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Technological approaches for recovery of petrochemical condensates

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Abstract: In the (petro)chemical industry, the importance of steam is highly emphasized as an essential heat transfer and reaction medium, as well as a diluent during crude feed cracking. The variety of process applications of steam lead to the generation of many condensates with different specifics hampering their direct reuse. As part of a project under the scope of the Institute for Sustainable Process Technology (ISPT) and together with several partners (Dow Benelux BV, Terneuzen, Ghent University, Evides Industriewater, KWR Water Research Institute, Kurita, Sitech) this research aims to achieve more efficient production of steam in the (petro)chemical industry by enhancing the recycling of condensates as high quality water and reducing the freshwater intake. In order to reach this goal, a specific research case was initiated at the site of Dow Benelux BV, Terneuzen.

Keywords: reuse; condensate; petro(chemical)

Introduction

The petrochemical production process itself generates condensate streams at elevated temperatures, in which complex organics such as aromatic and oxygenated compounds and emulsion breakers are still present. Due to the nature of these pollutants, such streams are sent to the Waste Water Treatment Plant (WWTP).

By strategically by-passing the WWTP and applying an individual treatment on the condensate, a higher energy efficiency, an improved water recovery and lower load to the WWTP can be achieved. Different treatment approaches were preselected; Membrane Distillation (MD) and Membrane Aerated Biofilm Reactor (MABR), Figure 1.

MD is a thermally driven (possible low grade waste heat) process operating in the range between 30°C–80°C and applies a microporous hydrophobic membrane for the separation of a vapour from a liquid stream.

In order to achieve higher effluent purity, a biological treatment step was also considered. An MABR was selected, where the membranes serve as oxygen supplier (~200mbar) for the treatment and as a support for the development of biofilm. The wastewater surrounding the membranes provides the carbon source needed for the growth of the biomass.

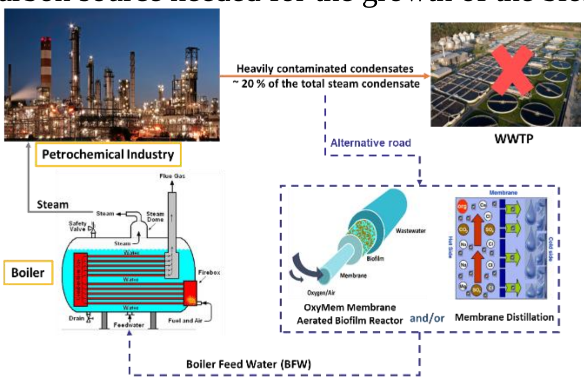

Figure 1. Project scope and concept - higher steam/condensate recycling ratio

Material and Methods

Due to the available waste heat in the condensate from Dow Benelux, MD was chosen as a technique for simultaneous water and energy recovery. The influence of key operational conditions on the process efficiency, such as ΔT, $T_{average}$, flow rate and pH in the range from 9.5-13 were studied in a lab scale Direct Contact MD (DCMD), treating a synthetic solution containing main pollutants.

The experimental set-up consisted of an acrylic MD module with an active surface area of 163 cm^2 and counter current supply of feed and distillate. The temperatures on both sides of the membrane were maintained by two heat exchangers and detected by Resistance Temperature Detector (RTD). The collected data was continuously logged via the program LabView. The values selected for these parameters were chosen to be comparable to a full scale MD configuration and to indicate their influence on the amount and quality of the obtained distillate. Based on a Design of Experiments (DOE) approach, for each studied parameter a high (ΔT = 20°C; $T_{average}$= 60°C, flow rate = 90L/h) and a low level (ΔT = 10°C; $T_{average}$= 40°C, flow rate = 60L/h) were given and different combinations of conditions were tested.

To study the biological removal efficiency of the main carbon substances, an MABR pilot with two identical 55L reactors designed by OxyMem, Ireland was installed at the site of Dow. The pilot was operated in series. It was inoculated with sludge from the WWTP of the company and it was initially fed with synthetic mixture gradually replaced by a real condensate stream. In order to assure all necessary elements for a healthy biofilm, macro (N and P) and micronutrients were additionally added. The pilot system was operated for 1.5 years at an HRT of 10h per reactor, which resulted in a feed flow rate to the system of ~130L/day.

Results and Conclusions

Within the MD experiments it was observed that the higher the $T_{average}$ and the flow rate, the flux generated from the system increases. The pH values of the feed solution have an impact on the rejection efficiency of the present organic components due to the influence on their dissociation constants. For example, the main group of the carbon pollutants in the condensate, with pKa around 4.8 at 25°C, were greatly rejected, which could be hypothetically explained by the presence of their unprotonated forms.

On the other hand, the most toxic substance in the condensate was less retained at a pH ranging from 9.5 -10.5 as its pKa value is 9.99. This physicochemical characteristic could lower its removal efficiency since partially it would be still present in protonated and more volatile form. On the other hand, when pH values of ~13 were reached in the feed, all constituents were rejected by the membrane from 97.72% to 99.98%.

The removal efficiency of the first MABR was mainly dependent on the Total Organic Carbon (TOC) load and the thickness of the biofilm. At lower feed concentrations (e.g. 9gTOC/day) and optimal biomass growth on the silicon fibers, the first bioreactor was able to remove all main carbon pollutants from 80% up to 99.3%.

When very high TOC load of 21g/day was gradually reached and fed to the system, the operation in series of the MABR pilot reactors was proven beneficial and lead to a final effluent values below detection limits for all identified and known components. The polishing effect of the second reactor was experienced at conditions aiming to achieve the expected on full scale TOC load.