Cascade units for neon isotopes production
by rectification method

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Basics of neon separation into isotopes by distillation method at $T = 28$ K are discussed. The required numbers of transfer units of the top and bottom column sections at different loads are calculated. The experimental characteristics of packed rectification columns are presented and examples of the cascade outlined. A scheme of cryogenic circuit based on the high-pressure throttle neon cycle with intermediate nitrogen cooling is presented. The necessity and the technical ability to create the driving difference of pressures between columns of various stages demonstrated.

1. Introduction

Nearly one hundred years ago A.J. Thomson has determined for the first time existence of stable elements isotopes ^{20}Ne and ^{22}Ne [1]. ^{21}Ne was discovered in the twenties. Neon isotopes are widely used in modern high technologies. ^{20}Ne + ^{22}Ne mixtures are object of research of the physicists, who study mechanism of photonuclear reactions. Isotopic anomalies help in disclose secrets of our planetary system formation. In particular, astronomers have found out that ^{22}Ne monoisotope is produced when some meteorites are heated. At the same time the total content of ^{21}Ne and ^{20}Ne doesn't exceed 1% (nearly two orders lower than in neon extracted from the Earth atmosphere). Neon isotopes gas mixture (^{20}Ne + ^{22}Ne) is an active medium in gyroscopes, the operation of which is based on Szeemann's effect [2]. They are resistant to the mechanical influences and have stable scale factor. Besides navigation, such devices are in demand in different areas of fundamental research in physics. Very perspective is the sphere of application of the rarest of the neon isotope ^{21}Ne. Physicians believe that its nuclear and physical properties allow using it as an alternative to ^{3}He isotope in magnetic resonance imaging diagnostics of lungs ventilation.

2. Neon separation into isotopes by rectification method

In 1913 the first mass spectrometer, which was invented a year earlier, was used for separation of neon isotopes samples. Separation of ^{20}Ne and ^{22}Ne isotope pair for laboratory and industrial purposes is also possible by methods of thermal diffusion and chromatography [1,3]. Neon is at the limit of application of distillation method, which is considered to be effective at molecular masses less than 20 [4]. Separation coefficient of ^{20}Ne and ^{22}Ne isotopes between liquid and vapor phases in equilibrium at temperatures $27\,\text{K} \leq T \leq 30\,\text{K}$ is $\alpha = 1.040$–1.032 [5]. Nevertheless, the low-temperature rectification is considered to be the most perspective method of neon separation [6]. This statement becomes even more powerful, if one of the target products is ^{21}Ne.

Let's consider the process of the ^{20}Ne + ^{22}Ne binary mixture separation. Illustratively let's consider y–x diagram with the reference to the high-boiling isotope. Figure 1(b) shows that the graph is symmetric to the typical diagram,
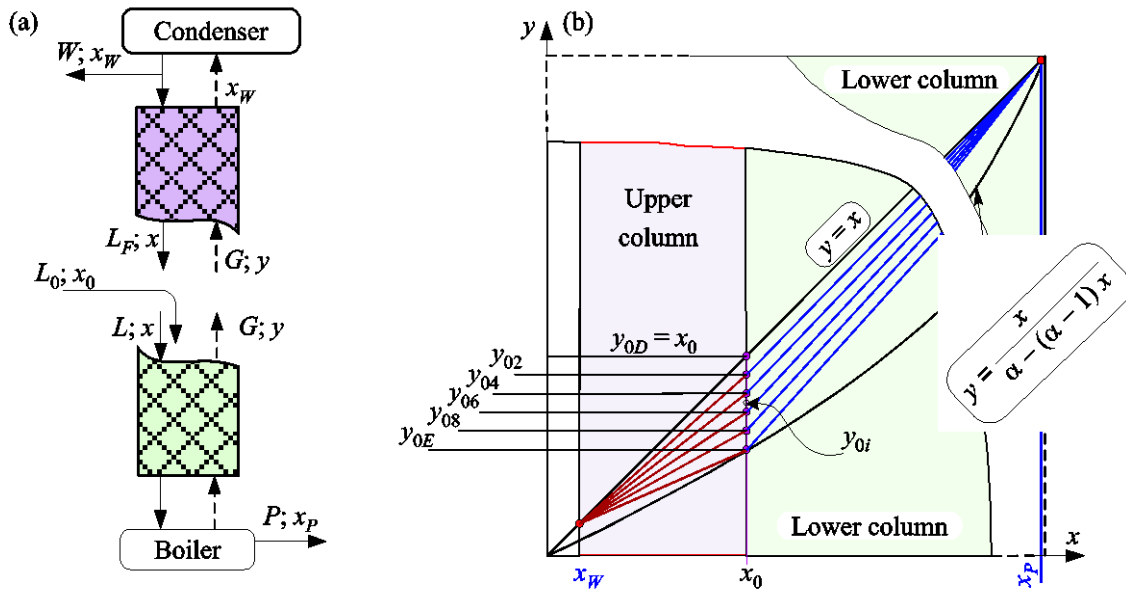
Fig. 1. Material flows (a) for the top and bottom sections of the column and operating lines (b) in *y–x* diagram built according to high-boiling component (arbitrary scale); L_0, W and P are, correspondingly, flow rate of supplying isotope mixture, of waste (enriched with [20]Ne) and of target product ([22]Ne).

constructed with the reference to the low boiling component of mixture. This fact allows avoiding unnecessary recalculations of concentration and provides information on the contents of the target product ([22]Ne) in streams and sections of the column immediately.

Table 1 shows the results of calculation of the number of theoretical plates (NTP) for the top and bottom sections of the column. Isotope concentrations of the streams, accepted in calculation, are the following:

– initial mixture with $x_0 = 0.0925$ ([22]Ne natural isotope ratio of 9.25%);

– bottom section of the column product $x_P = 0.9999$;

– waste stream, removed in the upper part of the column, $x_W = 0.015$.

At such concentrations of the waste flow W we lose 15% of the target product, and the level of extraction is $C = 0.85$, where

$$C = \frac{(x_0 - x_W)x_P}{(x_P - x_W)x_0}. \tag{1}$$

In accordance with the definition of the NTP, it was accepted that liquid and vapor are in equilibrium at each elementary rectification stage. In general case the equation for the upper column operating line is as follows:

$$y = \frac{L_F}{G}(x - x_W) + x_W, \tag{2}$$

where L_F and G are the flow rates of liquid (reflux) and of vapor, mol/s; x is the concentration in liquid phase at the arbitrary section of the upper column, mol/mol (Fig. 1(a)).

The corresponding equation for the lower column is:

$$y = \left(\frac{L_F + L_0}{G}\right) \ x - x_0 \ + y_{0i}. \tag{3}$$

Table 1. Specifications of operating conditions on the top and bottom sections of the rectification column at the liquid feed by neon having "natural" concentration of the high-boiling component ($x_0 = 0.0925$) and outflowing streams $x_W = 0.015$ and $x_p = 0.9999$. E is description of the mode, degree of equilibrium in the stream delivery point; λ'_F is angular coefficient of lines in the $x_W - x_0$ area; N'_T, N''_T are NTP; y_{0i} is coordinate of the working lines crossing at $x = x_0$; λ''_F is angular coefficient of lines in the $x_0 - x_P$ area.

$E = \dfrac{y_{0D} - y_{0i}}{y_{0D} - y_{0E}}$		Top section		Bottom section			Total N_T, pieces
		$\lambda'_F = \dfrac{L_F}{G}$	N'_T, pieces	y_{0i}	$\lambda''_F = \dfrac{L_F + L_0}{G}$	N''_T, pieces	
No-load. $E = 0$		1.0 (diagonal)	52.3	$y_{0D} = x_0 = 0.0925$	1.0	316	368
Intermediate conditions	$E = 0.2$	0.992	59.8	$y_{02} = 0.0919$	1.00066	327	387
	$E = 0.4$	0.984	70.6	$y_{04} = 0.0913$	1.00132	340	411
	$E = 0.6$	0.977	88.3	$y_{06} = 0.0907$	1.00199	357	445
	$E = 0.8$	0.969	125.6	$y_{08} = 0.0901$	1.00265	384	510
Minimal reflux $E = 1$		0.961 (equilibrium curve)	∞	$y_{0E} = 0.0895$	1.00331	∞	

Here L_0 and x_0 are flow rate and concentration of the vapor feed stream, mol/s; x is concentration in the liquid phase at the arbitrary section of the lower column, mol/mol; y_{0i} is ordinate of the intersection of the top and bottom sections operating lines of the column (Fig. 1(b)).

In the case when initial mixture is loaded to the column as a liquid, the ordinate of points y_{0i}, where operating lines intersect, will be on the vertical line $x_0 = 0.0925$ within the segment limits $y_{0D} - y_{0E}$. The calculation model considers: "no load" mode, corresponding to the absence of selection of the product $P = 0$ ($y_{0D} = x_0$); maximal loading in the case of minimal reflux (y_{0E}), as well as four intermediate modes: $y_{02}, \ldots, y_{08}$. The operating lines are spaced from the diagonal $y = x$ by 20, 40, 60 and 80% of to the maximal distance, characteristic for the mode of minimum reflux (y_{0E}). For the accepted concentrations of streams, the relative flow rate of the product P/L_0 varies with increasing of the loading from $E = 0$ up to $E = 1.0$ within the range of 0–0.0033. Therefore, the volume of the product having 99.99% isotopic concentration of ^{22}Ne does not exceeds one third of a percent from the flow rate of the supply substance L_0.

As our calculations show, the number of theoretical plates is calculated by hundreds. As the height of the transfer unit for the applied types of the packing makes dozens of millimeters (see Table 2), a column producing ^{22}Ne with isotopic quality of 99.99% and extraction coefficient $C = 0.85$ must have a considerable size. The height of the mass exchange part may reach 15–20 m. Such sizes lead to a considerable external heat leakage and complicate the cryogenic support of the unit.

Factor of separation q of column and number of theoretical plates N_T in the case of no extraction of product ($P = 0$) are specified by the Fenske formula [7]:

$$q = \frac{x_P}{x_W}\left(\frac{1 - x_W}{1 - x_P}\right) = \alpha^{N_T}, \qquad (4)$$

where α is separation coefficient of binary system ($\alpha = 1.037$ for isotope pair ^{20}Ne–^{22}Ne) [5].

3. Separation of neon isotopes in cascade of rectification columns

If the height of a single column is limited (see Table 2), it is impossible to obtain the high quality x_P of (^{22}Ne) product. For this reason, the separation of isotopic components has to be made stage-by-stage. On some stages of separation the accumulation of ^{21}Ne isotope contained in the initial mixture in 0.28% concentration is performed.

Figure 2 outlines schemes of successive concentration of the high-boiling ^{22}Ne and intermediate ^{21}Ne + ^{22}Ne isotopic components. Naturally, x_W mixtures enriched with low-boiling ^{20}Ne are removed from the waste mixture circuits.

The first scheme (Fig. 2(a)) provides multiple processing of intermediate fractions in the same column [6]. Obviously, the performance of such method is low and to increase it the cascade connection of several columns is applied (Fig. 2(b)). The feature of the second scheme is the return of waste fractions x_{W2} and x_{W3} to the previous sections (*1* and *2*) for reprocessing. For this purpose at each next step the pressure relative to the previous one is increased: $P_1 < P_2 < P_3$. Both in the first and the second case (Figs. 2(a), (b)) the feed of bottom product x_{Pi} to the column for re-separation processes is accompanied by a number of unproductive processes.

The resulting intermediate fractions x_{Pi} must be forcedly heated up to ambient temperature, collected in a gas tanks, compressed, cleaned of impurities, cooled, and then let in another column (option (b)) or in the same column (option (a)). Unfortunately, these procedures result in losses of expensive isotopic components, enriched by the target products (^{21}Ne + ^{22}Ne).

More perspective, in our opinion, is third option (Fig. 2(c)), where the valuable products are supplied directly to the subsequent stages of cascade (x_{P1} — to the column *2*, x_{P2} — to the column *3*, etc.) in cold state. Thus, less valuable products, enriched by predominant component ^{20}Ne are supplied to the block *9* for collection, storage and purification of fraction. The scheme presented in Fig. 2(c) can function without returning of waste streams.

Table 2. Comparative characteristics of the packed rectification columns, used by authors for neon separation into isotopes (in the no-load mode: $E = 0$). x_W and x_P are concentrations of the high-boiling component ^{22}Ne; SP is spiral-prismatic packing; SC is spiral-cylindrical packing.

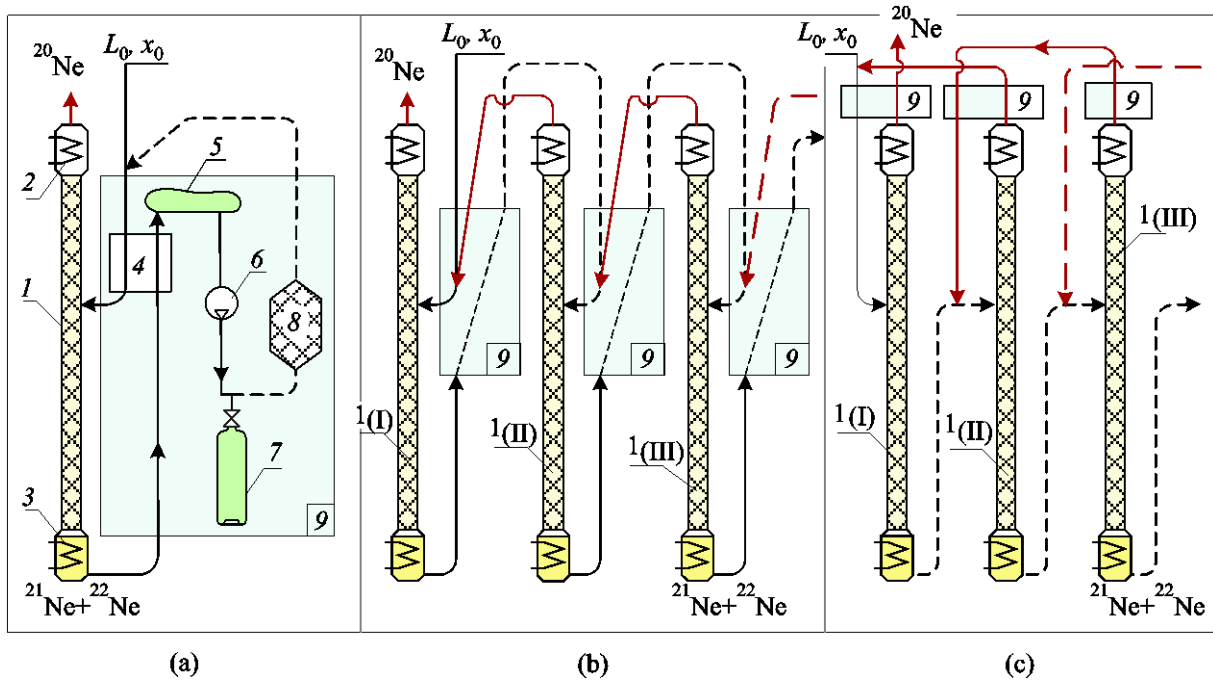| Diameter, mm	x_W	x_P	NTP, N_T, pieces (4)	Height of the theoretical plate, mm	q is separation factor (4)	Specific surface area of packed bed, m^2/m^3
22	0.003	0.985	275	28.7	21 800	5300–SP
25	0.004	0.983	263	30.0	14 400	5200–SP
25	0.02	0.98	215	30.5	2 400	5000–SP
32	0.06	0.92	150	42.0	180	4000–SC
35	0.05	0.95	160	40.1	360	3500–SC
50	0.01	0.5	130	50.4	100	3500–SP
50	0.015	0.4	105	61.0	45	1900–SC

Fig. 2. Options of the multistage separation of isotopic compounds: on the basis of the same rectification column (a); cascade connection of columns with heating of intermediate fractions, enriched by target products (b); cascade connection of columns with heating of intermediate fractions, depleted by target products (c). *1* is rectification columns; (I)–(III) is number of the stage; *2* is condenser; *3* is vaporizer of the bottom section of the column; *4* is heat exchanger; *5* is gasholder; *6* is compressor; *7* is receiver; *8* is adsorber; *9* is collection, storage and fractions purification block.

In this case x_{Wi} fractions are collected and used, e.g., for preparation of mixtures with modified (different from natural) isotopic ratio.

For the operation of the circuit shown in Fig. 2(c), the driving difference of pressure between the stages $P_1 > P_2 > P_3$ must be maintained. Such driving pressure difference can be achieved through the different thermal loading in vaporizers of bottom section of the column *3* (Fig. 3(a)). An important operating advantage of the scheme, shown on Figs. 2(b) and 3(a), is the decreased pressure in the end column III. Thus the coefficient of relative volatility (separation factor) of the isotope pair $^{20}Ne + ^{22}Ne$ is increased with reduction of the working pressure [5].

In Figs. 2 and 3 all stages are conventionally shown as columns of the same diameter. Meantime most cascade units use circuits with step-by-step decreasing performance of elements [8]. Decrease of the flow rate $x_{01} > x_{02} > x_{03}...$ allows reducing the time required to achieve the stationary state in the columns of cascade. For illustration of this phenomenon we will introduce the special factor — relative performance of rectification devices:

$$\omega = \frac{L_0}{V} = \frac{L_0}{k\phi (v_1 + v_2 + v_3)} \text{ h}^{-1}. \quad (5)$$

Here L_0 is the flow rate of the product processed, norm. dm^3/h; $v_1 + v_2 + v_3$ is the total hydraulic volume of the column, dm^3, that consists of volumes of packing sec-

tion (*1*), of condenser (*2*) and of bottom section of the column (*3*), correspondingly (see Figs. 2 and 3); $\phi = 0.16$–0.18 is the filling fraction of volumes 1, 2, 3 by liquid neon; $k = \rho_G/\rho_L = 1450$ is volume of neon, norm. dm^3, produced at evaporation of 1 dm^3 of liquid ($\rho_G = 0.829$ g/dm^3 is density of gaseous neon at $P = 0.1$ MPa and $T = 293$ K; $\rho_L = 1206$ g/dm^3 is density of liquid neon).

As it follows from data provided in Ref. 6 and results of our tests, the size ω for the primary column of cascade in the mode of ^{22}Ne production is $\omega_{22} = 0.10$–0.12.

When the target product is ^{21}Ne, the relative flow rate is decreased up to $\omega_{21} = 0.014$–0.018. Being a nominal index, factor ω, at the same time, shows what amount of time necessary for initial accumulation of target products in columns. If this factor is not taken into account and there is no replacement of isotope products in reflux, which fills the cavities of devices, it is possible to produce only partly enriched products. Production of concentrated substances is possible only as a result of accumulation of sufficient volume of target product in columns (especially end sections). Minimum time (hours), required for stabilizing of concentrations, to a first approximation is

$$\tau = \frac{x_m}{\varpi \ x_{01}} \text{ h}, \quad (6)$$

where $x_m = 0.5(x_{01} + x_{P3})$ is the average concentration of the target product in the columns of the cascade, mol/mol.
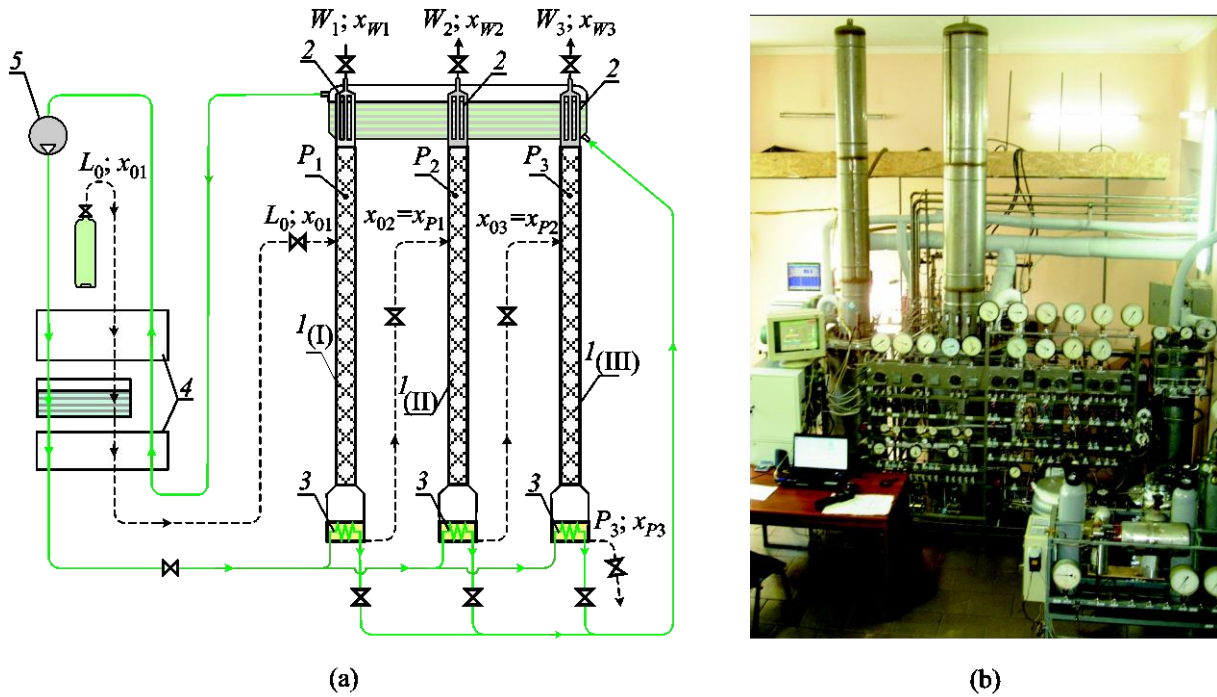
Fig. 3. Cryogenic cascade setup maintenance identical to Fig. 2(c). *1–4* are the same as in Fig. 2; *5* is compressor of the neon throttle cycle cooled by liquid nitrogen.

Taking into account empiric values of ω_{22} and contents of ^{22}Ne in the initial neon stream having natural composition ($x_0 = 0.0925$), one gets $\tau_{22} \approx 100$ h. Analogically, for ^{21}Ne ($x_0 = 0.0028$) production the necessary time is $\tau_{21} > 20\,000$ h! To reduce this period the deep concentration (saturation of reflux by target product) is applied usually only at the end columns of the cascade. The same result can be achieved by reduction of volume (diameter) of columns of end cascades and by increase of the initial section size. According to Eqs. (4) and (5), the initial section determines the quality of the target product, supplied to the separation circuit. In other words, only the high performance at initial stage can provide the operation of low-capacity output column.

Meantime, practical implementation of this technical solution doesn't give the expected result. An attempt to increase the flow rate in the initial column by increasing diameter of its section results in the sharp drop of the separation factor q (Table 2). The degree of extraction of target products (1) accumulating in the packing as a reflux, is decreased. This negative phenomenon can be leveled by using several small-scale columns forming initial stages of cascade (Fig. 4(a)). Theoretically, all columns of the cascade must be unified, and their number at all stages must be gradually decreased [9]. Such reduction will lead to redistribution of streams between sections. This will, in turn, affect the inclination of the operating lines expressed by Eq. (3) (Fig. 4(b)).
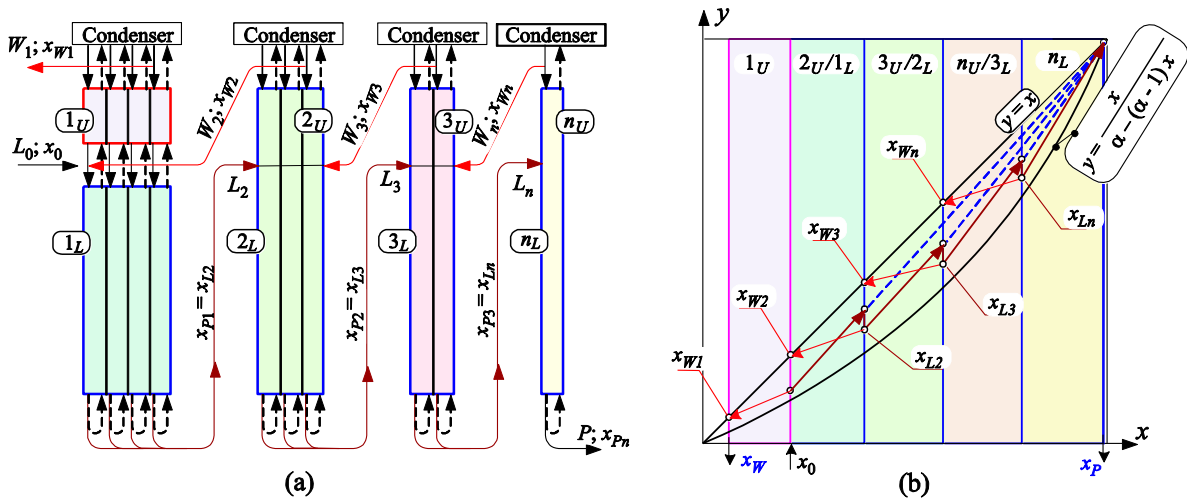

Fig. 4. Cascade setup (Figs. 2(c) and 3(a)), formed from the same type columns (a) and character of operating lines (b) in *y–x* diagram built according to high-boiling component (arbitrary scale).

The research carried out allows creating the series of industrial units for production of neon isotopes with concentration up to 99.99%.

4. Conclusions

Ukraine is traditionally a leading exporter of rare gases. Our country produces about a half of the world amount of high purity neon. Future progress in isotope technologies is an actual and logical part of the integrated technological sequence of the light inert gases production from atmospheric air.

Rectification is an effective method of separation of gases with relatively small molecular weight. However due to almost identical physical properties of isotope components the separation coefficient doesn't exceed 1.040. It results in a large number of theoretical plates and in considerable column height (> 15 m). Cascade scheme of the rectification devices assembly makes it possible to reduce several times vertical dimensions of the unit, as well as heat leakage and maintenance costs of cryogenic process.

According to the technical solutions presented in this article, a series of cascade units for Ne separation into isotopes was created. Under conditions of the limited available height of rectification columns the record results on ^{21}Ne enrichment are obtained, as well as ^{20}Ne и ^{22}Ne with isotope concentration more than 99.99% were produced.

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