Thermally driven adsorption heat pumps: recent advancements and future technical challenges

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Problématiques Scientifiques et Technologiques dans les Procédés Frigorifiques et Thermiques à Sorption
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SUMMARY

① Basics
② Current market Situation
③ R&D priorities
  ① Novel Adsorbent Materials
  ① Adsorbent coatings
  ① Adsorption machine components
  ① Machine optimization and control
④ Recent advancement at CNR-ITAE
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Thermally Driven ADsorption Machines

Operating Principle

[Diagram showing the cycle of bed 1 and bed 2 condenser and evaporator connections]
Thermally Driven ADSorption Machines

PERFORMANCE AND DRAWBACKS

😊 Less studied and developed than liquid sorption
😊 Not a mature technology
😊 Few products on the market

Environmental aspect

😊 Can be efficiently driven by a heat source at a temperature as low as 60-80 °C
😊 Environmental friendly refrigerants (water)
😊 Silent operation
APPLICATIONS

HEAT SOURCES FOR ADSORPTION CHILLERS

- (Low-grade) waste heat recovery
- Tri-generation
- Air conditioning in vehicles or boats
- Solar cooling

Heat sources for adsorption chillers:

- Solar collectors
- District heating
- Automotive waste heat
- CHP units, process heat
- District heating

Heatsources
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Brief history of adsorption chiller development

1980 – 1990
Early studies and prototypes

1990 – 2000
No commercial products strong enough to survive, apart the Mycom silica gel/water chiller

2000 – today
Reliable products developed
(better heat transfer quality, materials, controls)

Specific Cooling Power ~ 5-10 kW/m³

Meunier, Guilleminot, Pons et al. in Paris (AC/Meth, Zeolite/H2O)
Tchernev in USA (zeolite/water)
Shelton in USA (AC/Ammonia)
Spinner in Perpignan (hygroscopic salts)
Cacciola and Restuccia in Italy (zeolite/water)
Groll in Germany (metal hydrides)
Alefeld in Germany (zeolite/water)
**Current market situation**

**Small size Units**

- **Vaillant**
  - zeoTHERM
  - VAS
  - heat pump
  - gas-fired
  - zeolite/water
  - 10 kW
  - Germany

- **Sortech AG**
  - ACS08-15
  - chiller
  - water-fired
  - silica gel/water
  - 8 kW - 15 kW
  - Germany

- **Invensor**
  - LTC10-18
  - chiller
  - water-fired
  - zeolite/water
  - 10-18 kW
  - Germany

- **SWAC-10**
  - chiller
  - water-fired
  - silica gel/water
  - 10 kW
  - China

*Before 2012*
Current market situation

**Small size Units**

- **SolabCool**
  - Chiller
  - Water-fired silica gel/water
  - 4 kW
  - Netherlands

- **eCoo**
  - Chiller
  - Water-fired silica gel/water
  - 12 kW
  - Germany

- **Vitosorp 200-F**
  - Heat pump
  - Gas-fired zeolite/water
  - 16 kW
  - Germany

- **AQSOA**
  - Chiller
  - Water-fired zeolite/water
  - 10 kW
  - Japan

- **heat pump**
  - Gas-fired AC/ammonia
  - 10 kW
  - Available in 2014
  - UK

**After 2012**
Current market situation

HIGH-CAPACITY CHILLERS

AdRef-Noa
chiller
water-fired
zeolite/water
105kW - 430kW
Japan

Ad3
chiller
water-fired
silica gel/water
35 to 600 kW
USA

NAK/NAK-C
chiller
water-fired
silica gel/water
50 to 430 kW
Germany

NUS-VEG
chiller
water-fired
silica gel/water
35 to 500 kW
Poland
The current market for solid sorption heat pumps is very small, due to:

- High capital costs
- Still too big and too heavy to compete with conventional systems
- Lower thermal efficiency and power density than liquid sorption systems

Advanced prototypes realized at:

Warwick University (UK)
ECN (NL)
SJTU (Ch)
CNR ITAE (IT)
Adsorption chillers/heat pumps development

Main actors involved

- Vaillant
- Viessmann
- Fraunhofer ISE
- Greenchiller.de

Asia

- Nagoya University
- Mitsubishi Plastics
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Future challenges

- Today a limited number of materials is used!
- New or modified adsorbents needed
- Stability over several thousand cycles

Materials

- Compact, lightweight, high surface area HEXs and adsorbent reactors
- Compact and low cost evaporator and condenser
- Coated adsorbent reactors

Components for adsorption machines

- Advanced control strategies
- Compact and modular system designs

Machine optimization control & integration
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Development of advanced adsorbent materials

The adsorbent material is a key-element of an adsorption machine

Initially, adsorption heat transformers were realized using not optimized adsorbents (Zeolite 4A, X, silica gel)

New generation of adsorption machines requires novel adsorbent materials with optimal adsorption properties

\[ \Delta W = \Delta W \]
“New” adsorbent materials

- Classical zeolites (4A, 13X, DDZ 70 UOP)
- Microporous silica gel (e.g. Fuji Davison type RD)
- Aluminophosphates (SAPO34, AQSOA FAMZ02 from MITSUBISHI Plastics)
- Porous Carbons (ammonia and alcohols adsorbate)

Composite Adsorbents «salt in matrix» (Selective Water Sorbents)
Modified Zeolites (dealuminated zeolites, MeAPO)
Metallic Organic Frameworks (MOFs) (Major trend)

The solution must be stable and cheap.
SWS-Selective Water Sorbents

<salt> ∙ n <sorbate>

<sorbate> = water, methanol, ethanol, ammonia

Ca(NO₃)₂ + 2 H₂O = Ca(NO₃)₂·2H₂O
BaBr₂ + 8 NH₃ = BaBr₂·8NH₃
LiCl + 3 CH₃OH = LiCl·3CH₃OH
LiBr + 3 C₂H₅OH = LiBr·3C₂H₅OH
SWS-Selective Water Sorbents

SORPTION CHARACTERISTICS

Water Uptake, \( w(\text{g} \, \text{H}_2\text{O}/\text{g} \, \text{dry sorbent}) \)

- SWS-2L 25 mbar
- SWS-1L 23.4 mbar
- SWS-1S 24.4 mbar
- Micro-Silica gel Grace 25 mbar
- Meso-Silica Gel KSK 25 mbar

Temperature, \( T \, (°C) \)

[Graph showing water uptake as a function of temperature for different sorbents.]
MOF-Metall Organic Frameworks
Commercially available MOFs: (BASF - Basolite®)

**Basolite® C300 (HKUST-1):** Copper-based MOF, trimesate trianions as linkers. It is also known as Cu(BTC).

<table>
<thead>
<tr>
<th>Property</th>
<th>Basolite C300 (HKUST-1)</th>
<th>Basolite F300</th>
</tr>
</thead>
<tbody>
<tr>
<td>Particle size distribution</td>
<td>15.96 μm</td>
<td>~ 20 μm</td>
</tr>
<tr>
<td>Surface area</td>
<td>BET surf. area 1500-2100 m²/g</td>
<td>BET surf. area 1300-1600 m²/g</td>
</tr>
<tr>
<td>Bulk density</td>
<td>0.35 g/cm³</td>
<td>0.35 g/cm³</td>
</tr>
<tr>
<td>Cost</td>
<td>~ 95 €/(10 g)</td>
<td>~ 85 €/(10 g)</td>
</tr>
</tbody>
</table>

**Basolite® F300:** Iron-based MOF, trimesate trianions as linkers.
**MOF-Metall Organic Frameworks**

**STABILITY ISSUE**

![Graph showing water uptake vs temperature for different adsorption steps.]

ΔW = -6 wt %

**BASOLITE C-300**: Water adsorption capacity reduction after 5 ad/desorption steps!
Database of Adsorbent Materials

A DATABASE of adsorbent materials was created within the IEA - Annex 34 “Thermally Driven Heat Pumps for Heating and Cooling”

Databasing of adsorbents is continuing within the new Annex 43 “fuel driven sorption heat pumps”.

![Graph showing water uptake versus temperature for various adsorbents]
### Overall comparison of adsorbents

<table>
<thead>
<tr>
<th>Material</th>
<th>Ability to be regenerated at low T</th>
<th>Maximum adsorption capacity</th>
<th>Hydrothermal stability</th>
</tr>
</thead>
<tbody>
<tr>
<td>AQSOA – Z02</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>NaY UnionCarbide</td>
<td>-</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>NaY CBV-100</td>
<td>-</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>DDZ70</td>
<td>-</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Fuji Davidson</td>
<td>+</td>
<td>-</td>
<td>+</td>
</tr>
<tr>
<td>Basolite C300</td>
<td>+</td>
<td>+</td>
<td>-</td>
</tr>
<tr>
<td>SAPO 34</td>
<td>+</td>
<td>+</td>
<td>-</td>
</tr>
<tr>
<td>Siogel</td>
<td>+</td>
<td>-</td>
<td>+</td>
</tr>
<tr>
<td>Basolite F300</td>
<td>+</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

**AQSOA Z02 is the best material for low T application**
SUMMARY

Basics

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Novel Adsorbent Materials

Adsorbent coatings

Adsorption machine components

Machine optimization and control

Recent advancement at CNR-ITAE
Intensification of the heat transfer quality in adsorbers is a key-factor for development of dynamically efficient adsorption refrigeration and heat pump systems.

### Heat Transfer Characteristics

<table>
<thead>
<tr>
<th>Type</th>
<th>Heat Transfer Quality</th>
<th>WHTC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Granular (loose grains)</td>
<td>$\lambda_{eq} = 0.09 \text{ W/m K}$</td>
<td>$\lambda_{eq} = 10 \text{ W/m K}$</td>
</tr>
<tr>
<td>Consolidated (mechanically compressed)</td>
<td>$\lambda_{eq} = 0.4 \text{ W/m K}$</td>
<td>$\lambda_{eq} = 0.6 \text{ W/m K}$</td>
</tr>
<tr>
<td>Coated HEXs (dip coating) (direct synthesis)</td>
<td>$\lambda_{eq} = 10 \text{ W/m K}$</td>
<td>$\lambda_{eq} = 20 \text{ W/m K}$</td>
</tr>
<tr>
<td></td>
<td>$\lambda_{eq} = 100-400 \text{ W/m}^2 \text{ K}$</td>
<td>$\lambda_{eq} = &gt;1000 \text{ W/m}^2 \text{ K}$</td>
</tr>
</tbody>
</table>
Coated adsorbers

DEVELOPMENT STEPS

Grains - coating - synthesis

Performance enhancement

Development steps

150-times enlarged

designed by Witte, K.T.
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Utilization of compact, lightweight, high surface area HEXs is mandatory for realization of dynamically efficient adsorbent beds

**Components for Adsorption Machines**

Optimization of the HEX design
- (H&M transfer properties, thermal mass, flow field)

Optimal configuration of the “adsorbent – HEX” (AdHex) unit
- Optimal adsorbent mass per 1 m² of HEX
- Optimal size of the adsorbent

Corrosion
- Is it a real issue?
- Coatings offer a barrier effect

**OPEN ISSUES**
Increased dynamic efficiency of the AdHex unit asks for compact and efficient evaporator and condenser.

- The heat transfer between tube wall and refrigerant and between tube wall and chilled water circuit have to be increased through:
  - Increasing of the specific surface area
  - Improvement of the heat transfer coefficient
  - Increasing the volume flow and the turbulence inside the tube
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Early studies on improved cycles for high regeneration T

Today the trend is to use low regeneration T.

Most developers are using the simple cycle, especially for low temperature applications.
Machine optimization

Management Strategy

Identification of the optimal cycle time for a given operating condition

Very short duration of the isosteric stages

Desorption rate is faster than adsorption, due to higher temperature and vapor pressure

Up to 30% COP increasing
Basics

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ITAE’s Coating Technique

Inorganic (clay-based) binder

Organic binder – in collaboration with UNIME
Preparation of the Coated Adsorbers

Coating technique: The original lamella HEX in aluminum was coated by pouring a SAPO-34 zeolite – polymeric binder (5 wt.%) solution through the lamellas ...

...drying at room temperature, then heating at 120 °C in oven.

• binder thermally resistant in the T-range of application
• coating thickness can be controlled (0.1-0.7 mm) by multi-layer deposition
The prepared adsorbers
ITAE coating performance evaluation

HEX filled with grains → Coated HEX

- **Cycle time, min**: 10 → 5
- **Wall Heat Trans. Coeff., W/m²K**: 10 → 100
- **Specific cooling power W/kg_{ads}**: 20 → 300
Adsorption Chiller for Automotive Applications

STRALIS 520

- Overall volume: 150 L
- Overall weight: 59 kg
- Chilling capacity: 2,3 kW
- Min. air temperature: 9 °C
- COP: 0,2
- Regeneration temp.: 80 °C
- Adsorbent: Zeolite

- SCP: up to 600 W/kg
- Very competitive weight considering commercial products!
- Volume density higher than 10kW/m³!
## Solar Cooling System for Residential Application

<table>
<thead>
<tr>
<th>Technology of solar thermal collectors</th>
<th>Evacuated tubes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of evacuated tubes</td>
<td>90</td>
</tr>
<tr>
<td>Total thermal collectors area [m²]</td>
<td>9.6</td>
</tr>
<tr>
<td>Heat storage volume [m³]</td>
<td>0.5</td>
</tr>
<tr>
<td>Tilt angle [°]</td>
<td>20</td>
</tr>
<tr>
<td>Gas Boiler nominal Power [kW]</td>
<td>20</td>
</tr>
<tr>
<td>AHP cooling Power [kW]</td>
<td>8</td>
</tr>
<tr>
<td>Required Cooling Load [max, kW]</td>
<td>2.43</td>
</tr>
<tr>
<td>Cold delivering system</td>
<td>Flat radiant panel</td>
</tr>
<tr>
<td>Overall radiant surface [m²]</td>
<td>28</td>
</tr>
</tbody>
</table>
Test facility for Trigeneration Systems

- 75 kW heat source up to 99 °C
- 15 – 50 °C discharging T ability
- 2 – 20 °C Low T simulation ability
- 1500 litres High Temperature Storage
- 1000 litres Low Temperature Storage
- Variable flow hydraulic pumps
- High accuracy sensors
- Pressure drop measurements
- Full automatic operation (overnight tests!)
- UNI-EN 12977 – III (possible tests on storages for solar application)

Testing of chillers up to 35-40 kW cooling
Thermal energy storage test (max charging rate 75 kW – discharging 63 kW)
ICE or Fuel cell Cogenerator
Conclusions

Development will be mainly technological

- Better materials
- Enhanced heat transfer/HEX
- Optimized management strategy
- Techno-economic optimization

Scientific issues

- Material science (adsorbents, etc.)
- From thermodynamic to adsorption dynamics
Thank you!