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PROJECT OF LABORATORY RECTIFICATION COLUMN FOR PERIODIC WORK

PROJEKT LABORATORYJNEJ KOLUMNY REKTYFIKACYJNEJ DO PRACY OKRESOWEJ

Abstract

The paper presents a project of a rectification column working periodically for the production of ethyl alcohol. The project contains an assumption of a steady concentration of the distillate. Thee range of change in the reflux from 1.7 to 13 required to obtain that concentration was calculated. With 50 litres of feed containing 9 mol % ethanol, about 10 litres of distillate was obtained, which has 70 mol % ethanol. Ceramic Raschig rings with a diameter of 15 mm, which, in a column, occupy a height of 0.5 m, were used. The height of the entire column was 0.67 m.

Keywords: rectification column, ethanol, heat balance column

Streszczenie

W artykule przedstawiono projekt kolumny rektyfikacyjnej pracującej okresowo do otrzymywania alkoholu etylowego. W projekcie założono stałe stężenie destylatu i wyznaczono zakres zmiany liczby powrotu od 1,7 do 13, konieczny do jego otrzymania. Z 50 litrów surówki zawierającej 9% mol. etanolu uzyskano ok. 10 litrów destylatu o stężeniu 70% mol. Jako wypełnienie zastosowano ceramiczne pierścienie Raschiga o średnicy 15 mm, które zajmują w kolumnie wysokość 0,5 m. Natomiast wysokość całej kolumny, jest równa 0,67 m.

Słowa kluczowe: kolumna rektyfikacyjna, etanol, bilans ciepła kolumny

1. Nomenclature

R – reflux
x_i – mole fraction in the liquid phase
y_i – mole fraction in the gas phase
n_t – the number of theoretical shelfs
α_{AB} – the average coefficient of relative volatility
ρ – density
M_i – molar mass
T – temperature
a – specific surface of fill
$\dot{V}_{\mathrm{mol}}$ – molar flow of steam
ϕ – degree of usability of the surface
S_k – cross-sectional area of the column
r_r – molar heat of evaporation
i_i – enthalpy
D, S, W – mol quantity of distillate, feed and decoction
t_{wS} – boiling temperature of feed
t_o – surrounding temperature
C_{wi} – specific heat of feed
V_{mol} – amount of steam moles
$\dot{Q}_{sk}$ – heat stream from condensed vapor
k – heat transfer coefficient
d_z – external diameter
d_w – internal diameter

2. Introduction

After World War II, in Poland, there were about 1200 agricultural distilleries eligible for commissioning and 15 industrial distilleries adapted for the processing of molasses. The agricultural distilleries were grouped into 'State Agricultural Enterprises' and industrial distilleries into the 'POLMOS' State Enterprise of the Spirits Industry. These companies also included alcohol rectification plants, vodka factories and yeast plants. The production of spirits in post-war Poland was ran by three distilleries, which converted cellulose alkalis to alcohol. These operated within the paper industry, and several branches producing fruit spirits.

In 1991, the Ministry of Finance approved the introduction of a certain amount of spirits into gasoline. This allowed producing a fuel containing 5% anhydrous alcohol. It was practically insignificant for the alcohol market. Bioethanol is a dehydrated alcohol, which improves car fuels by increasing their octane number, reducing the concentration of carbon monoxide by 20–30% and the concentration of hydrocarbons in the exhaust gases by 10%. In 1997, more than 50% of domestic ethanol was consumed in addition to fuel, which accounted for about 100 million litres of spirits. In subsequent years, the consumption was already smaller [1].

In 2007, the production of agricultural distilleries in the EU accounted for about 10% of ethanol production. Apart from Poland, agricultural distillate was also obtained on a larger scale in Austria and Germany. In other countries, the distilleries operated rather locally. Agricultural distilleries in Poland operate depending on the demand reported from the fuel and spirits sector. Table 1 shows the production of agricultural distillate (raw spirit), the number of active agricultural distilleries and the production of bioethanol in Poland in 1994–2006. In 2009, the consumption of bioethanol as an additive for gasoline was at 293.6 thousand m^3, of which 56% came from domestic production; the remainder came from imports. The total production of ethanol in Poland in this year amounted to 205.8 thousand m^3. In 2009, there were 179 distilleries craft, of which 14 produced bioethanol as a bio component [2, 3].

Table 1. Production of agricultural distillate (raw spirit), number of active agricultural distilleries and bioethanol production in Poland in 1994–2006 [3]

Year	Agricultural distillate, mln l	Active agricultural distilleries	Bioethanol, mln l
1994	210	b.d.	27.0
1995	245	950	63.0
1996	278	900	100.9
1997	240.6	840	110.6
1998	208	700	99.8
1999	167.2	620	88.5
2000	173.3	380	51.5
2001	181	350	69.4
2002	210	330	82.8
2003	210–219.6	300	76.2
2004	195	242	45.2–48.5
2005	ok. 230–241.5	220	110.8
2006	259	217	161

In 2016, 98 million litres of vodka were produced. This is less than in 2012, when more than 102 million litres were produced, or 2011 when the production was over 103 million litres. The reason for the reduced production was a 15% increase in excise duty on strong alcohol, which was introduced on January 1, 2014 (Fig. 1). In Poland, excise duty represents 75% of the price of a half a litre of vodka. In the year 2016, the spirits sector transferred 11 billion zlotys to the state budget [4].

A different situation concerns the export of Polish vodka, which has been developing dynamically since the accession of Poland to the EU. Over the last 10 years, its sales have increased three fold. In 2003, Polish producers sold 15 million litres of vodka abroad. In 2013, the export of spirit drinks increased from 44.5 million litres to 50.75 million litres. In 2017, exports amounted to 51 million litres. Polish spirits are best sold in France and in the USA (Fig. 2) [5].

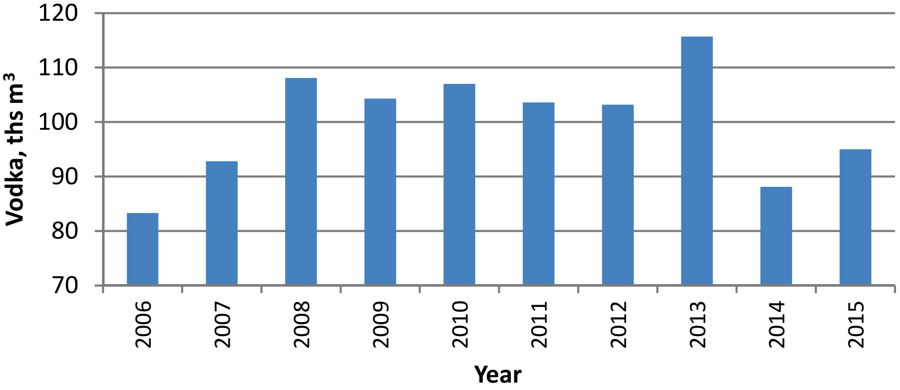

Fig. 1. Annual production of vodka in years 2006–2015 [4]

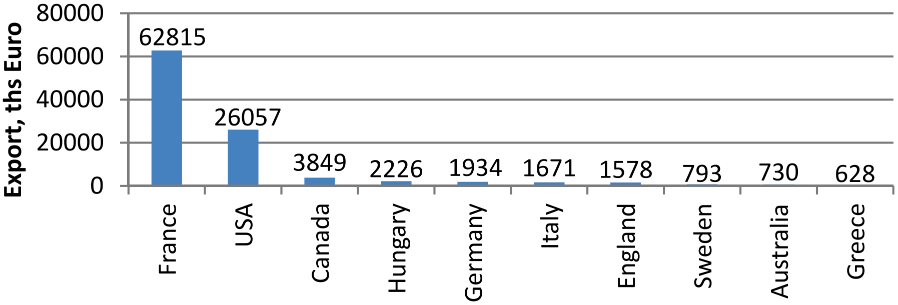

Fig. 2. The largest recipients of Polish vodka [5]

3. Project of periodic rectification column

In periodic rectification, the boiler is filled with a liquid mixture, which is heated to the boil point. The steam passing through the column is enriched in a more volatile component and the liquid in the less volatile component with a higher boiling point. At the top of the column, where the temperature is lower, the vapor is condensed and is collected as a distillate. As a result, we obtain mixtures of fractions that differ in condensing temperatures. In the boiler, a residue rich in less volatile component remains. The periodic rectification is used to separate small amounts of mixtures.

3.1. Project assumptions

The calculations assumed the process of periodic rectification carried out at a constant composition of distillate, for which reflux varies from R_p to R_k. The feed was 50 dm^3 in volume and contained a 25% vol. ethanol in water solution. The concentration of ethanol in the distillate was set at 0.7 mol·mol^{-1} (x_D), and in the residue – 0.01 mol·mol^{-1} (x_W).

3.2. Determining the reflux

To calculate the minimum reflux for the beginning and end of the process, the following formula (1) was used:

$$R_{\min} = \frac{x_D - y_i^*}{y_i^* - x_i} \tag{1}$$

where index 'i' is the composition of the feed (S) at the beginning of the rectification or composition of the residue (W) at its end. The star was the determined equilibrium concentrations corresponding to real concentrations.

The real reflux was calculated from equation (2). The coefficient of excess reflux (β) for the working calculations is taken in the range of 1.2–2.5 [6]. In order to more accurately select the reflux, an optimisation calculation would have to be made. For the purposes of this project, the value of $\beta = 2$ was assumed.

$$R = \beta \cdot R_{\min} \tag{2}$$

In order to receive a constant composition of distillate $x_D = 0.7$ mol·mol^{-1} (it was assumed), the reflux during rectification should be changed from 1.7 to 13.4 (Tab. 2). The total amount of distillate received (D) is 0.27 kmol (Fig. 3).

Table 2. The reflux for the beginning and the end of rectification

R_{minp}	R_p	R_{mink}	R_k
0.8	1.7	6.7	13.4

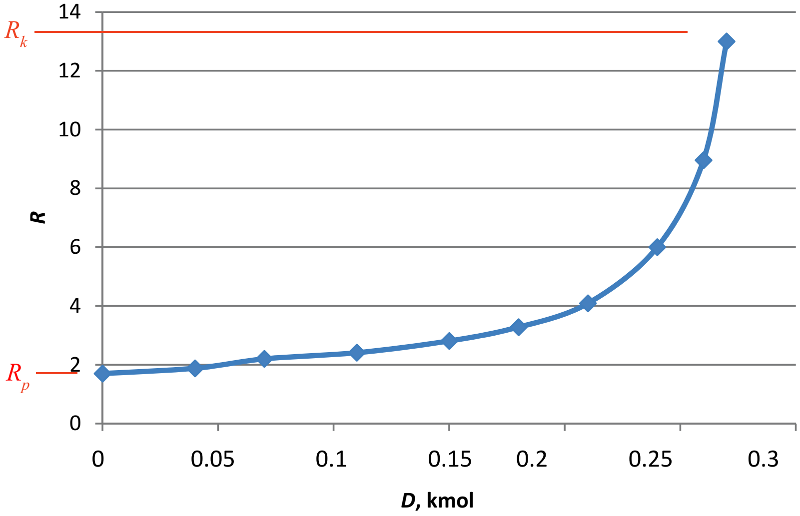

Fig. 3. Change of the amount of distillate depending on the change of the reflux

3.3. Determining the number of theoretical shelfs

3.3.1. McCabe-Thiele Method

McCabe-Thiele's graph method for determining theoretical shelfs is based on the introduction of equilibrium triangles between the operating line at the beginning of the rectification and the liquid-vapor equilibrium line. Figure 2.2 indicates the existence of four equilibrium steps. The first one is a boiler; therefore, the number of theoretical shelfs (n_t) is three (Fig. 4).

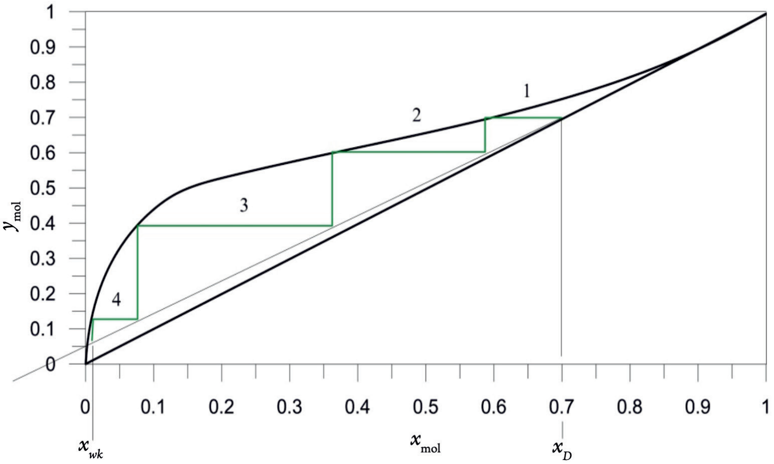

Fig. 4. Determination of theoretical shelfs by McCabe-Thiele methodology

3.3.2. Analytical method of Fenske

Fensky's analytical method uses average relative volatility at the boiling point of ethanol and water. The number of theoretical shelfs is calculated from the equation (3).

$$n_t = \frac{\log\left[\dfrac{x_D \cdot (1-x_{Wp}}{x_{Wp} \cdot (1-x_D)}\right]}{\log(\alpha_{AB})} - 1 \tag{3}$$

The calculated relative volatility factors at the boiling point of ethanol and water are 2.31 and 2.25, respectively. The number of theoretical shelfs determined by this method equals three.

3.4. Selection of column fill

As a fill, Raschig ceramic rings of Ace ChemPack were selected. Table 3 shows the characteristics of the rings used [7].

Table 3. Specification of Raschig ceramic rings

Specification of Raschig ceramic rings	
ring diameter, mm	15
ring height, mm	15
wall thickness of the ring, mm	2
specific surface (a_r), $m^2 \cdot m^{-3}$	330
free volume, $m^3 \cdot m^{-3}$	0.7
the number of items in 1 m^3	250 000
bulk density, $kg \cdot m^{-3}$	690

3.5. HETP and the height of the fill

In order to calculate the height equivalent of the theoretical plate (*HETP*), the equations of Granville (4) and Delzenne (5) were used. The fill height was determined for the average value of *HETP* [7].

$$HETP = \left(8.8 \cdot 10^{(-4)} \cdot \frac{a_6}{a_r}\right) \cdot \frac{M_{S\rho S}}{T} \tag{4}$$

$$HETP = HETP_o \cdot \left[1 + 0.7 \cdot \log\left(\frac{D_k}{D_o}\right)\right] \tag{5}$$

In the formulas, a surface area of the 6 mm (a_6) diameter rings equal 790 $m^2 \cdot m^{-3}$, $HETP_o$ = 0.762 m, and the diameter of D_o = 0.915 m for the selected reference column, were assumed. The diameter of the column is 0.7 m (D_k). The average *HETP* was 0.16 and the fill height was 0.5 m (h_w).

3.6. Mass transfer coefficient

The mass transfer coefficient (6) was calculated for the gas phase as the product of the mass transfer unit (h_{oG}) (7) and the number of mass transfer units (N_{oG}) (8) [9].

$$K_{oG} = h_{oG} \cdot V_{oG} \tag{6}$$

$$h_{oG} = \frac{\dot{V}_{\mathrm{mol}}}{h_w \cdot a_r \cdot \varphi \cdot S_k} \tag{7}$$

$$N_{oG} = \int_{y_p}^{y_k} \frac{1}{y^* - y} \cdot dy \tag{8}$$

The mass transfer coefficient in the gas phase assumes the value:

$$K_{oG} = 2 \cdot 10^{(-3)} \left[\frac{\text{kmol}_A}{m^2 \cdot s \cdot \frac{\text{kmol}_A}{\text{kmol}}} \right]$$

3.7. Column height

The total height of the column (9) was calculated as the sum of the heights: above the mist eliminator – 0.07 m (h_1), the mist eliminator – 0.02 m (h_2), the condenser – 0.05 m (h_3), space under the grate – 0.01 m (h_4) the grate – 0.02 m (h_5) and the fill column – 0.5 m (h_w).

$$H_k = h_w + h_1 + h_2 + h_3 + h_4 + h_5 \tag{9}$$

$$H_k = 0.67\ \text{m}$$

3.8. Heat balance of rectification column

In the aim, which was determined to calculate the heat loss from the rectification process to the environment, the heat balance of the rectification column was prepared (10) [10, 11].

$$Q_w + Q_p = Q_d + Q_{sk} + Q_{\text{wyw}} + Q_{\text{str}} \tag{10}$$

The heat needed to produce the right amount of steam (11).

$$Q_w = r_D \cdot \int_0^D R dD + r_D \cdot D \tag{11}$$

Heat use to warm the feed in the boiler (12).

$$Q_p = C_{Ws} \cdot (t_{wS} - t_o) \cdot S \cdot M_S \tag{12}$$

Condensation heat of vapor (13).

$$Q_{sk} = r_D \cdot V_{\text{mol}} \tag{13}$$

Heat of residue, which remained in the boiler after the process end (14).

$$Q_{\text{wyw}} = i_w \cdot W \tag{14}$$

Heat received with distillate (15).

$$Q_d = i_D \cdot D \tag{15}$$

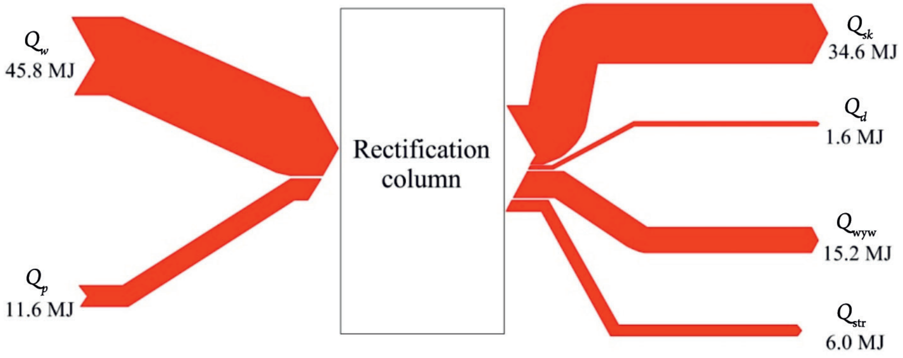

Fig. 5. Chart Sakey's for rectification column

The amount of heat lost to the environment during the rectification process based on the energy balance of the column is equal to 6 MJ (Q_{str}) and represents about 10% of all outgoing streams. Most of the energy was required to condense the resulting vapours (Fig. 5).

3.9. Selection of the pot and condenser for the column

3.9.1. Condenser

In order to select the condenser, it was necessary to calculate the heat exchange surface (16).

$$A = \frac{\dot{Q}_{sk}}{k \cdot \Delta T_m} \tag{16}$$

where ΔT_m is the logarithmic difference of temperature in the condenser.

Logarithmic diameter of the coil (17).

$$d_n = \frac{d_z - d_w}{\ln \frac{d_z}{d_w}} \tag{17}$$

Coil length (18).

$$L = \frac{A}{\pi\left(\frac{d_n}{d}\right)} \tag{18}$$

In addition, from the following formula (19), the amount of water flowing through the condenser was calculated at 57.2 $\mathrm{kg \cdot h^{-1}}$.

$$\dot{m}_{\text{wody}} = \frac{\dot{Q}_{sk}}{c_w \cdot \Delta T_m} \tag{19}$$

From the above formulas, a condenser cooling area equal 0.11 $\mathrm{m^2}$ was calculated along with a coil diameter of 9 mm and a coil length of 3 m. For these values, a condenser was selected in the form of a tube with an internal coil (Tab. 4).

Table 3. Condenser characteristics [12]

Condenser	
tube diameter of the condenser, mm	70
length of pipe, mm	400
coil length, mm	3000
coil diameter, mm	10

3.9.2. Pot

The pot of the column was selected from available materials with the assumed volume of 60 dm^3. The tank is made of stainless steel, acid resistant AlSi304. Its specification is shown in Table 5.

Table 4. Characteristics of the pot [13]

Pot	
volume, dm^3	60
height, mm	340
diameter, mm	480
wall thickness, mm	1.4
net weight, kg	5

4. Conclusions

- Ethyl alcohol can be obtained in the laboratory using a rectification column for period work, which is suitable for a small amount of feed.
- At work, 25% vol. ethanol in feed was assumed. At such concentrations of ethanol, there is resistance to gamma-rayed Saccharomyces cerevisiae strains only.
- Periodic rectification can be carried out in two different ways by establishing a constant concentration of ethanol in the distillate by changing the reflux or vice versa.
- The calculations show that a change in reflux between 1.7 and 13 would allow the ethanol concentration in the distillate to be maintained at about 70 mol%. This method can be technically difficult to achieve and requires constant process parameters control, but it is possible to obtain a high concentration product already in the first rectification cycle. The concentration of ethanol in the residue remains small.
- The project used ceramic Raschig rings with a diameter of 15 mm, which occupy a column height of 0.5 m. The height of the entire column is 0.67 m.
- Heat losses in the column were obtained at an acceptable level of 10%.

References

[1] Łączyński B., *Skrócony kurs gorzelnictwa rolniczego*, Wydawnictwo Sigma-NOT, Warszawa 1993.

[2] Jarociński J., Jarosz K., *Gorzelnictwo i drożdżownictwo*, Wydawnictwo Szkolne i Pedagogiczne, Warszawa 1994.

[3] Kupczyk A., *Perspektywy rozwoju polskich gorzelni rolniczych*, Rynki Alkoholowe v 7/2007, 60–65.

[4] Biernacka P., *Metody kompleksowej analizy składu produktów ubocznych procesu fermentacji alkoholowej w półproduktach i produktach spirytusowych*, Rozprawa doktorska, Politechnika Gdańska, Gdańsk 2012.

[5] Ministerstwo Skarbu Państwa – Polski rynek wódki, http://www.msp.gov.pl/pl /przeksztalcenia/serwis-gospodarczy/wiadomoscigospodarcze/28430,Polski-rynek-wodki.html (access: 10.06.2017).

[6] Pawłow K.F., Romankow P.G., Noskow A.A., *Przykłady i zadania z zakresu aparatury i inżynierii chemicznej*, WNT, Warszawa 1971.

[7] AceChemPack – ceramiczne pierścienie Raschiga, http://www.tower-packing.com/ceramic /ceramic_rasching_rings_random_packings.html (access: 10.06.2017).

[8] Ziółkowski Z., *Destylacja i rektyfikacja w przemyśle chemicznym*, Wydawnictwo Naukowo-Techniczne, Warszawa 1978.

[9] Hobler T., *Dyfuzyjny ruch masy i absorbery*, Wydawnictwo Naukowo-Techniczne, Warszawa 1976.

[10] Ciborowski J., *Inżynieria procesowa*, Wydawnictwo Naukowo-Techniczne, Warszawa 1973.

[11] Raznjevic K., *Tablice cieplne z wykresami*, Wydawnictwo Naukowo-Techniczne, Warszawa 1983.

[12] Mojamaszyna – skraplacz, http://mojamaszyna.pl/chlodnica-destylator-3-metry-rurki -wezownicy-fi-10-i6600199556.html (access: 10.06.2017).

[13] Destylandia – zbiornik 60 l, http://destylandia.pl/index.php?id_product=2068

[14] &controller=product (access: 10.06.2017).