Molten Salt Reactors in Gasification and Gas Purification

Presenting author:
Ville Nikkanen

Place:
6th International Freiberg Conference on IGCC & XtL Technologies
Dresden, Germany

Time:
19th of May 2014
Table of Contents:

- Applications and Research
- Tar Cracking Process in Molten Carbonates
- Properties of Molten Carbonates
- Conclusion
- Contacts and Additional Information
1. Applications for Molten Salts and Carbonates:

- **Applications for molten salts**
  - Different applications in which liquid media and high temperatures are needed or beneficial
  - Few industrial applications e.g. in $\text{SO}_2$ oxidation in $\text{H}_2\text{SO}_4$ production.
  - Carbonate melts are less used in the industry

- **Research fields**
  - Molten Salt Fuel Cells ($\text{CO}_3^{2-}$)
  - Direct gasification molten salts (1970’s)
  - Thermal energy storing in solar thermal power plants ($\text{NO}_3^-$)
  - Cooling in 4th generation nuclear power plants (Exotic mixtures)
  - Gas purification ($\text{CO}_3^{2-}$)
  - **Molten carbonates in reality**
1. Applications in Gasification:

- Molten salt reactor integration with a gasifier
  - Small or medium scale
    - Fluidized bed gasifiers for gas engines
      - High temperature gas is used to heat the Molten Salt Reactor
      - Tars are partly eliminated
  - Tar cracking before heat recovery and gas engine
  - Less maintenance in downstream processes
  - Almost complete (strong-) acid gas removal
    - Less corrosion in heat recovery
    - $\text{H}_2\text{S}$ and other weaker acids are only partly removed
2. Molten Carbonate Gas Purification Process:
3. Properties of Molten Carbonates:

- Benefits of molten salt gas purification
  - Eliminates and separates partially several impurities at one stage
  - High temperatures and pressures can be used
  - High heat transfer rates and high thermal capacity
  - Simple structure
  - No solid-solid blockages – carbon formation less harmful

- Challenges
  - Complex chemistry
  - Transformation of mixture during operation
  - High corrosivity
  - Evaporation of salts at highest temperatures
  - Pressure drop

M. Kawase and M. Otaka, *Removal of \( H_2S \) using molten carbonate at high temperature*, Waste Management 33, 2013
2. Tar Cracking:

- **Catalytic window**
  - Molten carbonates have a slight catalytic effect in tar cracking

![Graph showing the conversion rate of benzene vs. temperature. The graph illustrates the catalytic effect of molten carbonates compared to thermal processes.](image-url)
3. Physical Properties of Molten Carbonates:

- **Viscosity**
  - Viscosity of molten carbonates is low (2-5 mPa·s) at high temperatures (800°C)
  - Low viscosity increases the contact between the syngas and molten carbonates and lowers the pressure drop over the reactor.

- **Surface and interfacial tensions**
  - Surface tensions of molten carbonates are high (200 mN/m)
  - High surface tension decreases the gas-liquid contact between syngas and molten carbonates

- **Solubility of compounds**
  - Gas solubilities are reported to be low, which decreases also contact
  - Metals dissolve to molten salts, which might increases catalytic effects

3. Reactivity of Carbonates:

- Reactivity and stability of Molten carbonates
  - Alkali carbonates are the most stable carbonates
    - Decomposition to oxides only at very high temperatures
    - Low tendency to reduction

- Chemical absorption
  - Carbonates react with different impurities
    - HCl, HBr, HF (fast reaction)
    - H$_2$S (equilibrium)
    - HCN (equilibrium)
  - Chemical absorption $\leftrightarrow f (T, P, p_{gases}, C_{MCO3}, C_{Solid \ carbon}, C_{Impurities})$
3. Exhausted Salt and Regeneration:

- Exhausted salt
  - Particles and chemical impurities affect to properties
    - Silica ashes and particles increase viscosity
    - Chemical absorption increases the melting point
    - Carbon content increases hydrogen sulfide absorption
    - Corrosivity of molten salt increases

- Utilization of exhausted salt?
  - Probably waste
  - Recovery of potassium and lithium
    - Sodium carbonate ~ 300–800 €/ton
    - Potassium carbonate ~ 800–1 200 €/ton
    - Lithium carbonate ~ 5 000–10 000 €/ton

4. Conclusion:

- **One possible approach for syngas cleaning**
  - Operates at high temperatures
  - Eliminates or separates partly several harmful compounds in one step
  - Possibly great potential in gas purification

- **Challenges**
  - Corrosion
  - Complex chemistry and increase of melting point during operation
  - Regeneration of salt
    - Potassium and especially lithium are expensive
  - Complete purification is not achieved
    - Vulnerable downstream processes are not applicable without deeper purification
5. Contacts and additional information:

- **Contact:**
  - ville.nikkanen@ict.fraunhofer.de
  - www.ict.fraunhofer.de
  - stephan.seidelt@eifer.org
  - http://www.eifer.uni-karlsruhe.de

- **Patents:**
  - EIFER holds a patent on this technology

- **Funding:**
  - European 7th framework: Fuel From Waste
Thank you
for your attention.

Ville Nikkanen
ville.nikkanen@ict.fraunhofer.de