



# A novel salt separator for the supercritical water gasification of biomass



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## ABSTRACT

The production of synthetic natural gas (SNG) via supercritical water (or hydrothermal) gasification (SCWG or HTG) offers the possibility to exploit the energetic content of biomass with a high water content. Separation and recovery of inorganic constituents present in the feed stream is crucial, as these constituents can lead to blocking of the plant, and to fouling and poisoning of the gasification catalyst. In addition, the recovery of salts offers the potential of producing a fertilizer as a valuable by-product.

A new salt separator design for the SCWG process was tested with two different setups using model solutions with water/2-propanol/Na<sub>2</sub>SO<sub>4</sub>/K<sub>2</sub>SO<sub>4</sub>. The separation and recovery efficiency proved to be superior compared to the previously used salt separator. The sulfur recovery increased by a factor of 3.5–7 and the sulfur accumulation decreased by a factor of 2–10 using the novel design.

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## 1. Introduction

Synthetic natural gas (SNG) produced from high-moisture biomass is a carbon dioxide neutral alternative to fossil fuels. At the Paul Scherrer Institute (PSI) a process was developed [1] that uses hot, compressed water as process medium. Energy intensive drying of the biomass feed is thus avoided. The process consists of mainly three steps: heating up of the feed to supercritical water conditions, the salt separation, where the inorganic constituents of the biomass are removed, and a catalytic gasification in supercritical water. The latter step uses a Ru/C catalyst and the methanation is carried out at pressures and temperatures above the critical point of pure water ( $T_C = 374\text{ °C}$ ,  $p_C = 22.1\text{ MPa}$ ). The inorganic constituents of the biomass feed provide some challenges as they can lead to blocking of the plant as well as to fouling and poisoning of the catalyst. Hence the salts have to be separated from the process stream prior to gasification. Additionally, a recovery of the salts provides the opportunity to use them as fertilizer in biomass production; thus making the whole process more economical and closing nutrient cycles.

Several studies with model substances as well as with real biomass have been carried out in our group. Schubert et al. [2–5]

studied the separation and recovery performance of the KONTI-2 and the SALSAN test rigs, using model salt solutions as feedstock. Their main finding was that so called type 2 salts, which exhibit a discontinuous solubility line and hence precipitate as a solid, are the most problematic salts to separate and recover. Type 1 salts, with a continuous solubility line from the critical point of pure water to the critical point of pure salt, could be efficiently separated and recovered from the process stream.

The original salt separator design used by Schubert et al. [2–5] consists of a vertical pressure vessel with a dip-tube through which the preheated feed is introduced into the vessel. The preheated feed stream mixes quickly with the contents of the salt separator, held at supercritical water conditions. Ideally, the salts from the feed separate and accumulate at the cooler bottom of the salt separator, where they re-dissolve in subcritical water and can be withdrawn as concentrated brine. The organic fraction of the feed dissolves in the hot compressed water and is fed to the catalytic reactor through an outlet at the top of the salt separation vessel (Fig. 1).

Another study on salt precipitation and scaling prevention in a flow reactor using ternary salt solutions was carried out by Makaev et al. [6]. They also used a vertical reactor, but with the feed inlet at the bottom of the vessel and just one outlet at the top. The objective of this study was to avoid the formation of a solid phase by adding type 1 salts to a solution initially showing type 2 behavior.

Earlier studies [7–9] on salt separation and precipitation were related to the Supercritical Water Oxidation (SCWO) process and

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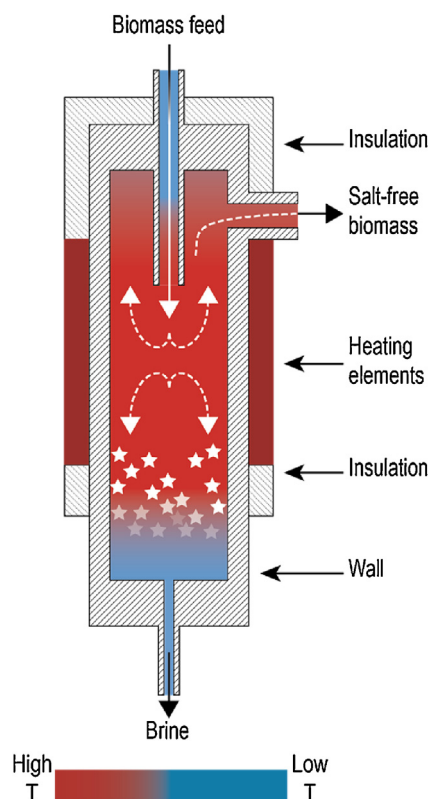


Fig. 1. Schematic of the salt separation and recovery in the original outline of the salt separator as used by Schubert et al. [2–5]. Stars represent precipitated salt.

dealt with the solubility of salts in water above the critical temperature and pressure of pure water, as well as with crystallization processes which occur under these conditions. Several types of salt separators for the SCWO process have been developed in order to solve the scaling problems caused by precipitating salts [10,11].

The main difference between using such a salt separator for SCWG instead of SCWO is the mode of heat supply. In SCWO heat is provided homogeneously inside the salt separator by the oxidation reactions, whereas in SCWG the heat is provided by an external source via heat transfer from the walls of the salt separator.

In the present study we tested a new salt separator design and compared it to the one used by Schubert et al. [2–5]. In this new design, the feed is introduced through a riser tube from the bottom of the reactor. We investigated the new salt separator design in two different configurations, using model solutions and real biomass. The results showed a significantly improved salt separation efficiency compared to the dip-tube salt separator.

## 2. Conceptual idea

The main idea behind the salt separation vessel is to make use of the unique properties of hot compressed water. The solubility of organics increases dramatically [12] with increasing temperature as the static permittivity of water decreases under such conditions [13]. For electrolytes, this leads to a reduced solubility (see e.g. Fig. 3 in [14]).

In the salt separator design used in previous studies in our group, [2–4,15,16] the preheated feed stream was injected into the upper hot zone of the reactor. This caused several problems, such as the deposition of precipitated salts and the formation of coke.

Our new design ‘inverts’ the old one, featuring a riser tube, which injects the cold feed at half-height into the salt separation vessel. The lower part of the salt separator is kept at temperatures below

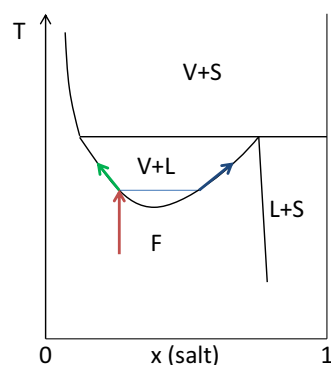


Fig. 2. Sketch of an isobaric cross-section of a phase diagram of type 1a. F: one-phase fluid; V: vapor phase; L: liquid phase; S: solid phase.  $x$ : molar fraction of salt in the mixture. (For interpretation of the references to colour in the text, the reader is referred to the web version of this article.)

374 °C. At these conditions, the salts stay dissolved. Towards the upper, hotter end of the separator, the feed starts to separate into a dense salt-rich phase (or a solid, in the case of a type 2 salt) and a less dense salt-lean phase. The organic phase also rises to the top and dissolves in the less dense phase as the solubility of non-polar species in water increases as water reaches temperatures above its critical point. The less dense phase, consisting mainly of water and organics and being depleted in salts, rises further towards the top of the salt separator where it is withdrawn and fed to the gasification reactor.

This idea can be visualized in an isobaric cross section through the phase diagram of a typical type 1a salt (Fig. 2). As the temperature of the salt solution rises upon injection into the salt separator (red arrow in Fig. 2), it separates into a salt-rich liquid phase (blue arrow in Fig. 2) and a salt-lean vapor phase (green arrow in Fig. 2). The vapor phase rises in the separator due to buoyancy, whereas the heavier liquid phase starts to accumulate at the bottom.

For a type 2 salt (Fig. 3) the precipitation of the solid salt happens as soon as the temperature crosses the solubility line (red arrow in Fig. 3). As the solubility is highly related to the static permittivity and hence also to the density of the fluid, this precipitation takes place around the pseudo-critical point (in terms of pure water), where the density of the fluid drops rapidly. Ideally, the formed particles settle down to the subcritical zone of the vessel where they re-dissolve in subcritical water. The virtually salt-free vapor phase (green arrow in Fig. 3) rises and leaves at the top of the salt separator. The use of a non-preheated feed enhances the effect of having a lower temperature at the bottom of the salt separator.

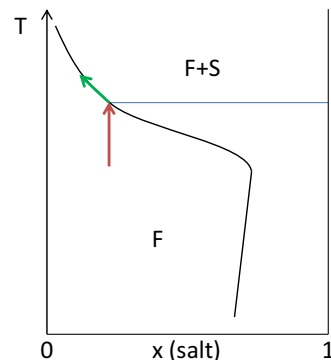


Fig. 3. Sketch of an isobaric cross-section of a phase diagram of type 2 above the pressure of the lower critical endpoint  $p_c$ . F: one-phase fluid; S: solid phase.  $x$ : molar fraction of salt in the mixture. (For interpretation of the references to colour in the text, the reader is referred to the web version of this article.)

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