



SPE 171427

New low temperature process of CO₂ recovery from natural gases

Salavat Z. Imaev, Lev A. Bagirov, Vasily E. Borisov, Evgeny V. Voytenkov, ENGO Engineering, Ltd.

Copyright 2014, Society of Petroleum Engineers

This paper was prepared for presentation at the SPE Asia Pacific Oil & Gas Conference and Exhibition held in Adelaide, Australia, 14–16 October 2014.

This paper was selected for presentation by an SPE program committee following review of information contained in an abstract submitted by the author(s). Contents of the paper have not been reviewed by the Society of Petroleum Engineers and are subject to correction by the author(s). The material does not necessarily reflect any position of the Society of Petroleum Engineers, its officers, or members. Electronic reproduction, distribution, or storage of any part of this paper without the written consent of the Society of Petroleum Engineers is prohibited. Permission to reproduce in print is restricted to an abstract of not more than 300 words; illustrations may not be copied. The abstract must contain conspicuous acknowledgment of SPE copyright.

Abstract

Low-temperature processes seem to be the most promising for the extraction of CO₂ from gases with high acid components content. The present paper contains the research results of using supersonic separation technology (3S-separation) for the extraction of CO₂ from natural gases. 3S-separation technology is based on separation of selected components of natural gas, effected by gas expansion in a supersonic Laval nozzle, in which a strong gas cooling is achieved due to the conversion of potential energy into kinetic energy. Condensation and separation of the target components are implemented in a cooled flow inside the nozzle.

This paper analyzes the various technological schemes of CO₂ extraction. The results of tests of model 3S-separator, confirmed the high efficiency of CO₂ separation, are represented. It is proven, that units for CO₂ recovery from natural gas, based on low-temperature separation processes in supersonic separators, allow CO₂ concentration in processed gas below 2%.

Introduction

It is estimated that about 30% of global natural gas resources have significant amounts of CO₂. The largest reserves of natural gas with high CO₂ content are located in South-East Asia, Australia, North Africa, Middle East and USA.

The necessity to follow strict parameters of acid components content in the sales gas leads to an extremely high capital and operation costs of construction of gas processing plants (for the gas with abnormally high acid components content). That is why large number of gas fields with high CO₂ content still cannot be developed at an adequate level. This primarily relates to giant Natuna field, which belongs to Indonesia. CO₂ content of this deposit is exceeding 70% by volume.

Technologies of acid components from natural gas removal can be divided into the following four groups [1-13]:

- **Absorption processes**, which are usually used for low pressure streams with low CO₂ content of 3-25%. These methods are not suitable for very high CO₂ concentration streams because of the large solvent recirculation and consequently large heat duty in the stripper for solvent regeneration;

- **Adsorption processes** are used for reducing CO₂ content from 3% to 0.5%. Not applicable for high CO₂ concentration streams since it needs frequent regeneration of adsorbent;

- **Membrane processes** of separation are based on predominant permeability of separate components through the separation membrane. Flexible for different CO₂ concentration streams, but as for the high acid components content gas processing it is necessary to have multilevel treatment system, which complicates the process and increases energy costs for the gas compressing.

- **Low-temperature processes** of acid components separation are based on CO₂ and H₂S condensation in conditions of temperature fall. These processes seem to be the most promising for the treatment of gases with anomalously high acid components content. A few methods of low-temperature separation have received attention in the literature, among them: Ryan Holmes process, Controlled freeze zone method (CFZ), Cryocell method, Sprex method. Only one of above mentioned methods - Ryan Holmes process - is used industrially. However, due to necessity of using an essential number of rectification columns, this method has not gained wide application. The other processes have passed only pilot production tests and for various reasons are not used in industrial scale.

In recent years there is a special interest to advanced technologies, enabling acid components removing from natural gas. One of these technologies is technology of 3S-separation [14-16].

3S-technology specification

The technology of 3S-Separation (SuperSonic Separation) is based on natural gas cooling in the supersonic swirling gas flow.

Supersonic flow is implemented by means of convergent-divergent Laval nozzle. In this nozzle, the gas picks up speeds faster than the speed of sound in gas. At that, a rapid cooling of gas, caused by the conversion of a portion of flow's potential energy into kinetic energy, takes place.

Progressive low-temperature 3S method of CO₂ separation, which can be used for natural-gas with high CO₂ content stripping, will be considered and analyzed in this paper.

The expansion of natural gas, even to a small Mach numbers ($M \sim 1.3-1.5$), makes it possible to cool the gas down to temperatures, sufficient for condensation not only of components, heavier than propane, but even heavier than ethane, such as CO₂ and H₂S. At that Cryogenic temperatures of natural gas can be achieved without any additional sources of cold, such as chillers, turbo expanders, etc.

In 3S-technology the selection of condensate drops, condensed in a supersonic nozzle and containing target components, is implemented under the influence of centrifugal forces. The centrifugal force field is created by flow swirling in the chamber of supersonic nozzle.

The basic scheme of 3S-technology device (hereafter referred to as 3S-separator) is shown in Fig. 1.

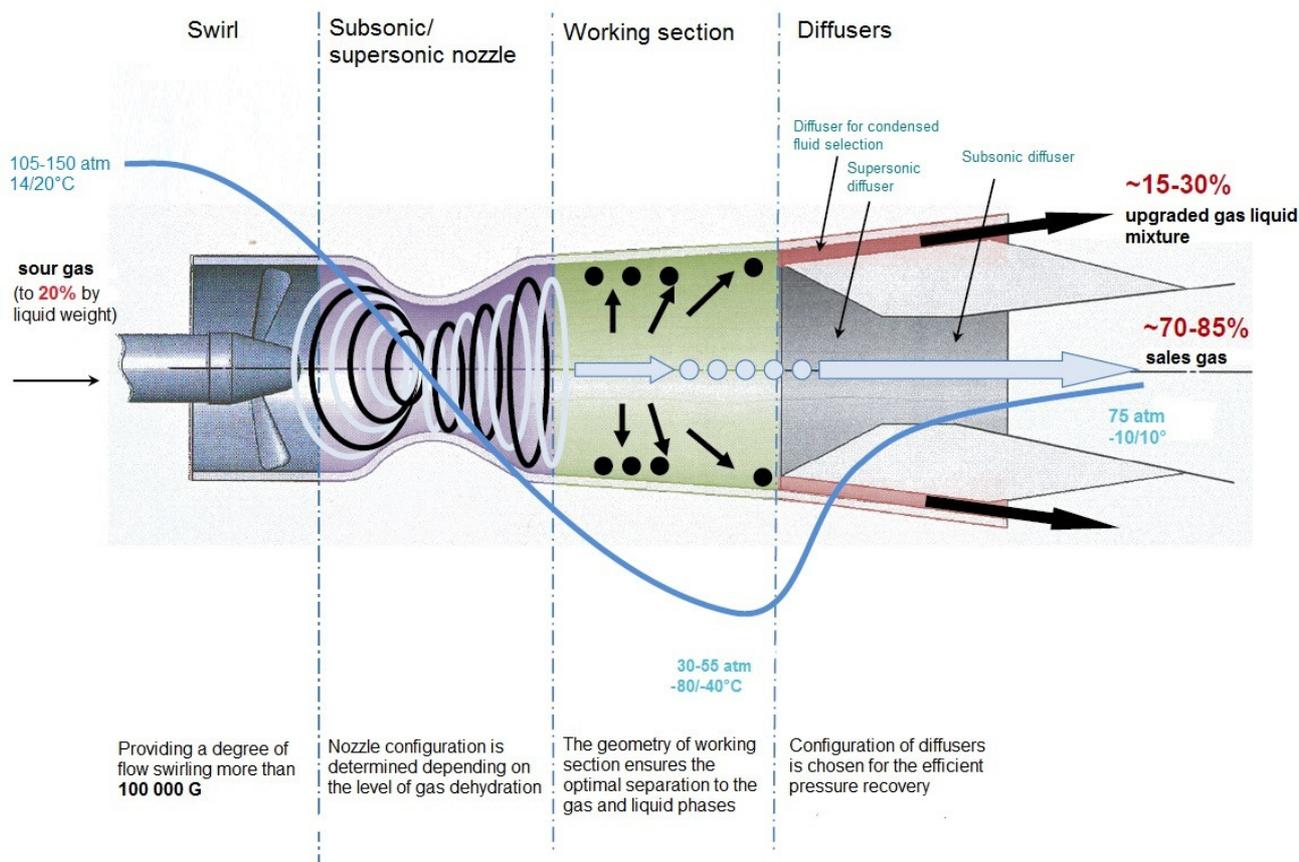


Fig.1 Basic scheme of 3S-separator

3S-separator comprises a swirling device, subsonic and supersonic nozzle, working section, a device for condensed fluid selection and diffusers.

The use of diffuser at the outlet of 3S-separator's working section, due to the diffusion, makes it possible to converse a flow potential energy into kinetic energy, which causes the gas pressure at the outlet of diffuser, higher than the static pressure of gas in a supersonic nozzle, in which the condensation of the target component takes place.

3S-technology as a method and devices, based on this method, are patented in Russia and CIS countries, as well as in USA, China, Brazil, Canada, Australia, UK, France, Netherlands, Spain, Italy, Malaysia, Thailand and Indonesia and other countries. At present two supersonic separation devices are in commercial service. These devices had been mounted at gas processing facilities of "Rosneft", JSC and at the gas field of Chinese public company "Petrochina".

3S-Separator, mounted in 2007 in JSC "Rosneft" (Gubkinskoe complex gas treatment plant (CGTP)) allowed to decrease the hydrocarbon and water dew points by 20°C, compared with the standard scheme with Joule-Thomson valve, used previously on the site. This Separator is still in successful operation and provides a treatment of about 80 000 nm³/h of natural gas at the inlet gas pressure of 70-80 atm.



Fig.2 3S-separator at Gubkinskoe CGTP, JSC "Rosneft"

In 2011, 3S-separation unit was successfully launched by Petrochina Company at YAHA field in China. This separation unit, consisting of two 3S-Separators, enables to decrease hydrocarbon and water dew points in sales gas more than by 20°C, compared with the standard scheme with Joule-Thomson valve, used before. The gas pressure at the inlet of the unit was 108 atm., the gas flow rate was 160 000 Nm³/hr.



Fig.3 3S-separation unit at YAHA field («Petrochina»)

Presently, 5 units of 3S-separators are being installed on different gas processing facilities.

The main advantages of 3S-technology over traditional technologies of hydrocarbons separation are the following:

- small dimensions of the unit (footprint), and consequently, capability of placing in a sufficiently small area, capability to incorporate additional equipment to the whole complex of equipment, assembly and installation cost reduction,
- low capital and operating costs,
- environmental safety,
- the absence of moving parts,

- no requirement for routine maintenance,
- the possibility of using the usually wasted gas formation's energy,
- higher efficiency compared to conventional gas separation equipment.

Basic principles of 3S-technology using for carbon dioxide recovery

The process flow scheme of carbon dioxide recovery device, based on the principle of 3S-technology, is shown in Fig. 4.

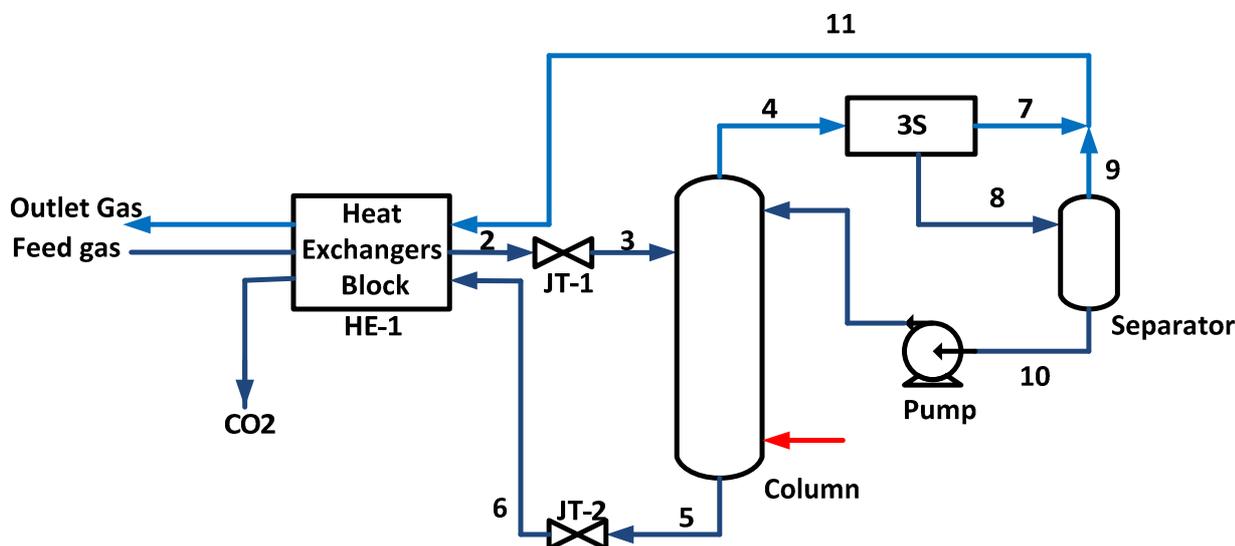


Fig.4 Basic scheme of 3S-separation unit for CO₂ recovery from natural gases

3S-separator functions as follows: dry inlet gas, containing large amount of CO₂, is cooled in heat-exchangers block, and after the preliminary expansion, it is fed to rectification column. In rectification column occurs a fractionating of inlet mixture, at that condensate, generally containing liquid CO₂, is sampled in the bottom of the column; condensate, containing ethane, methane and CO₂, is sampled at the top of the column. Gas from the column is delivered to the inlet of 3S-separator, to be cooled in the supersonic nozzle, and the carbon dioxide, remaining in gas, is condensed. Two-phase flow is directed from 3S-separator to the conventional gas-liquid separator. Separated liquid, containing CO₂, is pumping and then it flows to the column as a reflux liquid. Gas from separator is mixed with processed gas from 3S-separator, cooled in heat-exchangers block and finally fed to consumers. Condensate from the bottom of the column is throttled, heated in heat-exchangers block and directed to the compressor for injection.

The optimum level of gas pressures at the inlet of the unit – more than 40 atm. At that, the range of outlet pressure is usually from 20 to 25 atm.

In proposed device, separation of carbon dioxide is carried out in two stages. In the first stage through the gas cooling in heat exchangers, gas is cooled to temperatures -40 - -70°C (depending on desired level of gas from CO₂ purification and inlet gas pressures). At such range of temperatures a portion of CO₂ is condensed. In this regard, since the condensed carbon dioxide is a good dissolvent, hydrocarbon components of natural gas dissolve rapidly in liquid CO₂. Therefore, the bulk of the input stream before the column is in the liquid phase. Stripping of light hydrocarbons occurs in the column by liquid heating in the bottom part of the column. Owing to this, liquid condensate at the outlet of column, sampled in the bottom of the column, mainly contains liquid CO₂; a gas from the top of the column contains light hydrocarbon components, such as methane, ethane, propane, and CO₂. Depending on selected mode of the column, CO₂ content in gas at the outlet of the column may vary from 10 to 20 mol% at any even very high CO₂ concentration in the inlet gas.

In the second stage, the gas is treated in 3S-separator, where through the extremely strong gas cooling, in a supersonic nozzle could be achieved such low temperatures, that CO₂ concentration in the gas phase could be up to 2% mol or higher, depending on the requirements to the sales gas.

Figure 5 shows the phase diagram of the inlet gas changes on the pressure-temperature plane. The segment *AB* refers to the gas cooling in the block of heat exchangers, the segment *BC* – is a gas flow throttling in the choke, *CD* shows the gas passage through the column, the segment *DE* concerns to the gas cooling in the supersonic nozzle of 3S-separator, the segment *EF* refers to the gas passage through the diffuser of 3S-separator, and the segment *FG* shows the gas heating in the block of heat exchangers.

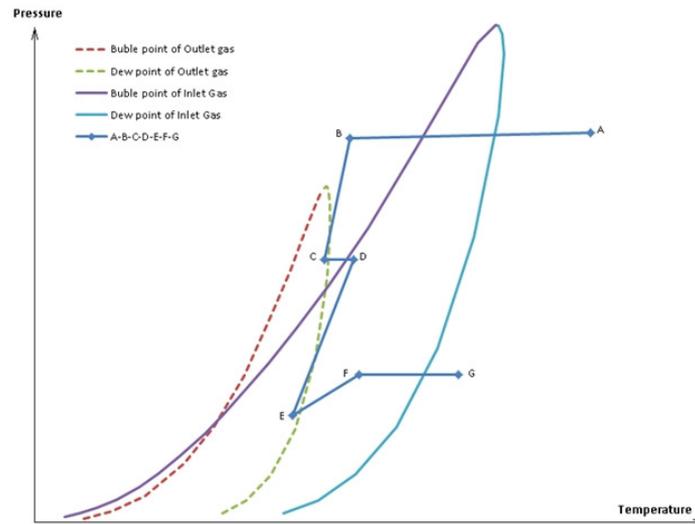


Fig.5 Phase diagram of the inlet gas changes on the pressure-temperature plane

In tables 1 and 2 there are examples of design parameters of flows at the inlet and outlet of 3S-separator for two cases, where the gas at the inlet of the unit has a high carbon dioxide concentration. Table 1 - corresponds to the case, when according to the customer's requirements, the outlet gas may have a CO₂ concentration of 13%, as it will be burned at the power plant. Table 2 presents data for more complex 3S-separation unit than shown in Fig. 4. In this case, CO₂ concentration in the outlet gas is 2%.

Table 1

	Unit	Inlet gas	Outlet CO2	Outlet Gas
Vapour Fraction		1,00	1,00	1,00
Temperature	C	45,0	-10,0	-9,6
Pressure	MPag	6,7	0,1	2,5
Molar Flow	m ³ /h (gas)	11776,6	8351,6	3425,1
Mass Flow	kg/h	18053,9	15153,2	2900,8
Mole Frac (Nitrogen)		0,004000	0,000011	0,013727
Mole Frac (CO2)		0,712018	0,949584	0,132736
Mole Frac (Methane)		0,268007	0,030888	0,846199
Mole Frac (Ethane)		0,011000	0,012814	0,006577
Mole Frac (H2S)		0,004975	0,006703	0,000761

Table 2

	Unit	Feed Gas	CO2	Outlet Gas
Vapour Fraction		1,00	1,00	1,00
Temperature	C	40,0	19,0	30,0
Pressure	MPa	6,0	0,5	2,5
Molar Flow	m ³ /h	145830,0	105100,2	40727,9
Mass Flow	kg/h	217924,8	188633,8	29290,5
Mole Frac (CO2)		0,606770	0,831241	0,027542
Mole Frac (Methane)		0,308422	0,056799	0,957700
Mole Frac (Ethane)		0,037684	0,049821	0,006374
Mole Frac (Propane)		0,023786	0,032969	0,000096
Mole Frac (i-Butane)		0,003828	0,005312	0,000000
Mole Frac (n-Butane)		0,008120	0,011267	0,000000
Mole Frac (i-Pentane)		0,001847	0,002563	0,000000
Mole Frac (n-Pentane)		0,004689	0,006506	0,000000
Mole Frac (Nitrogen)		0,002329	0,000020	0,008287
Mole Frac (n-Hexane)		0,000334	0,000463	0,000000

Mole Frac (n-Heptane)		0,001184	0,001643	0,000000
Mole Frac (n-Octane)		0,000667	0,000926	0,000000
Mole Frac (n-Nonane)		0,000231	0,000321	0,000000
Mole Frac (H₂S)		0,000005	0,000007	0,000000
Mole Frac (n-Decane)		0,000075	0,000104	0,000000
Mole Frac (n-C11)		0,000022	0,000031	0,000000
Mole Frac (n-C12)		0,000005	0,000007	0,000000
Mole Frac (n-C13)		0,000001	0,000001	0,000000

To prove the efficiency of 3S-technology for above listed schemes, ENGO Engineering developed an experimental setup, which allows testing 3S-separator in a wide range of pressures, temperatures and CO₂ concentrations in the inlet gas.

Description of the experimental unit

The main possible difficulty of the 3S-separator operating at low temperatures could be excessive overcooling of the mixture during adiabatic expansion, at which temperature of condensate droplets becomes lower than temperature of solidification. In this case, coagulation of frozen particles would be impossible and therefore the separation process could not be started up. Thus, it is necessary to organize the process in such a way that coagulation happens prior to solidification of micro-particles i.e., the process should be a thermodynamically nonequilibrium one. Also, the process should be nonequilibrium in a boundary layer, because due to the overcooling, crystals can be formed on the walls.

That is why the primary objective of experimental setup developed was the final adjustment of 3S-technology at a mode of possible crystalline CO₂ genesis in a supersonic separator.

Figure 6 shows a basic scheme of experimental unit.

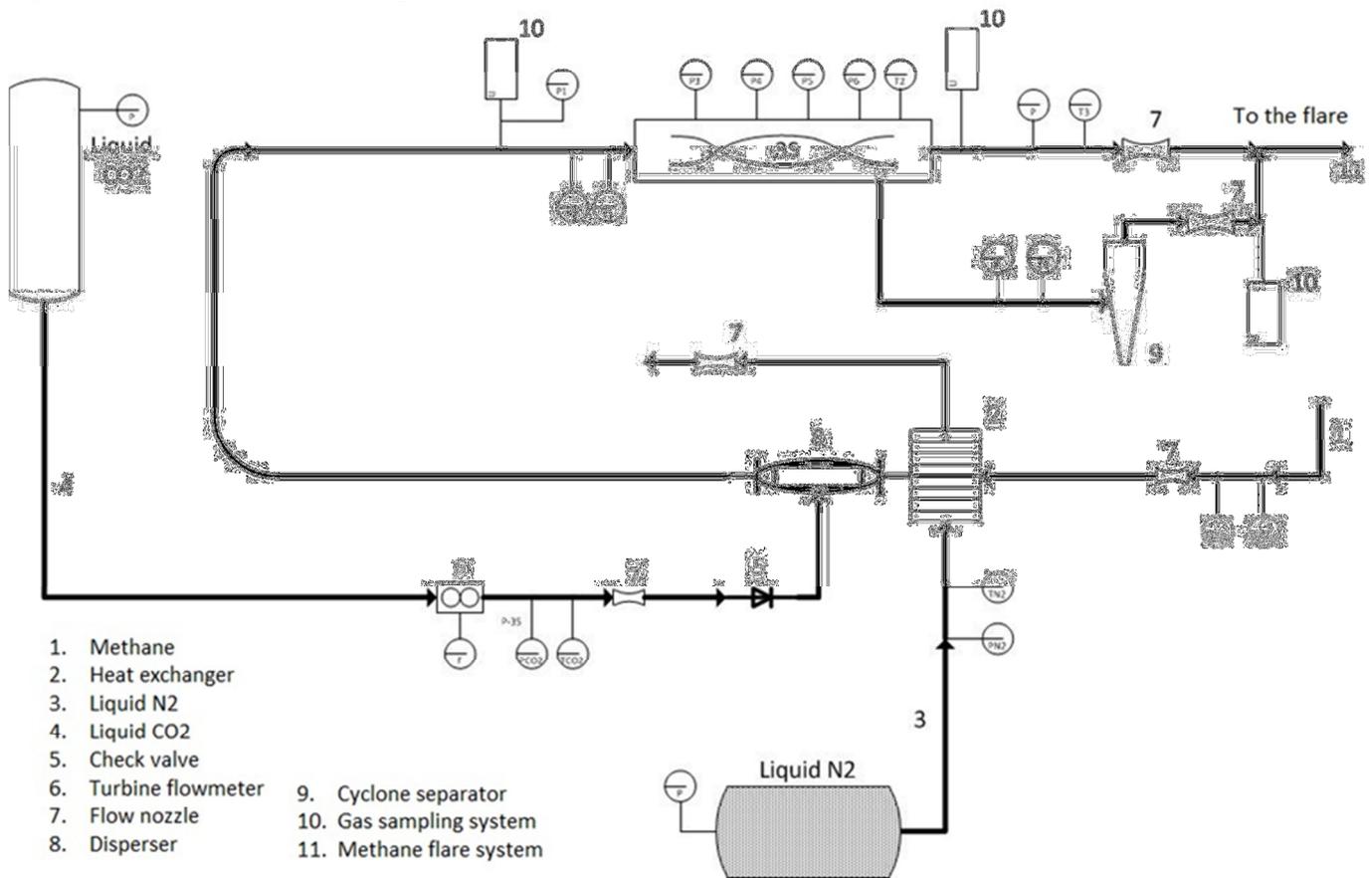


Fig.6 Scheme of experimental unit

The test setup consists of the following systems:

- investigated **3S-separator** (see Fig. 7 showing a picture of the unit)

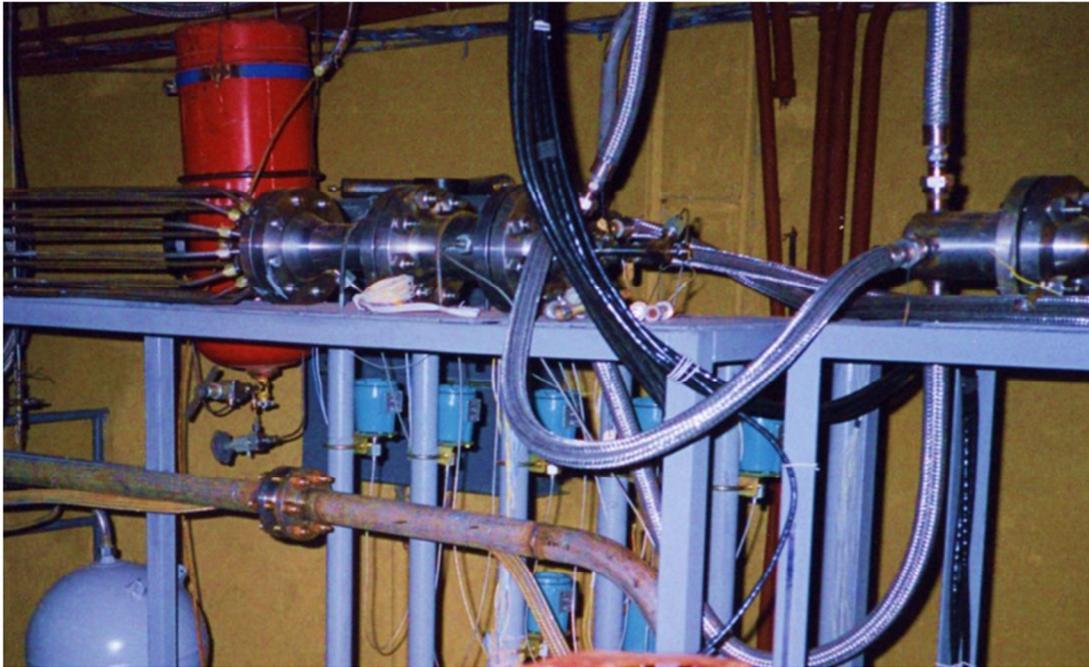


Fig.7 3S-separator, mounted at the experimental unit

- The **methane injection system 1** consists of a high pressure methane source, control valve and a **flow nozzle 7**.
- **Heat exchanger 2**, where the preliminary cooldown of methane flow occurs, caused by the liquid nitrogen evaporation;
- The **feed system 3**, supplying liquid nitrogen into the heat exchanger (**liquid nitrogen supply system 3**), consists of a vessel with liquid nitrogen and a pressure-feed system.
- The **liquid CO₂ supply system 4**, used for mixing liquid CO₂ with methane, includes CO₂ storage vessel and nitrogen pressure-feed system. The Carbon dioxide supply line is equipped with **check valve 5**, CO₂ **turbine flowmeter 6** and a **flow nozzle 7**; after which the carbon dioxide is delivered into the methane line by means of the **disperser 8**. A check valve prevents methane from entering into the carbon dioxide line;
- **Two phase flow separation system** (for the flow from 3S-separator) comprises **cyclone separator 9**;
- **Gas sampling system 10**. Samples are taken at three points of the test setup - from the feed mixture at the inlet of 3S-separator, at the outlet of 3S-separator and in the gas line at the outlet of **cyclone separator 9**. For each test point there is a metal container and two remotely operated valves to take samples during each test run;
- A **methane flare system 11** is installed at the outlet of the test setup. The flare system also prevents accumulation of methane and its uncontrolled ignition;
- **Instrumentation and controls system** is installed at different points of test setup to obtain the required operation conditions of test run and to analyze performance of the test setup. It consists out of a number of thermocouples, pressure gauges and above-stated flow nozzles and turbine flowmeters. The sensor signals are measured and recorded by National Instruments device and a PC.

The sequence of test setup experiments is the following. During the preparation for the experiment the required amount of liquid nitrogen and liquid CO₂ is supplied from permanent storage tanks to the supply system vessels. These supply vessels are designed for supercharger pressure. The desired pressure values in these vessels can be set at closed components supply line.

Each test run begins with methane supply and setting of its required pressure at the inlet of 3S-separator, while at the same time it is required to control the methane flame presence at the flare at the outlet of test setup. Then the liquid nitrogen line is opened to the heat exchanger. Carbon dioxide supply valve will be opened, when the temperature of methane at the inlet of separator falls down to a required level. And after the stabilization of its injection conditions, gas sampling is done. Then the supply of CO₂ and methane are closed and the methane line is blown down using gas nitrogen. Samples are taken and sent to the portable containers for further analysis by a gas chromatograph.

Test results of 3S-separator with mixtures of Methane and CO₂

Tests of 3S-separator were carried out at ENGO Engineering Laboratory in Moscow. The purpose of the tests was to investigate conditions at which it is possible to purify CH₄+CO₂ mixture to concentrations less than 3% mol. For that purpose, inlet mixture was cooled down to (-60) - (-70)°C.

The same equipment as in the previous series of experiments was used during the laboratory tests, but the gas-dynamic channel was specially designed. Separation of two-phase boundary layer was implemented at a rate of 18-20% from total gas mass flow rate through 3S-separator.

Some test results are shown in Fig. 8.

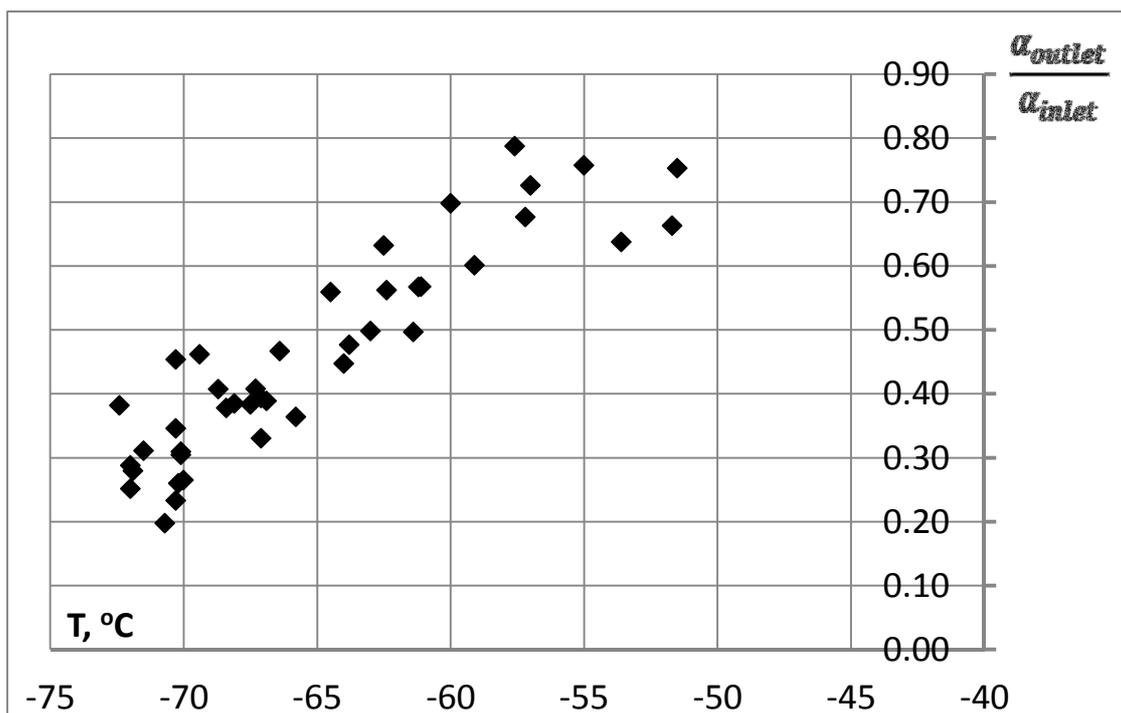


Fig.8 Dependence of 3S-separators operating efficiency
 α_{outlet} - concentration of CO₂ (mol.) at the 3S outlet,
 α_{inlet} - concentration of CO₂ (mol.) at the 3S inlet,
 T – gas temperature at the 3S inlet

As it follows from presented data, the main factor, which determines high rate of mixture purifying, is the temperature of the inlet mixture.

During experiments, it has been shown, that in order to achieve a high rate of acid gas removal the inlet temperature should be below -60°C. Only at these conditions it is possible to purify natural gas to CO₂ concentration less than 4% mol.

Also the following factor helps to achieve high rate of mixture purifying: due to the centrifugal effect, mixture pressure in the core of the flow is 25-30% less than at the periphery, which leads to additional adiabatic cooling of mixture flow.

The course of tests demonstrated the effectiveness of 3S-technology for CO₂ separation and also proved the fact that crystallization processes have no time to develop in the nozzle of supersonic separator. A coagulation and separation processes, taking place in the nozzle, are accompanied by supercooled droplets, which are not crystallized yet.

Conclusions

Available technology of supersonic separation can be used for carbon dioxide removal from natural gases. 3S-technology is most effective for natural gas with high CO₂ content stripping, especially when it is difficult to use conventional technologies. Proposed schemes of 3S-separation units can provide CO₂ concentration in the outlet of the unit less than 2 % mol. (at any CO₂ content in the inlet gas).

Tests of 3S-separators, conducted on hydrocarbon mixtures, containing CO₂, have shown that the developed 3S-separator provides the desired efficiency of CO₂ separation from natural gases.

References

- [1] Mehdi Panahi, Cryogenic CO₂/H₂S capture technologies for remote natural gas processing, Trial Lecture, 2011
- [2] http://www.fischer-tropsch.org/DOE/DOE_reports/GRI/gri-86_0009-1/86_0009-1_Part4_Pages_298-409.pdf
- [3] E. Keskes, C.S. Adjiman, A. Galindo, and G. Jackson, a physical absorption process for the capture of CO₂ from CO₂-rich natural gas streams, Chemical Engineering Department, Imperial College London, <http://www.geos.ed.ac.uk/ccs/Publications/Keskes.pdf>
- [4] J. Hao, P.A. Rice, S.A. Stern, Upgrading low-quality natural gas with H₂S and CO₂ selective polymer membranes: Part I. Process design and economics of membrane stages without recycle streams, *Journal of Membrane Science*, 209, 1, 177-206
- [5] A. S. Holmes, J. M. Ryan, Cryogenic distillation separation of acid gases from methane, US patent, 1982
- [6] J. A. Valencia, B. K. Mentzer, Processing of High CO₂ and H₂S Gas with Controlled Freeze Zone™ Technology, ExxonMobil Upstream Research Company GASEX 2008 Conference
- [7] J. A. Valencia, P. S. Northrop, C. J. Mart, Controlled Freeze Zone™ Technology for enabling processing of high CO₂ and H₂S gas

reserves, ExxonMobil Upstream Research Company IPTC 12708 (2008)

[8] B.T.Kelly, J. A. Valencia, P. S. Northorp, C. J. Mart, Controlled Freeze Zone™ for developing sour gas reserves, Energy Procedia 4 (2011), 824-829

[9] C. Condon, M. Parker, Shute Creek Gas Treating Facility Project Updates, The Wyoming Enhanced Oil Recovery Institute 5th Annual Wyoming CO₂ Capture Conference, 13 July 2011

[10] Bruce W. Klint, Peter R. Dale, Charles Stephenson Low Quality Natural Gas Sulfur Removal and Recovery CNG Claus Sulfur Recovery Process // Pilot Plant Test Program/ DOE Contract DE-AC21-92MC29470

[11] A. Hart and N. Gnanendran, Cryogenic CO₂ Capture in Natural Gas, Energy Procedia 1 (2009), 697-706

[12] http://www.total.com/MEDIAS/MEDIAS_INFOS/239/EN/sour-gas-2007.pdf

[13] F. Lallemand, F. Lecomte and C. Striecher, "Highly Sour Gas Processing, H₂S bulk removal with the Splex Process", IPTC 10581, 2005

[14] Korytnikov R.V., Yakhontov D.A., Bagirov L.A., Dmitriev L.M., Imaev S.Z. Industrial tests of supersonic separation technology at low temperature separation unit of UPMT of "1-S" gas complex treatment unit of Zapolyarny oil and gas fields' complex// Petroleum engineering Journal, №6, 2012

[15] Andreev O.P., Minigulov R.M., Korytnikov R.V., Bagirov L.A., Imaev S.Z. Technological schemes of GPP based on 3S-technology for the northern oil-gas condensate fields //Science and Technology of Gas Industry Journal, №2, 2009

[16] Vadim Alfyorov, Lev Bagirov, Leonard Dmitriev, Vladimir Feygin, Salavat Imayev, John R. Lacey. Supersonic nozzle efficiently separates natural gas components // Oil & Gas Journal, May 23, 2005