A new hydrate based process for drying liquids

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Abstract:
Clathrate hydrates are crystalline solid structures formed by entrapping a small gas or liquid molecule within a water molecule cage. Research not only focuses on inhibition of hydrate formation to prevent blocking of natural gas pipelines, but also on its potential as a separation method. Applications include separation of CO₂, CH₄, H₂S, H₂, N₂, and desalination. We present a novel process for drying a high-temperature hydrate former: chlorine. Chlorine with more than 20 ppm water content severely corrodes stainless steel, which requires use of expensive tantalum. Here, we dry liquid chlorine in a rotor-stator spinning disc unit (RSSD), which has heat transfer coefficients up to 10 kW/m²/K, independent of flow rate [1]. The liquid chlorine is cooled below the hydrate formation temperature of 28 °C. The lighter hydrates are separated from the dry liquid chlorine in the centrifugal force field in the unit. The hydrates are consecutively melted to form liquid water, liquid (wet) chlorine two-phase flow which is also separated in the centrifugal force field. The wet liquid chlorine is recirculated. Benefits of this novel drying process are (1) compactness of the RSSD heat exchanger, minimizing tantalum investments, (2) blocking of the equipment by sticky hydrates is prevented by the rotation, and (3) no chlorine contamination by drying agents, e.g. sulphuric acid or zeolite.

The water concentration is measured in batch experiments (50 mL) with dichloromethane (DCM), as a model compound for liquid chlorine. The initial water content and cooling temperature are varied to evaluate the influence of supersaturation and supercooling. Temperature of -10 °C results in a shorter induction time (20 min) of hydrate formation and thus faster water removal rate (equilibrium reached after 40 mins) in comparison with temperature of 0 °C (induction time - 1.5 h; equilibrium reached after 2h). Higher heat transfer rates by increased stirring (500 RPM) accelerate water removal, with equilibrium water content reached instantaneously at -10 °C. The RSSD experiments are performed at residence times of 36 s and 57 s, -7 °C and 0 °C, and 0-1000 RPM rotation speeds. The same trends as in the batch experiments are found: lower temperature, increased rotation, and increased residence time enhance the performance. Equipment blocking was occasionally found at 0 RPM only.

In conclusion, the results show that the RSSD heat exchanger facilitates an elegant, energy-efficient water removal process that can be applied to removal of trace amounts of water from hydrate forming liquids.

Reference 1:
Reference 3:
Reference 4:

Highlight 1: Elegant process that can be applied to water removal from hydrate forming liquids.
Highlight 2: No blockage of the equipment by sticky hydrates due to high shear force caused by rotation
Highlight 3: High heat transfer in the compact RSSD heat exchanger minimizes material investments.