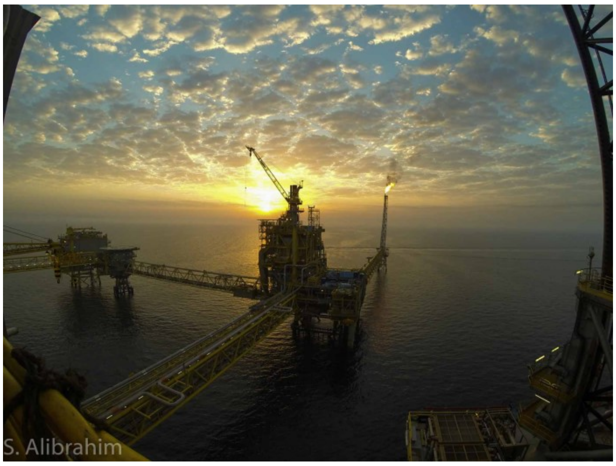


Associated petroleum gas (APG): from incineration to full disposal

Basic definitions

Oil and gas hydrocarbon deposits are often adjacent to each other, forming oil and gas producing regions, which contributes to the interpenetration of oil or gas production technologies, but most importantly, leads to the creation of a unified infrastructure through which several important technological, economically advantageous and environmentally advanced options can be additionally implemented. In reality, many oil fields are located in remote areas. If at the same time, the oil produced contains a significant amount of the gases dissolved in it or if large gas caps accumulate over the surface of the oil reservoir, then there will inevitably be problems with the utilization of this gas, called Associated Petroleum Gas (APG). For a long time, oil producers got rid of it in a simple and reliable way - by burning associated gas in flares. Another popular option was the injection of gas back into the reservoir. However, at present, in connection with the tightening of environmental standards, as well as a general increase in the culture of oil production and the advent of new technologies, more and more projects are being implemented for the beneficial utilization of associated gas, which is a valuable type of hydrocarbon feedstock, with significant commercial returns.

The main component of associated petroleum gas is of course methane, as is the main element of natural gas. But the problems created are not so much by the presence of methane in the oil, but rather by the presence of other gases in the composition of the associated gas, such as ethane, propane, butane, nitrogen, carbon dioxide and others, as well as third-party liquids. As a result, wet gas cannot be routed to gas pipelines since it requires preliminary cleaning, dehydration and separation. Such gas cannot be used as a raw material for petrochemistry without additional processing or used as fuel for electricity generation and sometimes cannot even be pumped back into the formation. The procedures necessary to get associated gas especially in hard-to-reach areas are quite expensive and require qualified personnel and special equipment. Therefore, the straightforward struggle of environmental organizations and governments with oil companies against the flaring of associated gas is not always effective, since solving this problem requires flexible legislative, economically mutually beneficial and affordable high-tech solutions, which together pose a serious challenge.

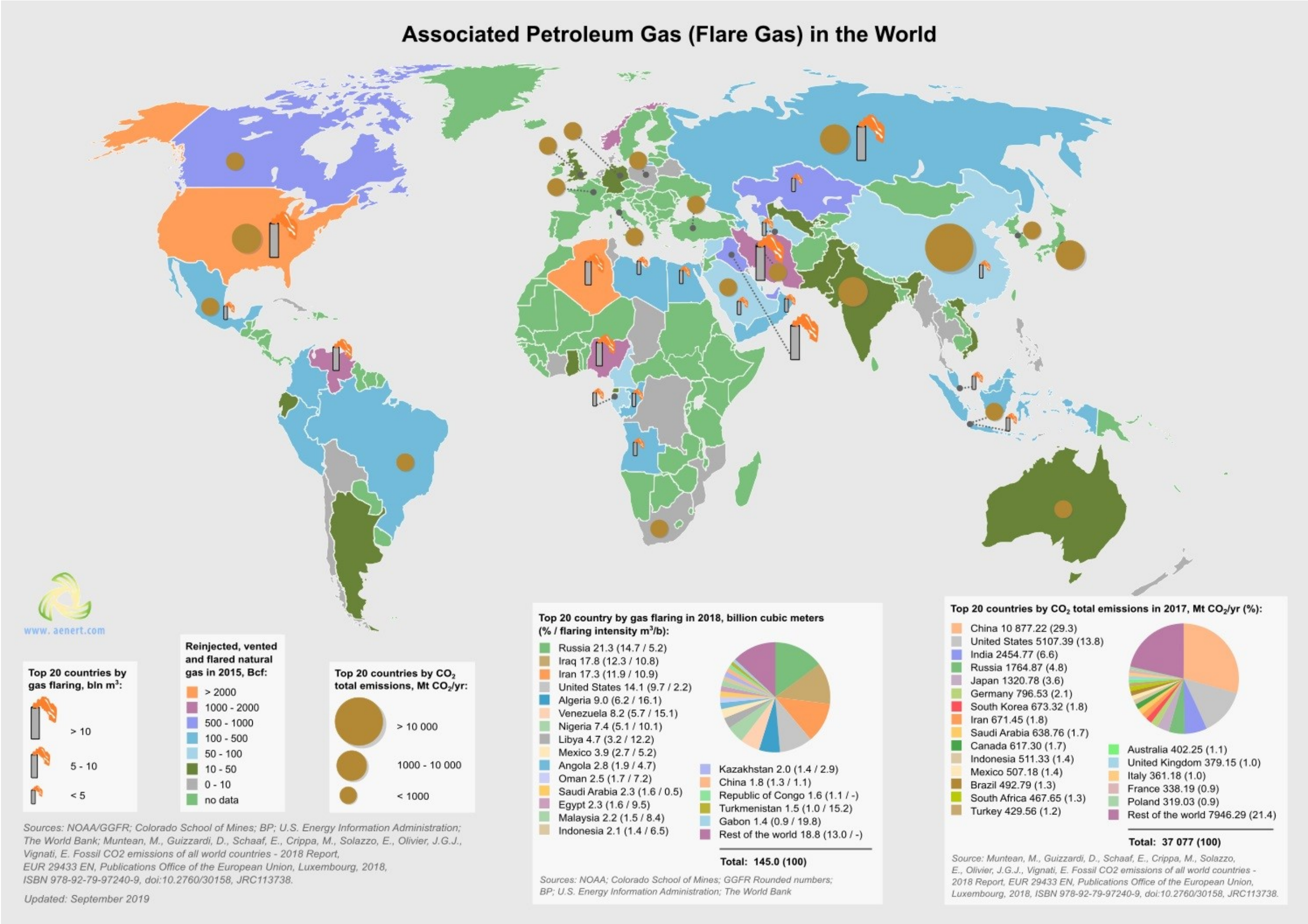
The World Bank, which is the main organizational centre for the indication and resolution of associated petroleum gas problems, launched the "... zero routine burning by 2030" (The World Bank, "Zero Routine Flaring by 2030) [1]. The accompanying documents of this initiative note that about 140 billion m^3 of associated gas are burned annually in the world, and more than 300 million tons of CO_2 are emitted into the atmosphere ("As a result, thousands of gas flares at oil production sites around the globe burn approximately 140 billion cubic meters of natural gas annually, causing more than 300 million tons of CO_2 to be emitted to the atmosphere "). The volume of combustion is quite comparable with the annual production of natural gas of such large producers as Qatar, China, Norway or Australia. In addition, as the World Bank notes, this volume of gas could produce 750 billion kWh of electricity, which corresponds to the annual consumption of Africa .

Fig. 1 presents data from various sources characterizing the level of combustion, direct emissions into the atmosphere, and re-injection of associated petroleum gas (Vented and Flared Gas; Reinjected Gas). Statistical data on carbon dioxide emissions in the top 20 countries of the world are given below.

According to [2-3], in 2018 about 150 billion cubic meters of associated petroleum gas were burned in the world, in Russia - 21.3, Iraq - 17.8 and Iran - 17.3 billion cubic meters. Obviously, the volume of associated gas production will largely depend from the volume of oil production, therefore, a specific indicator is additionally applied - the volume of combustion to the volume of production. The results look completely different. The absolute leader according to version [2] is Cameroon, where in 2018 this figure was more than 40 m^3 per barrel. The burning level of more than 10 m^3 per barrel for the first 30 oil-producing countries was exceeded by Iraq, Iran, Algeria, Venezuela, Nigeria, Libya, Egypt, the Republic of Congo, Turkmenistan and Gabon. For three leading oil producers - the USA, Russia and Saudi Arabia, this indicator was 2.2, 5.2 and 0.5 m3 per barrel, respectively. The change in combustion volumes for most of the largest producing countries over the past five years can be seen in Fig. 2 [3].

Combustion volumes in Iran, Iraq, Russia and the United States increased substantially. Oil companies of Kazakhstan, Malaysia, and Venezuela reduced the volume of combustion by more than one Bcm (the latter against the background of a significant decrease in production). Nigeria, Indonesia and Mexico reduced volumes by one Bcm. In total, the volume of emissions over this period increased by 1.1 Bcm.

Figure 1. Associated Petroleum Gas (Flare Gas) in the World

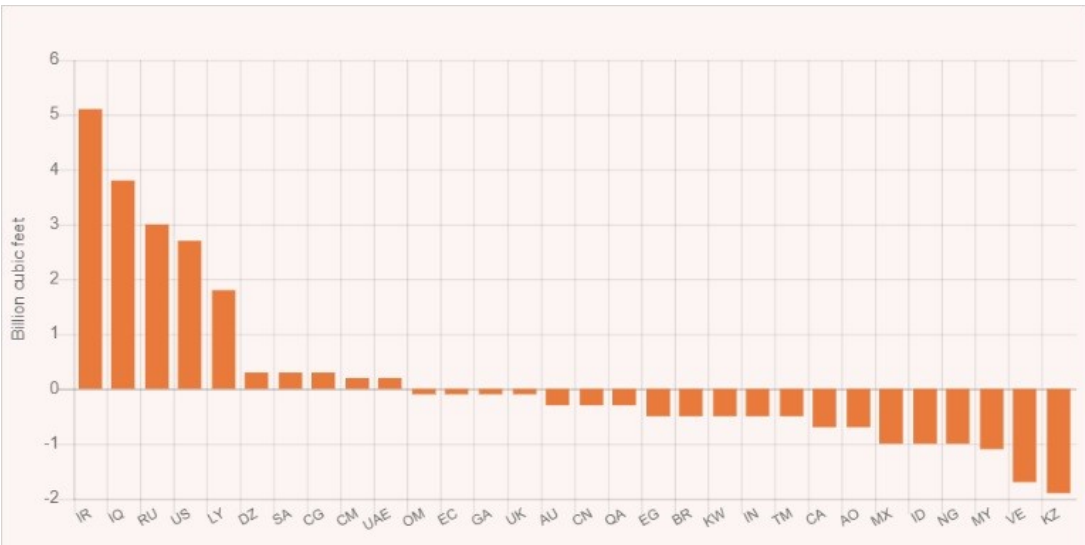


Source: on the map

[*Associated Petroleum Gas (Flare Gas) in the World[0.6 MB]*]

According to [3], a huge leap in gas burning volumes occurred in the USA, where between 2016 and 2018, i.e. in just three years, it increased from 8.9 to 14.1 Bcm or by 5.2 Bcm or by almost 60%. Obviously, this is primarily due to the increase in shale oil production.

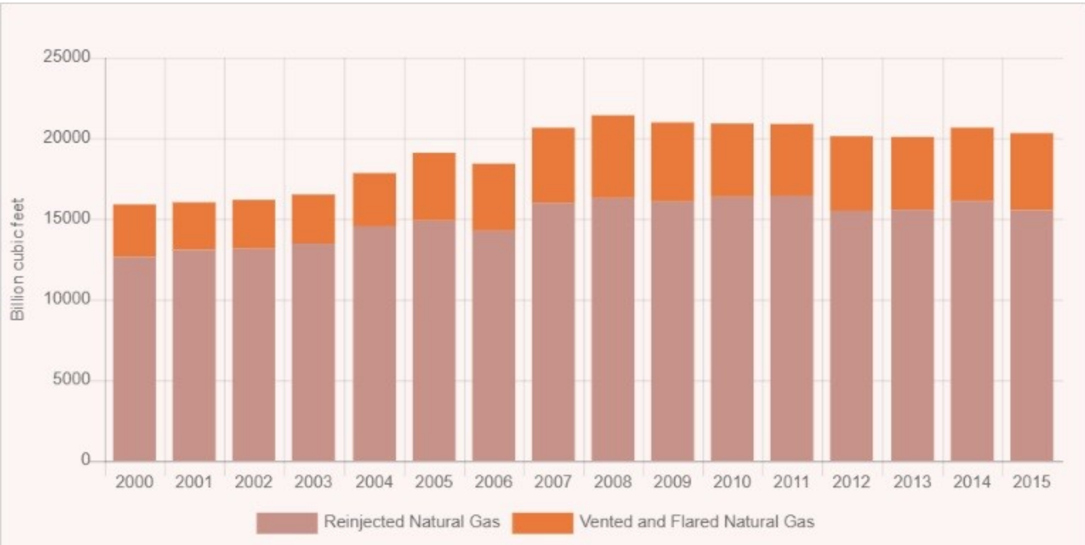
Fig. 2. Gas flaring data in 2014-2018



Source: NOAA, Colorado School of Mines, GGFR Rounded numbers

When methane is burned, carbon dioxide, the main by-product of industrialization, is released into the atmosphere, which largely determines the development of the greenhouse effect of the Earth. Countries with annual CO_2 emissions of more than a thousand Mt are China (10 877.22), USA (5107.39), India (2454.77), Russia (1764.87) and Japan (1320.78) [4]. However, direct methane emissions are much more dangerous, as their global warming potential over a 100-year cycle is 28 times greater than that of carbon dioxide [5]. Currently, direct methane emissions are prohibited in many countries, including associated gas production, in addition, it is difficult to obtain real statistics on this indicator. Nevertheless, such data, although in combination with the volume of combustion, until recently, were recorded in [6]. On the map of Figure 1, data on vented emissions, combustion, and re-injection volumes (Vented, Flared and Reinjected Gas) are summarized for 2015 [6]. As a result, countries were ranked (in colour) by this indicator, which can be seen on the map above. The largest volume of utilized gas was demonstrated by the USA - 3701.8 Bcf, Algeria - 2845.3 Bcf, Iran - 1605 Bcf and Norway - 1553.8 Bcf. The volumes of re-injection in this case amounted to - in the USA more than 92%, in Algeria - more than 95%, in Iran - 68% and Norway - 99.3%. In fig. 3 you can see the annual volumes of gas produced in the United States from 2000 to 2015, which were Vented, Flared and Reinjected. The overall growth of these indicators over this period amounted to more than 30%, and approximately equally for Vented + Flared and Reinjected gas. It should be noted that the U.S. Energy Information Administration uses a special technique to determine the type of well (oil or gas) depending on the ratio of production of these hydrocarbons, however, accounting is carried out for all types.

Fig. 3. Vented, Flared and Reinjected Gas data in 2000-2015, USA



Sources: U.S. Energy Information Administration/ Sep 13, 2019

The data for Russia are very controversial. According to [6], in 2015, 360 Bcf or a little more than 10 Bcm was burned or released into the atmosphere (data on re-injection are not available). According to [3], this figure in 2015 was 19.6 Bcm, and in 2018 - 21.3 Bcm. On the other hand, as follows from a Government source in Russia [7], in 2015 the volume of associated gas burning amounted to about 10 Bcm, and in 2018 about 12 Bcm, with production of about 90 Bcm. It is also noted here that the level of APG utilization this year was quite high and amounted to 86.2%.

The United States is the world leader in associated gas production. According to estimates [8], the volume of production here from 2013 to 2018 more than doubled from 4114 to 8634 Bcf or almost to 250 Bcm, which is about 12% of the total natural gas production in the country [9]. Production in the main oil producing regions of the country - Permian, Bakken, and Eagle Ford has increased significantly. In addition, an increase in associated gas production in the USA saw a record production of natural gas plant liquids (NGPLs) as a valuable raw material for chemical production and a by-product of wet gas purification [9].

Mainstream technologies

In the current production practice of associated petroleum gas utilization, there are a number of widely used technologies, in addition, there are several more promising and commercially viable options that are at the stage of local application, industrial development, or even experimental study, however, the utilization volumes corresponding to these options have not yet been commensurate with the volume of disposal technology of the first group. The following technologies are widely used [10-15]:

- - gas transportation through gas pipelines;
- - gas flaring;
- - re-injection of gas into the oil reservoir.

Associated gas can be transported through pipelines to gas processing plants or directly to consumers only if the associated gas meets the technical parameters of the local gas transportation system, which means that the content of external gas and other impurities in it is satisfactory. The second condition is the availability of pipeline infrastructure in the place of oil production. These conditions greatly limit the possibilities for utilization by direct transportation.

Flaring, as mentioned above, is an extremely undesirable procedure, both in terms of environmental consequences and taking into account the loss of a valuable resource. Nevertheless, it should be emphasized that gas flaring is a necessary technological operation, which should always be present to some extent at hydrocarbon production and processing enterprises. This is required to ensure safety in emergency situations, as well as, for example, when it is impossible to ensure full compliance of the infrastructure capacities for gas utilization at different periods of field operation. In this sense, the presence of burning torches is an inevitable attribute of modern oil production, which, however, does not mean justification for the large-scale burning of the main volumes, instead of other disposal options. It does not mention venting - direct methane emissions into the atmosphere, as the most harmful phenomenon, however, under certain conditions it is also a technological inevitability, especially in emergency situations. It is also important to note that modern methods of associated gas flaring provide high efficiency in the conversion of methane and other hydrocarbons to carbon dioxide, water and a small amount of carbon monoxide.

Re-injection is the most ambitious way to utilize associated gas. If this leads to an increase in oil recovery, then the method becomes a good complement to the commercial return of the field, in addition, non-hydrocarbon gases, such as CO_2 or nitrogen, are utilized. However, if EOR (enhanced oil recovery) methods cannot be implemented, re-injection will result in the loss of potentially valuable products, especially if dry gas is exposed to it, although the oil company can benefit by reducing the amount of fines for burning.

Less common methods of associated gas utilization, nevertheless present in real practice and confidently developing, are [10, 15]:

Gas Processing (natural gas plant liquids (NGPLs);

Gas to Power (Power generation);

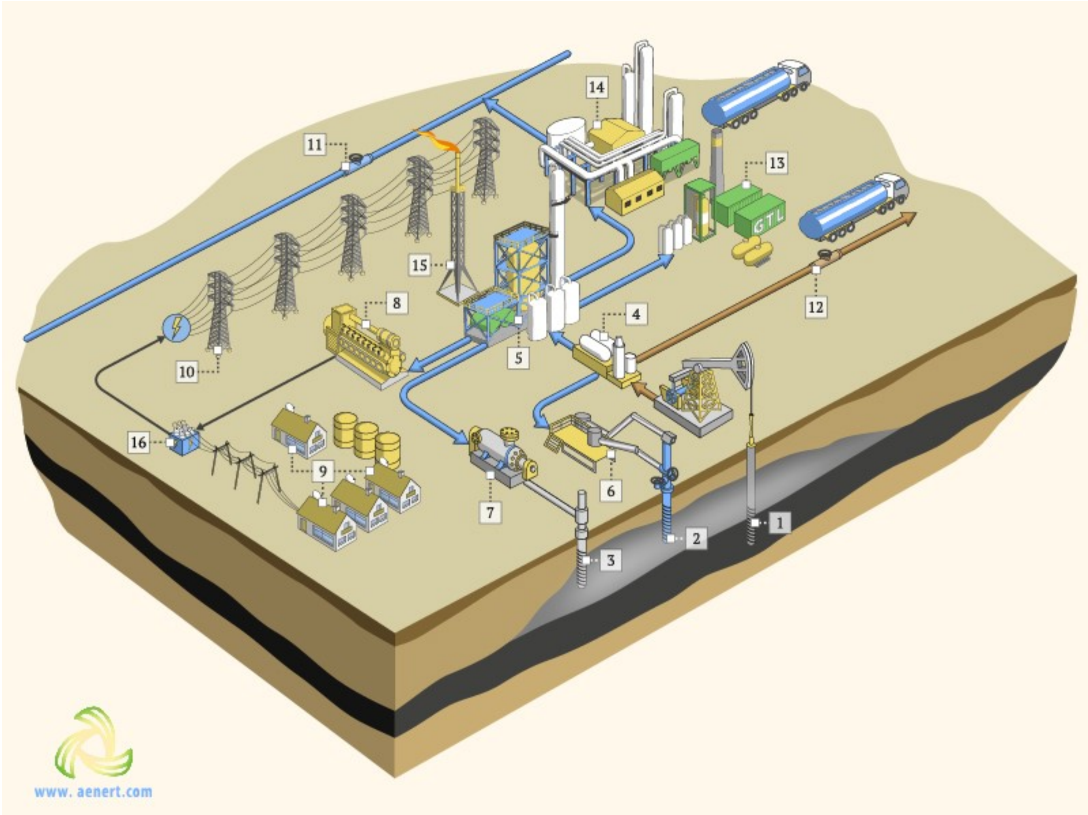
Compressed Natural Gas (CNG);

Liquefied Natural Gas (Small Scale LNG plants);

Gas to Liquids (Microchannel GTL)

A simplified scheme of production and methods of associated petroleum gas utilization is shown in Fig. 4. The main areas of these processes are the oil and gas production unit; primary separation section, where oil is separated from gases, water and other impurities; gas treatment unit; nodes for further use of associated gas.

Fig. 4. A simplified scheme of production and methods of utilization of associated petroleum gas



1. *Production well;* ***2.*** *Water injection well;* ***3.*** *Gas injection well;* ***4.*** *Oil separator;* ***5.*** *Treatment unit;* ***6.*** *Water treatment;* ***7.*** *Pump gas;* ***8.*** *Gas generator;* ***9.*** *In-situ users;* ***10.*** *External users;* ***11.*** *Gas pipeline;* ***12.*** *Oil pipeline;* ***13.*** *GTL plant;* ***14.*** *Gas processing plant;* ***15.*** *Flare stack;* ***16.*** *Transformer*

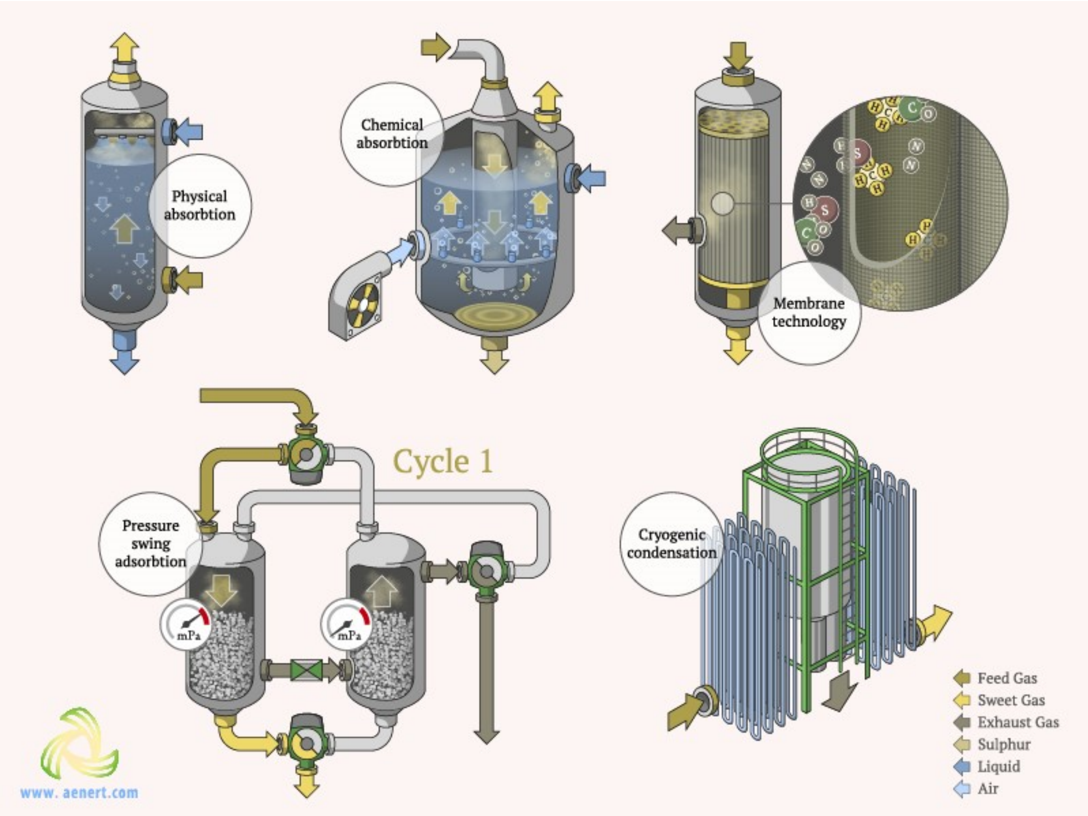
Depending on the field, when producing oil, in addition to associated gas, a significant amount of water with dissolved mineral salts, as well as various mechanical impurities, are simultaneously extracted. Therefore, the first operations after production are separation, i.e. separation of oil from gas, dehydration, removal of Hydrogen Sulphides, Carbon Dioxide and other aggressive impurities, which is often called "sweeting". Further, associated gas, if it contains methane within the established standards, can be subjected to almost any of the above methods of disposal. If the associated gas is wet, i.e. it contains a large number of other gas components in addition to methane, it is further processed, i.e. separation of natural gas liquids (NGLs) [10, 16].

For the separation and purification of gases, various technological processes are used, for example, physical or chemical absorption, membrane systems, cryogenic condensation and others (Fig. 6).

For example, low-temperature condensation and absorption processes are often used to isolate NGLs from associated gas, membrane technologies are very effective in separating sulphur-containing compounds and CO, and other absorption technologies are effective in gas drying.

With the appropriate infrastructure, NGLs can be sent to specialized gas processing plants to produce petrochemicals, and dry methane to the pipeline system. If such infrastructure is not available, then options such as Gas to Power, Compressed Natural Gas (CNG), Liquefied Natural Gas, Gas to Liquids are used. The choice of options is determined by the manufacturer depending on the volume of associated gas production, the location of the field and economic indicators [10, 16, 17, 18]. The technologies of Aspen Engineering Services (NGL Pro process) companies, which include dehydration, compression, cooling and conditioning with a separation efficiency of 80%, are widely known for processing associated gas, as well as CleanSmart turnkey membrane autonomous mobile installations or plug and play or Membrane Technology & Research Inc. See [19] for more details.

Fig. 5. Separate treatment options for industrial gases



The simplest and at the same time effective method of disposal is the Gas to Power technology, which allows the generation of thermal and electric energy. This is especially important if you take into account the high cost of electricity during oil production, and even more so if it is generated through diesel generators. In this case, gas-fired reciprocating engines or industrial gas-fired turbines are most often used. For example, the company Jenbacher (General Electric) supplies gas engines with a capacity of up to 9.5 MW to the market, which are capable of providing local heat and electricity supply with an efficiency of up to 90% [20]. However, there are certain requirements for the content of the gas mixture, which should not have a noticeable proportion of heavy components. This technology is applicable for small volumes of associated gas production, as well as in combination with other utilization technologies [16-17]. The main suppliers of equipment for the production of electricity from associated gas are also APR Energy; Capstone; LPP Combustion, LLC; OPRA Turbines; Turboden (part of Mitsubishi Heavy Industries) - all supplied by Mobile Gas Turbine. Moser Energy Systems, Wärtsilä - are the suppliers of gas engines and gas generators [19].

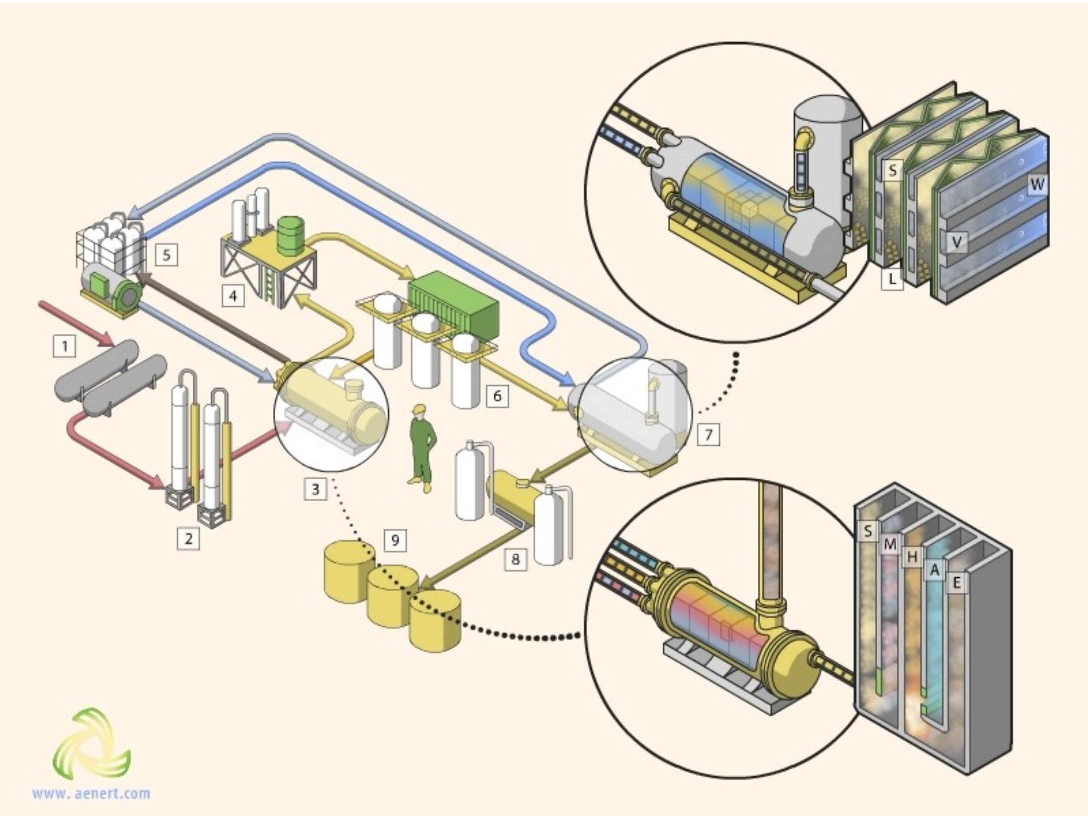
Fig. 6-7. Gas processing plants. Left - Gas treatment plants OMV in Aderklaa, Lower Austria. On the right is SIBUR, the largest associated petroleum gas refinery plant in Russia

Recently, with the invention of Small-scale CNG, mainly from General Electric [19], this technology is increasingly used. At the same time, gas is pressured of 100-250 bar to reduce the volume up to 300 times. The gas must first be cleaned of CO_2 and H_2S, N_2. The advantage of such plants is its relatively low capital cost, the disadvantage is the cost of transporting the product. Another disposal option may be gas liquefaction at Small Scale LNG plants. For example, Galileo's Cryobox® plants produce up to 9013 gpd (gallons per day).

The installation cost, including cleaning, is US$600 per tonne of liquefied gas per year FOB, and operating costs are approximately US$1 MMbtu. General Electric's «plug-and-play» installations provide between 25 k and 1,200 k gallons of LNG per day. Among the other suppliers of this technology Beerensgroup, Calvert Energy Group, Chart Industries, Expansion Energy, Linde Cryostar are noted in [19].

Over the past 20 years, a significant breakthrough has been made in the creation of small-sized, primarily microchannel, gas to liquid - GTL technologies, which have continued the already mastered large-scale technologies, primarily in factories in Qatar, Malaysia and South Africa. The technologies are based on the principles of producing syngas from natural gas through steam methane reforming - SMR and the processes of converting carbon monoxide and hydrogen with a catalyst into various hydrocarbon molecules using the Fischer – Tropsch process. A simplified diagram is shown in Fig. 8. Despite significant technical difficulties (many are limited only to the first part of the process - syngas production) GTL microchannel technologies have undeniable advantages, as they ultimately provide liquid fuel that has simpler solutions for use, storage and transportation. In addition, the final product of this technology may be synthetic oil, which operators mix with the produced oil and route it to pipelines.

Fig. 8. Simplified GTL microchannel technology



1. *Gas treatment;* ***2.*** *Desulfurization;* ***3.*** *SMR microchannel reactor;* ***4.*** *Compressor station;* ***5.*** *Boiler & Cooling Water Unit;* ***6.*** *Hydrogen membranes;* ***7.*** *F-T microchannel reactor;* ***8.*** *Product separation unit;* ***9.*** *Stock of liquid hydrocarbons;* ***S*** *- Syngas(H2+CO);* ***L*** *- Liquid hydrocarbons;* ***V*** *- Vapor;* ***W*** *- Water cooling;* ***M*** *- Methane+Steam;* ***H*** *- Hydrogen;* ***A*** *– Air;* ***E*** *- Exhaust*

So far, GTL technologies are the most expensive of those used for associated gas utilization. In addition, GTL processes are characterized by strict adherence to temperature conditions and pressure in reactors, as well as high requirements for catalysts. Nevertheless, these technologies are being improved and have significant prospects for the oil industry, given the relaxed requirements for the composition of the source gas compared to other technologies. The main suppliers of industrial equipment of mini-GTL are [19]:

- The Calvert Energy Group, offering modular mobile plants with the ability to produce 50 or 100 barrels per day (plant size 50 bbl / day and 100 bbl / day) of Diesel, Naptha, Jet fuel. Approximate Capex $47k - $52k / bbl, OPEX ~ $0.03 / litre of produced fuel. The expected life of the catalyst is three years.

- CompactGTL is one of the pioneers in this technological area, as well as Emerging Fuels Technology, GasTechno Energy & Fuels, Greyrock, Siluria, Primus Green Energy.

For more information on research on these and other similar technologies, see [21-24].

Research and innovations

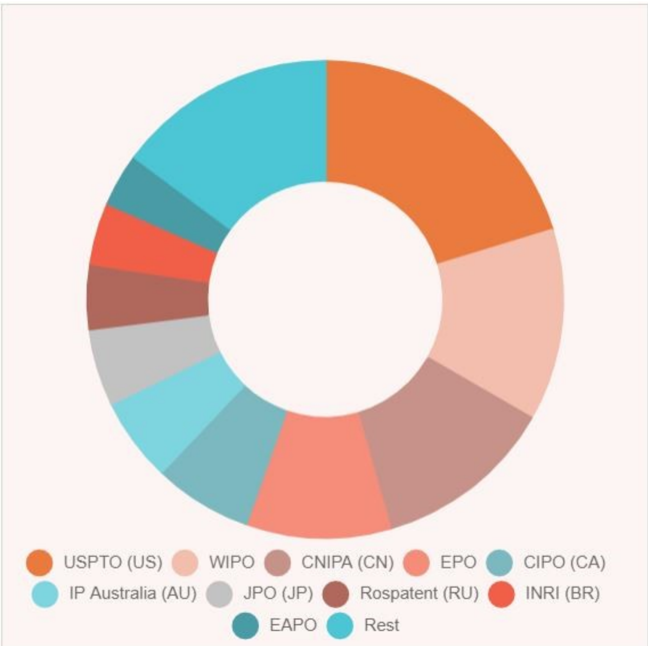
Associated gas utilization is an intensively developing area, annually enriched with a large number of scientific research and patent solutions. Below are the statistics and a brief analysis of the totality of patent applications registered over the past 10 years (2009 - 2018) in the patent offices of the world on topics related in one way or another to associated petroleum gas. The research methodology is available on the Advanced Energy Technologies website. 2887 patent applications submitted by 1,065 applicants from 29 countries and registered in 36 patent offices of the world were selected for consideration.

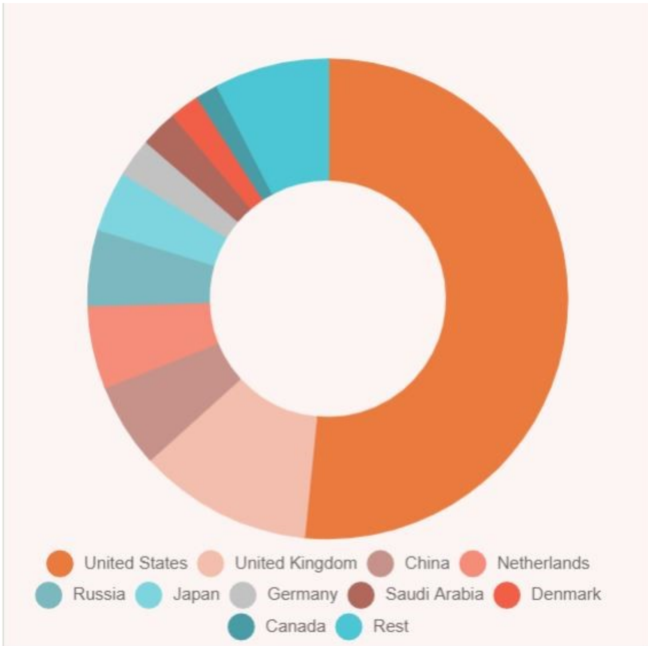
The largest number of patent documents was registered by the US Patent Office - 587 or more than 20% of the total number (Fig. 9). 374 applications were registered in the international patent office WIPO, and 356 in the Chinese CNIPA, which amounted to 13 and 12.3%, respectively.

In total, the top 10 patent offices accounted for about 85% of all applications for inventions. A significant number of patent documents (426) were issued outside the top 10.

The greatest activity on this topic over the period under review was shown by applicants from the USA - more than 51% of all applications were prepared by them (Fig. 10). Also, a significant interest in this topic was demonstrated by residents of the United Kingdom, who submitted 338 patent documents or 11.7% of the total.

Fig. 9-10. Left - Distribution of the number of registered patent applications on the topic "Associated Petroleum Gas" in the top 10 patent offices of the world. Right - Patent activity of residents of the countries of the world between 2009-2018 on the topic "Associated Petroleum Gas"





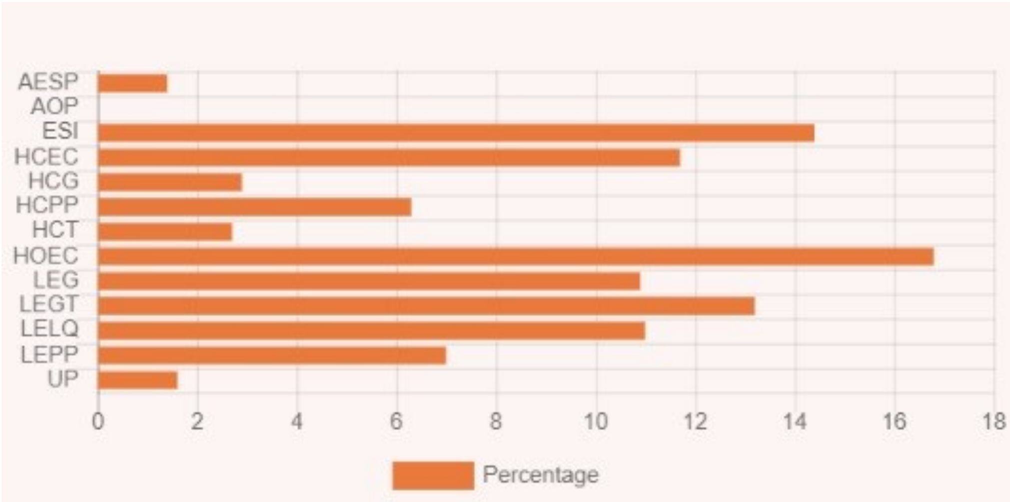
Source: Advanced Energy Technologies

The top 10 most active countries besides them included China, the Netherlands, Russia, Japan, Germany, Saudi Arabia, Denmark and Canada.

The most popular non-resident offices were USPTO (US), where they registered 197 patent applications or 34%, CNIPA (CN) -190 applications or 56%, EPO (Europa) - 207 documents or 73%, CIPO (Canada) - 183 applications or 95% and IP Australia - 158 patent applications or 96% of the total number accepted at this office. Representatives of 22 countries of the world filed their applications in the US Patent Office - more than in other offices, non-residents from 16 countries registered inventions in China, and non-residents from 15 countries in CIPO (Canada).

In their patent decisions, inventors most often dealt with problems associated with High OPEX / Equipment and consumables (mentioned in 16.8% of cases), Environmental and social impact (14.4%) and Low efficiency / Gas treatment (13.2%) - Fig. 11. The number of unrecognized or unaccounted for problems in the main list was insignificant - only 1.6%.

Fig. 11. Distribution of problems in patent documents

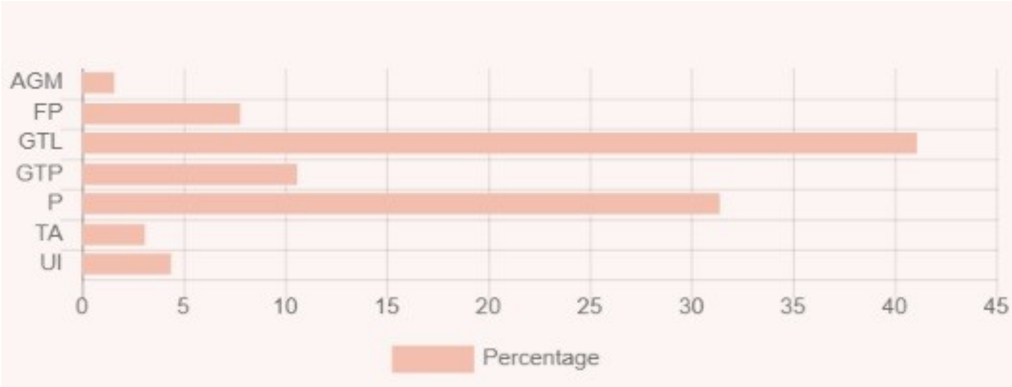


Source: Advanced Energy Technologies

***AESP** - Additional expenses on secondary processes; **AOP** - Administrative and organisational problems; **ESI** - Environmental and social impact; **HCEC** - High CAPEX / Equipment and consumables; **HCG** - High costs in general; **HCPP** - High cost of production processes; **HCT** - High costs of transportation; **HOEC** - High OPEX / Equipment and consumables; **LEG** - Low efficiency in general; **LEGT** - Low efficiency / Gas treatment; **LELQ** - Low efficiency / Location and quality of gas; **LEPP** - Low efficiency / Production process; **UP** - Unclear problem*

Among the technological processes, the inventors were primarily interested in the Gas to liquid technologies, which were mentioned in 1376 documents or in more than 41% of cases (Fig. 12). Technologically, gas preparation operations also had a significant share - 1,050 documents or 31.4%. It should be mentioned that several problems or technological elements can occur in one document at the same time, therefore, in these cases, accounting here is based on the total number of references to these indicators in the texts of patent documents, and not on the total number of applications.

Fig. 12. Distribution of patent documents by technological elements (applied technologies)



Source: Advanced Energy Technologies

***AGM** - Associated gas metering; **FP** - Flaring process; **GTL** - Gas to liquid; **GTP** - Gas to power; **P** – Preparation; **TA** - Transport and storage; **UI** - Underground injection*

A significantly smaller number of applications was addressed to the traditional processes of associated petroleum gas utilization - the Flaring process and Underground injection - 261 and 148 patent documents, respectively (12.2% in total). The largest number of patent applications for the considered period of time was registered by the American ExxonMobil Upstream Research Company (Table 1).

Table 1. Top 10 Applicants

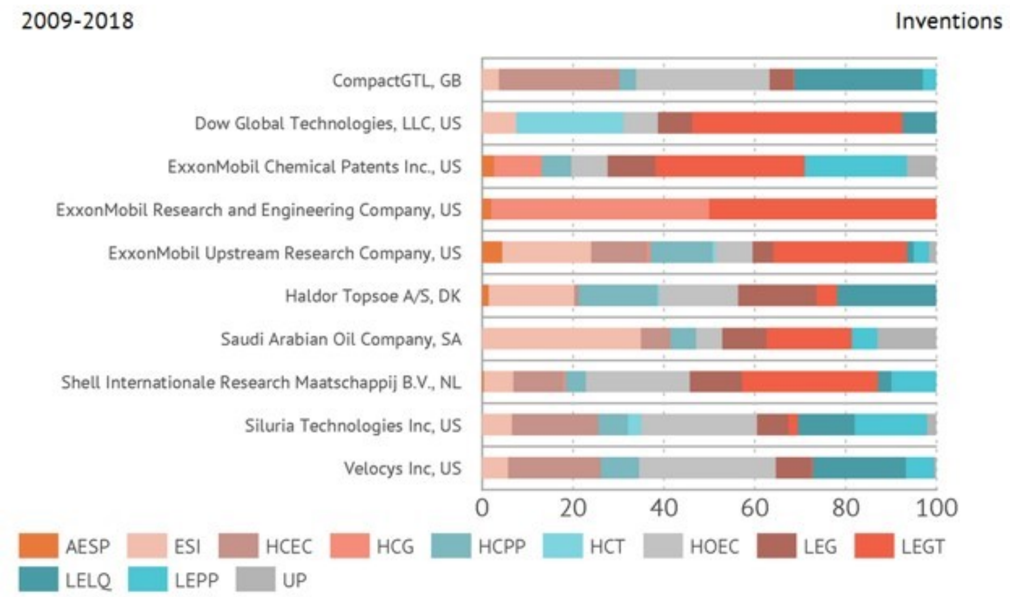
Status	Country	Name	Average rating	Total 2008-2017
Company	US	ExxonMobil Upstream Research Company	12	259
Company	US	Velocys Inc	15.5	197
Company	GB	CompactGTL	13.1	187
Company	NL	Shell Internationale Research Maatschappij B.V.	10.5	121
Company	US	Siluria Technologies Inc	12.7	88
Company	US	ExxonMobil Research and Engineering Company	11.5	74
Company	SA	Saudi Arabian Oil Company	13.3	69
Company	US	Dow Global Technologies, LLC	7.9	57
Company	US	ExxonMobil Chemical Patents Inc.	10.6	55
Organization	DK	Haldor Topsoe A/S	11.1	52

Source: Advanced Energy Technologies

Also, more than 100 applications were registered by the American Velocys Inc., CompactGTL from the UK and Shell Internationale Research Maatschappij B.V. from the Netherlands. The top 10 applicants included representatives from five countries - 6 companies from the USA and one company from the UK, the Netherlands, Saudi Arabia and Denmark. All applicants noted in Table 1 sought patenting in different countries of the world. For example, Velocys Inc. registered its documents in 13 countries of the world, Shell Internationale Research Maatschappij B.V., ExxonMobil Upstream Research Company and CompactGTL - in 16, and Saudi Arabian Oil Company - in 8.

The share distribution of patent applications of the top 10 applicants by problems and technological elements is presented in Fig. 13-14.

Fig. 13. Distribution of problems in patent documents of leading applicants

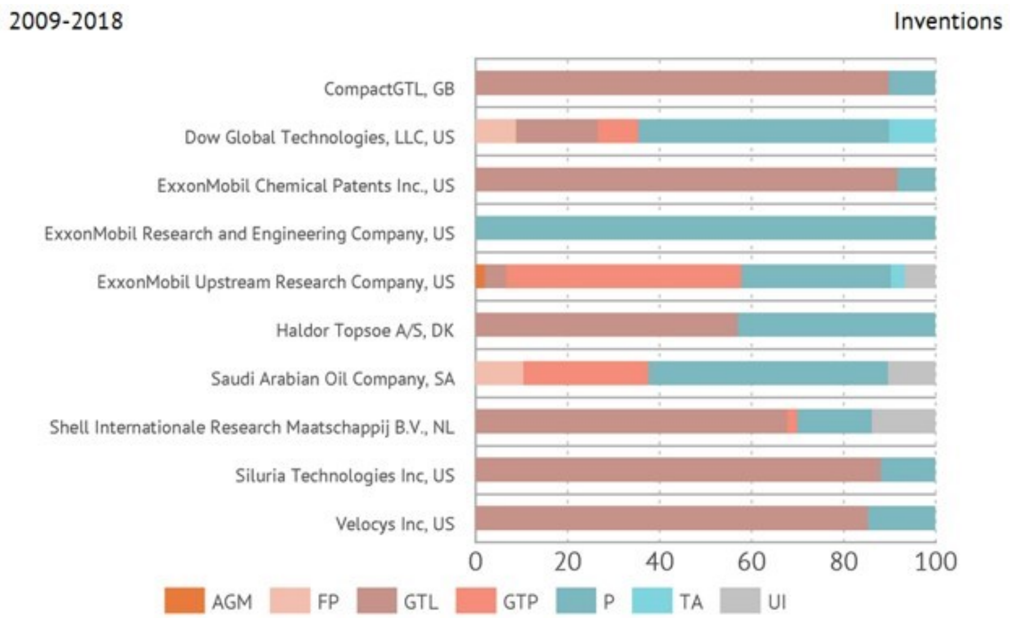


Source: Advanced Energy Technologies

AESP *- Additional expenses on secondary processes;* ***AOP*** *- Administrative and organisational problems;* ***ESI*** *- Environmental and social impact;* ***HCEC*** *- High CAPEX / Equipment and consumables;* ***HCG*** *- High costs in general;* ***HCPP*** *- High cost of production processes;* ***HCT*** *- High costs of transportation;* ***HOEC*** *- High OPEX / Equipment and consumables;* ***LEG*** *- Low efficiency in general;* ***LEGT*** *- Low efficiency / Gas treatment;* ***LELQ*** *- Low efficiency / Location and quality of gas;* ***LEPP*** *- Low efficiency / Production process;* ***UP*** *- Unclear problem*

The most consistent was ExxonMobil Upstream Research Company, which mainly addressed the issues of High costs in general and Low efficiency / Location and quality of gas. Velocys Inc. and CompactGTL - High CAPEX / Equipment and consumables and Low efficiency / Location and quality of gas, and Saudi Arabian Oil Company - Environmental and social impact.

Fig. 14. Distribution of patent documents by technological elements (applied technologies) among the top 10 applicants



Source: Advanced Energy Technologies

AGM *- Associated gas metering;* ***FP*** *- Flaring process;* ***GTL*** *- Gas to liquid;* ***GTP*** *- Gas to power;* ***P*** *– Preparation;* ***TA*** *- Transport and storage;* ***UI*** *- Underground injection*

Gas to liquid and Preparation technologies clearly prevail among the rest of the majority of the represented companies.

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