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Proceedings of European Congress of Chemical Engineering (ECCE-6)
Copenhagen, 16-20 September 2007

# Investigation of application of extractive distillation method in chloroform manufacture

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## Abstract

The research of a purification process of chloroform from impurities by a method of an extractive distillation is submitted. Comparison the schemes of chloroform purification is executed on the basis of two separation agents: ethylen glycol and 2-phenoxyethanol. On the basis of economical criterion the expediency of usage of the separation agent 2-phenoxyethanol is shown.

Keywords: Extractive distillation, chloroform, mathematical model

## 1. Introduction

The chloroform manufactured on the basis of a chlorination of methane, contains impurities of ethane - ethylenic series and demands special stage of purification. The main difficulty is introduced by separation of closely boiling impurities, in particular, 1,1 - dichlorethane and cis - dichloroethylene.

Some ways of purification of chloroform are known:

1. A chlorination of impurities up to higher-boiling derivatives by excess of chlorine with initiation of reaction by a solar lamp irradiation [1] or by contact with porous material at heightened temperature [2] with the subsequent distillation. The lacks of these methods are : it is possible selectively to eliminate only cis - dichloroethylene, while at a chlorination of a 1,1-dichlorethane the chloroform is simultaneously chlorinated. At finishing of the content of a 1,1-dichlorethane 0,02 % in product the loss of chloroform up to 50 % can be reached.
2. In considerable losses of chloroform results also the method of purification by reaction of impurities with etching acid at the presence of pentachlorated antimony as catalyst with the subsequent separation of impurities by an adsorption on molecular sieves.
3. There is a set of methods of chloroform purification, where the sulfuric acid in combination, for example, with a formic aldehyde acts.

In operational manufacture of chloromethanes the chloroform subject to purification by an oleum (batch process by duration about 6 hours), then neutralize by alkali liquor and subject to dewatering by azeotropic distillation [3]. This method, as well as previous, results in losses of chloroform at all stages of purification. Besides, it demands the consumptions of reactants (oleum, alkali), that results in formation of waste (spent sulfuric acid and spent alkali liquor).

## 2. The extraction distillation method

In this research the method of an extractive distillation for the solution of the indicated problem of purification of chloroform is offered. For this purpose by the authors the selection of separation agents is carried out and for the selected separation agents on the basis of the conducted experimental researches the thermodynamic model of a vapour-liquid equilibria in a multicomponent system 1,1 - dichlorethane - cis - dichloroethylene - chloroform - carbon tetrachloride - separation agent is constructed. With usage of the basic equation of an extractive distillation the efficiency of selected separation agents application is demonstrated. The best selection agents have appeared the substances of glycol class . On the base of a vapour-liquid equilibria researches the selection of the separation agents was carried out.

The calculation of change of a relative volatility closely boiling components at the introducing of the separation agent was conducted on an equation [4]

$$lg\frac{(\alpha_s)_m}{\alpha_m}=\frac{F_{1s}-F_{2s}}{1-x_s} \quad (1)$$

Here $x_s$ is concentration of separation agent. The function F for a ternary system consisting from components 1 and 2 given mixture and separation agent ("s") is determined by expression

$$F=x_1 lg\gamma_1+x_2 lg\gamma_2+x_s lg\gamma_s \quad (2)$$

where $\gamma_1$ , $\gamma_2$ , $\gamma_s$ - activity coefficients of component 1, 2 and separation agent, respectively.

Value of selectivity S

$$S=\frac{(\alpha_s)_m}{\alpha_m} \quad (3)$$

expresses mean increase of a relative volatility coefficient of components of considered binary mixture conditioned by presence of the separation agent.

In the tables 1, 2 the values of a difference $\frac{F_{1s}-F_{2s}}{1-x_s}$ and selectivity S calculated on the equilibrium data for two investigated separation agents ethylen glycol and 2-phenoxyethanol are submitted.

It is visible, that the difference of functions of state F is positive, that speaks about fulfilment of the main disparity of extractive distillation.

The values of selectivity S demonstrate, that the first component (1,1-dichlorethane or cis - dichloroethylene) at interaction with the separation agent becomes more volatile, than, if the separation agent was not.

In work the dependences of activity coefficients from mole fraction of ethylen glycol and 2-phenoxyethanol in binary mixtures formed by substances, present during an extractive distillation have investigated.

From the obtained data it follows, that in systems a 1,1-dichlorethane - ethylen glycol, cis - dichloroethylene - ethylen glycol and 1,1-dichlorethane - 2- phenoxyethanol , cis - dichloroethylene - 2- phenoxyethanol of selectivity values for ethylen glycol and 2-

phenoxyethanol are approximately identical. Allowing selectivity values it is possible to draw a conclusion, that gaining of ethylen glycol or 2- phenoxyethanol to systems a 1,1-dichlorethane - chloroform and cis - dichloroethylene - the chloroform should produce increase of a relative volatility of 1,1-dichlorethane and cis - dichloroethylene.

The purpose of an extractive distillation is the distillation of 1,1-dichlorethane and cis - dichloroethylene impurities from chloroform together with distillate. At the same time it is necessary, that the concentration of chloroform was maximum in cube, and the concentration of 1,1-dichlorethane and cis - dichloroethylene was minimum taking into account the requirements of impurity level in the chloroform product.

n fig. 1, 2 influence of distillate flow rate on the contents of the main impurity of 1,1-dichlorethane and chloroform in a bottom product of extractive distillation column (separation agent 2-phenoxyethanol) is shown.

Table 1. Values of a difference $\frac{F_{1s}-F_{2s}}{1-x_s}$ and selectivity S for the ethylen glycol separation agent.

| 1,1-dichlorethane - chloroform | | | cis - dichloroethylene - chloroform | |
|---|---|---|---|---|
| $x_i$ | $\frac{F_{1si}-F_{2si}}{1-x_s}$ | $\left(\alpha_{si}\right)_m / \alpha_{im}$ | $\frac{F_{1si}-F_{2si}}{1-x_s}$ | $\left(\alpha_{si}\right)_m / \alpha_{im}$ |
| 0,9 | 0,3537 | 2,2579 | 0,0491 | 1,1198 |
| 0,8 | 0,2812 | 1,9109 | 0,0393 | 1,0948 |
| 0,7 | 0,2162 | 1,6455 | 0,0310 | 1,0742 |
| 0,6 | 0,1597 | 1,4444 | 0,0232 | 1,0550 |
| 0,5 | 0,1110 | 1,2915 | 0,0164 | 1,0385 |
| 0,4 | 0,0717 | 1,1797 | 0,0106 | 1,0248 |
| 0,3 | 0,0408 | 1,0986 | 0,0061 | 1,0139 |
| 0,2 | 0,0182 | 1,0429 | 0,0025 | 1,0059 |
| 0,1 | 0,0047 | 1,0110 | 0,0008 | 1,002 |

Table 2. Values of a difference $\frac{F_{1s}-F_{2s}}{1-x_s}$ and S selectivity for the sectioning agent 2-phenoxyethanol.

| Cis - dichloroethylene - chloroform | | |
|---|---|---|
| $x_i$ | $\frac{F_{1si}-F_{2si}}{1-x_s}$ | $\left(\alpha_{si}\right)_m / \alpha_{im}$ |
| 0,989 | 0,2916 | 1,9571 |
| 0,984 | 0,2939 | 1,9677 |
| 0,976 | 0,2960 | 1,9771 |
| 0,95 | 0,2962 | 1,9780 |
| 0,90 | 0,2968 | 1,9795 |

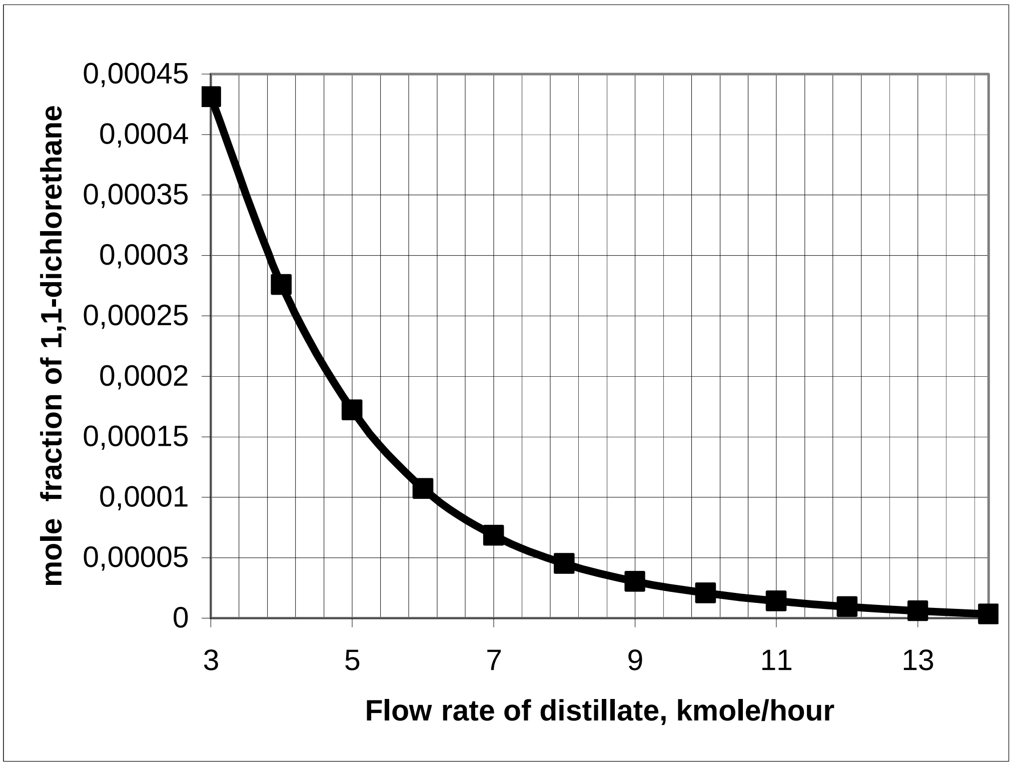

Fig. 1. Dependence of the content of 1,1-dichlorethane in cube of extractive distillation column from quantity of distillate.

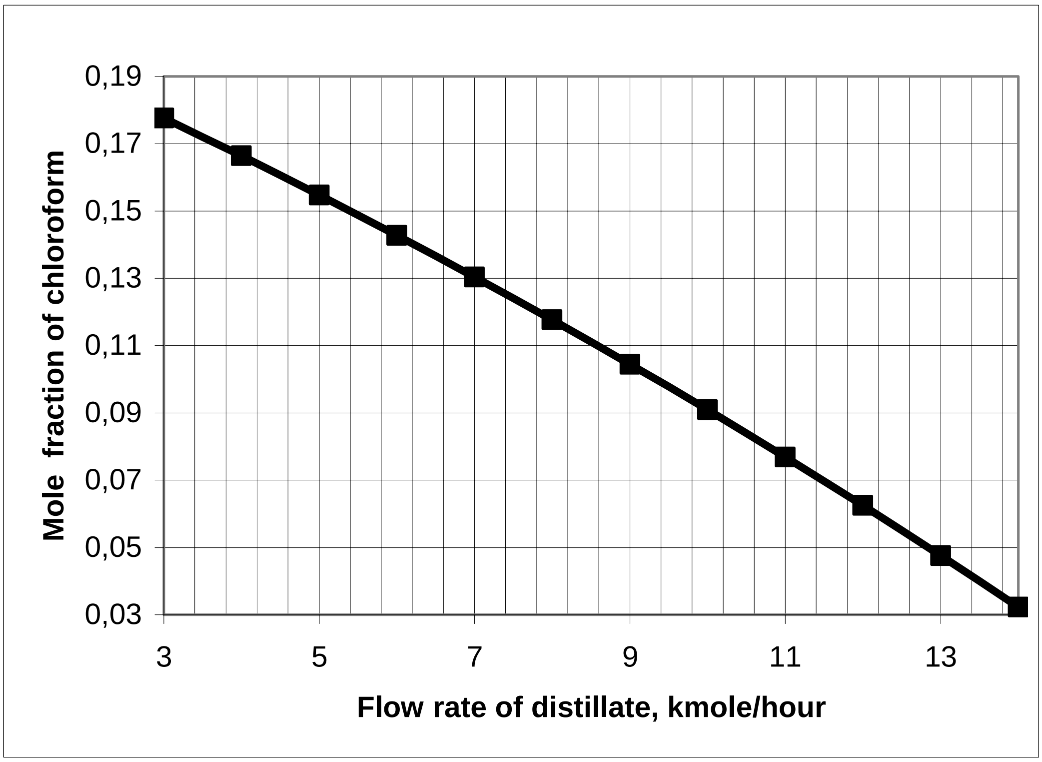

Fig.2. Dependence of the content of chloroform in cube of extractive distillation column from quantity of distillate.

The nature of the obtained dependences speaks about necessity of search of optimum quantity of distillate flow rate. At limitation on total quantity of impurities in a bottom product of extractive distillate column, not superior 0,025 %, the optimum distillate flow rate has equal 9 kmole/hour.

In a fig. 3 the dependence of the content of the main impurity of 1,1-dichlorethane in a bottom product of extractive distillation column from reflux number is shown. As well as it was necessary to expect this influencing was essential.

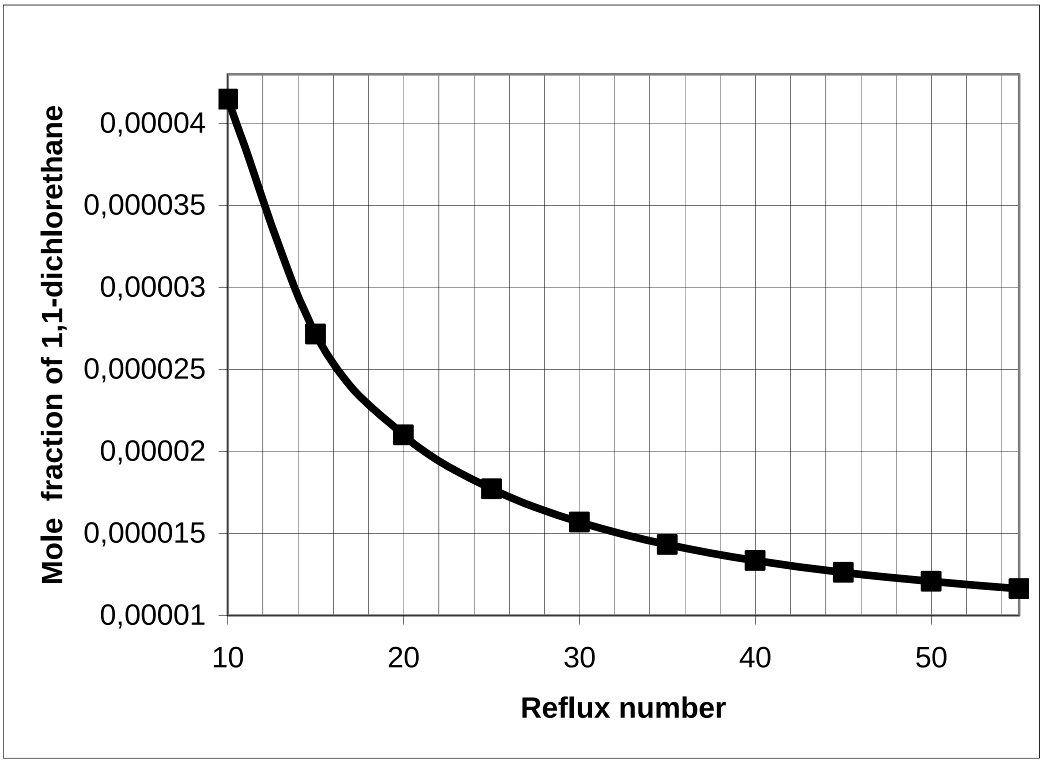

Fig. 3. Dependence of the content of 1,1-dichlorethane (separation agent 2-phenoxyethanol) in bottom product of extractive distillation column from reflux number.

It is interesting to learn influencing of quantity of separation agent flow rate on separation of impurities in column. For this purpose quantity of the separation agent and its input step was varied.

It was obtained, that under increasing of quantity of separation agent flow rate the decreasing of concentration in a bottom product both impurity of 1,1-dichlorethane and chloroform take place. Therefore quantity of separation agent flow rate was determined by optimization at limitation on impurity level in grocery chloroform. (60 kmole/hour).

For final selection of the separation agent the simulation of three-column scheme for separation 1,1-dichlorethane - cis – dichloroethylene - chloroform - carbon tetrachloride mixture was conducted. In the first column of the scheme the separation of carbon tetrachloride is carried out. In the second column the process of extractive distillation with separation of impurities of 1,1-dichlorethane and cis - dichloroethylene with distillate is carried out. At last, in the third column after separation of separation agent in the evaporator the final clearing of chloroform from impurities and separation agent is realized.

The matching of two separation schemes with usage of ethylen glycol and 2-phenoxyethanol as the separation agents has shown, that the grocery chloroform of demanded quality (contents of a 1,1-dichlorethane no more than 0,002 %, and common impurity level no more than 0,025 %) can be obtained in both schemes at approximately identical regime and design parameters. Therefore it was expedient to compare the schemes with allowance for of cost of the separation agents. Such matching is listed in table 3.

Table 3. Matching of two schemes of chloroform purification on the basis 2- phenoxyethanol and ethylen glycol

| The scheme with 2- phenoxyethanol | The scheme with ethylen glycol |
|---|---|
| 1. Costs of heating steam, \$/year | |
| Heat required for evaporation of mixture by heating steam in column bottom:<br>$Q_{\mathrm{ev}} = (R+1)\cdot D\cdot\sum_{i=1}^{N}\left(y_i\cdot r_i\cdot M_i\right)$ | |
| $Q_{\mathrm{ev}} = 3300518{,}61$, kJ/hour | $Q_{\mathrm{ev}} = 3143997{,}83$, kJ/hour |
| Costs of evaporation in column bottom, \$/year | |
| $E_{\mathrm{e}} = 97880.95$ \$/year | $E_{\mathrm{e}} = 93239.14$ \$/year |
| 2. Costs on separation agent $E_{\text{separation agent}}$, \$/year | |
| Total quantity of the separation agent: $m_{\text{separation agent}}$, kg/year | |
| $m_{2-phenoxyethanol} = 21899{,}76$ kg/year | $m_{\text{ethylen glycol}} = 18386{,}26$ kg/year |
| Costs on separation agent $\mathrm{E}_{\text{separation agent}}$, \$/year | |
| $\mathrm{E}_{\text{2-phenoxyethanol}} = 743.77$ \$/year | $\mathrm{E}_{\text{ethylen glycol}} = 16902.17$ \$/year |
| Costs on heating steam and separation agent $E_{total}$, \$/year | |
| $E_{total} = 98624.72$ \$/year | $\mathrm{E}_{\text{total}} = 110141.31$ \$/year |

The obtained outcomes have shown, that taking into account the cost of separation agent the usage of chloroform purification scheme with 2-phenoxyethanol is more economically justified.

## 3. Conclusions

1) The ecological saving technology of chloroform purification from impurities is investigated.
2) On the basic equation of extractive distillation the applicability of 2-phenoxyethanol and ethylen glycol as separation agents in the scheme of purification of chloroform from closely boiling components are investigated and justified.
3) The simulation of three column scheme of chloroform purification is conducted and the regime parameters of the scheme with application of ethylen glycol and 2-phenoxyethanol are determined.
4) The basic design parameters of columns of carbon tetrachloride separation , extractive distillation and final purification of chloroform in the separation scheme with usage of ethylen glycol and 2-phenoxyethanol are determined.
5) Matching the separation schemes on the basis of ethylen glycol, 2- phenoxyethanol is conducted and expediency of usage of the separation agent 2- phenoxyethanol also is revealed.

## Table of symbols:

$(\alpha_s)_m$, $\alpha_m$ – express average value of a factor of a relative volatility of the first and second components in all range of their concentrations accordingly in presence and in absence of the separating agent;
F – function of state of a system (equation (2));
S – value of selectivity;
$x_s$ – concentration of the separation agent in mixture;
Y – activity coefficient.

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This work was executed at partial financial support of Ministry of education and science of Russian Federation. The project РНП 2.1.2.2881.