Technology Offer

Exergy Efficient Chlorine Separation

Ref.-No.: 1402-5465-LC

Three novel processes to separate Cl_2 from unconverted HCl in the anode outlet stream of a electrochemical gas-phase reactor were developed at the MPI for Dynamics of Complex Technical Systems. The novel processes lead to a higher reaction yield in gas-phase reactor and have an reduced energy demand compared to the Bayer UhDenora state-of-the-art process.

Background

Chlorine is employed in the the industrial production of plastics, sanitary and medical products as well as organic solvents amongst others. Interestingly, one third of all substances produced with the aid of Cl_2 do not contain Cl_2 themselves and 50 % of the employed Cl_2 is being discharged in form of side products like HCl or chloride salts. As the market for hydrochloric acid is saturated, recycling of HCl by means of its electrochemical oxidation to Cl_2 is favourable.

In an electrochemical gas-phase reactor gaseous HCl is lead to an anode at a membrane permeable for protons. An anode outlet stream comprising Cl_2 and unconverted HCl is formed by oxidation of the HCl at the anode, whereby the protons diffuse through the membrane to a cathode and react with a cathode gas comprising O_2 or an O_2-comprising gas, thereby forming water. The cell voltage of this gas-phase reactor is 0.97 V at 4000 A/m2 and 1.09 V at 5000 A/m2, which makes this novel reactor significantly more efficient than the current state-of-the-art liquid phase reactor in the Bayer UhDenora process. Subsequent to the gas-phase reactor, Cl_2 is separated from unreacted HCl in the anode outlet stream.

Three novel separation techniques were developed which can be combined with the electrochemical gas-phase reactor. In the following these three separation techniques are described in detail. As a benchmark for evaluating their performance, the currently most energy-efficient industrially employed process from Bayer and UhDenora was chosen, which employs a liquid phase reactor. It is shown that the energetic advantage of the gas-phase reactor can even be extended on the overall process level, taking said separation strategies into account.

Technology

All three offered technologies provide a method for separating Cl_2 from a gaseous anode outlet stream mass flow of an electrochemical cell reactor, which consists of Cl_2 and essentially anhydrous HCl.

Assuming that no oxygen is present in the HCl/Cl_2 mixture at the gas phase reactor outlet, the separation becomes more simple and energy-efficient.

Compared to Deacon like processes, a significant advantage of all three approaches is the possibility of recycling unconverted HCl.

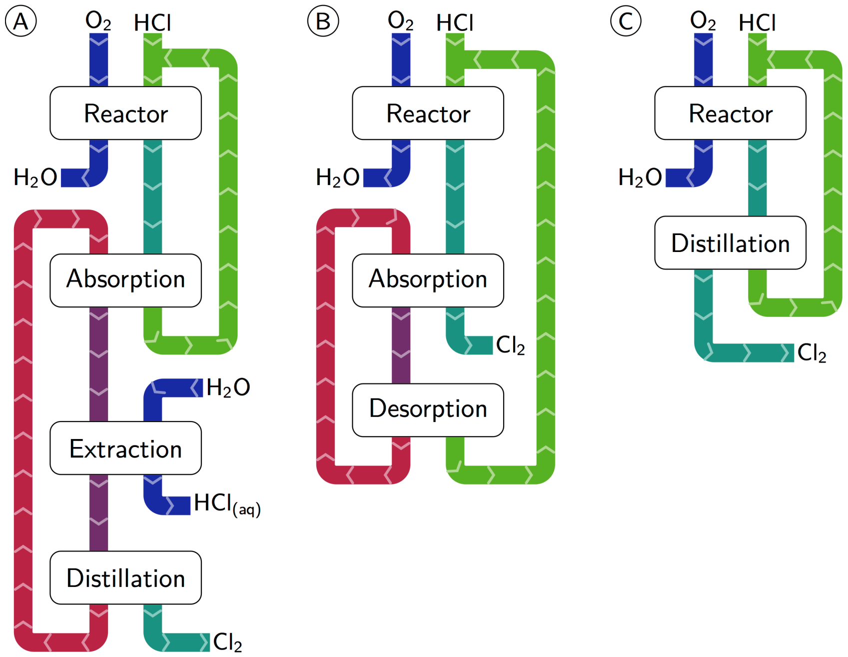

Fig 1: Graphical illustration of the proposed separation techniques: **A**: Absorption & Extraction, red: organic solvent cycle; **B**: Absorption with Ionic Liquid (red); **C**: Direct Distillation.

Therefore, the electrochemical gas phase process theoretically allows for very high overall conversions of up to 100 %. All three approaches are able to separate Cl_2 with a purity of at least 99.5 wt%.

Table 1: Total exergy consumption of the three separation techniques combined with an electrochemical gas-phase reactor; calculated in Aspen Plus depending on two different simulated single-pass conversions (i.e. content of Cl_2 in outlet stream of the reactor).

Process Variant	Single-Pass Conversion	Exergy Consumption
Bayer UhDenora State of the Art	23%	42.3 MW
1A: Absorption and Extraction	80%	27.0 MW
	60%	28.4 MW
1B: Absorption in Ionic Liquid	80%	27.0 MW
1C: Direct Distillation	80%	26.3 MW
	60%	26.5 MW

1A: Separation via Absorption and Extraction

In a first step the anode outlet stream is exposed to a nonpolar organic solvent (s. fig. 1A). In a range of common organic solvents, for example chloroform, benzene and alkanes, the solubility of Cl_2 is distinctly higher than the one of HCl. The mass flow of the solvent is adjusted to adsorb most of the Cl_2. Thus, a gas flow containing essentially HCl remains, which is suitable for direct recycling into the electrochemical cell reactor. In this way, a high overall conversion of HCl can be achieved even at moderate single-pass conversions in the electrochemical cell reactor, hence a low cell potential is possible.

The Cl_2 containing solution is procured to a second step. By extraction with water, the small amount of HCl being absorbed besides Cl_2 is removed completely from the organic solvent due to the highly exergonic dissociation reaction. By subsequently absorbing pure HCl from step 1, concentrated hydrochloric acid can be produced. The remaining organic phase contains Cl_2 and traces of water only. Thus, Cl_2 can be desorbed in a distillation column and discharged as a product stream while the organic solvent leaving at the bottom of the distillation column is recycled.

The exergy demand of the overall process including the gas phase reactor and this separation method is about 64 % of the demand of the overall state-of-the-art process including the electrochemical reactor (s. table 1).

1B: Separation Absorption in Ionic Liquid

Alternatively, the absorption in step 1 can be accomplished by an ionic liquid. In this case, the mass flow is adjusted to absorb the HCl completely, leaving a gas flow containing essentially Cl_2. Due to the significantly higher selectivity for HCl, no second separation step as in approach 1 is necessary. In a subsequent desorption step – by reduced pressure and increased temperature – the HCl is separated from the ionic liquid, allowing a recycling into the electrochemical cell reactor as well as the absorption in water to produce concentrated hydrochloric acid (s. fig. 1B).

The exergy demand of this process is about 64 % of the demand of the state-of-the-art process (s. table 1) – comparable to the first technique. Since no cooling streams below room temperature are needed, the requirements of the respective additional cooling cycles (for example for the distillation column in the first method) will be lower and its efficiency higher. Additionally, less devices are needed.

1C: Separation via Direct Distillation

A third approach for the separation uses the direct distillation of the outlet stream at elevated pressure of 1–12 bar (s. fig. 1C). Here, the overhead product mass flow essentially comprises HCl, which can be recycled into the electrochemical reactor or led into an absorber to form concentrated hydrochloric acid.

The bottom product comprises the Cl_2. The exergy demand of this overall process is about 62 % of the demand of the state-of-the-art process (s. table 1). Also this variant comprises the least amount of devices. However, it also has the lowest condenser temperature in the head of the column, leading to the need for a more effortful cooling cycle.

Advantages over the Bayer UhDenora state-of-the-art process

- reduced energy demand
- recycling of HCl into reactor possible contrary to Deacon process
- HCl is dissolved in water at a late step reducing the demand for corrosive resistant equipment
- higher reaction yield in gas phase reactor
- smaller device compared due to higher single pass conversion, and for approach 2 and 3 also less devices.

Patent Information

- EP patent application filed November 28th 2017.
- PCT patent application WO2019105955 filed November 28th 2018, nationalized in EP, US, CN

Literature

- Bechtel S., Vidakovic-Koch T., Sundmacher K.: "Novel process for the exergetically efficient recycling of chlorine by gas phase electrolysis of hydrogen chloride"; Chemical Engineering Journal 346 (2018) 535–548
- Bechtel S., Vidakovic-Koch T., Sundmacher K.: "Energy-Efficient Gas-Phase Electrolysis of Hydrogen Chloride"; Chem. Ing. Tech. 2019, 91, No. 6, 795–808
- Bechtel, S., Song, Z., Zhou, T., Vidaković-Koch, T., Sundmacher, K.:"Integrated process and ionic liquid design by combining flowsheet simulation with quantum-chemical solvent screening.", Comput. Aided Chem. Eng. 44: 2167-2172.
- Bechtel, S., Sorrentino, A., Vidaković-Koch, T., Weber, A. Z., Sundmacher, K.: "Electrochemical gas-phase oxidation of hydrogen chloride to chlorine: Model-based analysis of transport and reaction mechanisms." Electrochim. Acta 324: 134780.
- Bechtel, S., Vidaković-Koch, T., Weber, A. Z., Sundmacher, K.: "Model-based analysis of the limiting mechanisms in the gas-phase oxidation of HCl employing an oxygen depolarized cathode." J. Electrochem. Soc. 167: 013537.

Contact

Dr Lars Cuypers

Senior Patent- & License Manager
Chemist

Phone: +49 (0)89 / 29 09 19 - 21
eMail: cuypers@max-planck-innovation.de