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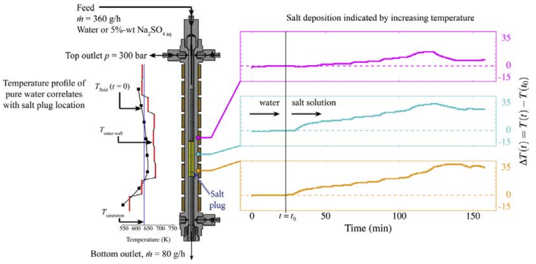
Investigation of Na_2SO_4 removal from a supercritical aqueous solution in a dip-tube salt separator

S. Viereck[a], Z.R. Jovanovic[b,*], A. Haselbacher[b], A. Steinfeld[b]

[a] Solar Technology Laboratory, Paul Scherrer Institute, Villigen PSI, CH-5232 Villigen Switzerland
[b] Department of Mechanical and Process Engineering, ETH Zürich, Sonneggstrasse 3, CH-8092 Zurich Switzerland

GRAPHICAL ABSTRACT



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ABSTRACT

Solar-driven hydrothermal gasification is an efficient process to exploit the energetic potential of biomass containing high amounts of water. This process requires effective removal of the type-2 salts from the feedstock as their precipitates can plug the equipment and poison the gasification catalyst. This work investigates the effect of the axial temperature profile on type-2 salt deposition in a dip-tube salt separator operated with an aqueous Na_2SO_4 solution as model feed and presents a method for online detection and monitoring of the growth of the deposits. Our results suggest that preventing the salt deposition at the wall of the separator by controlling the axial temperature profile is not possible. The online monitoring of the salt deposition is thus indispensable for scheduling the timely removal of the salt deposits.

1. Introduction

Hydrothermal gasification (HTG[1]) offers the potential for efficient production of methane and hydrogen from biomass containing large amounts of water (75%-wt. and above) [1,2]. Such feedstock is not suitable for conventional thermal gasification processes [3–5] because the energy required for drying the feedstock decreases the energy efficiency of these processes to impractical levels [6,7]. Drying of the feedstock may be circumvented by gasifying under hydrothermal conditions (p = 300 bar and T = 673–773 K) [1,8] to maintain the water in liquid or supercritical state. To increase the fuel yield even further, the required process heat can be supplied from concentrated solar power [9].

The solar-driven HTG process combines (1) a solar trough concentrator for heating a heat-transfer fluid (HTF) to temperatures in the range of 573–873 K, (2) a thermal energy storage for storing the solar energy and supplying the HTF in the absence of sufficient solar irradiation, and (3) an HTG plant [9]. The HTG plant comprises three main unit operations: (a) compression of the biomass feedstock, (b) superheating of the compressed feedstock to hydrothermal conditions, and

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* Corresponding author.
E-mail address: zjovanovic@ethz.ch (Z.R. Jovanovic).

[1] HTF: Heat-transfer fluid, HTG: Hydrothermal gasification, ID: internal diameter, MFC: Mass-flow controller, MTC: Multipoint thermocouple, OD: outer diameter, PID: Piping and instrumentation diagram.

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(c) catalytic biomass gasification [2]. As the solvation properties of water under hydrothermal conditions are similar to those of non-polar solvents such as hexane [1], the salts contained in the feedstock separate in the superheater: some separate into a dense salt brine and a salt-lean phase (type-1 salts such as NaCl, K_3PO_4, or KNO_3) while some precipitate as solids (type-2 salts such as Na_2SO_4, K_2SO_4, or Na_2CO_3) [10]. If not removed prior to gasification, the separated salts can lead to plugging of process equipment, fouling of heat-exchanger surfaces, and poisoning and fouling of the gasification catalyst [1]. Due to the importance of salt separation, the superheater is thus more commonly referred to as the salt separator.

As the salt separator is also the process step with the highest energy demand [7,9,11], it is the preferred point for integrating solar energy into the HTG process. The strategy to transfer the solar energy stored in the HTF to the salt separator has to be chosen such that the resulting temperature profile inside the salt separator drives an effective separation and removal of the salts. Based on the temperature profile reported by Schubert et al. [12] to be effective for the separation of type-1 salts, our previous work [13] discusses suitable heat-exchanger strategies for dip-tube salt separators. This type of separator, initially proposed by Hong et al. [14], consists of a vertically aligned cylindrical pressure vessel into which the salt-containing feed is introduced through a dip tube and heated to hydrothermal conditions through the outer walls of the separator. For type-1 salts, the dense salt brine formed under hydrothermal conditions collects in the colder bottom part of the salt separator where it is withdrawn. For this kind of separation, the dip-tube separator configuration is a particularly attractive option due to its simple design and operating principle.

Ideally, the dip-tube salt separator could also be applied for the separation of type-2 salts as precipitated salt particles would settle down to the colder bottom part of the separator, where they would redissolve in subcritical water and also form a brine. In reality, however, Peterson et al. [15,16] reported that type-2 salts deposit at the inner wall of the salt separator. Schubert et al. [17] also reported that type-2 salts plugged the salt separator. This suggests that the dip-tube salt separator cannot be employed in the HTG of low-cost, abundantly available feedstock such as algae, manure, or sewage sludge that contain type-2 salts [1,18,19]. However, neither Peterson et al. nor Schubert et al. investigated how the axial temperature profile inside the salt separator impacts the deposition and re-dissolution of precipitated salt particles. The first objective of this work was thus to explore the effect of the axial temperature profile on salt deposition.

If salt deposition cannot be avoided, build-up of salt deposits inside the separator should be detected to schedule their removal before they obstruct the flow through the separator. Peterson et al. [15,16] explored using neutron radiography to visualize the deposition of type-2 salts in a dip-tube salt separator. In spite of providing detailed information about the separation and deposition of salts, this method is rather impractical and expensive when applied during continued operation as it requires a neutron source and construction of the salt separator from special materials that do not attenuate neutron radiation considerably. Rogak and Teshima [20] reported a practical and cost-effective method for the detection of salt build-up at the inner wall of a tubular reactor that is based solely on the temporal evolution of the temperatures at the outer reactor wall. The second objective of this work was thus to adapt and implement the method of Rogak and Teshima to a dip-tube salt separator and evaluate its performance. In addition to experimentally demonstrating the applicability of this method, we used a radial heat-transfer model to correlate the variations in the outer separator-wall temperatures to an increase in the overall heat-transfer resistance induced by the growing salt deposit.

2. Experimental

2.1. Feed preparation

All the experiments in this work were performed with a 5%-wt. aqueous Na_2SO_4 solution because of its well-characterized phase behavior [10,21,22]. The solution was prepared by dissolving anhydrous Na_2SO_4 powder (VWR International GmbH, Switzerland) sieved through a 600 μm mesh sieve into deionized water having an electrical conductivity <5μS/cm. After vigorously shaking the container filled with the salt solution, the container was placed in an ultrasonic sound bath (Telsonic Ultrasonics TPC-280, Telsonic AG, Switzerland) for 15 min to dissolve the remaining salt crystals and release the air remaining in the water.

2.2. Experimental set-up

The piping and instrumentation diagram (PID) of the experimental set-up is shown in Fig. 1.

The central element of the set-up is the salt separator (SA-2-01[2]) fabricated from Zircaloy-2 by SITEC-Sieber Engineering AG (Maur, Switzerland). As shown by Fig. 2a, the separator is a 444 mm high, 30 mm outer diameter (OD)/12 mm internal diameter (ID) vertically mounted cylindrical vessel. The salt solution is introduced from the top through a 78 mm long, 0.76 mm ID/1.59 mm OD dip tube made of 304 stainless steel. A multipoint thermocouple (MTC, manufactured in-house) is used to measure the temperature profile along the centerline of the salt separator. The MTC comprises ten 0.25 mm K-type thermocouples of different lengths (TTR-2-10–TTR-2-19) bundled together in a 3.1 mm OD thermowell (measurement points are indicated in Fig. 2a & b). The MTC's tip is placed 10 mm below the exit of the dip tube. The salt separator is heated with nine cylindrical electrical heating bands (H-2-01–H-2-09, LCS Isotherm, Germany), each delivering a heating power of up to 210 W at a maximum temperature of 723 K. Each heater is equipped with a K-type thermocouple (TTR-2-01–TTR-2-09) (see Fig. 2b) measuring the temperature at the heater/salt-separator interface (i.e., the outer separator wall in contact with a heater). The heaters are controlled independently in either manual or automatic mode. In the manual mode, a specific power input is assigned to each heater; this was the preferred mode of operation since the thermocouple in the heating element could then be used detect salt deposition. In automatic mode, the power supplied to each heating element is adjusted to maintain a set-point temperature at the heater/separator interface. In either of the modes, the electrical power delivered to each heating element is modulated via a phase-onset controller Kemo M012 and a direct current and pulse converter M150 (Luedeke Elektronik, Germany).

An HPLC pump (Pump-1-01, Waters 515, Waters AG, Switzerland) was used to pump the feed from the feed container (Tank-1-01 or Tank-1-02) into the salt separator. The flow rate of the feed was measured by the loss-in-weight of the feed container placed on a calibrated balance (Balance-1-01, Kern PBS, Kern & Sohn GmbH, Germany). The flow rate of the (nominally) salt-rich stream leaving the salt separator at the bottom outlet was controlled using a mass-flow controller (MFC, Liqui-Flow-4-01, Bronkhorst Liquiflow L29, Bronkhorst AG, Switzerland). The (nominally) salt-lean stream leaving the salt separator at the top was collected in a container placed on a second balance (Balance-3-01, Bosch BSG, Bosch Wägesysteme GmbH, Germany). The flow rate of the top-outlet stream was determined from the recorded weight-gain of the container over time. The pressure in the separator was adjusted at the top outlet by a manual backpressure valve (V-3-04, Tescom Backpressure regulator, Tescom GmbH & Co. KG, Germany).

Data acquisition and control were performed with Labview

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[2] The label refers to the PID in Fig. 1.