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# THE RECYCLED ALCOHOLS PURIFICATION OF DIOCTYL PHTHALATE PRODUCTION OF JSC "SALAVATNEFTEORGSINTEZ"

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*The block of recycled alcohols rectification of dioctyl phthalate production of JSC "Salavatnefteorgsintez" have been considered. The scheme of the recycled alcohols rectification has been suggested and its optimization has been done for the purpose of recovery of 2-ethylhexanol corresponding the specifications of State Standard 26624-85.*

Keywords: *2-ethylhexanol, rectification, quality, one-column scheme, two-column scheme*

Dioctyl phthalate (DOP) is the most widespread plasticizer. Its part of world market of plasticizers is about 70 %. DOP is used for plasticization of vinyl resin, vinyl chloride copolymers, polyvinylidene chloride in production of a cable elastron, artificial leathers, general mechanical rubber goods, polymer building materials, packaging films [1].

DOP synthesis is carried out by esterification of phthalic anhydride by 2-ethylhexanol (2-EH) in presence of a catalyst. In the synthesis process by-side reactions occur. These reactions lead to formation of undesirable products such as unsaturated components, ethers, water et al. These components are separated from the end product together with 2-EH in the following stages: distillation of excess alcohols and residual water, stripping volatile components by direct steam, after settling. Reuse of the recycled alcohols without preliminary purification from undesirable products will lead to quality reduction of the product DOP. In order to avoid this, purification of the recycled alcohols is carried out.

In this work the block of the recycled alcohols purification of DOP production of JSC "Salavatnefteorgsintez" have been considered. This block assigns for 2-EH recovery corresponding to the specifications of State Standard 26624-85 [2]. The specifications to 2-EH according State Standard 26624-85 are presented in Table 1.

The existing scheme of the recycled alcohols purification is presented in Fig. 1.

 

The recycled alcohols heating up in a heat exchanger 2 are pumped into a column 1. Process of the recycled alcohols purification is carried out under vacuum. The column 1 is supplied by a remote heat exchanger 3. Temperature of top of the column 1 is regulated by input of the liquid from bottom of the column 1 through a heat exchanger 4 into rectifying section of the column 1. Light components vapors are routed from top of the column 1 to a heat exchanger 5 where it is condensed and cooled. Purified 2-EH from bottom of the column 1 are involved again in the process of DOP synthesis.

Table 1

The specifications of State Standard 26624-85 for 2-EH

| Name of a value | Standard | |
|---|---|---|
| | Superior | The first |
| 2-EH content, % mass | 99,0 | 98,0 |
| Aldehydes and ketones content, % mass | 0,5 | 1,5 |
| Unsaturated components content, % mass | 0,05 | 0,1 |
| 2-ethyl-4-methylpentanol content, % mass | 0,02 | 0,05 |
| Water content, % mass | 0,1 | 0,2 |

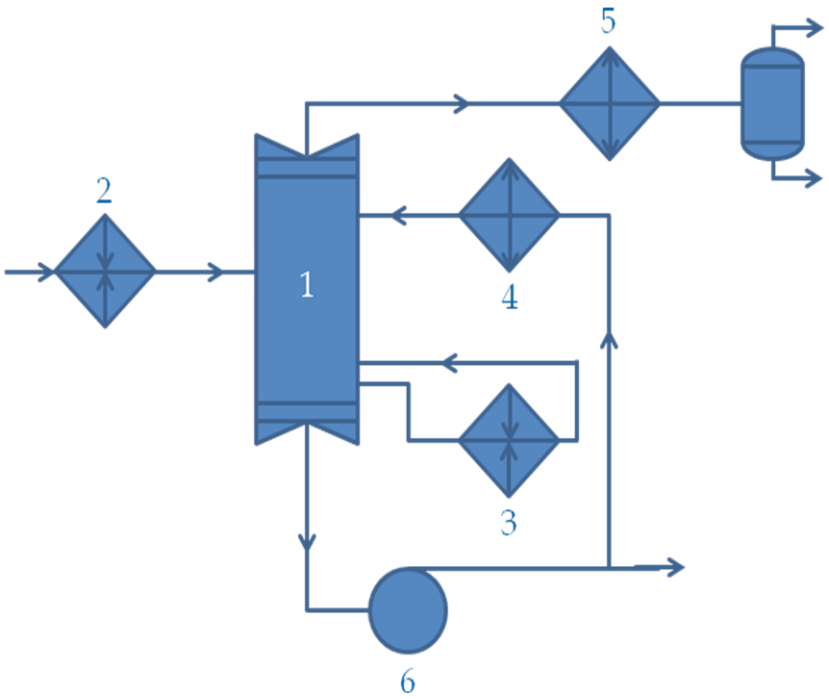


Figure 1. The existing scheme of the recycled alcohols purification in JSC “Salavatnefteorgsintez”:
1 – column; 2, 3, 4, 5 – heat exchangers; 6 – pump

The mathematical model of this scheme has been done in HYSYS. Activity model UNIQUAC [3] has been chosen as thermodynamic package. Model adequacy and tray efficiency have been checked on the basis of an experimental running data. Data obtained by modeling and experimental running are given in Table 2.

Table 2

Comparison of experimental and calculation data

| Parameter | Data | |
|---|---|---|
| | experimental | calculation |
| Feed stock flow rate, $m^3/h$ | 1,8 | 1,8 |
| The end product flow rate, $m^3/h$ | 1,69 | 1,69 |
| Water content in the end product, % mass | 0,66 | 0,51 |
| Specific gravity of the end product | 0,831 | 0,830 |
| Water content in the distillate, % mass | 2,41 | 2,34 |
| Aldehydes content in the distillate, % mass | 5,29 | 5,28 |
| Specific gravity of the distillate | 0,82 | 0,821 |
| Feed stock temperature, °C | 120 | 120 |
| Temperature of top of the column, °C | 70 | 72 |
| Temperature of bottom of the column, °C | 105 | 105 |
| Reflux rate, $m^3/h$ | 0,2 | 0,2 |
| The tray efficiency | – | 0,621 |

The next task of the research was selection of operation regime of the column and optimal feed tray for the purpose of production 2-EH corresponding to the specifications of State Standard 26624-85. For this, three feeds different composition have been considered (Table 3). Composition of the feed is changed because of undesirable reactions such as formation of unsaturated components, ethers, water et al. The results, obtained at selection of regime of column work, are presented in Table 4.

Table 3

The feed composition using for modeling

| Value name | Feed 1 | Feed 2 | Feed 3 |
|---|---|---|---|
| 2-EH content, % mass | 94,73 | 96,74 | 97,25 |
| Aldehydes and ketones content, % mass | 0,88 | 0,15 | 0,35 |
| Unsaturated components content, % mass | 1,07 | 0,38 | 0,52 |
| 2-ethyl-4-methylpentanol content, % mass | 0,23 | 0,21 | 0,19 |
| Water content, % mass | 0,90 | 0,65 | 0,34 |

Table 4

The operation regime of the column at the feeds different composition

| Value name | Feed 1 | Feed 2 | Feed 3 |
|---|---|---|---|
| 1 | 2 | 3 | 4 |
| Feed stock temperature, °C | 105 | 105 | 105 |
| Feed stock flow rate, kg/h | 1050 | 1050 | 1050 |
| Reflux rate, $m^3/h$ | 8,1 | 8,1 | 7,9 |
| Reflux ratio | 36,01 | 39,27 | 37,40 |
| The end product flow rate, kg/h | 863,0 | 885,7 | 870,1 |
| The end product: | | | |
| 2-EH content, % mass | 97,58 | 97,87 | 98,38 |
| Aldehydes and ketones content, % mass. | 0,03 | 0,01 | 0,02 |
| Unsaturated components content, % mass | 0,09 | 0,09 | 0,12 |
| 2-ethyl-4-methylpentanol content, % mass | 0,25 | 0,23 | 0,21 |
| Water content, % mass. | – | – | – |
| Temperature of top, °C | 55,1 | 54,1 | 54,1 |
| Temperature of bottom, °C | 136,3 | 136,4 | 136,3 |
| Pressure of top, kPa | 8,00 | 8,00 | 8,00 |
| Pressure of bottom, kPa | 21,33 | 21,33 | 21,33 |
| Number of the trays | 30 | 30 | 30 |
| Feed tray (counting from the bottom) | 15 | 15 | 15 |

Modeling in HYSYS have been allowed to determine the dependences of quality change of the end product on the feed tray at constant reflux ratio for feed 1 (Fig. 2).

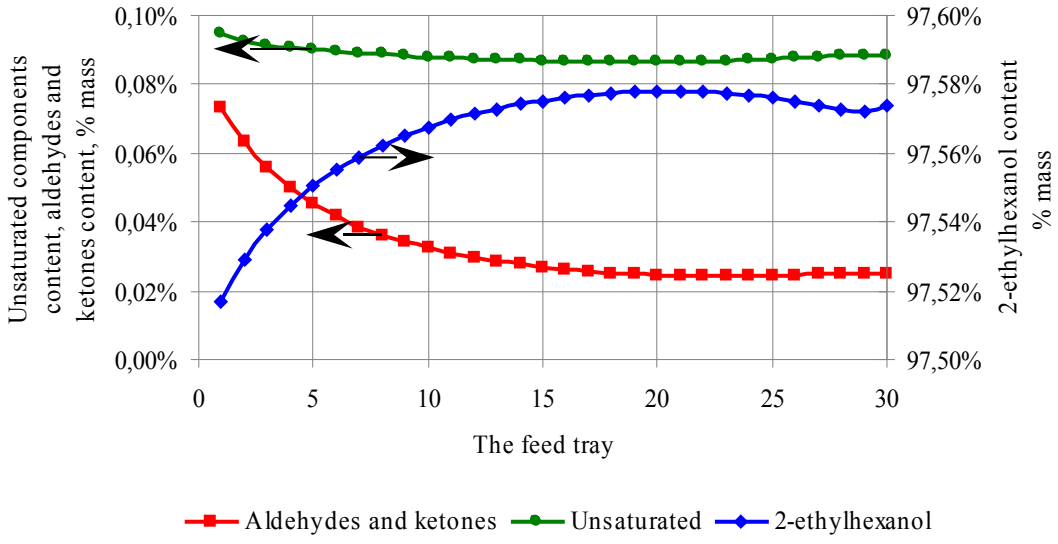


Figure 2. Dependences of aldehydes and ketones content, unsaturated components content, 2-EH content in the end product on feed tray in the column 1

From Fig. 2 we can see that the end product contains maximum 2-EH quantity and minimum unsaturated components quantity, aldehydes and ketones quantity when the feed tray is 20$^{th}$. If the feed is supplied on tray from 15$^{th}$ till 25$^{th}$, content of these components insignificantly differs from its content in case of feed supply on 20$^{th}$ tray. Because at the present time the feed is routed on 15$^{th}$ tray, therefore it does not make sense to change the feed tray. Dependences of aldehydes and ketones content, unsaturated components content and 2-EH content on the feed tray are the same at use of feeds the other composition.

At modeling of work of the column 1 we could not obtain quality of the recycled alcohols corresponding to the specifications of State Standard 26624-85: unsaturated components content exceeds acceptable, 2-EH content is lower than required. Therewith more than 15 % of 2-EH containing in the recycled alcohols withdraws from the column 1 together with the distillate. It depends on that vapours of 2-EH and other components rise to the top of the column vaporizing from the bottom. Part of the bottom liquid, which was in equilibrium with these vapours, is cooled in the heat exchanger and pumped to upper tray of the column as reflux. As a result of that just small part of 2-EH containing in the vapours crosses to liquid phase, the other part rise and leave the column together with light components.

Thereby it is impossible to achieve required quality of 2-EH by purification with one column, because water, aldehydes and ketones containing in the recycled alcohols is lighter than 2-EH, but majority part of unsaturated components is heavier than 2-EH.

To decide that problem the scheme of the recycled alcohols rectification including two columns has been considered (Fig. 3): the first is for water and light components removing, the second is for heavy components removing.

The recycled alcohols are pumped into a column 1 through a heat exchanger 2 where they are heated up to no more than 105 °C. Process of the recycled alcohols rectification is carried out under vacuum. The column 1 is supplied by the remote heat exchanger 3. Temperature of top of the column 1 is regulated by reflux. Light components vapors are routed from top of the column 1 to the heat exchanger 4 where it is condensed and cooled. Part of the formed condensate is routed to the top of the column as reflux, the other part of the condensate is sent to local waste water treatment.

The flow from bottom of the column 1 is pumped continuously for the end product separation to the middle section of a column 6. The column 6 is supplied by a remote evaporator 7. Temperature of top of the column 6 is regulated by reflux. 2-EH vapors are routed from top of the column 6 to a heat exchanger 8 where it is condensed and cooled. Part of the formed condensate is routed to the top of the column as reflux. Balance part of the condensate is pumped continuously to esterification process.

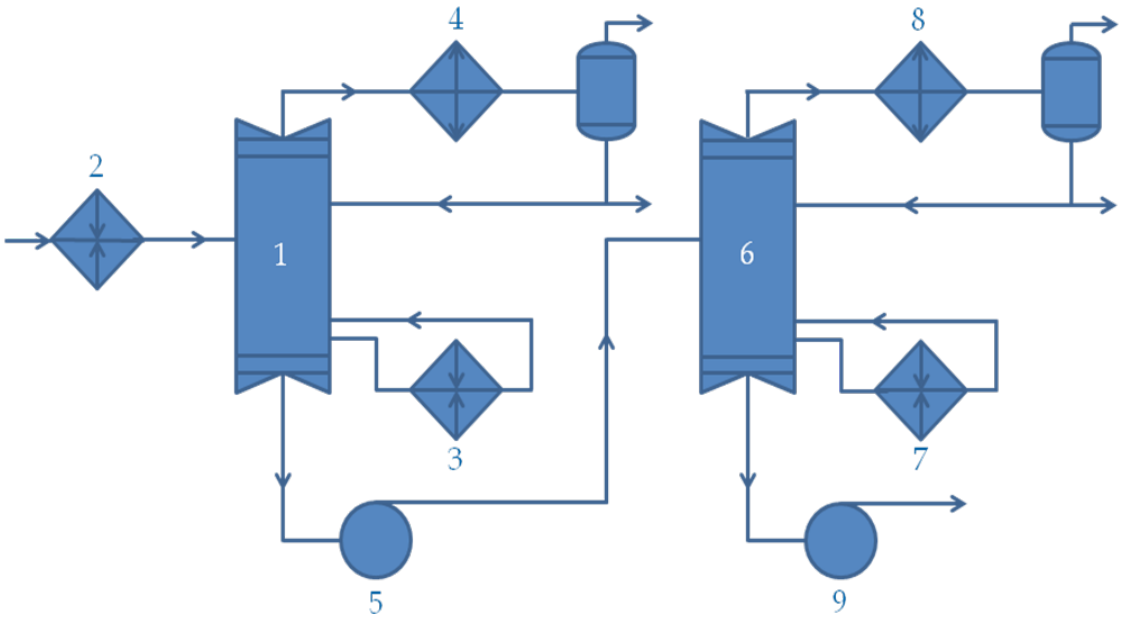


Figure 3. Offered scheme of the recycled alcohols rectification in JSC«Salavatnefteorgsintez»:
1, 6 – columns; 2, 3, 4, 8 – heat exchangers; 5, 9– pumps; 7 – evaporator;

The model of this block has been done in HYSYS. Selection of operation regime of the columns and optimal feed tray, which ensure recovery of 2-EH required quality has been done (Table 5). The dependences of quality change of the end product on the feed tray at constant reflux ratio for feed 1, which have been obtained as a result of modeling, are presented on Fig. 4 and Fig. 5.

Table 5

The operation regime of the columns at the feeds different composition

| Value name | Feed 1 | Feed 2 | Feed 3 |
|---|---|---|---|
| Column 1: | | | |
| Feed stock temperature, °C | 105 | 105 | 105 |
| Feed stock flow rate, kg/h | 1050 | 1050 | 1050 |
| Reflux rate, m3/h | 3,3 | 3,2 | 3,1 |
| The end product flow rate, kg/h | 1002 | 1030 | 1033 |
| Water content in the end product, % mass | – | – | – |
| Temperature of top, °C | 88,5 | 92,4 | 85,1 |
| Temperature of bottom, °C | 136,5 | 136,4 | 136,4 |
| Pressure of top, kPa | 8,00 | 8,00 | 8,00 |
| Pressure of bottom, kPa | 21,33 | 21,33 | 21,33 |
| Number of the trays | 30 | 30 | 30 |
| Feed tray (counting from the bottom) | 15 | 15 | 15 |
| Column 6: | | | |
| Feed stock temperature, °C | 136,9 | 136,9 | 136,9 |
| Reflux rate, $m^3/h$ | 15,8 | 15,8 | 15,8 |
| Reflux ratio | 13,54 | 13,53 | 13,22 |
| Distillate flow rate, kg/h | 976,0 | 977 | 1000 |
| Distillate: | | | |
| 2-ethylhexanol content, % mass | 99,00 | 99,00 | 99,00 |
| Aldehydes and ketones content, % mass | – | – | – |
| Unsaturated components content, % mass | – | – | – |
| 2-ethyl-4-methylpentanol content, % mass | 0,02 | 0,01 | 0,01 |
| Temperature of top, °C | 143,2 | 143,2 | 143,2 |
| Temperature of bottom, °C | 174,8 | 173,1 | 173,4 |
| Pressure of top, kPa | 50 | 50 | 50 |
| Pressure of bottom, kPa | 71 | 71 | 71 |
| Number of the trays | 30 | 30 | 30 |
| Feed tray (counting from the bottom) | 23 | 23 | 23 |

From Table 5 we can see that 2-EH quality completely corresponds to the specifications of State Standard 26624-85 at use of two-column scheme of the recycled alcohols rectification.

From Fig. 4 we can see that the feed tray of the column 1 slightly influences on the end product quality. Therefore it does not make sense to change the feed tray from $15^{th}$ to another tray. From figure 5 we can see that change of the feed tray in the column 6 from $15^{th}$ to $23^{rd}$ will lead to increase of the end product yield. Dependences of alde-

hydes and ketones content, unsaturated components content, 2-EH content on the feed tray are the same at use of feeds the other composition. Therefore the feed tray in the column 6 should be changed to 23rd. It will decrease reflux ratio and consequently duty on the evaporator.

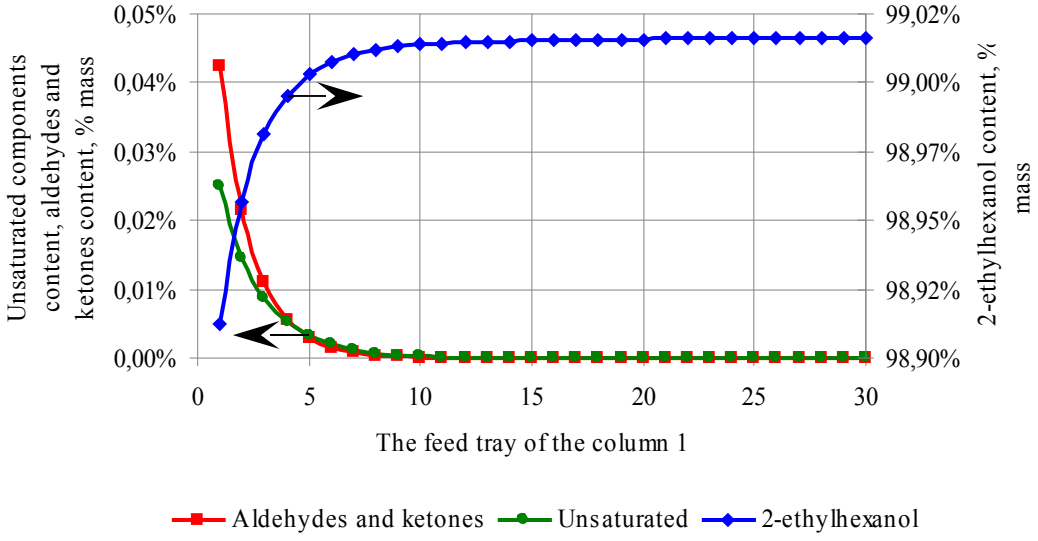


Figure 4. Dependences of aldehydes and ketones content, unsaturated components content, 2-EH content in the end product on feed tray of the column 1

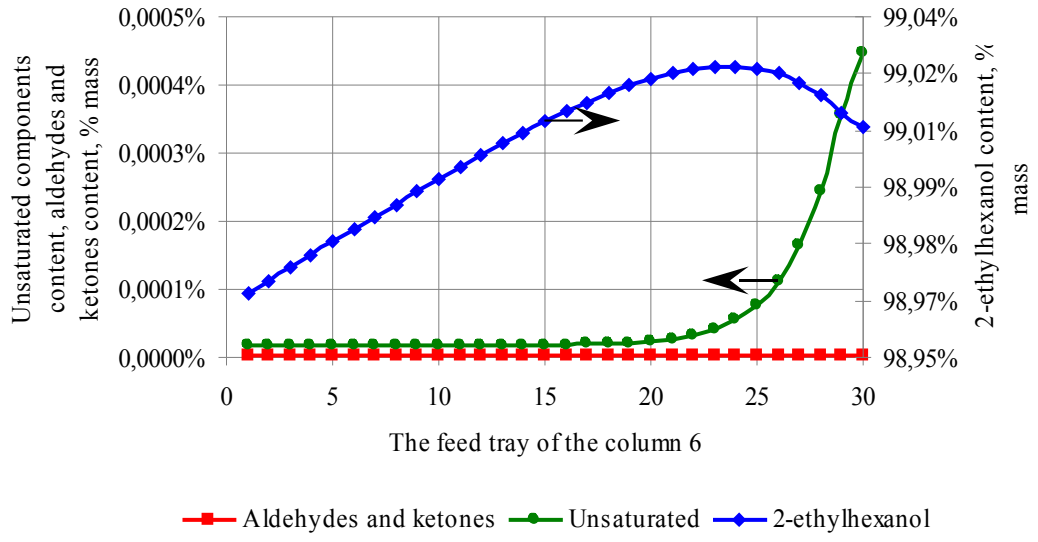


Figure 5. Dependences of aldehydes and ketones content, unsaturated components content, 2-EH content in the end product on feed tray of the column 6

Thereby use of the scheme of the recycled alcohols purification including only one-column will not allow to recovery of 2-EH corresponding to the specifications of State Standard 26624-85. It is necessary to use two-column scheme for recovery of 2-EH required quality.

## References

1. Диоктилфталат, химические свойства, формула // Компания "Русьхим". URL: http://www.ruschem-spb.ru/dioktilftalat/ (дата обращения 18.05.2010).

2. ГОСТ 26624-85. 2-этилгексанол технический. Технические условия. – М.: Изд-во стандартов, 1986. – 18 с.

3. Ghanadzadeh H. Gilani, Khiati G., Haghi A.K. Ghanadzadeh Gilani H. Liquid–liquid equilibria of (water + 2,3-butanediol + 2-ethyl-1-hexanol) at several temperatures // Fluid Phase Equilibria. – 2006. – Vol. 247 – P. 199 - 204.