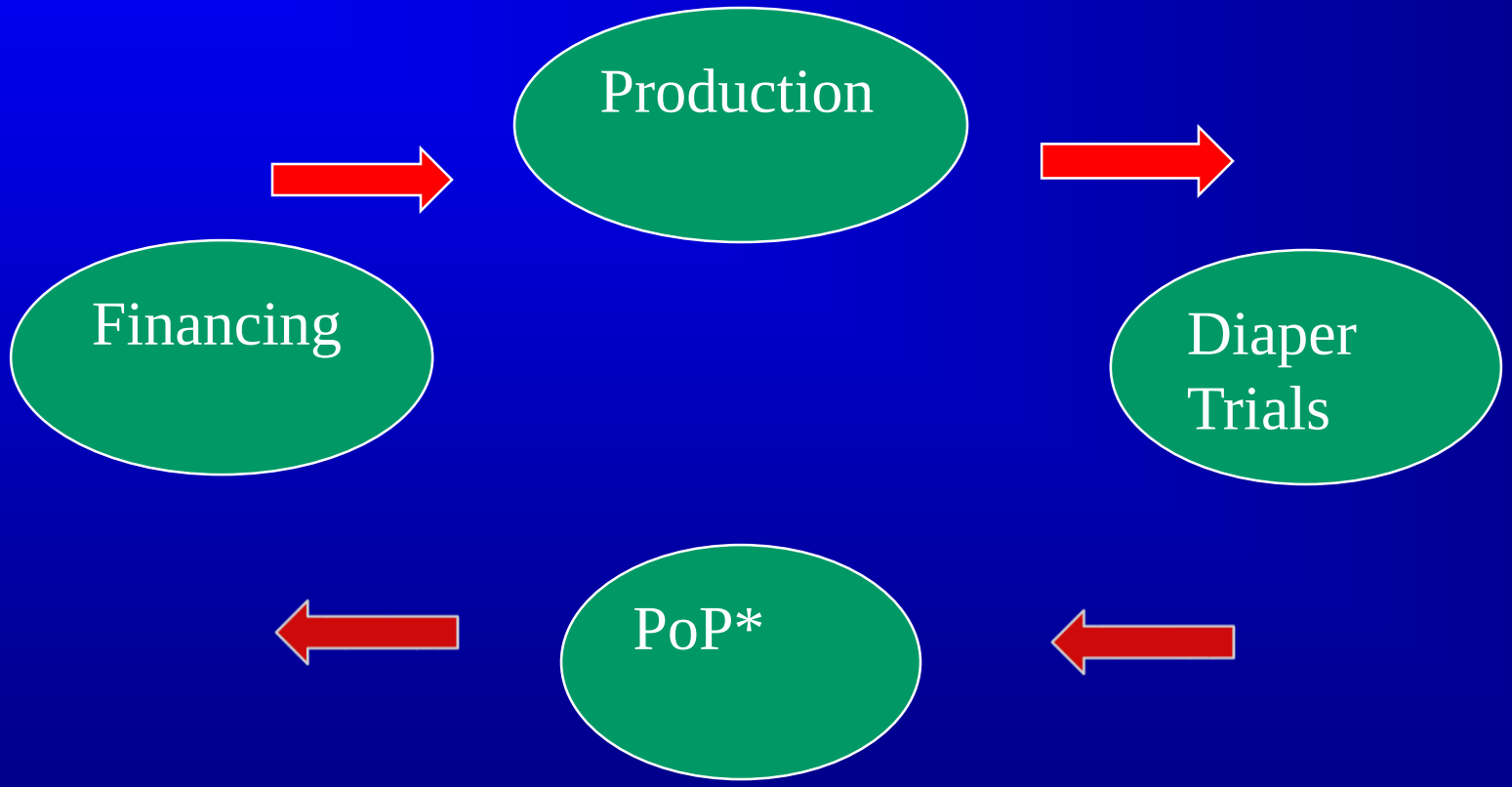
No production = no large quantities for diaper trials

No diaper trials = no proof of performance

No proof of performance = no investment

Exotech Bio Solutions

Chicken & Egg:



* Proof of Performance

Exotech Bio Solutions

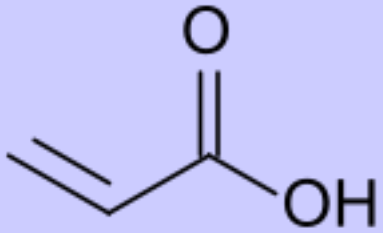
- 10-15 years of search for partners to invest and commercialize
- Too soon?

- Focus now appears to be on Gelesis with $60 MM IPO filed April 1st 2015
  - ‘weight loss capsule for patients with obesity & type 2 diabetes’

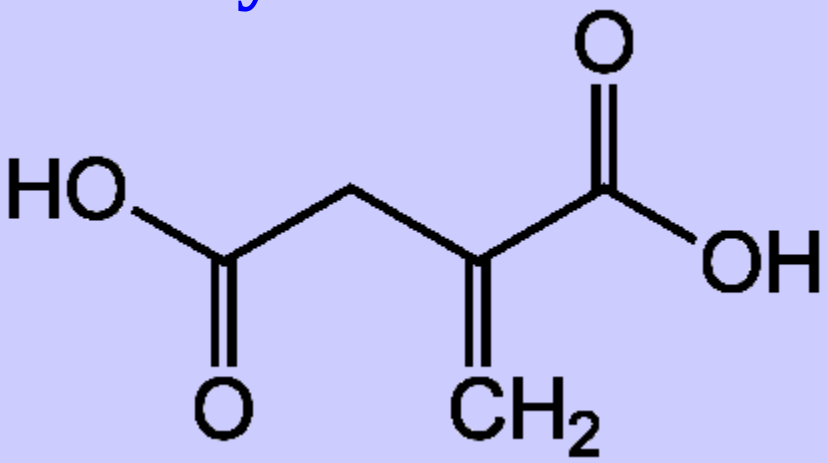
Are there other possible chemistries for SAP with similar carboxyl functionality?

- Aspartic acid
- Itaconic acid
- Glutamic acid

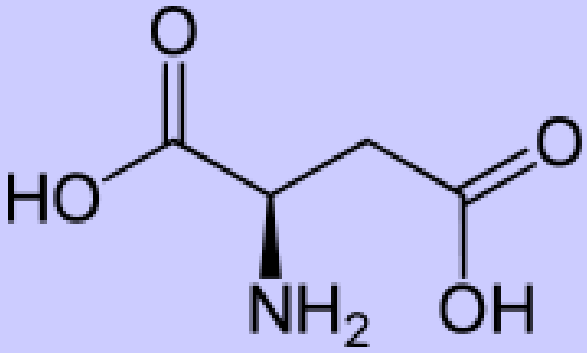
Other chemistries
Similar carboxyl functionality



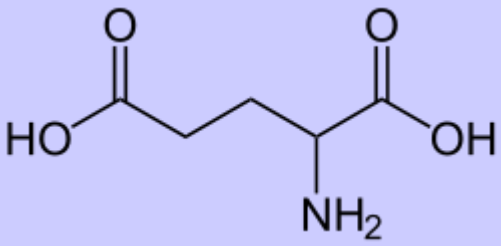
Acrylic Acid 1:1



Itaconic acid 1:2



Aspartic acid 1:1



Glutamic Acid

Polyaspartic acid

Donlar Biopolymers – early 2000's
CRC – high teens
AUL – low teens
Off color (yellow/ brown…)

Polyaspartic acid – other references

- **EP 0 866 084 A2 Production process of cross-linked polyaspartic acid resin (1998, Irizato et.al. Mitsui)**

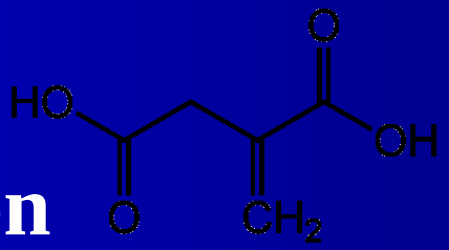
A process is disclosed for producing with good productivity a cross-linked polyaspartic acid resin having biodegradability and high water absorbency

- **Novel Superabsorbent Composite Based on Poly(Aspartic Acid) and Organo-Kaolin - Journal of Macromolecular Science, Part A: Pure and Applied Chemistry Volume 51 , Issue 10 , 2014**

Itaconic acid

Itaconix – New Hampshire based start up

Itaconix



Need to use dual carboxyl function

5 new products close to launch markets oil & gas, emulsions, detergents, others

Sodium polyacrylate works very well for SAP

Hygiene customers will not, in our view, pay extra for renewable or biodegradable

REMINDER:

Natural or Renewable does not equal ‘Biodegradable’

Sodium polyacrylate SAP will have the same profile physically and chemically whatever the feedstock used for the acrylic acid

What is Biodegradable?

OECD Test Guidelines No. 301 A-F:

DOC Die-Away Test (TG 301 A),
CO2 Evolution Test (TG 301 B),
Modified MITI Test (I) (TG 301 C),
Closed Bottle Test (TG 301 D),
Modified OECD Screening Test (TG 301 E)
Manometric Respirometry Test (TG 301 F)

What is Biodegradable?

OECD Test Guidelines No. 301 A-F:

The following pass levels of biodegradation, obtained within 28 days, may be regarded as evidence of ready biodegradability: 70% DOC (*dissolved organic carbon*) removal (TG 301 A and TG 301 E); 60% theoretical carbon dioxide (ThCO2) (TG 301 B); 60% theoretical oxygen demand (ThOD) (TG 301 C, TG 301 D and TG 301 F).

Does modified Sodium Polyacrylate meet this standard?

NO

Higher starch = improved degradation = lower SAP performance

Also, starch modified SAP tends to discolor

So What about ‘Low Oil’? (1)

- **Equivalence is constantly changing**
- **Corn $6 v. Oil $100 was attractive for some (*but both volatile*…)**
- **Long term pressure on global food chain**
- **Forecast excess of propylene will depress SAP price (July 2015 already < 40 cpp in US)**

So What about ‘Low Oil’? (2)

Low Propylene is an added challenge for Biobased Acrylic Acid

FT Commodities Global Summit 04/21/2015

China's taste for meat forces state grain trader to go global in search of feed

GREGORY MEYER — LAUSANNE

The head of Cofco, the Chinese state-owned grain trader, has laid out plans to turn the company into a publicly listed global powerhouse, highlighting Beijing's decision to relax its policy of food self-sufficiency.

Ning Gaoning, Cofco chairman, told a Financial Times conference in Lausanne that ***China's farm imports would rise from 120m tonnes to 200m** tonnes in a decade as people consumed more meat and milk***. "This is a transformation period in China," he said.

The diets of the country of 1.4bn have changed as living standards rose with industrialisation. More meat and dairy on tables has strained arable land and water resources, pushing China abroad in search of grain to feed livestock.

**** 1 MT meat requires 2-6 MT grain!**

Conclusions

- **No imminent threat to conventional Propylene based SAP**
- **Agricultural commodity giants are moving downstream into chemicals**
- **‘Renewable’ feedstock will face cost pressure if it competes with human food chain**
- **One or two startups may present credible future alternatives with cost base other than Propylene – YES, they might be eventually competitive BUT the installed SAP capacity base is a huge barrier to new entrants**

Acknowledgments:

Absorbent Technologies, Inc.
Archer Daniels Midland Company*
EDANA
Ekotec GmbH
Hy-Tec GmbH
Exotech Bio Solutions Ltd.
Itaconix Corp.
Myriant Corp.
Nanochem Solutions Inc.*
Novomer Inc.
OPX Bio
Tethis Inc.
Vitalico LLC.*
Yixing Danson Science & Technology Co., Ltd.

*** Unavailable or unwilling to contribute**

Thank you

Ian Davenport

ian@davenport.com
www.davenportinternational.com
917-605-1174

DAVENPORT INTERNATIONAL ASSOCIATES, LLC