Levulinic acid and derivatives: sustainable solutions for today and tomorrow

R. Parton
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› Levulinic acid and approach to bring it in the market

› GF B approach and products
Technology: The Reaction

A miracle

easy in lab not so easy in plant
DR OP IN OR NEW BIOBASED BUILDING BLOCKS?
NEW BUILDING BLOCKS: LEVULINIC ACID

DR OP-IN:

COMPETE ON PRICE

NEW BB:

IMPROVED PERFORMANCE
Levulinic acid: essential building block for a Green Future
LEVULINIC ACID

NEW VALUE OR DROP-IN?
Which chemicals from biomass:

Drop in: plant trees

New biochemicals: built a new value chain = plant seeds
Financial risk mitigation:

- Clarity on
  - market size
  - price elasticity

Saving & using existing assets base

Economy of scale (introduction) considerations
But !!
Drop-in competes on price

**Pro's**
- Known markets and properties
- Market development forecasts
- Downstream production established

**Con's**
- Competing price
- Bio-label main differentiator
New building blocks compete on functionality

Con’s
› Properties not know
› Application development needed
› Higher initial investment and risk

Pro’s
› Competition on functionality
› Bio-label added feature
› New business opportunities
› Later phase at large scale compete on price
levulinic acid: will it be a sequel of the future???
Focused and dedicated to market levulinic acid since 2008

2008
FOUNDATION
Mission: Bringing levulinic acid to the market by technology innovation

2009
FACILITY
Lease Caserta plant to develop and demo breakthrough technologies

2013
NEW FUNDS
New investor and rebranding Green Future to GF Biochemicals

2014
ORGANISATION
Key personnel from global leaders reinforce GF Biochemicals to further develop the technologies

2015
LEVULINIC ACID DEMO PLANT
Novel technologies implemented
Capacity 1,200 MT

2016
GFBIOCHEMICALS AMERICAS
Acquisition of Segetis assets, IP and trademarks

2017
COMMERCIALISATION ON LEVULINIC ACID & DERIVATIVES
Toll Manufacturing

2018-2022
LARGE SCALE PRODUCTION FACILITY

Growth strategy: by acquisitions of derivative technologies and partnerships with major companies
Problem for all biomass based products:

CAPEX hurdle

&

Growth rate vs choice of size
How to bring a new building block to the market?

- Market development via toll manufacturing
- Afterwards Investments in **CAPEX:**
Levulinic acid

Bio-based Building Block

GF: Ketal platform
GL platform
Applications: Levulinate ester-ketal platform

LEVULINIC ACID ➔ LEVULINATE ESTERS ➔ LEVULINIC KETALS ➔ POLYOLS & PLASTICIZERS

Solvents
Hansen plot
Asustainable multifunctional 1st order derivative of LA with large potential and broad application across a range of market segments
Levulinic acid, esters and ketals for personal care

› Levulinic acid:
  › Offers perfuming, skin conditioning and pH regulation

› Levulinic esters
  › Appreciated as fragrance ingredients

› Levulinic ketals:
  › Dissolve a wide range of actives
  › Bring difficult ingredients into formulations
  › Enable high water loading for moisturizing formulations
  › Broad compatibility
  › Light, dry emolliency
  › Biodegradable
# High solvency and dispersing power

<table>
<thead>
<tr>
<th>Solubility of Active Ingredients (in wt%) by Application Area</th>
<th>FC1100</th>
<th>FC1200</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Suncare</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sunscreen</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Avobenzone</td>
<td>20%</td>
<td>30%</td>
</tr>
<tr>
<td>Oxybenzone</td>
<td>20%</td>
<td>30%</td>
</tr>
<tr>
<td><strong>Skincare</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bioavailability Enhancer</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tetrahydropiperine</td>
<td>20%</td>
<td>20%</td>
</tr>
<tr>
<td>Benzoyl Peroxide</td>
<td>5%</td>
<td></td>
</tr>
<tr>
<td>Salicylic Acid</td>
<td>15%</td>
<td>11%</td>
</tr>
<tr>
<td>Resveratrol</td>
<td>1%</td>
<td>0.50%</td>
</tr>
<tr>
<td>Retinoic Acid (all-trans)</td>
<td></td>
<td>0.50%</td>
</tr>
<tr>
<td>Ubiquinone (Co-enzyme Q10)</td>
<td></td>
<td>20%</td>
</tr>
<tr>
<td>Dimethylmethoxy Chromanol</td>
<td>2.50%</td>
<td>2.50%</td>
</tr>
<tr>
<td>Skin Whitening</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tetrahydrodiferuloylmethane</td>
<td>20%</td>
<td>5%</td>
</tr>
</tbody>
</table>

- Brings difficult ingredients into formulation, enabling higher concentrations of actives.
- Dissolves a wide range of actives.
## Broad solubility gives formulation flexibility: oils

<table>
<thead>
<tr>
<th>Oil</th>
<th>Soluble with what % FC1100?</th>
<th>Soluble with what % FC1200?</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stearyl alcohol</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>Stearic acid</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>Castor oil</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>Beeswax</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>C12-15 alkyl benzoate</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>Stearine myristate</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>Isopropyl palmitate</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>Caprylic/capric triglycride</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>Mineral oil</td>
<td>--</td>
<td>50</td>
</tr>
<tr>
<td>Octyl methoxycinnamate</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>Cyclomethicone</td>
<td>--</td>
<td>50</td>
</tr>
<tr>
<td>Avocado oil</td>
<td>10</td>
<td>50</td>
</tr>
<tr>
<td>Sunflower oil</td>
<td>10</td>
<td>50</td>
</tr>
<tr>
<td>Almond oil</td>
<td>10</td>
<td>50</td>
</tr>
<tr>
<td>Squalene</td>
<td>--</td>
<td>50</td>
</tr>
<tr>
<td>Isododecane</td>
<td>--</td>
<td>50</td>
</tr>
<tr>
<td>Caprylyl methicone</td>
<td>--</td>
<td>50</td>
</tr>
</tbody>
</table>
Broad solubility gives formulation flexibility: water, solvent & alcohol

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Soluble with FC1100</th>
<th>Soluble with FC1200</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethanol</td>
<td>Infinite</td>
<td>Infinite</td>
</tr>
<tr>
<td>Isopropanol</td>
<td>Infinite</td>
<td>Infinite</td>
</tr>
<tr>
<td>Water</td>
<td>Infinite</td>
<td>3-5%</td>
</tr>
<tr>
<td>Hydroalcohol</td>
<td>Infinite</td>
<td>Infinite</td>
</tr>
</tbody>
</table>
Bring difficult ingredients into formulations: polymers

- Dissolve crystalline actives & polymers
  - High solubility limit
  - Broad substitution range

- Increased active loading
- Simplified formulation
- Simplified raw material inventory

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Wt. % in FC1100</th>
<th>Wt. % in FC1200</th>
</tr>
</thead>
<tbody>
<tr>
<td>nitrocellulose</td>
<td>Y</td>
<td>Y</td>
</tr>
<tr>
<td>cellulose acetate butyrate</td>
<td>14</td>
<td>≥25</td>
</tr>
<tr>
<td>acrylate/octylacrylamide copolymer</td>
<td>~5</td>
<td>~1</td>
</tr>
<tr>
<td>PMMA</td>
<td>1</td>
<td>&gt;10</td>
</tr>
</tbody>
</table>
Versatile match-makers

- Expand solubility range of ethanol
- Expand solubility range of water
- Bring water into anhydrous systems
Actives more tolerant to water with FC1100 than with ethanol
<table>
<thead>
<tr>
<th>Opportunities to use our Segetis product line</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Simplified formulation and inventory</strong></td>
</tr>
<tr>
<td>› Single formulation ingredient to replace many specialized ingredients</td>
</tr>
<tr>
<td><strong>Improved performance</strong></td>
</tr>
<tr>
<td>› Troubleshooting ingredient that allows formulators to expand the range of actives &amp; increase actives concentration</td>
</tr>
<tr>
<td><strong>Easy to use</strong></td>
</tr>
<tr>
<td>› Robust formulation latitude</td>
</tr>
<tr>
<td>› Compatible with many starting formulations</td>
</tr>
<tr>
<td><strong>Innovative ingredient combinations</strong></td>
</tr>
<tr>
<td>› Incorporates water into anhydrous systems</td>
</tr>
<tr>
<td>› Expands solubility of ethanol, w/ clarity</td>
</tr>
<tr>
<td><strong>Improved skin feel in natural formulations</strong></td>
</tr>
<tr>
<td>› Compliment to natural formulations to reduce greasiness</td>
</tr>
<tr>
<td>› Dry, silky after-feel</td>
</tr>
</tbody>
</table>
Levulinic Ketals in household and industrial cleaners

› Superior grease-cutting and soil removal
› High Stability in multi-component systems
› Low skin irritation & sensitization
› Good substantivity and skin feel
D-limonene replacement by Levulinic Ketals

› Powerful at neutral pH, easy handling
› Safe and Non-sensitizing
› No flash or VOC
› Renewable and bio-degradable
Levulinic ketals outperforms bio-based alternatives

<table>
<thead>
<tr>
<th></th>
<th>Glycerol ether</th>
<th>DBE</th>
<th>Dlimonene</th>
<th>Soy methyl esters</th>
<th>SV218</th>
</tr>
</thead>
<tbody>
<tr>
<td>Paraloid B-72 (acrylic)</td>
<td>1</td>
<td>1</td>
<td>4</td>
<td>5</td>
<td>1</td>
</tr>
<tr>
<td>Paraloid B-82 (acrylic)</td>
<td>1</td>
<td>1</td>
<td>3</td>
<td>6</td>
<td>1</td>
</tr>
<tr>
<td>Desmocoll 176 (TPU)</td>
<td>1</td>
<td>2</td>
<td>5</td>
<td>4</td>
<td>2</td>
</tr>
<tr>
<td>CAP-482-0.5 (cellulose acetate)</td>
<td>1</td>
<td>1</td>
<td>6</td>
<td>6</td>
<td>1</td>
</tr>
<tr>
<td>DER-661 (epoxy)</td>
<td>1</td>
<td>1</td>
<td>5</td>
<td>5</td>
<td>1</td>
</tr>
<tr>
<td>EPON 1001F (epoxy)</td>
<td>1</td>
<td>1</td>
<td>5</td>
<td>3</td>
<td>1</td>
</tr>
<tr>
<td>UCAR PKHH (phenoxy)</td>
<td>2</td>
<td>1</td>
<td>6</td>
<td>6</td>
<td>1</td>
</tr>
<tr>
<td>Polyvinyl Acetate</td>
<td>1</td>
<td>1</td>
<td>6</td>
<td>6</td>
<td>1</td>
</tr>
</tbody>
</table>

Key
1 Soluble
2 Almost Soluble
3 Slight Solubility
4 Swollen
5 Little Swelling
6 No Visible Effect

Solubility observations were made after 1.0 g resin and 9.0 g solvent were agitated for 24 hours at room temperature.

Paint strippers & brush cleaners, Graffiti-, Gum, rosin, & tar-, Adhesive removers
Method Detergent: 4 times more concentrated than traditional 2X concentrated detergents

Strong solvency and performance in acidic environments
Approved as food additives
Levulinic Ketals polyols

- Allows reduced isocyanate/catalyst content
- Less plasticized by hydrocarbon blowing agents
- No residual unsaturation
- Highly compatible
Levulinic-Ketal Polyol Technology: Many Design Variables

Levulinic-Ketal polyols are produced by reacting ketal monomers with a variety of initiators and, optionally, co-monomers:

\[
\text{I(OH)}_n + \text{EtO} - \text{EtO} - \text{O} - \text{O} - \text{EtO} - \text{H} + \text{catalyst} \xrightarrow{\text{heat}} \text{I} \left[ \text{O} \left( \text{EtO} - \text{EtO} - \text{O} - \text{O} - \text{EtO} - \text{H} \right)_y \right]_n
\]

AB monomer

The special levulinate ketal monomer creates rigidity and can be used to fine tune flexibility in polyols and polyurethanes and therefore properties.
Levulinic Ketal Polyols for Polyurethane Foam Applications

> **Amorphous**
  > No preheating required to melt
  > No phase transitions related to soft segment

> **Stiffer than polyester polyols, which enables**
  > Reduced isocyanate content
  > Lower polymer crosslink density

> **Synergistic effects with other polyol technologies**

<table>
<thead>
<tr>
<th>Foam Type</th>
<th>Application Examples</th>
<th>Levulinic Ketal Polyol advantages</th>
</tr>
</thead>
</table>
| Rigid Foams     | › Gap-filling sealant foams for construction  
                   › Roofing insulation board  
                   › Wall insulation  
                   › Appliance insulation  
                   › Automotive interiors | Improved modulus                                |
| Viscoelastic Foams | › Bedding  
                        › Furniture, seating | Reduced isocyanate usage                        |

> L-Ketal polyols offer better performance and more versatility versus other bio-based alternatives (seed-oil polyols like castor oil)
Levulinic acid Ketals
plasticizers

› Good hardness efficiency
› Phthalate-Free formulations with low fusion temperatures
› Rapid dry blend time
› Lower volatility then other plasticizers
› Improve processing of phthalate alternatives
Levulinic Ketals are excellent performing phthalate-free, bio-based plasticizers

Replace the phthalic anhydride core with levulinic ketal core

- Plasticizers rely on a phthalic anhydride core; this is modified to meet performance requirements

- In Ketal plasticizers the core is a biobased levulinic ketal

- The plasticizer properties can be modified in a similar way through choice of (biobased) R groups

Phthalate-free, Bio-based Plasticizers

<table>
<thead>
<tr>
<th></th>
<th>SG0159x</th>
<th>SG0158x</th>
<th>SG9200</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hardness Efficiency</td>
<td>Excellent</td>
<td>Good</td>
<td>Excellent</td>
</tr>
<tr>
<td>Fusion Temperature</td>
<td>Average</td>
<td>Excellent</td>
<td>Excellent</td>
</tr>
<tr>
<td>Volatility</td>
<td>Good</td>
<td>Good</td>
<td>Good</td>
</tr>
<tr>
<td>Color stability</td>
<td>Excellent</td>
<td>Average</td>
<td>Excellent</td>
</tr>
<tr>
<td>Non-polar Extraction</td>
<td>Average</td>
<td>Good</td>
<td>Excellent</td>
</tr>
</tbody>
</table>

- SG0159x: Primary plasticizer for all flooring types.
- SG0158x: Performance plasticizer for sheet flooring and VCT/LVT with HEXAMOLL® DINCH® and DOTP
- SG9200: Best combination --- low gelation temperature with excellent efficiency, volatility, and superior non-polar extraction. For all flooring types
Unique property profiles to flex PVC and flex PLA with Levulinic Ketas

**Low Migration into Nonpolar Media**

- Flexible PLA with Levulinic Ketal plasticizer
- Flexible PLA with competitive plasticizer (stress whitening when bent)
- Excellent compatibility with hydrophilic biopolymers

**Complex Viscosity of Plasticized PLA Formulations at 150°C**

- Lower the processing temperature of PLA
- Transmission >90% with Levulinic Ketal plasticizer

**60 phr PVC Formulation**

60 phr plasticizer, 2 phr Ferro SP175 in GEON 121A; % mass loss is normalized to plasticizer loading (assumes all mass loss is plasticizer)

- Ketal plasticizer has low compatibility with polyethylene → low migration into PE and other hydrophobic polymers

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**Graphs and Charts**

- Bar graph comparing extracts in Hexane
- Complex viscosity graph for plasticized PLA formulations

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GF Biochemicals
BENEFITS TO FLOORING

Phthalate-free PVC formulations with excellent performance

> Vinyl Sheet
  - Fast gelation: high throughput
  - Low gelation temperature: lower energy
  - Low volatility: better plasticizer utilization
  - Excellent heat-aged stability: good color retention

> Vinyl Tile
  - Fast dry blend time: high throughput
  - Low gelation temperature: lower energy
  - Excellent heat-aged stability: good color retention
Levulinic acid

\[ \text{Gamma valerolactone Platform} = \text{Next platform to be developed} \]
Green solvents and resins from lignocellulosic biomass

New European innovation project GreenSolRes will convert lignocellulosic feedstock into chemical building blocks and high added value products.
MOLECULE TREE

- Methylene-γ-valerolactone (monomer)
- γ-valerolactone (solvent)
  - 1,4-pentanediol (Polyester precursor)
  - Levulinate esters (biodiesel additive)
  - Diphenolic Acid (Bisphenol A substitute)
- BIOMASS
  - Cellulose
    - Glucose
      - LEVULINIC ACID
        - 2-methyl THF (solvent, fuel oxygenate)
        - Acrylic acid (monomer)
        - 5-amino Levulinic acid (herbicide)
        - Acetyl Acrylic acid (monomer)
        - Methyl ethyl ketone (solvent)
- LEVULINIC ACID
- 5-methyl-2-alkyl pyrrolidone (monomer)
- Adipic acid (monomer)
- Caprolactam (monomer)
- Hydroxypropionic acid (monomer)
- Succinic acid (monomer)
- LA-ketals (plasticizer/solvent)
- Methyl vinyl ketone (solvent)

GF Biochemicals
SUMMARY

> Levulinic acid
  • Huge potential to make numerous chemicals to develop biobased chemical industry
  • CAPEX and OPEX comparable or lower to lignocellulosic fermentation products

> GF B
  • First to bring lignocellulosic levulinic acid in the market
  • Commercialize levulinate ketal platform with applications as coupling agent, solvent, plasticizer, polyol, ....
  • Develop & commercialize gamma-valerolactone platform
Levulinic acid: Road to a flourishing bioeconomy
Shore A Hardness

Plasticizer - 60 phr in PVC

- SGP9200 is more efficient than DOP
- SG0159x is as efficient as DINP
- SG0158x is equivalent to phthalate-alternatives

60 phr plasticizer, 2 phr Ferro SP175 in GEON 121A (paste resin), cured 10 min. @ 200 °C
Shore A 15-sec hardness, 245 mil film thickness
SG0159X IS MORE EFFECTIVE THAN DOTP AND DINP IN FILLED TILE FORMULATIONS

50 phr plasticizer in GG2095 (suspension resin) with 40 phr CaCO3, 3 phr ESO (except SG0159x), 0.25 phr stearic acid, 2.5 phr Mark 1221
Cured 10 min. @ 160 °C
All three Segetis products show low gel temperature.

For sheet:
low gel & fusion temperature

For tile:
rapid blend time and lower fusion temperature

60 phr plasticizer, 2 phr Ferro SP175 in GEON 121A (paste resin)
Gel bar (gradient temperature bar) test, 6 mil drawdowns, recorded after 1 minute
LEVULINATE KETAL BASED FAST FUSERS ENABLE DINP PERFORMANCE IN NON-PHTHALATE FORMULATIONS

**Diagram Description:**
- **SG0158x** shows the same performance as **SGP9200**
- **Segetis fast fusers bring** gel points of DINCH and DOTP into DINP regime
- **Improve processing of DINCH and DOTP without sacrificing**
  - Hardness
  - Color

**Graph Details:**
- X-axis: % SGP9200
- Y-axis: Gel Temperature (°C)
- Data points for DINCH, DINP, and DOTP
- DINP/BBP range

**Experiment Details:**
- 60 phr plasticizer, 2 phr Ferro SP175 in GEON 121A (paste resin)
- Gel bar (gradient temperature bar) test, 6 mil drawdowns, recorded after 1 minute
SGP9200 IS ADVANTAGED IN VISCOSITY STABILITY COMPARED TO OTHER FAST FUSERS

60 phr plasticizer, 2 phr Ferro SP175 in GEON 121A (paste resin)
Brookfield viscosity at 21 °C.
DPGDB = dipropylene glycol dibenzoate

Benefits of fast-fusing with less viscosity build
Good storage stability of plastisols for sheet vinyl
EFFECTIVE CLEANING IN FORMULATION*

**Superior grease-cutting power**

<table>
<thead>
<tr>
<th>Percentage Soil Removed per Test Cycle</th>
<th>Segetis SV218</th>
<th>2-butoxyethanol</th>
<th>Water</th>
</tr>
</thead>
<tbody>
<tr>
<td>% Soil Removed</td>
<td>10</td>
<td>5</td>
<td>0</td>
</tr>
</tbody>
</table>

Ingredients:
- Water 91%, Sodium Citrate 0.5%, BIO-SOFT® N91-6 4.5%, Degreaser 4%

- Powerful grease and soil removal
- Enhances phase stability in aqueous solutions
- Ultimately biodegradable
- Chlorine-free

**Superior coupling ability**

<table>
<thead>
<tr>
<th>Improvement in Upper Cloud Point (g/C)</th>
<th>DDBSA</th>
<th>BioTerge PAS-85</th>
<th>DowFax C10-L</th>
</tr>
</thead>
<tbody>
<tr>
<td>Segetis SV388</td>
<td>20</td>
<td>15</td>
<td>10</td>
</tr>
<tr>
<td>GlycoEther (EGBE)</td>
<td>10</td>
<td>5</td>
<td>0</td>
</tr>
</tbody>
</table>

**Heavy-duty cleaning**

- **Heavy Duty Cleaning Agents**
  - 13-propanediol, SV388, Ethanol
  - Estimated percent stain removal 10% (10%), 40% (40%), 75% (75%), 90% (90%), 90% (90%)

- **Bio-based Coupling Agents**
  - d-limonene, DBE, SV218

Material: Formulation Aid 4.0%, Nonionic Surf. (Biosoft N25-7) 4.5%, Anionic Surf. 0.5%, Na Citrate 0.5%, DI Water 90.5%

Formulation stays homogeneous up to higher temperatures for better shelf life

*Testing protocols available on request*
Problem for all biomass based products:

CAPEX hurdle

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Growth rate vs choice of size