Recycling study of the fiber stainless steel from grinding swarf by using supercritical fluids.

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Introduction

The by-product produced from steel manufacturing process

Swarf + Cutting oil

Specified Waste! Why? It’s has cutting oil over 10% of total weight.
Where was Swarf come from?

- Briquette Swarf: 670 ton/year
- Grinding Swarf: 1250 ton/year
Swarf Characteristics

- The mean size 150 μm of the fiber structure

- A fiber structure of Swarf is valued ten times more than same price metal materials because its manufacture is difficult and complex.

SEM micrograph of Swarf
Problems of the Current Disposal Method

- Low recovery rate for making steel ≈ 47 ~ 48%
- Produce of much fume because the swarf contains oil over 10wt% of total weight

The Swarf Recycling Methods

- Vacuum Thermal Extraction
- Solvent Extraction
- Supercritical Fluids Extraction
Advantages of the Supercritical Fluids Extraction

- No residual oil in grinding swarf
- Extracted oil can be reused without any refinement
- No deforming during extraction
- Environment-friendly and energy efficient
- Recycle of extraction fluid easily facilitated
- Adjustable solvent power

That’s great!
<table>
<thead>
<tr>
<th>Department of Chemical Engineering</th>
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</thead>
<tbody>
<tr>
<td><strong>Experiment</strong></td>
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<tr>
<td><strong>Pressure (bar)</strong></td>
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<tr>
<td><strong>Liquid phase</strong></td>
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<tr>
<td><strong>Gas phase</strong></td>
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<tr>
<td><strong>Supercritical Fluid</strong></td>
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<td><strong>Good solvent power</strong></td>
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<td><strong>No surface tension</strong></td>
</tr>
<tr>
<td><strong>Gas-like viscosity</strong></td>
</tr>
<tr>
<td><strong>Liquid like-density</strong></td>
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| **Temperature (°C)**              |
| **SOLID**                         |
| **LIQUID**                        |
| **GAS**                           |
| **31.06 (T_c)**                   |
| **73.77 (P_c)**                   |

- **Temperature** (°C): 
  - Above 31.06 (T_c): GAS
  - Between 31.06 (T_c) and 73.77 (P_c): LIQUID
  - Below 73.77 (P_c): SOLID

- **Critical point**
- **Gas phase**
- **Liquid phase**
Experiment Condition

**Carbon Dioxide**
- Supercritical Condition
  - $T = 30 \, ^\circ\text{C}$, $P = 10, 15, 20, 25, 30\text{MPa}$
  - $T = 40 \, ^\circ\text{C}$, $P = 10, 15, 20, 25, 30\text{MPa}$
  - $T = 50 \, ^\circ\text{C}$, $P = 10, 15, 20, 25, 30\text{MPa}$

- Subcritical Condition
  - $T = 80 \, ^\circ\text{C}$, $P = 5, 10\text{MPa}$
  - $T = 90 \, ^\circ\text{C}$, $P = 5, 10\text{MPa}$

**Propane**
- Supercritical Condition
  - $T = 100 \, ^\circ\text{C}$, $P = 5, 10\text{MPa}$
  - $T = 110 \, ^\circ\text{C}$, $P = 5, 10\text{MPa}$

- Material: 13.4g swarf
- Solvent: carbon dioxide, propane
Experiment Apparatus

1. CO₂ or C₃H₈ cylinder
2. High pressure pump
3. Cooling circulator
4. Pre-heater
5. Extraction vessel
6. Metal basket
7. Thermocouple
8. Magnetic stirrer
9. Air bath
10. Pressure transducer
11. Rupture
12. Back-pressure regulator
13. Separator
14. Rotameter
15. Dry gas meter
Mathematical model

Single parameter model with **linear desorption kinetics**

Mass balance in bulk phase in the extraction cell

\[
\frac{\partial C}{\partial t} + \nu \frac{\partial C}{\partial z} + \frac{1 - \varepsilon}{\varepsilon} \rho \frac{\partial q}{\partial t} = 0
\]

Linear desorption kinetics can be written as:

\[
\frac{dq}{dt} = -k_d q
\]

The initial condition is:

\[q = q_0 \quad \text{at} \quad t = 0\]

The desorption profile:

\[q(t) = q_0 e^{-k_d t}\]

The mobile phase can be considered as an irreversible process because of the lack of information on effective diffusivity of oil in SCCO\(_2\) phase and the adsorption isotherms.
The comparison of removal of oil in extraction vessel (case 2) with removal of oil from swarf (case 1) under 20MPa, 40 °C.
1. Carbon Dioxide

Grinding oil concentration at different $k_d$ values

<table>
<thead>
<tr>
<th>T(°C)</th>
<th>P(MPa)</th>
<th>$q_0$(g/g)</th>
<th>$k_d$(min⁻¹)</th>
<th>t(min)</th>
<th>$\rho_0$(g/ml)</th>
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<tbody>
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<td>1.474</td>
<td>0.00409</td>
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<td>1.474</td>
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<td>0.01037</td>
<td>0.871</td>
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</table>
Effect of Temperature

10MPa

25MPa
Effect of Pressure

30 °C

40 °C

50 °C
Effect of CO₂ flow rate

40 °C, 20MPa
2. Propane

At Subcritical Propane state

At Supercritical Propane state
SEM Micrographs of the Swarf after extracting

- Vacuum Thermal Extraction
- Solvent Extraction (n-Hexane)
- Supercritical CO$_2$ Extraction
- Subcritical C$_3$H$_8$ Extraction
- Supercritical C$_3$H$_8$ Extraction
The feasibility of supercritical extraction to recycle the stainless steel by removing grinding oil from grinding swarf was tested.

In this work, the extraction efficiency depends on temperature and pressure. Also, as solvent flow rate increased, the extraction efficiency is increased. The experiment results was predicted by applying a one-parameter mathematical model assuming linear desorption kinetics. The predicted value showed good agreement with experimental data.

We could know from the SEM for the oil removed swarf that the steel fiber was deformed and oxidized by vacuum thermal extraction. However, by using supercritical fluids as a solvent, we could not only remove cutting oil from raw swarf, but also preserve the fiber’s own characteristics of swarf effectively.