New Developments and Applications of Resin Systems for the Treatment of Citrus Products Containing Pulp and Cloud

ICBC September 2008

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Two Types of Resin Processes

1. Cloudy products
2. Clear products

Citrus processing systems

Auckland - New Zealand
# Citrus Products Containing Pulp and Cloud

**Juices**
- Orange and Grapefruit concentrates
- Tangerine/Mandarin concentrates
- NFC

**Washes**
- WESOS (pulp wash)
- Orange core wash

**Extracts**
- Orange and Grapefruit peel
- Tangerine/Mandarin peel
- Lemon peel
- Whole fruit comminutes
Bucher Alimentech (BAN) Installations

36 CLOUDY CITRUS MACHINES

36 CLEAR PRODUCT MACHINES
Development of BAN Citrus Processing Technologies

1st Citrus processing equipment
   - 1984 Australia (debittering)

1st European installation
   - 1989 (Debittering and ratio adjustment)

1st USA installation
   - 1991 (Ratio adjustment/de-acidification)

1st Brazilian installation
   - 2007 (Debittering)
Cloudy Citrus Products

Problems to be addressed

• Bitterness
  - Limonin
  - Polyphenols
  - Naringin (grapefruit)

• Astringency
  - Polyphenols (peel extracts)

• High Acidity
Historical Solutions for Bitterness and Excess Acid

- Sugar was added to the juice to disguise bitterness

- In some countries alkalis were added to reduce the acidity of the products
Limonin Bitterness Formation In Citrus Juices

Limonin precursor synthesised in roots and stem and transported to the maturing fruit.

In the intact fruit (1) is converted to (2) in an Enzymatic controlled reaction. Enzyme confined to the neutral pH parts of the fruit flavedo, albedo, segment membranes, pith and seeds.

Enzymatic and acid induced conversion.

During the extraction, the Limonoate is dispersed into the acidic juice.

(1) Limonoate A-ring lactone-7-o-β-D-glucopyranoside (non bitter)

(2) Limonoate A-ring Lactone (non bitter)

(3) Limonoic Acid A-ring Lactone (non bitter)

(4) Limonin (intensely bitter)
# Bitterness and Astringency*

*Astringency, a problem with peel extracts.

<table>
<thead>
<tr>
<th>Effectiveness of Resins</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resin system 1</td>
</tr>
<tr>
<td>P495 only</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Before</th>
<th>After</th>
<th>Before</th>
<th>After</th>
</tr>
</thead>
<tbody>
<tr>
<td>Absorbance of Total Polyphenolics (Petrus Method)</td>
<td>-</td>
<td>-</td>
<td>3.60</td>
<td>0.41</td>
</tr>
<tr>
<td></td>
<td>3.30</td>
<td>2.12</td>
<td>3.30</td>
<td>1.58</td>
</tr>
<tr>
<td>Soluble Limonin (mg/L by HPLC)</td>
<td>70.0</td>
<td>1.50</td>
<td>70.0</td>
<td>6.60</td>
</tr>
</tbody>
</table>

Note same resins effect on different starting materials in table – lines 1 and 2
High Acidity

• Particularly at the beginning of a season with less mature fruit being processed

• In the USA high ratio (21~26) juice can be prepared using resins (21CFR 146.148)

• Will reduce the citric acid in the product, although the resins used will not materially affect the ascorbic acid (vitamin C) level
Solution for Bitterness and High Acid

USE RESIN TECHNOLOGY

Types of Resin Technology

• Ion Exchange

• Adsorption
Ion Exchange Applications

• Deionisation (DI)

• Acid Reduction (ratio adjustment)
Ion Exchange

Deionisation

- Applicable to clear juices
- Recovery of natural sugars by removing minerals, salts, organic compounds including polyphenols, colour bodies and other products

CITRUS APPLICATIONS

- Recover fruit sugars from citrus peels
Ion Exchange

Acid Reduction
- Applicable to all clear and cloudy products

CITRUS APPLICATIONS
- Increase ratios of citrus peel extracts and washes
- Where allowed, is used for production of low acid / high ratio orange juice
Deacidification – Ascorbic Recovery

Ascorbic Acid
• Inlet: 440mg/kg
• Outlet: 421mg/kg (composite of cycle)

**Graph 1**: Citrus Deacidification - 10 000 litres/hour. Ascorbic acid Sampled During the Run. (Initial ascorbic level = 440 ppm; Initial citric acid concentration = 1.0 %)
Adsorption Technology

- Debittering
- Reduction of Browning (Maillard)
- Hesperidin Reduction (clarified products)
Adsorption

Debittering

Reduction of Limonin and Naringin

CITRUS APPLICATIONS

- NFC
- Orange, Tangerine and Grapefruit Conc.
- Orange, Tangerine and Grapefruit Peel
- Orange and Grapefruit Washes
- Whole Fruit Comminutes
Adsorption

Colour Reduction

Reduction of Browning (Maillard reaction)

CITRUS APPLICATIONS

- Clarified lemon juice
- Peel extracts and comminutes
Citrus Processing Resin Technologies

Bucher Alimentech (BAN) Cloudy Products System

• **Centrifuge →** resin columns *with* external resin cleaning system

Others

• Clarification by UF → resin columns *no* resin cleaning system (*Bucher Alimentech use for clear products*)

• **Centrifuge →** resin *without* resin cleaning system
UF Membrane + Debittering Columns
Problems with UF System for Cloudy Products

- 100% cloud and pulp in one stream and 0% cloud and pulp in the other – recombination stability problems known

- Oil level must be below 0.01% (100 mg/l)

- When there is membrane failure, pulp clogs the resin bed, very difficult to clean – lost production

- **COST** of Membrane replacement

- **COST** of Energy

- Temptation to run cycles too long – less resin cleaning and risk of contamination – “The 4 a.m. Sunday syndrome”
BAN Cloudy system diagram
UF Membrane + Debittering Columns
Advantages of BAN Cloudy System

- Processes cloud and pulp up to 1% - no enzyming required - good recombination
- Resin is completely cleaned and regenerated every 3.5 to 5 hours. No bacteriological contamination
- No oil problem – can process up to 0.1% (1,000 ppm)
- If pulp gets into bed, immediately regenerate and continue
- Longer resin life
- NO membrane costs
- Energy costs significantly lower
- TOTAL OPERATING COST MUCH LOWER
Typical Processing Equipment

Continuous debittering plant
For cloudy juice
15,000 litres per hour
(65 ~ 70gpm)

6.0m L x 2.3m W x 5.5m H
(19’6” X 7’6” X 18’. approx)
Juice Process
Resin Transfer and Wash
Resin Return
Regenerate Resin
Development 1 - NFC

- NFC is becoming more important
- BAN process has been adapted to produce premium quality
- No separation of cloud from main stream important for product quality
- Dwell time in centrifuge + columns is much shorter than in UF + columns – better product quality
- Gas displace to minimize dilution
NFC Gas Displace
NFC Temperature Profile

TEMPERATURE PROFILE FOR BAN NFC ORANGE JUICE PROCESSING
(Actual Factory Conditions)

TIME COMPARISON
EX FINISHER TO STORAGE
BAN NFC .................30 min
UF NFC .................55 min
Development 2 - Core Wash Debittering

• Traditionally UF has been used because of the type of pulp.
• The problem of separating core wash pulp by centrifuge has been solved.
• Core Wash is mainly cloudy (BAN system better)
• Processing cost is high relative to product value.
• The BAN system reduces the cost of processing by at least 50%.
• Energy consumption is reduced by at least 75%.
• BAN Debittered Product is judged better quality.
Development 3 - Peel Extract Debittering

- Using BAN debittering the soluble solids can be upgraded to human food value
- The residual fiber can be used for human food also traditionally Animal Feed has been the end product
- This is an unstable market determined by factors outside the citrus industry
- The BAN system reduces the cost of processing and increases the output value
- Bio-actives can be produced from side streams
Development 4 - Flexibility

New Possibilities

• If a company wishes to process different products during the season or out of season

• It is possible to change over the resin beds in the processing columns in less than 6 hours. This is not possible in other resin systems
Resin Change - Over System
Recommended Debittering Resin P495

Choice of Resin

- Bucher Alimentech is not tied to one supplier
- The best resin for an application is selected
- Resins meet USA and European regulations
Service Life of Alimentech P495

COMPARISON OF THE DEBITTERING ABILITY OF P495 AFTER 8 YEARS SERVICE WITH NEW ALIMENTECH P495.
Feed Juice 35 ppm Limonin; Flow Rate 6 bv/hr.

- Absorbance of Total Polyphenolics (Petrus Method) & Limonin (mg/L)
- Total Flavonoids (mg/L as hesperidin)
- Soluble Solids (°Brix)

Graph showing the comparison of various parameters over the volume of citrus juice processed.
## Citrus Debittering - Typical Results

<table>
<thead>
<tr>
<th>Feed</th>
<th>°Brix</th>
<th>Input (mg/L)</th>
<th>Output (mg/L)</th>
<th></th>
</tr>
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<tbody>
<tr>
<td></td>
<td></td>
<td>limonin</td>
<td>naringin</td>
<td>limonin</td>
</tr>
<tr>
<td>Navel Orange Juice</td>
<td>12</td>
<td>13</td>
<td>-</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Navel Peel extract</td>
<td>4</td>
<td>50</td>
<td>-</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Valencia Peel extract</td>
<td>8</td>
<td>30</td>
<td>-</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Kinnow</td>
<td>11</td>
<td>18</td>
<td>-</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Grape fruit juice</td>
<td>10</td>
<td>25</td>
<td>600</td>
<td>&lt;5</td>
</tr>
<tr>
<td>Grape fruit peel extract</td>
<td>5</td>
<td>50</td>
<td>8000</td>
<td>&lt;10</td>
</tr>
</tbody>
</table>
Costs

- **Capital Costs** (65 ~ 70gpm (15,000 l/h) plant)
  USD $ 800,000 (typical)
  Columns + centrifuge cost is no more than UF + columns cost

- Latest Brazilian costs show this system capital cost is less than the UF equivalent system

- **Operating cost / ton** (60~65°Brix product)
  - BAN Process: US$ 25~50/ ton
  - UF Membrane Process: US$ 100~130/ ton
Benefits of BAN Process for Cloudy Products

• No alcohol or peroxide washes
• No membrane replacement
• Better recombination of cloudy products
• Longer resin life
• Low maintenance costs
• Processes high oil products
• Lower total operating cost
Summary of Developments

- NFC - Higher Quality
  - Lower Cost

- Core Wash - Better Quality
  - Lower Cost

- Peel Extract - Better Profitability
  - Lower Cost

- Flexibility – Short product change-over times
Bucher Alimentech Systems

CITRUS MACHINES IN 13 COUNTRIES

TOTAL MACHINES IN 23 COUNTRIES
Thank you!

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