Industrial wastewater collection using a separation technique

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A B S T R A C T
Water is an essential element within normal functioning throughout the chemical industry. The reuse of water, or more precisely water condensate collection, is very important during real chemical processes because it can reduce raw materials, energy losses, and costs, and can improve the operations of energy and process systems.

The effect of industrial activity on the environment has attracted considerable attention over the past few decades. Industry, therefore, has started looking at methods of reducing the volumes of produced wastewater. This paper presents the industrial separation of lower and higher temperature condensates’ collection using the heating utility of steam production, by separation techniques. The existing condensate collection regarding utilities’ preparation for steam-generation may no longer be optimal; the basic intention is that minimal changes in the system can produce an efficient improvement by using separate collections of low and high-temperature condensates, and the use of available heat with little heat flow rate loss. This separated water condensate collection preparation for the utility of steam production by using a separation technique and MINLP (mixed-integer nonlinear programming) was tested on an existing methanol process, which allowed for an efficient and additional 7% water condensate collection system for steam-generation.

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1. Introduction

Minimizing water-usage and waste-production reduces energy and utilities usage, as well as increasing process efficiency.

Water minimization within the process industry is becoming increasingly important as environmental legislation becomes more stringent, and awareness increases about the impact of industrial activities on the environment. Extensive work was carried out by Bagajewicz and Foo [1,2] on water-minimization during continuous processes. They developed methodologies for wastewater minimization during continuous processes, mainly using pinch-analysis techniques.

Those methods developed for water-minimization during continuous processes, can be roughly divided into insight-based and mathematical techniques. The former are mainly based on pinch-analysis techniques [3,4] that were originally developed for heat [5] and mass integration [6]. The former always consists of a two-step approach (targeting and design) when synthesizing a batch–water network that features minimum freshwater and wastewater flows for a given production schedule. On the other hand, mathematical methods [7,8] have their roots within an optimization framework. The mathematical techniques may be categorized by two subsections namely, with and without scheduling consideration.

Water condensate collection is very important during real chemical processes because it can reduce raw materials, energy-losses, and costs, and can improve the operations of energy and process systems [9,10]. Water is amongst the more important raw materials and utilities, therefore, it is reasonable to collect water during the process industries’ activities.

Couallier and co-workers reduced water consumption in beer distilleries by recycling the condensates for re-use during the fermentation phase. Recycling the condensates produced in beer distilleries for use during the fermentation phase enables a reduction in both water consumption and waste water rejection [11].

Water-minimization and energy-minimization problems have induced the development of conceptual design approaches within the field of water minimization [12,3].

There is substantial literature focusing on wastewater treatment technologies [13,14]. However it has always evaluated the environmental performance of technological applications [15] by comparing the effects of different wastewater treatment technologies [16,17].

This paper presents the separation of a single condensate collection into low and high-temperature reservoirs, using a separation technique, and by efficiently using them. This separation technique was compared with the above described methods. It...
was the simplest and provided fast and good solutions which, of course, are not global.

2. Separated water condensate collection by using a separation technique

Many industrial users of water are under increasing pressure to reuse water within their facilities. Their goal is to minimize the amount of wastewater, or more specifically condensates. Condensation is a changing of the physical state of matter from a gaseous phase into a liquid phase, and is the reverse of evaporation [18]. Upon the slowing-down of molecules within a material, the overall attraction forces between them prevail and bring them together at distances comparable to their sizes. Since the condensing molecules suffer from reduced degrees of freedom and ranges of motion, their prior kinetic energy must be transferred to a colder absorbing entity – either a center of condensation within the gas volume (colder molecules of the species, cold grains of dust, etc.), or certain contact surface. Condensation commonly occurs when a vapor is cooled and/or compressed to its saturation limit, and when the molecular-density within the gas-phase reaches its maximal threshold. Condensation is a crucial component of distillation, and an important laboratory and industrial-chemistry application.

Condensate, as produced during a process, could be collected for:

- utilities for steam-generation,
- preparation of raw materials.

The basis of a separation technique is to separate and then collected low and high-temperature condensates within low and high temperature reservoirs. This separation technique also takes into account that cooling by air-coolers would be done at below 100 °C and could, therefore, release much of the available energy for the preparations of utility systems.

The collection of all condensates, from low to high temperatures, into one reservoir is ineffective. The condensates should be collected separately:

- low-temperature (by 90 °C) condensate collection into a low-temperature reservoir and,
- high-temperature (about 120 °C or more) condensate collection into a high-temperature reservoir.

When using the proposed separation technique less heat flow rate is lost when heating the condensate for the preparation of a utility system. In this case the utility preparation only includes heating, as cooling is unnecessary. A separated collection avoids cooling and then re-heating.

The above-mentioned statement is also visually displayed in Fig. 1. Five condensates with different temperatures and mass flow rates (K1–K5) were collected within a reservoir. Firstly, all the condensates were combined together (Fig. 1a), then secondly as separate two-step (low and high temperature) condensation collections (Fig. 1b). The desired outlet temperature for the collected condensate was 130 °C. A lower heat flow rate into the heat-exchanger (H1) was needed in the case when separately collecting the condensates.

![Fig. 1. Collection of condensates: (a) together; (b) separately.](riovresererutarepmet-hgihriovresererutarepmet-wol)
If the condensate is collected for steam-generation, it makes sense that the available low-pressure steam can be added into the high-temperature condensate collection reservoir, (but not into the low-temperature), or directly added during the steam-phase, as far as possible. Low-pressure steam unnecessarily loses heat during condensation, when the condensate starts heating-up during the next stage.

3. Case study

This type of separated condensate collection was tested against an existing methanol process, by using the separation technique.

3.1. Condensate collection during the methanol process

This case study was based on the Lurgi methanol process [19] (Fig. 2). This methanol process is composed of three subsystems:

- production of synthesis gas
- production of crude methanol and,
- purification of methanol (F301, D301–D304).

The possibility of better conversion was studied regarding synthesis gas, whilst retrofitting the Lurgi process for low-pressure crude methanol production (without purification) from natural gas.

The raw material (natural gas) was first desulphurized (D101) and then heated up in a steam reformer (REA-1), where synthesis gas was produced from the raw material (natural gas) and steam, at 825 °C 15 bar:

\[ 3C_2H_6 + 6.5H_2O \rightarrow 2CO + 12H_2 + 1.75CH_4 + 2.25CO_2 \quad \Delta_rH^{298} = 196.17 \text{kJ/mol} \quad \text{(R1)} \]

\[ 3C_3H_8 + 10H_2O \rightarrow 3.5CO_2 + 17H_2 + 3CO + 2.5CH_4 \quad \Delta_rH^{298} = 277.88 \text{kJ/mol} \quad \text{(R2)} \]

\[ 3C_4H_{10} + 13.5H_2O \rightarrow 4.75CO_2 + 22H_2 + 4CO + 3.25CH_4 \quad \Delta_rH^{298} = 361.48 \text{kJ/mol} \quad \text{(R3)} \]

\[ \text{CH}_4 + H_2O \rightleftharpoons CO + 3H_2 \quad \Delta_rH^{298} = 206.08 \text{kJ/mol} \quad \text{(R4)} \]

\[ \text{CO} + H_2O \rightleftharpoons CO_2 + H_2 \quad \Delta_rH^{298} = -41.17 \text{kJ/mol} \quad \text{(R5)} \]

The hot-stream of synthesis gas was cooled in an E107 boiler, in E109, E110, E111 heat-exchangers with an EA101 air-cooler, and in an E112 water-cooler. The condensate was expanded in flashes: F1, F2, F107, and F108. All the condensates were collected (K1–K5) during the process. The synthesis gas was compressed in G201I and G201II two-stage compressors.

In the second subsystem, methanol was produced by the catalytic hydrogenation of carbon monoxide and/or carbon dioxide in a REA-2 reactor, using three main reactions (r = R6, R7, R8):

\[ \text{CO} + 2H_2 \rightleftharpoons \text{CH}_3\text{OH} \quad \Delta_rH^{298} = -90.77 \text{kJ/mol} \quad X_{\text{CO}} = 56\% \quad \text{(R6)} \]

\[ \text{CO}_2 + 3H_2 \rightleftharpoons \text{CH}_3\text{OH} + H_2O \quad \Delta_rH^{298} = -49.58 \text{kJ/mol} \quad X_{\text{CO}_2} = 30.5\% \quad \text{(R7)} \]

\[ \text{CO}_2 + H_2 \rightleftharpoons \text{CO} + H_2O \quad \Delta_rH^{298} = 41.19 \text{kJ/mol} \quad X_{\text{CO}_2} = 0.2\% \quad \text{(R8)} \]

The REA-2 high-pressure reactor was operated within the existing parameters, and the non-converted gas recycled. The inlet-stream of the reactor was heated by a process stream (HEPR). The stream

Fig. 2. Process flow-diagram of a low-pressure Lurgi methanol plant.
was then cooled using air (HEA) and water (HEW) coolers, before entering the flash (SEP). The liquid-stream during the separation was the product and the recycled gas-stream was compressed to 51 bar within a new, two-stage compressor (COMPI, 2) with intermediate water-cooling (HEW1). The purge gas was separated from the crude methanol in a F301 flash. Purification included the distillation columns (D301–D304).

During the methanol process, all the condensates were collected as utilities for 37 bar steam-generation (Fig. 3). The collected condensates were added to the freshly demineralization water (19791 kg/h) within the reservoir (Re1). The fresh-water and condensates were heated in a heat-exchanger (E111), followed by another collection of condensates into the reservoir (Re2), pumped using a pump (P1) at 50 bar, and then heated within heat-exchangers (E110, E102, REA2, E107, E104, E103). The necessary heat flow rates for the heating of a steam-generation system were obtained from synthesis gases (E111, E110, E107), the furnace-channel (E102, E104, E103), and the REA-2 reactor. All the hot steams, that allow for the heating of utilities regarding steam generation (cold streams), are presented in Table 1. The existing system (Fig. 3) was simulated using an Aspen Plus [20].

The existing steam-generation is presented by using a composite curve (Fig. 4), which allows for presenting a graphical transfer of heat flow rate into a utility preparation system, including all existing hot and cold streams (Table 1). The composite curve is a basic part of the pinch-analysis [21].

4. Retrofit system of condensate collection

The existing utility preparation system would be optimized, including the fact that the condensate collection would not be optimal, the air cooler would cool too much of the heat flow rate, and the heat would be exploited insufficiently within the furnace channel. The retrofit of the existing steam-generation system during the methanol process, would include these basic priorities:

- separately collected low and high-temperature condensates into low and high-temperature reservoirs, which is the basis of the separation technique,
- use of partly available heat from an air-cooler,
- use of additionally available heat within the furnace-channel.

Our first primary goal was the collecting of low and high-temperature condensates separately, so that condensates K3–K5 could be collected within a Re1 reservoir containing fresh-water. The high-temperature condensates K1–K2 could then be collected within a Re2 reservoir (Fig. 5). This alternative was the highest outlet temperature from reservoir Re2 (88 °C), which confirmed the correctness of separately collecting condensate. However, this temperature was then reduced to 80 °C because additional fresh water was entered into the system.

Secondly, an air-cooler with a temperature of 128 °C was used for synthesis gas heating, this temperature was too high and would have too-high a heat flow rate loss, therefore the E111 and E110 heat-exchangers were heated at 500 and 1000 kW higher heat flow rates for the demineralized water, and the inlet temperature of the air-cooler reduced to 101 °C (Fig. 5).

Thirdly, the existing furnace-channel had an available heat flow rate that could generate 7% more steam.
collection of condensates K1-K2

57331 kg/h
1.3 bar
67 °C
2180 kW
2.6 bar
25 °C
condensate
fresh water 24791 kg/h

All these advantages included within the existing steam-generation system could be increased by 7% without significant changes, and 5000 kg/h more of the fresh-water than was actually collected within the reservoir (Re1). K3–K5 condensates were collected within Re1, followed by heating in the E111, which has a 500 kW higher heat flow rate. K1–K2 condensates were collected into Re2, followed by pumping at 50 bar and heating in the E110, which had a 1000 kW higher heat flow rate. The demineralized water was heated into E102 using a lower heat flow than within REA2 with the same heat flow rate. The demineralized water was evaporated in E107 and E104 with additionally available heat within the furnace-channel, followed by overheating into E103.

The reconstruction of the steam-generation-system could be more effective, as all the available-heat was used during the process. 7% more steam could be produced by the existing system, which does not work at 100% capacity. The heat flow rate through the air-cooler was reduced by 23%. Condensates were collected over two stages – low and high-temperatures, separately. All the retrofitted hot streams, that allow for the heating of steam generation utilities (cold streams), are presented in Table 2. The retrofitted steam-generation is represented by using a composite curve (Fig. 6), including all retrofitted hot and cold streams (Table 2).

Special graphical profiles of hot (Fig. 7) and cold (Fig. 8) composite curves were created for the existing and retrofitted

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**Table 2**

Data of retrofitted steam-generation.

<table>
<thead>
<tr>
<th>Stream</th>
<th>Tₘ (°C)</th>
<th>Tᵢ (°C)</th>
<th>I (kW)</th>
</tr>
</thead>
<tbody>
<tr>
<td>E111 hot</td>
<td>110</td>
<td>101</td>
<td>2180</td>
</tr>
<tr>
<td>E110 hot</td>
<td>358</td>
<td>110</td>
<td>14,550</td>
</tr>
<tr>
<td>REA-2 hot</td>
<td>300</td>
<td>280</td>
<td>1600</td>
</tr>
<tr>
<td>E102 hot</td>
<td>287</td>
<td>240</td>
<td>2180</td>
</tr>
<tr>
<td>E107 hot</td>
<td>825</td>
<td>440</td>
<td>13,000</td>
</tr>
<tr>
<td>E104 hot</td>
<td>738</td>
<td>287</td>
<td>21,300</td>
</tr>
<tr>
<td>E103 hot</td>
<td>907</td>
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<td>10,400</td>
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<td>E111-C cold</td>
<td>25</td>
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<td>E110-C cold</td>
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<tr>
<td>REA-2-C cold</td>
<td>220</td>
<td>248</td>
<td>1600</td>
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<tr>
<td>E102-C cold</td>
<td>220</td>
<td>247</td>
<td>2180</td>
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<tr>
<td>E107-C cold</td>
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<td>248</td>
<td>13,000</td>
</tr>
<tr>
<td>E104-C cold</td>
<td>247</td>
<td>248</td>
<td>21,300</td>
</tr>
<tr>
<td>E103-C cold</td>
<td>247</td>
<td>500</td>
<td>10,400</td>
</tr>
</tbody>
</table>

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profiles. The profiles were very similar to each other, only the capacity of the retrofit had increased slightly.

Reconstruction is probably not an optimal, since it has not been optimized by mathematical methods. Reconstruction would exclude many modifications and thus reduce costs. The process is not operated at a 100% capacity, and consequently the existing processing units remain unchanged. The basic additional cost of reconstruction was 280 kEUR/a of fresh water (5000 kg/h, Table 3). Cost-analysis was assumed to be 10% of the additional costs for maintaining the expanded system (500 kEUR/a). The amount of steam generated would be increased by 2000 kg/h, bringing an additional income of 1600 kEUR/a. The total additional profit from the retrofitted steam production system was 820 kEUR/a.

5. Conclusions

Over the past decade, considerable design techniques have been developed in order to minimize the mass of water consumption.

Water is an immense asset, it is important for optimizing the collection of industrial wastewater, or more specifically water condensates. The collected condensates are also of use as raw materials or as a utility for produced-steam.

The separation technique is very important when separately collecting low and high temperature condensates into low and high temperature reservoirs, as this saves energy. Separated low and high temperature condensate separation when used for the utility preparation of a steam-generation heating system is more efficient because of no heat flow rate loss.

The existing condensate collection during the methanol process was modified in order to collect low and high-temperature condensates, separately. The cooling of air-coolers could be done at lower temperatures, as the inlet temperature in the air-cooler could be below 100 °C. All these improvements, including the unused-heat within the furnace-channel, would increase the generation of steam by 7%, and the use of available heat with little heat flow rate-loss.

By modification of the existing process, very little change would be needed for a better preparation of overheated-steam, as used in steam-turbines for producing electricity.

References