Speciality Chemicals
Manufacturing and Applications
Specialists in Supercritical Fluid technology
Russell Clarke

Chemsourse Symposia, Amsterdam June 23rd 2004

Website; www.thomas-swan.co.uk
Summary of Presentation

• What is a Supercritical Fluid (SCF)?
• Review of some chemistry in SCF?
• Overview of SCF facilities at Thomas Swan
• Overview of complimentary Thomas Swan Capabilities
What is a Supercritical Fluid (SCF)?

A Supercritical Fluid is a liquid at a temperature above its critical temperature and a pressure above its critical pressure.

The critical temperature of a gas is the temperature above which no amount of pressure will liquefy the gas. The critical pressure is the pressure needed to liquefy a gas at its critical temperature.
What is a Supercritical Fluid?
A. One Academic
B. One Industrial Partner

Thomas Swan OBE
Why collaborate on SCFs?

Mid 1990’s
- fear of ban on all chlorinated solvents

New Scientist
- “vending machine chemistry”
- “dial-a-molecule”
Reactions under SC conditions are not new...

1898  Villard - used Sc Ethene + Iodine to give 1,2-di-iodo ethane

1906  Ipatiev - First heterogeneous catalysed reaction: oligomerisation of ethene using ZnCl₂
...and were unknowingly used for many years

1913 BASF - ammonia synthesis
1923 BASF - methanol
1937 ICI - ethylene polymerisation
Why Use Supercritical Fluids (SCF’s)?

- They are solvents with some unusual properties.
- They combine the mass concentrations of a liquid with the transport/reaction rates of gases.
- Some novel/unusual chemistries are possible.
scCO₂ uses in extraction

- Plant oils
- Fragrances
- Fish oils
- Safrole
- Cashew nut oil
- Hops
- Fish oils
- Plant oils
• What is a Supercritical Fluid (SCF)?
• Review of some chemistry in SCF?
• Overview of SCF facilities at Thomas Swan
• Overview of complimentary Thomas Swan Capabilities
Reactions studied in SCFs

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Laboratory reactor

Reactants $\rightarrow$ Reactor + Catalyst $\rightarrow$ SC Fluid

Product(s) $\rightarrow$ Gas

Swan SCF® Process
Miscibility of $\text{H}_2$ and $\text{scCO}_2$

$T < T_c$

Liquid

$T > T_c$

Higher Concentration of “Dissolved” $\text{H}_2$ in $\text{scCO}_2$

Howdle, S. M., Healy, M. A., Poljakoff, M.

Trimethylcyclohexanone (TMCH)

Two standard routes:
- gas phase
- liquid phase

However, both methods problematic…

Swan SCF® Process
TMCH - gas phase process

- High reaction temperature (> 210 ºC) gives 3,3,5-trimethylcyclohexanol
- Difficult separation due to similar boiling points of alcohol, TMCH and isophorone
TMCH - liquid phase process

- Long reaction time (~4 hr)
- Low conversion (60-70%)
- Requires additional solvent (acetone)
TMCH - SCF process

- 100% conversion
- 100% selectivity
- Rapid reaction
- Improved catalyst lifetime (x 30)

Swan SCF® Process
SCF advantages . . .

- Higher conversion
- Higher selectivity
- Faster reaction
- Longer catalyst life
Hydrogenation of Acetophenone in scCO₂

Reaction parameters can be varied independently

Product distribution controllable
Selectivity of Hydrogenation Reactions
Reduction of Nitro-aromatics

Conventional routes

SCFT

No Detectable Hydroxylamine
Selectivity in SCF Hydrogenation

1% Pd on Deloxan
1.3 eq. H₂, 60 ºC, 120 bar

1% Pd on Deloxan
1.3 eq. H₂, 60 ºC, 120 bar

1% Pd on Deloxan
1.3 eq. H₂, 60 ºC, 120 bar
3-Ethylcyclohexene

Pt/MeOH, 20 bar
80% conversion
80% selectivity

Swan SCF® Process
3-Ethylcyclohexene

Pt/MeOH, 20 bar
80% conversion
80% selectivity

scCO$_2$, Pd/H$_2$, 32 ºC, 120 bar
100% conversion
100% selectivity

Swan SCF® Process
Conjugated aldehyde reduction (fragrance)

Conversion  95%
Selectivity  >99%

Swan SCF® Process
Hydrogenation of iso-α-acids (hop acids)

Conversion 100%
Selectivity >97%

Swan SCF® Process
Reduction of indoles – conventional

- Methods typically involve:
  - Boron/ silicon hydrides
  - Dissolving metals
  - Catalytic hydrogenation

- Yields often poor

Swan SCF® Process
SCF reduction of indoles

12% conversion
>95% selectivity

12% conversion
98% selectivity

100% conversion
100% selectivity
Rapid reaction

Swan SCF® Process
Continuous Supercritical Hydrogenation of Solid Substrates

• Problem
  – Solid reactants difficult to pump into reactor
  – Solid products may block depressurizing valves

• Answer
  – Dissolve reactant in a low boiling point organic solvent
Hydrogenation of solids in scCO$_2$

Starting compound dissolved in MeOH
**Hydroformylation**


Hydroformylation of Propylene, Akgerman *et al*, 4th Italian Conf. SCF & Applications

Batch Hydroformylation in SCF, US005198589A
Hydroformylation – current processes

Problems:

• Catalyst separation in homogeneous systems
• Catalyst leaching in heterogeneous systems
• Product selectivity in gaseous systems

Swan SCF® Process
Hydroformylation of 1-Octene

\[
\text{H}_2 /\text{CO} /\text{Deloxan HK1 2\%Rh} \quad \text{ScCO}_2 /150 \quad ^\circ\text{C}
\]

<table>
<thead>
<tr>
<th>Bar</th>
<th>Conversion</th>
<th>Aldehydes</th>
<th>n:iso</th>
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<tbody>
<tr>
<td>120</td>
<td>96%</td>
<td>71%</td>
<td>2.5 : 1</td>
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</table>
SCF hydroformylation

\[
\begin{align*}
&\text{H}_2/\text{CO (Syn gas)} \\
&\text{scCO}_2, \text{Rh catalyst}
\end{align*}
\]

- \( n:iso \ 50:1 \)
- No catalyst leaching giving greatly extended catalyst life

Swan SCF® Process
Synthesis of Ethers

Most routes cause considerable waste (e.g. salts, HCl, etc)

Acid catalysed isomerisation often gives unwanted by-products
Selective etherification of diols

MeO \text{100\%} OMe

\text{HO} \begin{array}{c} \text{+ MeOH} \\
\text{acid catalyst} 
\end{array} \begin{array}{c} \text{MeO} \\
\text{100\%} \\
\text{OMe} 
\end{array}
Selective etherification of diols

Selectivity controlled by temperature and pressure

+ MeOH
acid catalyst

100%

100%
Many useful downstream products

Swan SCF® Process
Supercritical Etherification

Reaction in scCO$_2$ gives 100% conversion at lower T and P than a typical process with liquid acid
Supercritical Etherification in scCO$_2$ at 200 bar

HO$_2$-C$_4$H$_8$-C$_4$H$_8$-OH $\xrightarrow{200 \, ^\circ\text{C}}$ C$_6$H$__{12}$O$_2$ + C$_5$H$_{10}$O$_2$ $86\%$

HO$_2$-C$_2$O$_2$-C$_4$H$_8$-OH $\xrightarrow{330 \, ^\circ\text{C}}$ C$_6$H$_{12}$O$_2$ + C$_5$H$_{10}$O$_2$ $95\%$
Acid - Catalysed Reactions

- Friedel Crafts Alkylation
- Ethers, Acetals & Ketals
Formation of Acetals & Ketales

scCO$_2$, 200 bar, Deloxan® ASP

\[\text{Formation of Acetals & Ketales} \]

**Conventionally yields are often low because the reactions are reversible**
Friedel-Crafts Alkylation

- need acid catalyst: AlCl$_3$, HF, etc.
- first alkyl group makes further substitution easier
- high dilution to prevent multiple alkylation

Usually a very dirty process
Friedel Crafts alkylation

Issues:
- Multiple alkylation
- Catalyst handling and disposal
- $n$-Alkylation not possible
SCF Friedel Crafts alkylation

- $n$-Alkylation possible?
- Selective mono-alkylation
- Acid catalyst can be regenerated
Friedel Crafts alkylation

SCF advantages . . .

• No corrosive waste streams
• Halogenated alkylating agents not required
Reductive amination

- Quantitative formation of benzylamine
- 100 bar N₂, 100 ºC
- Propionaldehyde - base abstraction of α-protons caused side reactions

D. N. Carter, PhD Thesis “Continuous Reactions in Dense Gases”, University of Nottingham, 2003
Oxidation

- 110 bar, 140 °C, 2.7 mol% O₂, continuous reaction
- 95% yield, >99.5% selectivity

Disproportionation

$$3 \xrightarrow{5\% \text{ Pd Deloxan}^{TM}} 2 \text{ + } \text{C}_6\text{H}_6 \quad 210 - 240 \, ^\circ \text{C}$$

- 100% conversion of cyclohexene

*F. R. Smail, PhD thesis “Continuous Organic reactions in Supercritical Fluids”, University of Nottingham, 2000*
Selective Esterification

- 50 °C, 200 bar
- 95% conversion, 85% selectivity

- 50 °C, 200 bar
- 100% conversion, 68% selectivity

W.K. Gray, University of Nottingham, unpublished results
Transesterification

$\text{Transesterification}$

- $200 \, ^{\circ}\text{C}$, 100 bar
- 100% selectivity, 75% conversion

$\text{W.K. Gray, University of Nottingham, unpublished results}$
Isomerisation

- Cis/trans ratio can be influenced in supercritical region
  - gas phase (low pressure), temperature variation gave no significant change in ratio
  - supercritical phase (higher pressure), temperature variation increased ratio from ~1.25 to 1.8

Diels Alder

- 35-40 °C, 70-270 bar
  - SCF density affected product distribution
    - endo:exo ratio passes through a maximum of ~ 3.8 at ~ 700 kg/m³


- 50 °C, 103 bar
  - Addition of silica (400 m²/g) gave increase in yield from 5% to 21%

Heck coupling

\[
\text{Pd/C, Et}_3\text{N} \quad \text{scCO}_2
\]

- 80 °C, 100 bar, 60 hrs, batch reaction
- 82% yield, unoptimised

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Laboratory reactor

- 300 bar
- 250 ºC
- 20 ml/min

Swan SCF® Process
SCF commercial plant

- 500 bar
- 200 ºC
- 100 kg/hr
SCF plant – reactor detail
• What is a Supercritical Fluid (SCF)?
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Thomas Swan & Co. Ltd.

- Privately owned company
  - Based in Consett, County Durham, UK
  - Facilities in Leicester – Sales office in USA.
  - Founded 1926
  - Emphasis on QA systems and environmental management
    - ISO 9001
    - ISO 14001
    - EMAS
    - OSHAS 18001
    - Responsible Care
Thomas Swan & Co. Ltd.

- **Turnover**
  - £25m (y/e March 31 2003)

- **Balance sheet**
  - Net assets £20m (March 31 2003)

- **Major activity**
  - Speciality chemicals manufacturer. 70% of turnover is own product sales, the remainder is contract & toll manufacture.

- **People**
  - 180 employees in Chemicals Business
  - 70 in other activities

- **Ownership**
  - Private & independent
    (3rd generation)
Thomas Swan & Co. Ltd.

Core business: chemical manufacturing and sales

- 70% own range of performance products
  - polymer / resin systems for coatings and rubber
  - bonding and adhesion promoters
  - speciality chemicals and intermediates

- 30% contract /toll manufacturing
  servicing many industries

- 70% of sales exported to 70 countries

- New processing technology
Support Equipment and Services

– *Pilot Plant*: Facilities include mainly glass vessels up to 200 litres with other equipment such as wiped film evaporator (operating to “near cGMP”).

– *Research and analytical development*: MS, HPLC, GLC, GC-MS, HPLC MSMS, NMR, IR, UV.

– *Materials testing*: Extruder, tensiometer, resiliometer, Shore hardness instrument, Tabor abrasor, paint testing equipment, viscometers.
Manufacturing facilities

- Approx 55 multipurpose and dedicated reactors
  - from 500 - 20,000 litres capacity
  - principally stainless steel or glass lined mild steel
  - Glycol cooling, hot oil and/or steam available
  - various overheads and receivers etc.

- Tank Farm - Bulk storage of raw materials and products.

- Solids Handling Equipment
  - centrifuges, dryers (including pressure/filter, rotary vacuum, ribbon, tray and fluidised bed)
  - grinding and milling etc.
Cyclopropyl Derivatives

- $R=H, \text{Alkyl}$
- $R=H, \text{Alkyl, Acetyl}$
Contract Manufacturing

• **Expertise**
  - Process development and scale up.
  - Statistical Process Control and Statistical Quality Control.
  - Expertise in handling amines, phenol, dimethyl sulphate, diethyl sulphate, isocyanates, hydrogen peroxide and mercaptans.

• **Rapid Solutions**
  - Rapid decision making capability and project implementation.
  - Flexible approach to meeting client needs
  - Sharing rewards from process improvements
### Contract Manufacturing

### Reaction Capabilities

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The challenge

To stop chemists thinking in terms of these.....

......and think in terms of........
The challenge

To stop chemists thinking in terms of these.....

......and think in terms of.........
Supercritical Processing at Thomas Swan

- Simple
- Safe
- Versatile

- Efficient
- Selective
- Clean

and therefore . . .

**ECONOMIC!**

Swan SCF® Process
Acknowledgements

- Thomas Swan & Co Ltd
- Dr SK Ross+group
- University of Nottingham
- Prof M Poliakoff + group
- Chematur Engineering
- NWA
- Johnson Matthey
- Purolite
- NWA
- VTT