A Critical Assessment of Synthetic Lubricant Technologies for Alternative Refrigerants

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Introduction

- *iso*-Butane R-600a ($\text{C}_4\text{H}_{10}$)
- Carbon Dioxide R-744 ($\text{CO}_2$)
- Ammonia R-717 ($\text{NH}_3$)
iso-Butane R-600a (C₄H₁₀)
Mineral Oil Issues

• ISO 10 to 22 mineral oils commonly used for R-600a. However, some issues have been observed related to the excessive solubility of R-600a in mineral oil
  – Foaming
  – Oil slugging (solubility: MO > esters > PAGs)
  – Reduction in energy efficiency

• Diester lubricant technology offers several advantages
  – Excellent lubricity
  – Reduced oil solubility
    • Reduced foaming
    • Improved energy efficiency of up to 5 %
  – Biodegradability
Chemistry of Diesters and POEs

Diester

Alcohol — Acid — Alcohol

- Diesters are less expensive than POEs

Polyol esters (POE)

Acid

Acid — Alcohol — Acid

Acid

- POEs are more soluble than Diesters
R-600a Lubricant Circulation Test

![Graph showing the mass of oil collected over time for Diester and Mineral Oil.](image-url)
Carbon Dioxide R-744 (CO$_2$)
**CO₂ Lubricant Issues**

- **Oil Transport**
  - Oil Solubility

- **High Pressure / High Load**
  - Wear Performance

- **Higher Level of water in Gas and Oil**
  - Formation of carbonic acid from the reaction of carbon dioxide and water

\[
\text{CO}_2 + \text{H}_2\text{O} \leftrightarrow \text{O=C} \text{OH} \text{OH} 
\]

- Effectiveness of drier
Schematic of CO$_2$ Miscibility Behaviour

<table>
<thead>
<tr>
<th>Lubricant</th>
<th>Miscibility</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mineral Oil</td>
<td>Immiscible</td>
</tr>
<tr>
<td>PAO &amp; AB</td>
<td>Immiscible</td>
</tr>
<tr>
<td>Diester &amp; POE</td>
<td>Miscible</td>
</tr>
<tr>
<td>PAG</td>
<td>Partial</td>
</tr>
</tbody>
</table>

Polyol ester

- Two Phases
- One Phase

PAG

- Two Phases
- One Phase

Oil Concentration (wt%) vs Temperature °C
CO₂ / Lubricant Phase Inversion

Temperature in °C

Density in g/cm³

-30 -20 -10 0 10 20 30 40

0.5 0.6 0.7 0.8 0.9 1 1.1 1.2

PAG
POE
MO
AB

CO₂

Hagita et al, Kobe, December 2000
Overview of CO$_2$ Solubility

- POEs
  - Other Ester
    - PVEs
      - PAGs
        - ABs
          - PAOs
            - Mineral Oil

- Lower Solubility

- Higher Solubility
Vapour Liquid Equilibria Data: CO$_2$ with ISO 32 POE, Diester & PAG
Vapour Liquid Equilibria Data: CO₂ with ISO 100 POE
Overview of CO\textsubscript{2} Lubricants

- Mineral oil (MO)
  - Very poor miscibility and solubility
    - Oil return and heat transfer issues
  - Phase inversion
    - Oil separation issues

- Poly \(\alpha\)-olefin (PAO) & alkyl benzene (AB)
  - Experience with process gas applications
  - Poor miscibility and solubility
  - Phase inversion
Overview of CO\textsubscript{2} Lubricants

• Diester
  – Esters have a very high solubility
    • may need to use higher viscosity grades.
  – Hydrolytic stability
  – Have been used for a number of years in CO\textsubscript{2} process gas applications

• Polyol ester (POE)
  – As for diesters but greater stability and cost
Overview of CO$_2$ Lubricants

- Single end capped PAG
  - Have been used for a number of years in CO$_2$ process gas applications
  - High levels of water in the oil
    - Dielectric strength
    - Material issues (e.g. PET)
  - Stability ?
- Double end capped PAG
  - Work well in automotive applications and overcome many of the above problems
  - Greater stability and reduced moisture sensitivity when compared to single-end capped
Chemistry of Polyalkylene glycols (PAG)

Polyalkylene glycol (PAG) - non end-capped

Polyalkylene glycol (PAG) - double end-capped

- Polar components attract water

- Endcap

- Polar components attract water

\[= \text{Polar component} \]

\[= \text{Non-polar component} \]
CO₂ Lubricant Additive Issues

- **Wear**
  - High load may need addition of anti-wear additive

- **Copper Plating**
  - Are copper deactivators required?

- **Foaming**
  - Very high solubility of esters, in certain systems, may require use of anti-foaming agents
Overview of Oil Use

- Ester, PAGs, PAOs and blends of these with other oil are all under evaluation.
  - Double end-capped PAGs are approved and used for:
    - Automotive sector
    - Heat pumps
  - Polyol esters and diesters are used for:
    - Heat pumps
    - Industrial & Commercial compressors
    - Vending machines
Ammonia R-717 (NH₃)
Overview of Ammonia Lubricants

- Poor solubility of hydrocarbons in ammonia
  - Mineral oil, PAO, AB
- Esters react with ammonia to form gels
  - Therefore should not be used
- PAGs have good solubility with ammonia. Double end capped EO/PO PAGs used
  - Low water uptake
  - Inverse solubility
  - Improved compatibility with mineral oil
  - Excellent stability
Overview of Ammonia Lubricants

• Flooded evaporators - Hydrocarbons
  – Blends of PAO, AB and hydrocracked oils
  – Poor miscibility with ammonia
    • Low foaming
    • Low dilution

• DX systems - Double end capped PAGs
  – Reduced refrigerant concentration (1:50)
  – Excellent heat transfer
  – Cost effective system
Conclusions

• Chemistry can be modified to optimise
  – Solubility
    • Wear, foaming, oil transport, heat transfer etc.
  – Stability
    • Drain interval
  – Materials compatibility
• Oil selection criteria is often based on logistical issues
  – One oil for several refrigerants e.g. CO$_2$ and CNG
• Synthetics offer a number of advantages for use with alternative refrigerants
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