“The Techno Rice”: An Industrial Application of Supercritical Fluid Technology in Taiwan

By Yi-Jen Liaw

FFTC-KU Risk Management on Agrochemicals through Novel Technologies for Food Safety in Asia
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OUTLINE

– Principle flow diagram and process description

– Design criteria for industrial scale
  • Raw material
  • Extraction conditions, solubility and optimisation
  • Types of extracts
  • Scale Up and feasibility of the process
  • Selection and sizing of components

– Applications on industrial scale

– New potential applications

– The Techno Rice
A SCF is defined as a substance above its critical temperature ($T_C$) and critical pressure ($P_C$). The critical point represents the highest temperature and pressure at which the substance can exist as a vapour and liquid in equilibrium.

$T_c = 31.1^\circ C$

$p_c = 73.8$ bar
Supercritical Fluid Extraction (SFE) is the process of separating one component from another (the matrix) using supercritical fluids as the extracting solvent.

Critical conditions:
- Temperature \((T_c) = 31.1 \degree C\)
- Pressure \((P_c) = 73.8 \text{ bar}\)
- Density \((D_c) = 0.467 \text{ gm/ml}\)

### Table 1: Comparison of average properties of gases, liquids and SCF

<table>
<thead>
<tr>
<th></th>
<th>Liquid</th>
<th>Supercritical (T - T_c)</th>
<th>Gas (at room (T) and (P))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific Gravity (\rho (\text{kg.m}^{-3}))</td>
<td>600 - 1600</td>
<td>100 - 900</td>
<td>0.6 - 2</td>
</tr>
<tr>
<td>Viscosity (\eta (\text{Pa.s}))</td>
<td>(10^{-3})</td>
<td>(10^{-5} - 10^{-4})</td>
<td>(10^{-5})</td>
</tr>
<tr>
<td>Diffusivity (D (\text{m}^2.\text{s}^{-1}))</td>
<td>(10^{-9})</td>
<td>(10^{-8})</td>
<td>(10^{-5})</td>
</tr>
</tbody>
</table>
Principle Flow Diagram of Supercritical Fluid Extraction

- Solid
- Liquid
- Gas
- Extractor
- Condenser
- Heat exchanger
- Critical point
- Supercritical Fluid
- Pump
- Separator
Principle Flow Diagram for industrial application
## Process Design Criteria

<table>
<thead>
<tr>
<th>Solubility in CO$_2$</th>
<th>Easily Soluble</th>
<th>Reduced Soluble</th>
<th>Not Soluble</th>
</tr>
</thead>
<tbody>
<tr>
<td>Esters, Alcohols</td>
<td>Edible oil from oil seeds</td>
<td>Sugars</td>
<td></td>
</tr>
<tr>
<td>Aldehydes, Ketones</td>
<td>Waxes</td>
<td>Fruit acids</td>
<td></td>
</tr>
<tr>
<td>Volatile Oil</td>
<td>Polyphenols</td>
<td>Starches</td>
<td></td>
</tr>
<tr>
<td>Aromas</td>
<td>Alkaloids</td>
<td>Proteins</td>
<td></td>
</tr>
<tr>
<td>Mono-, Sesqui – Terpenes</td>
<td></td>
<td>Mineral salts</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Glycosides</td>
<td></td>
</tr>
</tbody>
</table>
### Process Design Criteria

<table>
<thead>
<tr>
<th>Types of extractions</th>
<th>Types of extracts</th>
</tr>
</thead>
<tbody>
<tr>
<td>TOTAL EXTRACTS</td>
<td>Extracts containing all soluble substances - under selected processing conditions (spice extracts)</td>
</tr>
<tr>
<td>FRACTIONATED EXTRACTS</td>
<td>Partial extracts, obtained by specific separation conditions (essential oil fraction)</td>
</tr>
<tr>
<td>PURIFIED EXTRACTS</td>
<td>2-steps processing of a total extract to optimize the quality - colour enrichment, desodoration</td>
</tr>
<tr>
<td>SELECTIVE EXTRACTS</td>
<td>Active substance extracts, achieved by means of specific inline steps like adsorption (medicinal extracts)</td>
</tr>
</tbody>
</table>
Applications on Industrial Scale

1. Hops extraction
2. Coffee & Tea decaffeination
3. Extraction of herbs and spices
4. Rice treatment
5. Impregnation of wood
6. Edible oil extraction – roasted sesame oil
7. Cork cleaning
Hops extraction

- Since 1985
- Several companies: NATECO2 (DE), Nutrizeal (NZ), Pulawy (PL), Steinerhops (DE)

- Production capacity worldwide:
  - Around 90,000 tons of hops / year grown
  - Approx. 20,000 tons / year extracted by supercritical CO₂

- Advantages
  - Uniform extract quality (appear yellow colour), cleaner bitterness
  - No organic solvent residues in the product
  - Comply with the Reinheitsgebot (purity law)
  - Better storability of the extract
  - Easy dosing
Hops extraction

Process flow scheme

Hops extraction

Plant size: 3 x 5m³ / 325bar
Hops extraction

Nutrizeal plant (NZ): 3 x 850L / 550bar, 20% co-solvent; 4500kg CO₂/h
Decaffeination of Tea

- Since 1988 by EVONIK in Münchsmünster, Germany
- Plant was supplied under Schöller-Bleckman
- Plant size: 3 x 7 m³
- Still in operation
- Production capacity:
  - 3,000 tons of tea / year

Process description:

- Moisturizing the tea from 5 to 28%
- Loading of the extraction cartridge
- Extraction at 250 bar, 60°C for several hours
- Drying in fluidized bed back to 5% moisture
- Quality taste check, sensorial analyses
Decaffeination of Tea
Coffee – Extraction of caffeine

• Since 1992
• Plant was supplied under Schöller-Bleckman
• Still in operation – extractor closures revamped in 2013
• Plant size: 3 x 21.5m³ / 325bar

• Production capacity:
  – 10,000 tons of raw coffee / year
  – Approx. 200 tons of caffeine / year
Coffee – Extraction of caffeine

FLOW SHEET

CO_{2} Extraction Plant
coffee pretreatment, handling drying and despatch
Datum: 89-08-09 | Name: Wi
Coffee – Extraction of caffeine
Coffee – Extraction of caffeine
Coffee – Extraction of caffeine
Coffee – Extraction of caffeine
Extraction of spices

- Since 1996
- Several companies in India, Germany, Czech Republic
- Plant sizes: different
- Production capacity:
  - 100’s of Kilograms up to several tons / day
- Advantages
  - Solvent free products
  - Fractionated extraction of oleoresins and essential oils
  - Increased concentration of colorants
  - Uniform extract quality
  - Residues can be further used
  - Low process temperatures – aromas and fragrances are unchanged
  - Extracts are free of bacteria, mold, fungus and other contaminations associated with the raw material – sterilization effect
Extraction of spices

- 2 x 600 L / 550 bar
- 3 x 300 L / 550 bar
Rice treatment

- Since 1997
- Five King Cereals Inc. in Taiwan
- Plant size: 3 x 6m³ / 325bar; 20,000 kg CO₂/h
- Production capacity:
  - Around 90 tons of rice / day
  - Approx. 25,000 tons / year extracted by supercritical CO₂

Advantages

- Elimination of CO₂ soluble pesticides and lipids for longer stability against oxidation
- Much shorter cooking time; treated rice is aromatic, crunchy and tender at the same time
- Shelf life is substantially extended
- Processed brown rice requires no further rinsing and soaking in water
Rice treatment
Wood impregnation

- Since 2001
- Superwood in Denmark
- Plant size: 3 x 17 m³ / 170bar
- Production capacity:
  - 40,000 – 60,000m³ / year wood slab
- Advantages
  - The impregnation cycle lasts only about 3 to 5 hours
  - Controlled resin extrusion to the external surface
  - There is virtually no emission of solvents
  - During impregnation the fungicides are distributed homogeneously in the wood and the treated wood is dry and ready for use
  - The impregnated wood meets all quality requirements with minimal use of active components
Wood impregnation

Fungicide

Impregnation vessel

Recycled CO$_2$

CO$_2$

Recycled fungicide
Wood impregnation
Extraction of roasted sesame oil

- Since 2003
- U-max in South Korea
- Plant size: 2 x 3.8m³ / 550bar; 13,000kg CO₂/h
- Production capacity:
  - Around 7,000 Litters of oil / day
- Advantages
  - Much higher levels of antioxidants like sesamol and tocopherol as well as of bioactive compounds like phytosterols and selenium can be achieved
  - Enriched flavour results in a better taste
  - The germicidal properties of supercritical CO₂ further enhance the quality of the oil
  - An exploitable by-product of the process is the de-oiled sesame powder
  - The oil is fully extracted – high efficiency of oil extraction

Sesamin and sesamolin are minor components of sesame oil, on average comprising only 0.14% of the oil by mass

Extraction of roasted sesame oil

Sesamin

Sesamolin
Extraction of roasted sesame oil
Cork cleaning

Removal of TCA from fresh cork granulate for wine stoppers production

- Since 2004, the newest facilities was established at 2014.
- Oeneo Bouchage
- Plant size: 3 x 9 m³ / 150bar, 3 x 12 m³ / 130bar, 3 x 20 m³ / 130bar
- Production capacity:
  - 2,000 Mil. Cork stoppers / year
- Advantages
  - TCA level below 0.2 ng/L(ppt)
  - Conventional processes can reduce TCA up to 70%
  - Compressor process – saving of condensation energy compared to pump process
Cork cleaning

The most important secondary metabolite – formed by bacteria and fungi – is 2,4,6-trichloroanisole (TCA), which is responsible for the typical cork taint.

Eduard LACK, Helmut SEIDLITZ, NATEX Prozesstechnologie;
Dominique Tourneix, Oeneo Bouchage Rudolf Zobel, Moaad Bakali, Diamant Techoenologie S.A.

9th, International Symposium on Supercritical Fluids Arcachon, 18 – 20 May, 2009
Cork cleaning

FLOW SHEET DIAM CORK PROCESS

Extraction SC CO₂
P ≥ 80 bar ; T ≥ 40°C

Co – Solvent Pump

Extractor

Heater/Cooler

Compressor

Evaporator

Separator

CO₂ Tank
Cork cleaning

Courtesy of Diamante - Spain
Cork cleaning

Courtesy of Diamante - Spain
New potential applications

1. Supercritical extraction plants in GMP standard for medicinal production
2. Extraction of plastic polymers (PE, PVC, rubber recycling)
3. De-oiling of Magnesium- and Steel particles
4. Production of particles with scCO$_2$ (CPF, PGSS, RESS, SAS)
5. Aerogel production
6. Algae – Omega oils, Carotenoids
7. Impregnation of Plastics, Fibers
8. Dyeing of fibers
9. Cleaning of long pipes
10. Ceramics – debinding
11. Pasteurisation – Sterilisation with High pressure CO$_2$
12. Leather tanning with CO$_2$
13. Chemical reactions
14. Ionic liquids
15. Frosting of fresh fruits
“The Techno Rice”
Five King Cereals Industry Co. Ltd.
COMPANY MISSION

Strive for Quality
The Story of Techno Rice
FKCI was founded on March 14, 1997

FKCI is a company join venture founded by:

Yu Fong Cereal Co., a family own and operate rice milling company, got together with I-Mei Food Company, a leading food company in Taiwan, and Food Industry Research and Development Institute (FIRDI), a nonprofit organization
The research and development of “Techno rice” began under the assistance and supervision of FIRDI (Food Industry Research and Development Institute) in 1995,

It was a result of a three-year special cooperation project, supported by Council of Agriculture (COA) and the Ministry of Economics in Taiwan
The research and development work for the rice treatment with Supercritical CO$_2$ to ensure the safety of the rice with the science-based green technology so we called it “Techno Rice”
It all started from here:

The purpose of the development

- Removal of the oil and the fatty acids inside the rice bran to prevent the lipids oxidation.
- The germicidal properties of supercritical CO2 can extend the shelf life of the rice.
- Eliminating insects and their eggs.
- Removal of pesticide residuals and some of the heavy metal from the rice.
- Cleaning of the rice without leaving any organic solvent residue.
Exclusive Global Techno Rice Patent
making nutritious brown rice
tastier
providing rice that is
safer than ever
Realization

Five King signed 1998 a contract with NATEX of Austria, a world leading specialist in the field of Supercritical Fluid Technology and Expert for Scale-Up of new Applications to industrial scale.
It was the first set up of a Supercritical Fluid Rice Cleaning Plant in the world

The overall development of this project took four and a half years

Having successfully combined

• Agriculture and food industries;
• Local R&D Institution; and
• Novel technology.

This project serves as excellent model how traditional agriculture industries can use the novel technology to improve the quality of the produces, and increase competition for global market.
Process description

- The process is designed as cascade mode operation, where at:
  - the solvent, CO$_2$-circulation is continuous, and
  - the solid phase (rice) is batch-wise

- The plant is equipped with:
  - 3 extractors,
  - 1 separator S403,
  - 1 CO$_2$ washing column C701,
  - CO$_2$ circle and all necessary utilities.
3D designing
On site construction of Techno Rice plant
Acting Courser on the top of extractors
Middle section of extractors, separator and heat exchanger
Acting Courser on the bottom of extractors
Pressure pump
Acting Courser on the bottom of extractors – unloading the treated Techno Rice
Techno Rice was first introduced to the market in the year of 2000.
Techno Rice is still on the market at the very moment

Taipei FOOD EXPO 2016, June 24 - 27
Techno Rice is still on the market at this very moment.

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THANKS for your ATTENTION

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