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Method of purification of post-production condensates from polyester polyol production

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Nowadays, the topics of closed-loop and eco-design are raised very often, especially in the chemical industry. To combine development with these trends, Purinova Sp. z o.o. has focused on pursuing the closed-loop use of post-production condensate from polyester polyols production. To this end, purification and distillation processes have been adapted, both at the laboratory and production scale, to receive treated condensate with decreased Chemical Oxygen Demand (COD) index. The method involves connected purification of production condensate by returning condensate to the top of the distillation column during polycondensation and two stages distillation system afterwards. The method allows for decreasing COD index and contents of diethylene glycol and 1,4-dioxane. The resulting technology has consequently allowed the use of tailored distillation in the purification of post-production condensates in the production of polyester polyols. Furthermore, the quality of the condensate obtained allowed it to be used in the closed loop of the production plant.

Keywords: polyester polyols, distillation, condensate.

INTRODUCTION

Polyester polyols are obtained as the effect of the reaction of polycondensation of polycarboxylic acids with multifunctional alcohols[1]. The reaction utilises excess of hydroxyl groups, compare to stoichiometric, to achieve the product's appropriate particle size and functionality[2]. Water is the main by-product of polycondensation reaction between glycols and difunctional acids[3]. An exemplary diagram of polycondensation reaction is shown in Figure 1.

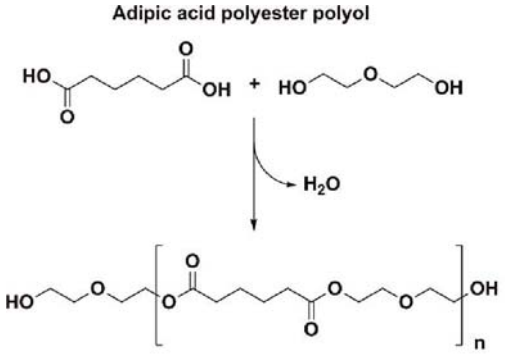


Figure 1. Reaction scheme for obtaining polyester polyols

The processes are carried out in a vacuum for the purpose of remove water and shifting the chemical reaction towards the formation of products and consequently – accelerating the chemical reaction[4]. Particles of substrate – glycols are collected together with the released water. The effect of entrainment of glycols with the water condensate is increased by means of vacuum and the flow of an inert gas stream, commonly nitrogen[5]. Diethylene glycol is one of the typically used bifunctional alcohols in the production of polyester polyols[6]. In the case of polycondensation of carboxylic acids with diethylene glycol, the side reactions generate a by-product in the form of 1,4-dioxane[7, 8] (Fig. 2).

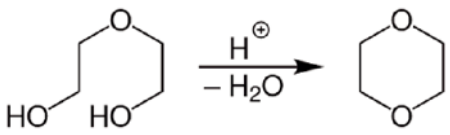


Figure 2. Reaction scheme for the formation 1,4-dioxane from diethylene glycol

All organic components contained in the post-production condensate, and in particular 1,4-dioxane and glycols used in the product recipe have a negative impact on its purity[9]. Condensate quality is commonly measured by an indicator in the form of Chemical Oxygen Demand (COD) index and the determination of the water content[10]. It is advisable to achieve the lowest possible COD index by limiting the number of organic compounds in the post-production condensate[11, 12].

Filled distillation columns aiming to separate the condensate components and to return the substrates to the reaction medium are used to increase the productivity of the reaction and to ensure pure water condensate[13, 14].

The commonly known methods of condensate purification include physical methods, such as distillation methods based on the differences in boiling temperatures such as distillation process[15, 16], including Pressure Swing Distillation[17], membrane distillation[18], and chemical, such as Wet Peroxide Oxidation (WPO)[19], for instance, utilising the Fenton reaction with the use of hydrogen peroxide in the presence of Fe^{2+} iron ions for the purpose of oxidising organic compounds[20, 21]. There are also physio-chemical methods, such as reactive distillation[22, 23] or photo-chemical methods using Fenton reaction supported with UV[24]. The known methods mentioned above are not enough to be simple implemented in full-scale production capacity without introducing large changes in the whole production process. There is necessity to provide a novel simple method according to specific production polycondensation process with diethylene glycol and phthalic anhydride as raw sources.

Optimisation of condensate quality brings benefits in numerous areas, first of all, an ecological because of the reduction of the emission of organic compounds outside the reaction medium[25], economical – decrease in the use of raw materials and optimisation of the mass balance, and of course, process benefits by increasing the supervision over the process carried out, retaining the stoichiometry of the chemical reaction[26].

Based on this study, we tried to find the best way to treat post-production condensate by two-step distillation process and parallel by in-situ optimization of the production process. Treated condensate should have reduced amount of impurities (mainly 1,4-dioxane), reduced COD index and finally, there should be possibility to close the loop by diverting the treated condensate to the technological process. The treatment process should reach also the economical goals of the production process by avoid using chemical compounds and it is also necessary to avoid expensive investments in production infrastructure.

EXPERIMENTAL SECTION

Materials

Polycondensation reaction was carried out using of phthalic anhydride flakes manufactured by BASF SE, diethylene glycol manufactured by PKN Orlen S.A. and catalyst tetra-n-butyl titanate as Tyzor TnBT produced by Dorf Ketal Specialty Catalysts, LLC.

Characterization

Chemical oxygen demand of samples was determined by the photometric method, according to Macherey-Nagel's method REF 985 012 using Nanocolor cuvette tests containing sulphuric acid, potassium dichromide and mercury sulfate. Samples are diluted in 1:10 or 1:20 ratio according to predicted COD index range (complies with producent procedure), and placed in cuvette test. Then samples are incubated (160 °C, 30 minutes) and after cooling down, are photometric measured, and compares to blank sample, in PF-3 photometer with included internal equation. The percentage of water in the tested samples was determined with the use of a KF Titrino automatic titrator utilising the electrometric titration method. The sample is dissolved in chloroform:methanol mixture (mixture proportion 3:1), then the mixture with dissolved sample is automatically titrated by Aquagent Complet 5 – provided by instrument producent. The diethylene glycol and 1,4-dioxane content were determined using the Shimadzu GC-2010 Plus gas chromatograph with Shimadzu GCMS-QP2010 SE mass spectrometer with a capillary column with polar filling – ZB-WAX plus produced by Phenomenex. The sample is dissolved in water and methanol, then separated in centrifuge (5000 rpm) and dissolved in internal standard solution. Analysis is provided with 1,00 ml/min flow with dozing temperature 250 °C at temperature program: 2 min at 60 °C, 10 °C/min to 220 °C, 20 °C/min to 260 °C and 2 min at 260 °C.

Apparatus

The distillation in laboratory scale was performed in a dedicated simple, cylindrical distillation steel reactor made from stainless steel and equipped with insulating jacket. Distillation reactor is heated through heating jacket powered by steam vapour which flow is automatically regulated due to required temperature set. Vapours generated during distillation flows by water cooler which is powered by cold water to condense these vapours. The distillate received is collected from the reactor to the condensate collector. Reactor volume is 5 dm^3 with additional 2 dm^3 condensate collector. Samples are collected by condenser and distilling reactor outlet placed in the bottom of reactor and condensate collector to a glass vessel and then are analized in laboratory. Distillation reactor scheme is shown in Figure 3.

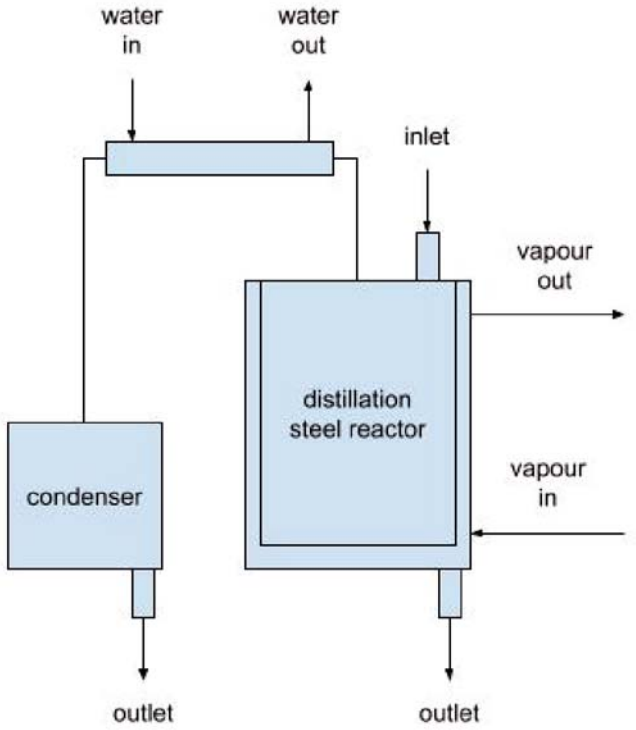


Figure 3. Distillation reactor scheme

RESULTS AND DISCUSSION

Purification of post-production condensates at laboratory scale

For the purpose of process optimisation and to measure possible effectiveness of condensate purification, laboratory-scale research was carried out. In effect, there is necessity to receive condensate purified from impurities as a diethylene glycol and 1,4-dioxane. In cases of different physical properties, mainly boiling temperatures, of diethylene glycol and 1,4-dioxane, the two-stage purification process was assumed in the distillation process.

Originally, condensate is dark and had an unpleasant odour. It is predicted to additionally improve samples' appearance and odour. Differences in colour and odour will be measured organoleptic.

The first stage involved the distillation of post-production condensate at the temperature of 100 °C at normal pressure. The aim of the first stage of the process is to separate the water and low boiling point substances from crude condensate. It utilised the significant differences in the boiling point of organic compounds contained in the condensate and water as the main component of the chemical mixture. A summary of the determined parameters is presented in Table 1.

The intended effects were achieved at the first stage of the distillation. The high-boiling condensate components, including the diethylene glycol remained in the depleted liquid. The low-boiling condensate components were collected in the form of distillate and forwarded to the second stage of distillation.

In the second stage, the distillation at normal pressure and temperature of 89 °C was selected based on the phase

Table 1. Characteristics of condensate and its distillation products, stage 1

	mass [g]	COD [mg/l]	content [% m/m]			
			diethylene glycol	1,4-dioxane	water	other*
crude	1 500	160 000	1.17	1.25	96.06	1.52
depleted liquid	120	111 930	12.44	0.00	87.49	0.07
distillate	1 380	2 400	0.19 *(–84%)*	1.38 *(+10%)*	98.23	0.20 *(–87%)*

* other, not recognized, contaminants and by-products

Table 2. Characteristics of condensate and its distillation products, stage 2

	mass [g]	COD [mg/l]	content [% m/m]			
			diethylene glycol	1,4-dioxane	water	other*
distillate from stage 1 (Table 1)	1 360	2 400	0.19	1.38	98.23	0.20
depleted liquid	1 285	1 500 *(–38%)*	0.07 *(-63%)*	0,00 *(–100%)*	99.84	0.09 *(–55%)*
distillate	75	1 143 500	0.89	34.53	63.54	1.93

* other, not recognized, contaminants and by-products

diagrams for the chemical mixture water – 1,4-dioxane[27]. This is theoretically the optimum temperature for carrying out azeotropic distillation and removing the 1,4-dioxane from the post-production condensate[13]. The aim of the second stage of distillation is to separate mainly 1,4-dioxane from distillate from the first stage and receive depleted liquid with decreased contaminant content and reduced COD index. A summary of the determined parameters is presented in Table 2.

The second stage of distillation resulted in a condensate with a significantly reduced amount of impurities. A reduction of the COD index between crude sample (160 000 mg/l) and two-stages treated condensate, received as depleted liquid from stage 2 of distillation (1 500 mg/l) was obtained at the level of 99%, with the simultaneous complete reduction of 1,4-dioxane and diethylene glycol.

Condensate after two stages of purification, as depleted liquid from the second stage of distillation, constitutes 86% of the primary stream of post-production condensate. Achieving the aforementioned indicators allows for utilising the condensate for technological purposes as an additional stream to refill pure technological water used in the production process, which in turn allows for a significant decrease in the generated liquid waste. At the same time, the operations carried out resulted in obtaining a significant reduction in the odour and colour of the condensate. Samples appearance before (left) and after (right) purification are presented in Figure 4.



Figure 4. Post-production condensate before (left) and after (right) purification by distillation process

Additional purification of the condensate during the process

The process of polycondensation of dicarboxylic acids with dialcohols in a semi-technical scale was carried out in an indirectly heated reactor with capacity 1000 dm^3 fitted with a mechanic stirrer, inert gas inlet and a distillation column connected with the post-production condensate collector with capacity 200 dm^3.

Raw sources such as phthalic anhydride and diethylene glycol and a catalyst were placed in a polycondensation reactor, then continuously mixed mixture, was deoxygenated by an inert gas flow into the reaction mixture. After 2 hours of deoxygenation, there was vapour heating system enabled to heat the mixture to operation temperature 180–190 °C. Water formed in polycondensation flows through condensate collection system and finally was collected in condensate collector. Polycondensation in such temperature was carried out until the moment when condensate increase in collector was stopped.

The condensate collection system was additionally fitted with an additional purification system for the condensate. To increase the effectiveness of the separation of condensate in the distillation column, a continuous condensate return to the top of the column was used. The such system causes a secondary separation of the condensate ingredients and the return of substrates to the reactors, effectively reducing the use of raw materials through the minimalization of losses, while at the same time reducing the number of impurities in the post-production condensate. Reactor scheme is shown in Figure 5.

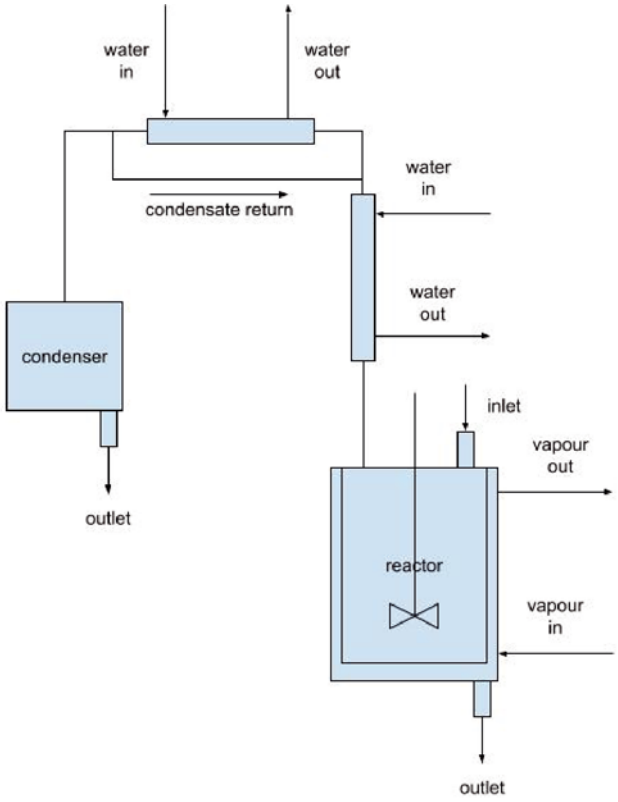


Figure 5. Polycondensation reactor scheme with condensate return line as a tool to additional purification

The effectiveness of the additional purification was defined through examining the basic parameters in the condensate without starting the system and comparing them with the parameters with the attached condensate repurification system. The defined parameters are shown in Table 3.

The losses of diethylene glycol have been eliminated during the repurification process, which is directly related to a significant reduction of the COD index by 50%.

Table 3. Additional purification efficiency

	Standard	Additional purification
Diethylene glycol	4.7%	LOQ*
1,4-dioxane	4.6%	4.6%
H_2O	90.4%	94.4%
COD	128,700 mg/l	64,800 mg/l

* – LOQ – below limit of quantification (less than 0.1%)

To determine the productivity of the repurification of condensate with time, condensate samples were collected during the production of condensate at 2-hour intervals; subsequently, the COD index, the contents of 1,4-dioxane and diethylene glycol were measured in the collected samples. The analytical results are presented in the diagrams (Fig. 6–8).

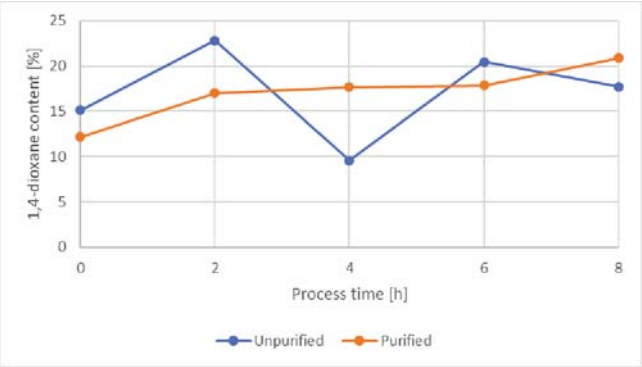


Figure 6. Dioxane content in the condensate during the process

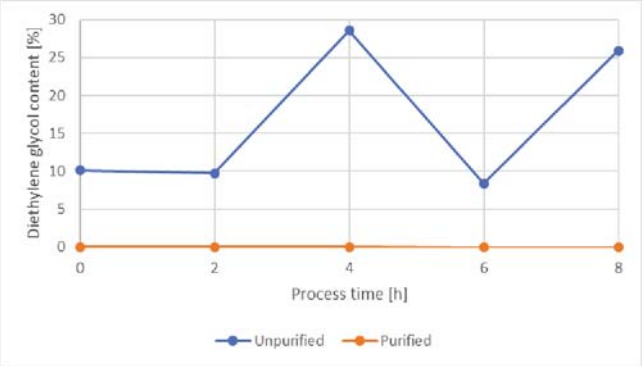


Figure 7. Diethylene glycol content in the condensate during the process

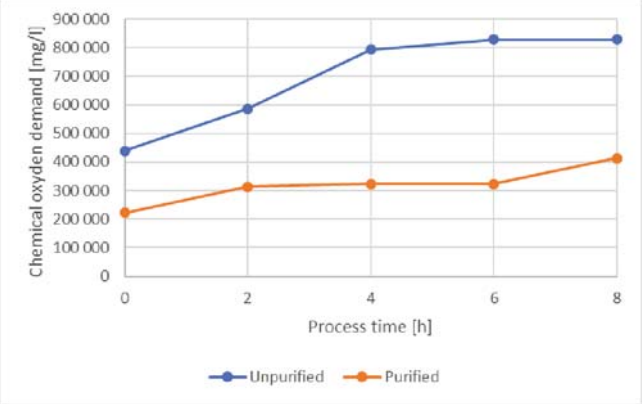


Figure 8. COD index in the condensate during the process

The conducted analyses confirmed the effectiveness of the additional purification system in the reduction of the amount of diethylene glycol in the post-production condensate and a simultaneous reduction of the COD index. The condensate repurification system is not efficient for separating 1,4-dioxane.

In the case of 1,4-dioxane (Fig. 6) and diethylene glycol (Fig. 7) contents, there are fluctuations during the process without an additional purification, caused by irregular flow of condensate in distillation column. With additional purification used, quantity of diethylene glycol and 1,4-dioxane in condensate during process remains stable during process because of more controllable flow in column.

Both additional purification and distillation steps have different selectivity of removal of various impurities, which is presented in Table 4. To remove both 1,4-dioxane and diethylene glycol, there are two steps needed: additional purification during the process with one-stage distillation or two-stages distillation without additional purification before that.

Table 4. Selectivity of methods in relation to impurities. X means that method is suitable to remove mentioned impurity from condensate

Method	1,4-dioxane	diethylene glycol
Additional purification		X
Distillation stage I	X	
Distillation stage II		X

Due to the selectivity of both of the developed methods, the condensate obtained in result of the polycondensation with the repurification system was diverted to the distillation system.

Condensate samples were collected from the distillation condensate in 2-hour intervals to determine the contents of 1,4-dioxane in the crude. The results are shown in Figure 9.

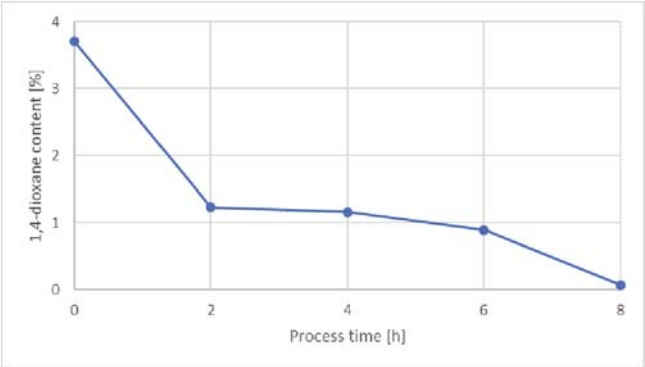


Figure 9. Dioxane content in the distillate during the distillation process

The use of combined repurification system during the process and the distillation of post-production condensate allowed for the effective removal of diethylene glycol and 1,4-dioxane. The quality of the purified post-production condensate allows it to forward for cooling in ventilation coolers and to return it to production systems. At the same time, the amount of the generated wastewater and the freshwater requirements necessary to top up the production systems were significantly reduced. Whole purification process with closing the loop is shown in Figure 10.

The condensate from the production of polyester polyols containing, among others, diethylene glycol and 1,4-dioxane is preliminarily repurified during the production process through diversion to the top of the distillation column at a controlled temperature. Subsequently, the repurified condensate is directed to the buffer as an intermediate condensate tank, from which it is directed to the distillation system. The distillation system was designed to allow either single-stage or two-stage distillation.

Single-stage distillation is used in the case of preliminarily purified condensates. For technological reasons as a longer production time with purification system enabled, the repurification system is either not used or used to a limited extent during the production of certain polyester polyols, without removing the entire diethylene glycol. In such cases, a two-stage distillation system is used for condensate purification.

The purified condensate is directed through the intermediate tank of purified condensate to the ventilation coolers, from where it can be forwarded directly to the technological system.

The depleted liquid from distillation can be directed as wastewater for disposal or used as fuel for heat recovery. Before the depleted liquid is diverted to its final storage location, it is routed via pipelines through process heating systems, where its heat is used.

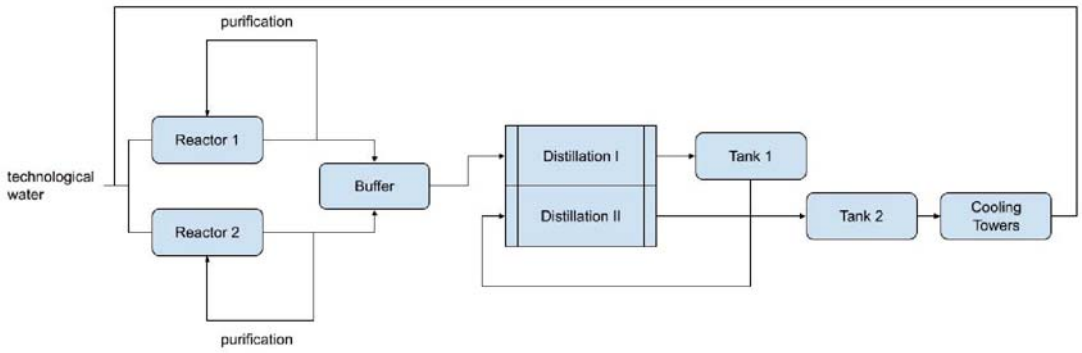


Figure 10. Post-production condensate purification system

CONCLUSIONS

The research carried out confirmed the expected assumptions related to the effectiveness of the distillation method in the purification of post-production condensates in the production of polyester polyols. There are novel purification system developed which results in reduction of contaminants in post-production condensate respectively: 1,4-dioxane by 100%, diethylene glycol by 95% and in effect chemical oxygen demand is reduced by 99%. Additionally, depending on current production requirements, there is possibility to use one of two possible ways to achieve treated condensate at the end: additional purification with one-stage distillation or only two-step distillation. The implementation of the repurification process and the condensate distillation system allows to obtain distillate of quality appropriate for diverting it to the technological system as a source of refilling pure water and closing the circuit, thus significantly limiting the amount of post-production waste.

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