Chemical and Petroleum Engineering, Vol. 40, Nos. 7–8, 2004

ANALYSIS OF MODERN NATURAL GAS LIQUEFACTION TECHNOLOGIES

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Liquefied Natural Gas – Energy Carrier of XXI Century

Over the past 30 years, a whole industry for production of liquefied natural gas (LNG) has come up and has been successfully functioning abroad, producing 100 Bm^3 of LNG a year. Experts predict that the volume of global LNG trade may grow by the year 2010 to 150 Bm^3 and more a year [1]. Note that abroad LNG production was stimulated to a great extent by export of huge quantities of natural gas (NG) from gas producing countries, such as Nigeria, Algeria, Indonesia, Libya, Malaysia, and others, to the countries of Western Europe, the USA, and Japan as well as by more economic supply by sea in the form of LNG. In the USA and in Western Europe, the share of LNG in the total gas consumption is more than 20%. Japan imports as much as 85% (45 Bm^3) of NG as LNG.

Also, a new segment of the fuel-energy branch of the industry associated with LNG production in mini-plants has come up and has been growing vigorously in developed countries. For example, in the USA and in Canada, about 300 LNG production and storage plants with outputs of 3–40 tons/h have been built and are in operation. The companies like Cryopack, Cryogas Engineering Ltd., and others are leaders in the field of construction of such plants. Natural gas liquefied in these plants is used for gas supply to population centers and as fuel for motor vehicles. For example, in the USA, motor vehicles are filled with LNG at numerous stationary gas stations, to which LNG from the mini-plants is delivered by specially built cryogenic methane carriers. A wide network of such gas filling stations has been created in California, Arizona, Colorado, Texas, Pennsylvania, etc.

At present, in Russia, there is practically no industrial LNG plant. However, because of aggravation of fuel-energy crisis and development of new fields on sea shelves, active debate concerning large-scale LNG production has begun in Russia [2, 3]. This is associated, on the one hand, with technoeconomic benefits of use of NG for gas supply to population centers and boiler houses far removed from gas networks, for use as motor fuel for various types of vehicles, and for creation of gas storage systems and, on the other, with proposed supply of NG by sea from the Ob Inlet and Sakhalin Island regions to foreign consumers.

Conditions of NG Liquefaction

Natural gas (NG) has no color and smell, is poorly soluble in water, and is explosive if present in a mixture with oxygen and air in 5.3–15% concentration. Under normal conditions, methane has a density of 416 kg/m^3 in liquid state and 0.717 kg/m^3 in gaseous state, its critical pressure is $45.8 \cdot 10^2$ kPa, critical temperature is –82.1°C, and boiling point at atmospheric pressure is –161°C. The viscosity of liquefied NG diminishes as the temperature rises. Its dynamic viscosity at the boiling point is $116 \cdot 10^{-7}$ Pa·sec.

Natural gas (NG) can be liquefied if it is cooled to or below the critical temperature. If NG is liquefied at the critical temperature, its pressure must not be below the critical. And if NG is liquefied below the critical pressure, its temperature must be below the critical.

For liquefaction of NG, use can be made of the principles of internal cooling when NG itself acts as the working medium as well as of external cooling when auxiliary (boosting) cryogenic gases with a lower boiling point (oxygen, nitro-

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Translated from Khimicheskoe i Neftegazovoe Mashinostroenie, No. 7, pp. 17–20, July, 2004.

gen, helium, etc.) are used to cool and condense NG. In the latter case, heat exchange between the NG and the boosting cryogenic gas occurs through the heat-exchange surface.

Liquefaction of NG based on the principle of internal cooling can be achieved as follows:

- by isoenthalpic expansion of the compressed gas (I = const, where I is the enthalpy), i.e., by throttling (using Joule–Thomson effect), in which the gas stream does not perform any work; and
- by isoentropic expansion of the compressed gas (S = const, where S is the entropy) with performance of external work whereby it is possible to produce additional cooling over and above what is produced by the Joule–Thomson effect because the work for expansion of the gas is performed at the expense of its internal energy.

In general, isoenthalpic expansion of compressed gas is used only in small- and medium-capacity liquefaction apparatuses where some overconsumption of energy can be ignored, whereas isoentropic expansion is used in large-capacity liquefaction apparatuses.

Liquefaction of NG based on the principle of external cooling can be achieved as follows:

- by using Stirling, Vieulemier-Taconis, and other types of cryogenerators where working media generally are helium and hydrogen, which allows the temperature on the heat exchanger wall to fall below the boiling point of NG if the thermodynamic cycle is closed;
- by using cryogenic liquids with boiling points below the boiling point of NG, such as liquid nitrogen and oxygen;
- by using a cascade cycle with the help of various cryogenic cooling agents like propane, ammonia, methane, etc., in which a gas easily liquefiable by compression produces upon evaporation the cold required for lowering of the temperature of another poorly liquefiable gas.

Technology of NG Liquefaction in Large LNG Plants

The global LNG production and consumption market has been growing toward supply of NG as an energy carrier from countries having surplus resources to countries experiencing deficits in this fuel as well as toward building storages for releasing peak loads. To date, 15 large LNG plants had been built and are in operation abroad. The output of the gas liquefaction plants has grown over the past 20 years from 0.6 to 3.0 million tons a year on account of application of more powerful equipment, which helps cut down consumption of energy for liquefaction. In general, in large LNG plants, use is made of cascade cycle (*propane – ethylene – methane* cascade) or cooling cycle on a mixed coolant with precooling with propane. A multicomponent mixture of hydrocarbons (*methane – ethane – propane – butane – pentane*) and nitrogen is used as the coolant.

Of late, increasing use is being made of single-flow cascade cycle combining the thermodynamic advantages of the cascade cycle and the simplicity of design of regenerative throttling cycle. A binary or multicomponent mixture of gases (*methane – ethane – propane*) with differing boiling points is used in this cycle as the coolant. The mixture undergoes compression in a compressor, passes through the final cooler where it is cooled with water, and finally flows into a separating vessel. The condensate containing essentially propane is separated (after throttling) from the gas mixture and is used for being cooled to 233–203 K required for cooling of the mixture and liquefaction of ethane. The liquefied ethane is used further as the coolant for cooling to 193–163 K required for liquefaction of the residue whose evaporation lowers the temperature further to 113–118 K. The cooling attained at different temperature levels is used to cool the compressed NG (methane) before throttling.

Construction of large NG liquefaction plants requires huge investments. The cost of a single NG liquefaction line with an LNG production capacity of 6 million tons a year at global prices is roughly US$3 billion. Because of the poor state of the Russian economy, construction of a large number of similar LNG plants in Russia in the immediate future is problematic. Moreover, studies have shown that potential LNG consumers in Russia are numerous and scattered across considerable distances from each other. Which is why construction of large LNG plants (except supply of NG to foreign consumers by sea) is not beneficial on account of heightened cost of transportation of this energy carrier by land over considerable distances.

For Russia, the most promising direction in industrial LNG production is construction of small mini-plants [4].

Mini-LNG Plants

Mini-LNG plants based on gas-distributing stations (GDS). In building mini-plants, depending on the type of GDS, intake pressure, and flow rate, diverse schemes and units are used for getting the highest NG liquefaction coefficient (efficiency) and lower LNG cost. As the main units (liquefiers) for plants liquefying NG from trunk pipelines at operating GDS, use is made of devices traditionally employed in cryogenic engineering, namely, throttling devices, truboexpanders, and vortex tubes.

Technology of LNG production based on throttling-vortex cycle. This technology is offered by a number of enterprises of the Northwestern region of the Russian Federation, such as Sigma-Gaz ZAO, Lentransgaz OOO, Krionord ZAO, etc. Initially, the technology of LNG production at GDS was based on use of vortex liquefier (Rank tube). A US.00.000 NG liquefaction plant based on use of a vortex cooler was tested at the Nikol'skoe GDS of Lentransgaz. The key technical characteristics (specifications) of the plant are: minimum operating pressure 3.5 MPa, gas flow rate 2000–7000 m^3/h, LNG output 100–500 kg/h, mass 3700 kg, and occupied area 6 m^2. The test data confirmed the operational fitness of the plant, but presence in the NG of large quantities of moisture and other impurities contributing to fouling of the heat exchangers do not allow uninterrupted LNG production process without special measures for cleaning and drying of the gas [6].

The advantages of this technology are: no energy cost, the required cooling for NG liquefaction being produced only through utilization of the energy of the pressure of the compressed gas from the trunk gas pipeline, simplicity, and relatively low capital investment. The disadvantages are: low liquefaction coefficient (2–4%), concentration of the target product, namely methane, does not meet standard requirements, and servicing is labor- and time-consuming because of the need for commutation (reversal) of the recuperative heat exchangers.

Later on, for raising liquefier efficiency, the experts of Sigma-Gaz developed a scheme for LNG production at GDS making use of classical throttling cycle and an additional external forward-flow cooling loop that includes a separating vortex tube and two reversible freezing heat exchangers.

Note however that for wide application of this technology and profitable LNG production, it is essential that the liquefaction coefficient be not less than 5%. This means that the gas pressure at the plant inlet must not be less than 6 MPa and the flow rate over a year, more than 30000 m^3/h. In Russia, only a small number of GDS has such parameters. Large GDS's with a steady seasonal flow rate of hundreds of thousands of cubic meters of gas per hour have an average inlet pressure of 3.5–4.5 MPa and an average outlet pressure of 1.2 MPa. Gas-distributing stations having such parameters make it possible to get liquefaction coefficients in the 0.5–2% range by the throttling or throttling-vortex cycle, which renders LNG production by the proposed technology unprofitable.

Technology of LNG production based on turboexpansion cycle. The LNG production technology proposed by the experts of Sibkriotekhnika OAO, is efficient from the cost point of view. This technology is based on use of the existing GDS's and turboexpansion NG liquefaction cycle [7]. Natural gas liquefiers operating on partial liquefaction principle and realizing free pressure drop at GDS's are connected in parallel to the pressure regulating devices of the GDS's in such a way that the unliquefied part of the NG being processed by them is discharged into the production gas pipeline of the GDS. The liquefaction coefficient is about 10%.

The effectiveness of construction of mini-LPG plants making use of pressure drop at the GDS with inclusion of a turboexpander in the technological circuit has been confirmed by the experience of work of US gas companies. Unfortunately, this promising NG liquefaction technology cannot be quickly put into practice in Russia for lack of domestic series-produced expanders with a capacity of 70000 m^3/h and an expansion ratio of 4–5. Also, a serious obstacle to construction of mini-LNG plants at GDS based on turboexpansion cycle is their high cost (US$2.5–3.0 million).

Technology of LNG production based on compression-expansion cycle. The experts of the Geliimash Scientific-Production Association suggest that an alternative solution to the problem of LNG production could be construction of compact NG liquefiers with capacities of up to 300 kg/h based on use of compression-expansion cycle, which is classical in cryogenic engineering [8]. This technology can be used both at automobile gas-filling compressor stations (AGFCS) and for construction of self-contained NG liquefaction plants located right on trunk gas pipelines. Six basic designs of NG liquefiers have been worked out. Application of each of them depends on the conditions of the input parameters of the NG. The major advantage of such liquefiers is that it is possible to employ existing equipment (compressors, expanders, heat exchangers, accessories, etc.). However, as the experts of Geliimash point out, the reverse side of the apparent simplicity of the basic NG liquefier designs is low thermodynamic efficiency, low liquefaction coefficient, and high specific (unit) cost. And what is more, in order to put this LNG production technology into practice, it is essential to solve the problem of series-production of reliable domestic compressors as well as the problem associated with large volume of waste gas (about 97%). Without solution of these problems, the proposed basic NG liquefier designs for LNG production cannot be put into practice.

Technology of LNG production based on throttling-separation cycle with precooling. In July 2001, the Lentransgaz company put into operation for the first time in Russia a mini-NG liquefaction plant operating on this cycle at an AGFCS (automobile gas-filling compressor station) in Petrodvorets (Leningrad region). The capacity of this mini-LNG plant is about 25 tons/day at a plant cost of 20 million rubles and a cost recovery time of 4 years [9].

A loop for external cooling of high-pressure gas with a K-127 two-stage Freon refrigerating machine made at the Moscow plant Kompressor was used as the equipment for raising LNG output based on throttling-separation cycle.

The experts of Lenavtogaz believe that the cost of LNG produced on the basis of AGFCS would roughly be the same as the cost of A-92-grade gasoline [10].

Technology of LNG production based on utilization of liquid nitrogen from metallurgical works. Domestic experience shows that for NG liquefaction, liquid nitrogen can be used effectively. In the former USSR, work in this direction was carried out at the Institute of Gas of the Academy of Sciences of Ukraine. Based on the results obtained, LNG plants with capacities of up to 500 kg/h were built. In these plants, NG was condensed with liquid nitrogen. Nitrogen consumption was 2 tons/1 ton of the LNG produced. The incoming gas was cleaned and dried in two alternately operating low-temperature regenerators from a KZh-300 oxygen plant. About 3% of the incoming gas was withdrawn for regeneration. The pressure at the plant inlet was 0.6 MPa.

Similar plants can be run effectively as a part of the GDS of integrated metallurgical works, where there is a surplus of liquid nitrogen produced with the help of technological plants for separation of air into oxygen used in metallurgical processes and nitrogen.

Technology of LNG production based on heat and electric power plants. Currently, there are about 490 heat and electric power plants (HEPP) in Russia. More than 80% of these use NG as the fuel. In general, these energy plants are hooked to gas mains having a pressure not below 2 MPa, which is excessive for normal functioning of gas burners. The gas pressure drops due to throttling with irreversible loss of energy for pressure drop. Thus, a unique possibility arises for utilization of the excess pressure of the incoming NG for building mini-LNG plants at the currently operating HEPPs.

The technology of LNG production at HEPPs using pressure drops is being employed abroad widely for more than 30 years [11]. In 1996, the US company San Diego Gas and Electric K° put into operation an NG liquefaction plant at the South Bay heat and electric power plant (HEPP) at a cost of US$2.7 million. The technical characteristics of the HEPP are: NG consumption 700,000 m^3/day, pressure at the plant inlet 2.1 MPa, and pressure in the boilers (burners) 0.2 MPa. Expansion cycle was used as the liquefaction method. The purpose of the plant was to stockpile NG for operation in the peak load period. During this period, LNG is withdrawn from the storages by cryogenic pumps and fed into an evaporator, after which it runs into the gas burners in gaseous state.

In Russia, there is experience now as to how to use excess pressure at HEPPs not only for LNG production but also for electric power generation by dropping the pressure of the supply-line gas for its liquefaction. In 1995, for the first time in Russia an industrial plant consisting of two DGA-5000 expander-generator units with a capacity of 5 MW each was put into operation at the HEPP-21 of Mosénergo (Moscow District Administration of Power Engineering Facilities). With the help of this technology, it is virtually possible to recover a part of the energy consumed by the gas pumping units for building in the trunk gas pipeline the pressure required for transporting the gas as well as of the energy irrecoverably lost upon its throttling at the electric power plant. Operational experience has shown that in only one year of operation this plant generates 24 MkW·h of additional electric power [12].

Use of this experience for NG liquefaction at HEPP would make it possible to build in Russia about 400 mini-LNG plants with a high economic efficiency because no electric power is consumed in this case for LNG production.

Production of LNG applying Stirling technologies. Application of Stirling technologies jointly developed by A. F. Mozhaiskii Military and Outer Space Academy and Stirling Technologii Innovation and Research Center can significantly enhance the efficiency of NG liquefaction plants [13–15].

In Stirling NG liquefaction technologies, the main units are cryogenic gas machines (CGM) operating on Stirling cycle, which used to be employed earlier in plants for liquefaction of various industrial gases and for liquid nitrogen production.

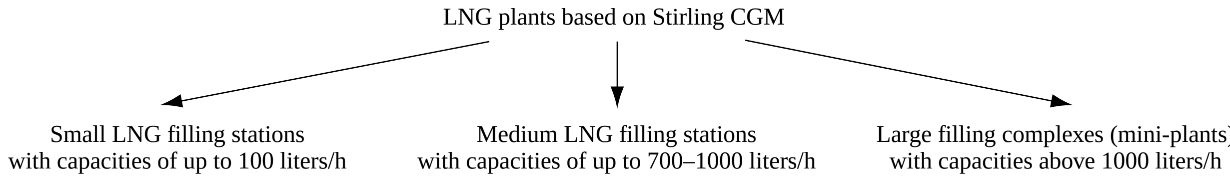

Fig. 1. Classification of LNG plants based on Stirling CGM.

Stirling CGMs are liquefiers whose action is based only on external cooling. The NG liquefaction process takes place at atmospheric pressure, which allows NG liquefaction plants based on Stirling CGM to be compact and easily serviceable. An important feature of Stirling CGMs is the possibility of 100% liquefaction of the fed low-pressure gas. The efficiency of the NG liquefaction cycle with application of Stirling CGMs is almost 2–2.5 times as much as the efficiency of simple throttling and expansion NG liquefaction cycles.

Basing on Stirling technologies, LNG plants varying in function and output can be built (Fig. 1).

At present, several versions of multicylinder Stirling CGM are being made abroad. Their capacities allow them to be used for construction of large LNG complexes.

For instance, at an incoming NG pressure of less than 2 MPa, a PPG-2500 CGM is capable of ensuring an LNG output of 5–6 tons/day. If this CGM is installed, only electric energy that cools the water and NG need to be supplied. The start-up lasts 15 min and takes place automatically. The manufacturing company guarantees a full operating period (mean-time-between-failures) of 8000 h and an overhaul period (interrepair service life) of not less than 20000 h.

Based on the designs (engineering solutions) worked out at the Stirling Technologii IITs, in 2001 a Russian enterprise organized a small-scale construction of garage LNG filling stations around a domestic Stirling CGM that forms a part of a ZIF-1000 air separation plant. According to a preliminary estimate, the cost of one liter of LNG obtained in series-produced modular NG liquefaction plants based on Stirling technologies is not higher than two rubles. The cost recovery time of the garage stations based on Stirling CGM is not more than 2.5 yr.

Application of Stirling technologies makes it possible to build LNG plants irrespective of where they are located: they can be hooked directly to trunk gas pipelines, GDS, AGFCS, low-pressure municipal gas supply networks, etc.

The prospect of application of Stirling technologies for building mini-LNG plants has been appraised abroad as well. For example, the world's most renowned German company Linde AG, which is engaged in cryogenic technologies, developed a liquefier with a Stirling CGM and a drive from a gas engine for which trunk pipeline NG is used as the fuel.

In the future, it is proposed to build around Stirling CGM having a drive from a Stirling engine fully automatic LNG plants that require no external electric energy. Application of Stirling engines will help achieve reduced toxicity in operations with organic fuel, reduced noise and vibrations, and saving of up to 20% fuel in comparison with conventional internal combustion engines. In the recent decade, Stirling engines began to be widely used abroad. For instance, during the years 1996–1998, in Sweden a series of submarines with 100 kW Stirling engines have been put into operation, in Japan Mitsubishi successfully tested Stirling engines with a power of more than 600 kW, in Germany MAN built a 700 kW Stirling engine, and so on.

REFERENCES

1. O. A. Ben'yaminovich, "Cold and gas industry," *Kholodiln. Delo*, No. 5, 2–3 (1997).
2. N. G. Kirillov, "Energy security of Russia and resource saving as the major line of development of Russian power industry," *Énergetich. Polit.*, No. 1, 13–20 (2002).
3. N. G. Kirillov, "Energy saving strategy of economic development of Russia," *Gorn. Promysh.*, No. 2, 4–7 and 61–63 (2002).

4. N. G. Kirillov, “Strategy for use of natural gas until 2020,” *Gaz. Promysh.*, No. 2, 22–26 (2002).
5. B. G. Bergo and E. V. Karpov, “Technology of liquefied natural gas production,” *Potentsial*, No. 1, 60–63 (2001).
6. V. E. Fin’ko, “Prospects of use of liquefied natural gas,” *Gaz. Promysh.*, No. 2, 58–60 (2000).
7. A. K. Grezin, A. V. Gromov, et al., “Use of liquefied natural gas as an energy carrier – a task of national importance,” *Kholodiln. Tekh.*, No. 9, 6–8 (1999).
8. B. D. Krakovskii, O. M. Popov, and V. N. Udut, “Choice of design of natural gas liquefier,” *Kholodiln. Tekh.*, No. 9, 26–27 (1999).
9. I. L. Khodorkov, “Russia’s first standard-sized mini natural gas liquefaction plant at AGFCS,” *Kholodiln. Biznes*, No. 4, 12–13 (2001).
10. N. A. Koreshonkov, “Problems of gas filling in road and river transport,” *Prirod. Gaz v Kachestve Motor. Topl.* (Natural Gas as a Motor Fuel), No. 5–7, 16–20 (1995).
11. B. V. Smirnov, *Production, Transportation, Storage, and Regasification of Natural Gas Abroad* [in Russian], Moscow (1967).
12. A. M. Vasil’ev “Energy saving and ecology,” *Khim. Neftegaz. Mashinostr.*, No. 4, 77–78 (1996).
13. N. G. Kirillov, “Concept of infrastructure building for liquefied natural gas production for urban road transport,” *Kholodiln. Tekh.*, No. 7, 27–31 (2002).
14. N. G. Kirillov, “Application of Stirling technologies for liquefaction of trunk pipeline natural gas,” *Neftegaz. Tekhnol.*, No. 1, 15–18 (2001).
15. N. G. Kirillov, “Liquefied natural gas: social, ecological, and energy aspects of use in transport,” *Industr.*, No. 4, 26 (2001).