Cryogenics in Russia: Development of Basic Cryogenic Cycles

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Three important and very successful ideas were born in the former Soviet Union, moved out and introduced worlwide: (i) The Low Pressure Expander (turbine) and low pressure cycles for air separation, developed and introduced by P.L. Kapitza, (ii) The One Flow Cascade with Multicomponent Refrigerant for liquefaction and treatment of natural gas, developed and introduced by A.P. Klimenko (Klimenko Cycle), and (iii) "Mixed Gas Refrigeration", a refrigeration concept developed since the 1960ies at the Moscow Power Engineering Institute. The history and thermodynamics of these cycles will be discussed.

KAPITZA CYCLE

It is well known that the air liquefaction system developed by Carl Linde in 1895 was the first commercially successful cryogenic system. Most of the modern industrial cryogenics was later developed based on inventions of Carl Linde.

The works of Linde were highly appreciated by D. Mendeleew and N. Umov in Russia. Moscow University purchased the air liquefier made by Linde in 1898, thus the first cryogenic laboratory for education purposes was organized in Russia.

Though the process developed by Linde (Figure 1a) was relatively simple and reliable, it had some disadvantages, the major one of which was poor efficiency and thus high power consumption. Today we know, that the thermodynamic efficiency of the cold part of the Linde´s system η_e was lower than 10 % due to the huge temperature difference between warm and cold streams in the heat exchanger.

Of course, C. Linde, as well as other engineers and inventors, tried to improve the efficiency of the process (Figure 1b). For example, C. Linde introduced an additional precooling system based on a classic ammonia refrigerator. That way he managed to reduce a temperature difference between the warm and cold streams in heat exchanger, consequently reducing the temperature of the stream before throttling valve, and increasing efficiency of the process.

George Claude (Figure 1c) developed another solution in 1902; he introduced in to the cycle an additional cryogenic piston-expander. This idea can be interpreted as introducing a precooling circuit, which allows reducing the temperature difference in heat exchangers. The other advantage of the Claude's process is that the energy of the high-pressure air was better utilized in the cycle, due to the fact that the expansion in the engine is more efficient compare to expansion through a throttle valve. Utilizing his cycle G. Claude received almost the same result as C. Linde, but at a lower operation pressure (~60 bar compared to 200—220 bar in the Linde´s system). That was a great innovation.

Peter Kapitza developed further the idea of G. Claude; he developed a highly efficient turbine-expander (isentropic efficiency higher than 80 %) and reduced the operation pressure further to 6—8 bar. The temperature difference in the heat exchanger was reduced, the expansion losses in the turbine were small, so the cold part of this process was practically loss-free compare to the original Linde´s system; the efficiency of the cycle was increased essentially.

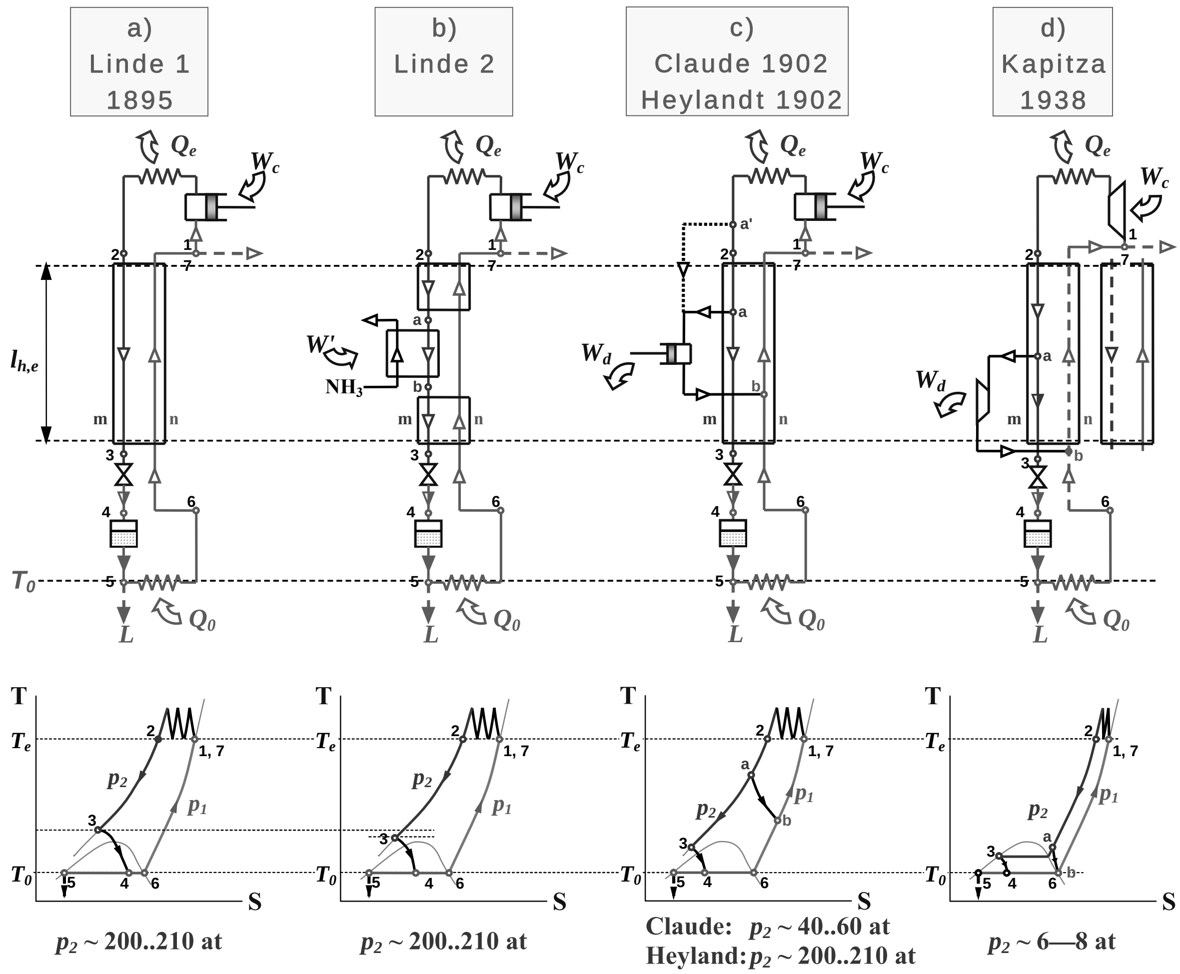

Figure 1 Basic Cryogenic cycles for air liquefaction

The idea to reduce operating pressures from customary 200-220 bar to much lower 6-8 bar was so new, that the Peter Kapitza had some problems with cryogenic community accepting his idea, especially in Germany, where the leading cryogenic engineer Helmuth Hausen (Linde, Höllriegelskreuth b. München) was very cautious about Kapitza´s invention. In a publication [11] Mr. Hausen wrote "the air liquefaction process of Kapitza does not bring any advantages conc. power consumption compared to the conventional high pressure processes even in spite of low operation pressure, probably [it does not bring any advantages] conc. mass, required space and production costs…The highest value of the efficiency 83 %, which is given by Kapitza, cannot be taken as proper value for the cooling capacity[1]".

Incidentally H.Hausen conceded that the low pressure process could be valuable for air separation systems, if the predicted efficiency of the Kapitza turbine would be confirmed. A similar position was voiced by P.Grassmann [10]. But the caution (discretion) of H. Hausen was interpreted by many other specialists as a kind of pessimism acc. Kapitza cycle. Finally it decelerated introducing of the process proposed by Kapitza in the air separation industry though could not stop it.

In this connection it is useful to remember the discussion between Kapitza on one side and several Russian professors on the other side. The position of Kapitza´s opponents was based on two following claims:

1. It is impossible to have an expander with adiabatic efficiency $\eta_{ad} > 0.83$ (the best turbine-expander of Linde-company had $\eta_{ad} = 0.6..0.65$ at that time).
2. The cycle of low pressure air separation must inevitable have efficiency lower than the cycle of high pressure.

[1] original text „...das Luftverflüssigungsverfahren von Kapitza trotz der Anwendung sehr niedriger Drücke gegenüber den bekannten Hochdruckverfahren keine Ersparnis an Energieaufwand, vermutlich auch nicht an Gewicht, Platzbedarf und Herstellkosten zu bringen vermag…Der höchste Wert des Wirkungsgrades von 83%, den Kapitza für seine Turbine angibt, kann aber ... nicht als maßgebend für die Kälteleistung angesehen werden".

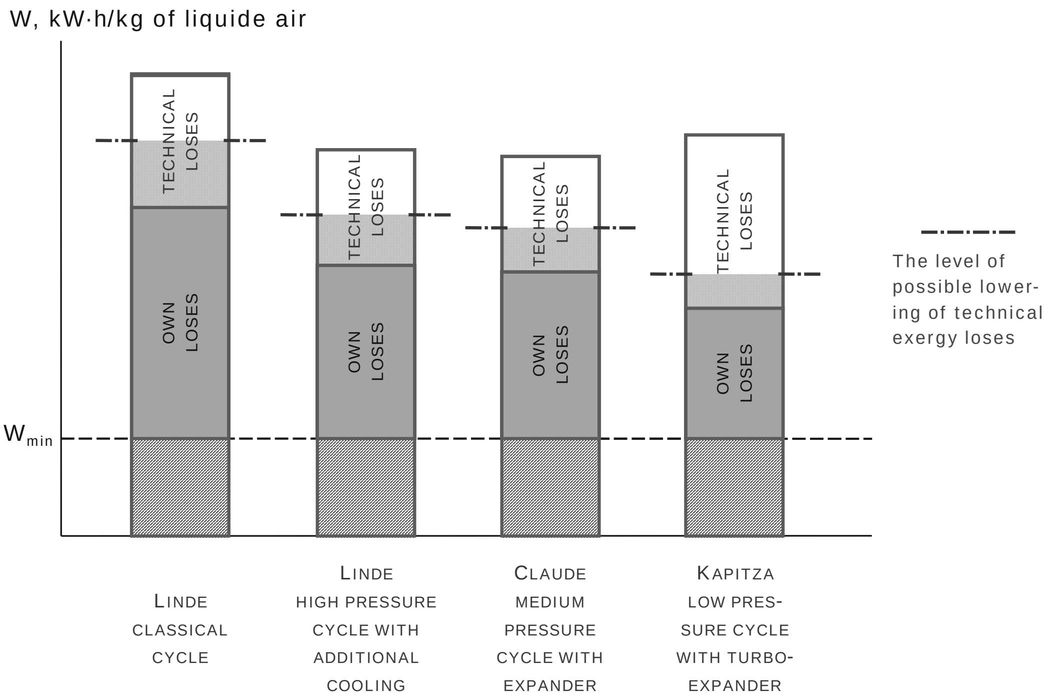

Figure 2 Distribution of losses in basic cryogenic cycles for air liquefaction

Both these statements were based on experience of that time, which later collapsed, proven by time. To understand it, it is necessary to analyze the problem with the help of thermodynamics. Today we know that all the thermodynamic losses can be divided into two groups — own losses Σd_0 and technical losses Σd_t (Figure 2). The own losses are inherent to given object and truly can't be eliminated. In opposite the technical losses can be reduced by proper operations in principle to „zero". P. Kapitza realized it in full scale. Introducing his radial inflow low temperature turbine-expander Kapitza eliminated most technical losses Σd_t by radical transformation of turbine-design, taking into consideration the high density of the cold compressed air even in the region of wet vapor).

The situation acc. the second claim was more complicated. The Kapitza´s opponents were absolutely correct in evaluation of the Kapitza cycle-performance. But they did not take into consideration the possible significant reduction of technical lossed Σd_t in Kapitza´s process by further development, especially concerning application of Kapitza-cycle for air separation. Of course, the own losses Σd_0 are increasing by lowering of working pressure by changing from Claude-process to Kapitza-process (the opponents of Kapitza were correct). But the technical losses d_t can be lowered still further at the same times by low pressure p_m. In the long run the total efficiency significantly grew, especially by large systems.

What we can learn from it. At the first, for analysis of given process it is necessary to divide the losses of exergy on d_t and d_0. The final decisions must be made based on the analysis of both Σd_t and Σd_0. In the case of Kapitza´s cycle the own losses in turbine-expander are absent at all; in this system there are only technical losses of exergy, which can be lowered in principle to zero.

Moreover, we can learn from it, that it is sometimes necessary not to restrict the attention on the present situation, but to analyze other possibilities and future trends, which could be connected not with thermodynamic aspects only, but also with economical aspects too.

Kapitza´s opponents were brilliant specialists, but they think on the level of preconceived ideas based on the better models of low temperature systems in that time. In opposite Kapitza was a physicist, he wasn't tied with cryogenics engineering traditions. He was a master of scientific original decisions, and used methods of scientific investigation. Sometimes it is of advantage to look on the problem from outside to achieve an essential improvement of an established technology.

Today the low-pressure air separation plants use different variations of the processes proposed by Peter Kapitza and run successfully all over the world.

KLIMENKO CYCLE

A.P.Klimenko worked in 1950's on the liquefaction of the natural gas. The main challenge was that the classic liquefaction processes known by 1950's (from C. Linde to P. Kapitza) were developed for pure substances[2], mainly for a gaseous cryogen (the liquid fraction develops, collected and withdrawn from the process just after the throttle valve) and could not maintain liquid neither in the heat exchangers, nor in the expanders. In contrast, the natural gas begins to liquefy at temperatures close to the ambient temperature, because the natural gas is a mixture, which consists of many components (most of them are hydrocarbons, like methane, ethane, propane, butane etc; other components are of non-organic nature like nitrogen, helium, carbon dioxide, H_2S, etc). Therefore it is very difficult to use the classical methods to liquefy natural gas.

The conventional method for liquefaction of natural gas used in 1950's employed a cascade system consisted of at least three separate refrigerators with different refrigerants. Propane was conventionally used for the first stage with cooling temperatures of ca. 240 K, ethylene for the second stage with cooling temperatures of ca. 200 K, and methane for the third stage (Figure 3). The cascade system is a very efficient system. But it has some disadvantages, the main of them being the complexity and high number of hardware-components (for example at least three compressors).

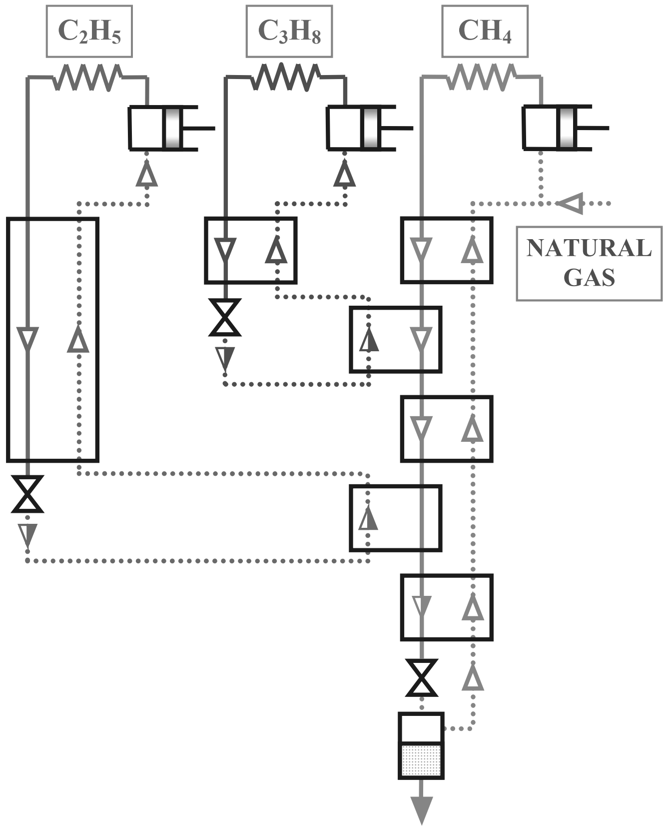

Figure 3 Classical cascade method for liquefaction of the natural gas (Keesom).

A.P.Klimenko realised that it was necessary to develop new liquefaction methods, taking in consideration special properties of natural gas. His idea was very simple; he decided to take the refrigerants "required" for a cascade system (methane, ethane/ethylene and propane) from natural gas directly during the process of liquefaction. This way, Klimenko transformed the complex composition of the natural gas from disadvantage into advantage.

The simplified flowsheet of the Klimenko process is shown in Figure 4. The refrigeration required for the cooling of the natural gas is provided by a circulating mixed refrigerant stream containing components such as butane, propane, ethane, methane and nitrogen. The heat of compression is removed in the aftercooler with water. In the first stage the mixed refrigerant stream, as a result of being compressed and cooled, is partially condensed, and the two phases are separated in the first separator. The vapor proceed as separate stream to the next heat exchanger, where heat is transferred to the returning refrigerant stream. The vapor is thereby partially condensed and proceeds from the first heat exchanger to the second phase separator, where the phases again separated. The liquid phase from the first separator is expanded in the first throttle valve before being separated from the cycle. These steps – partial condensation, separation, subcooling, and expansion repeated in the second and the third stage of the separation process.

Consequently, some hardware components (for example several compressors) are not required any longer; it makes the system simpler and more reliable. The capital expenditure can be reduced over the conventional cascade system. Additionally, the Klimenko process is very versatile; it is possible to produce not only LNG, but other gas products, like gaseous or liquid ethane, propane, butane and other natural gas components.

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[2] Although the air is a mixture of nitrogen, oxygen, argon and other gases, the thermodynamic of the air is very similar to the thermodynamic of an single component refrigerant like nitrogen or oxygen.

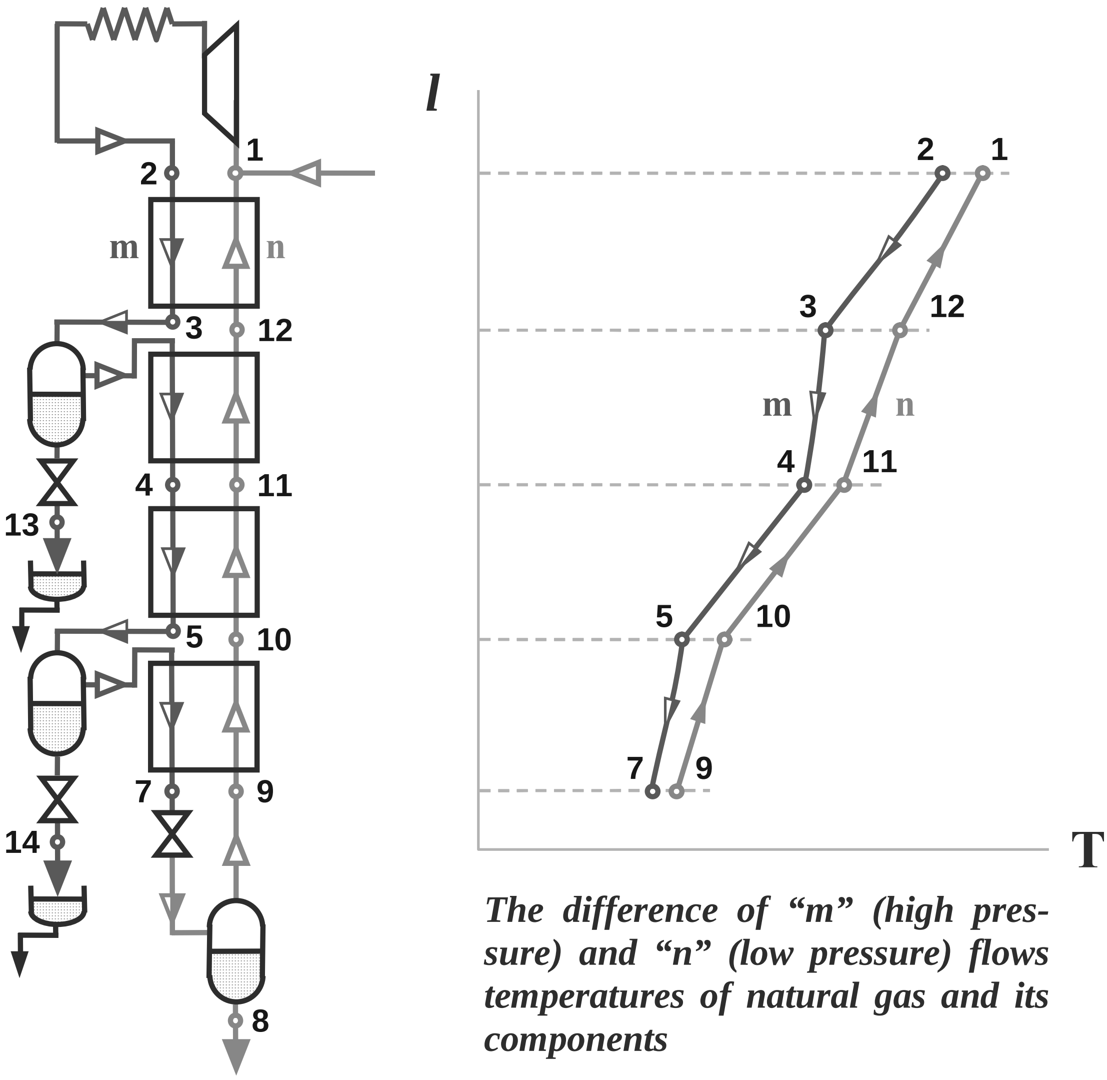

Figure 4   Flowsheet of the Kleemenko cycle

The thermodynamic analysis of the Klimenko cycle shown, that the temperature differences in the heat exchanger are very small, consequently the thermodynamic losses in the heat exchanger are small. Surprisingly, the losses in the throttle device are also very small. That is because of throttling of liquefied refrigerant.

One can say, that Klimenko follows the same principle like C. Linde, G. Claude and P. Kapitza. But (and that is absolutely new) the losses in the cycle were reduced neither by introducing an external refrigerator (like C. Linde), nor by introducing an expander (G. Claude, P. Kapitza). That was (using of mixed refrigerants) absolutely new in the low temperature refrigeration.

The Idea of Klimenko was developed further intensively in 60'ies and 70'ies. Now each industrial gas company develops systems for liquefaction of natural gas based on the mixed refrigerants. These processes are based on the Klimenko cycle.

MIXED REFRIGERANT CYCLE

In the early seventies, the author and Gresin worked on a refrigeration system for electronic component cooling with the goal of developing a high efficiency one stage cooling system without any additional precooling or machinery based on an a Klimenko idea to improve the classical refrigeration process developed by C. Linde by using of mixed refrigerants.

As a first step the Klimenko process was realized in small scale as a closed cycle (Figure 5) [1]. The system had an efficiency comparable to that of classical refrigeration cycles with expander. That system turned to be impractical due to the high number of hardware components, such as separators and throttle valves.

In a further development investigations showed that it was possible to reduce the number of separators in the system, and finally the separators were eliminated due to the use of a special refrigerant mixture. A mixed refrigerant Joule Thomson system for liquid nitrogen temperatures was invented. It combined the simplicity of the classical C. Linde process and high efficiency. The report about our mixed refrigerant system was presented to the International Congress of Refrigeration.

The mixed refrigerant Joule Thomson system looks very similar to the classical C. Linde´s system, but with some fundamental differences. One of them is that Linde´s process takes place mainly in the gas state, where as the mixed refrigerant Joule Thomson process happens mainly in the two-phase region – the mixed refrigerant condenses in the high pressure flow *m* at the warm side of heat exchanger and evaporates in the low pressure stream *n* at the cold side of the heat exchanger. Therefore the apparent heat capacity of a mixed refrigerant is a composition of the real heat capacity c_p and the heat of vaporization *r:*

at the high pressure side: $C_m = r_m + c_{p,m}$,

at the low pressure side: $C_n = r_n + c_{p,n}$.

Because the heat of vaporization *r* is higher than the real heat capacity c_p ($r >> c_p$) and the heat of vaporization *r* is only slightly pressure dependent ($r_n \approx r_m$), the heat capacity of the high pressure stream and the heat capacity of the low pressure streams are very close. As a result the temperature difference in the heat exchanger and the losses are very small (the mean temperature difference is less than 15 K for optimized mixtures). This is an essential feature of a mixed refrigerant Joule Thomson process.

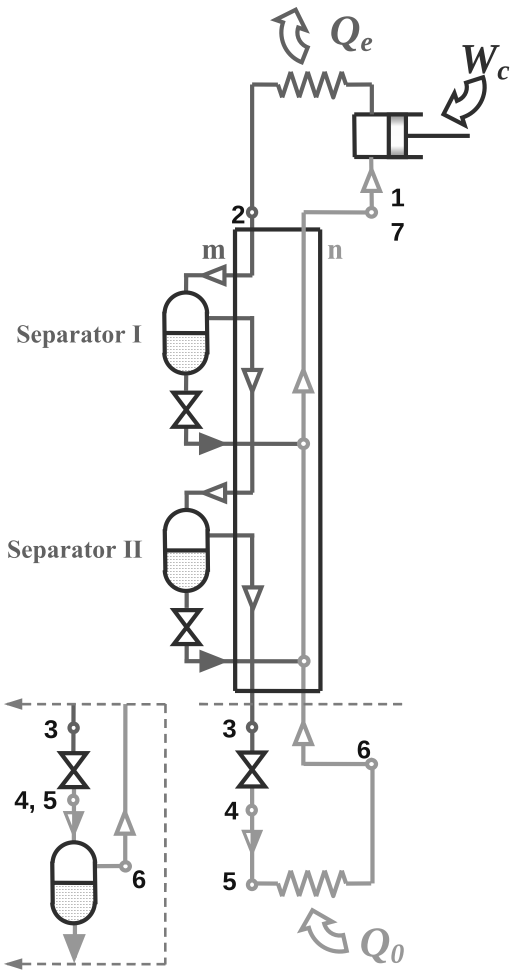

Figure 5 The first small-scale mixed refrigerant system

In the classical processes developed by Linde (JT with precooling), Claude and Kapitza the relative high losses in heat exchangers are compensated by additional precooling or machinery. In the mixed refrigerant process the losses in the heat exchanger are so small, that precooling and/or expanding is not necessary.

The next steps in optimization of the mixture composition were related to different requirements as refrigeration below 77 K, shortening cool down time, etc. The further development shows the other interesting effects:

- the splitting of some liquid mixtures (like nitrogen-hydrocarbons) into two separate unmixible liquids: low-boiling liquid (mainly nitrogen) and high-boiling liquid (mainly hydrocarbons). Because the low- boiling liquid (mainly nitrogen) boils at the constant temperature, it is possible to build the mixed refrigerant systems with very constant cooling temperature.
- The very short cool down time, essentially shorter than for the conventional nitrogen JT-systems, may be achieved.
- The cooling temperatures below 77 K (practically down to solid temperature of nitrogen - 63 K) can be achieved with a single stage mixed refrigerant JT-system, however the efficiency of the system is less in this case.

Based on the mixed refrigerant JT technics the refrigerators as well as liquefiers and gas cooling systems can be developed.

All the methods developed lead to the invention of a new class of small scale industrial systems based on a mixed refrigerant Joule Thomson system.

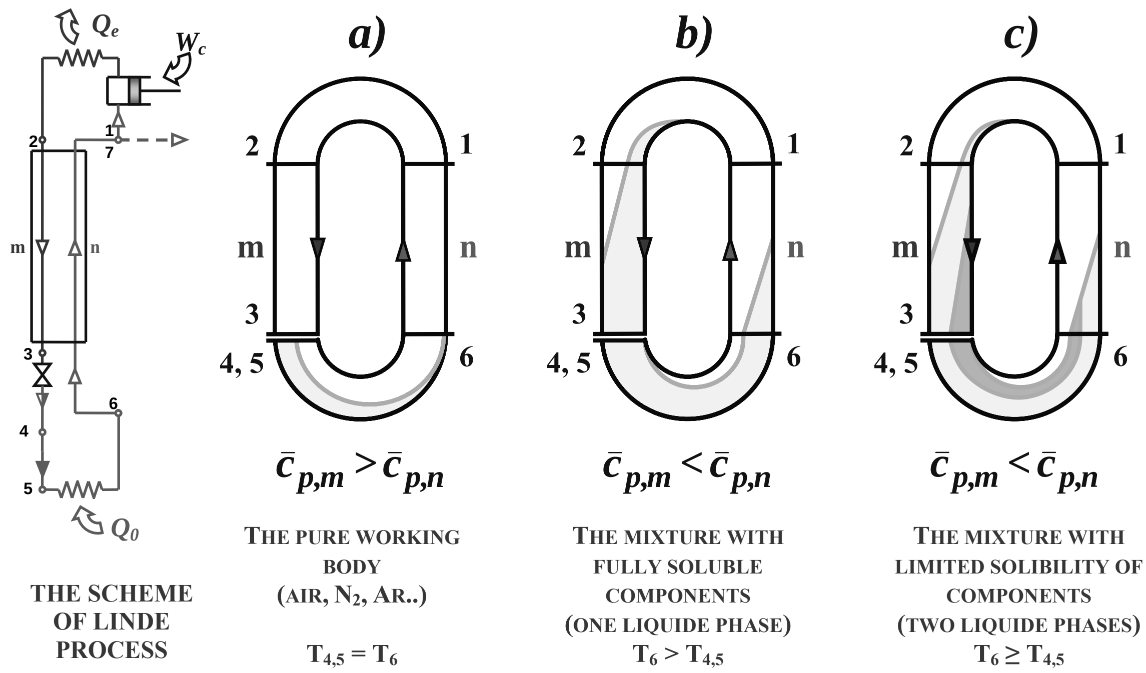

Figure 6 Mixed refrigerant Joule Thomson system

CONCLUSION

Three important and very successful ideas were born in the former Soviet Union, moved out and introduced worlwide: (i) The Low Pressure Expander (turbine) and low pressure cycles for air separation, developed and introduced by P.L. Kapitza, (ii) The One Flow Cascade with Multicomponent Refrigerant for liquefaction and treatment of natural gas, developed and introduced by A.P. Klimenko (Klimenko Cycle), and (iii) "Mixed Gas Refrigeration", a refrigeration concept developed since the 1960ies at the Moscow Power Engineering Institute.

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