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An Introduction to Liquefied Natural Gas as a Cryofuel

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1. Background

Introduction

Energy, food, and water are three basic needs of any society. Given that about 5 billion people want to live like about 500 million of us do, global energy demand is increasing steadily and will continue to do so for decades. Natural gas plays a key role in meeting global and U.S. energy demands. Bill Gates once said "Convergence of Factors to Change an Entire Industry comes along only Once… maybe Twice in every Lifetime"… Technological advances in the U.S. have unlocked massive quantities of natural gas from shale deposits, resulting in an abundant supply that should easily last many decades. This sustained situation created two important consequences (i) the price of pipeline natural gas (PNG) is low and stable; and (ii) more significantly, the price of PNG is decoupled from the price of crude oil. The convergence of these factors created a paradigm shift, causing the U.S. to change from importing this fuel to exporting it. As a result, cheap domestic natural gas has given us real, sustainable fuel choices in the transportation sector. Driven primarily by large price savings of $1.00-$1.50/equivalent gallon, vehicle owners are beginning to convert from diesel/gasoline to liquid and compressed natural gas fuels (LNG and CNG). This short article presents an introduction to the cryogenic fuel LNG.

Characteristics of Natural Gas

Natural gas is a mixture composed primarily of methane, but may also contain ethane, propane and heavier hydrocarbons. Small quantities of nitrogen, oxygen, carbon dioxide, sulfur compounds and water may also be found in natural gas. LNG is simply liquefied natural gas. The liquefaction process requires the removal of some of the non-methane components such as water and carbon dioxide from natural gas to prevent them from freezing into solids when the gas is cooled to about -162 °C (-260 °F or 111 K for methane at one atmosphere pressure). As a result of the liquefaction process, LNG is typically ~95 %-98 % methane. Natural gas is a flammable gas however LNG is not flammable until vaporized. Natural gas is very buoyant in air. Cold vaporized LNG is heavier than air until it warms to ~-160 °F above which it becomes buoyant. The cold NG freezes water vapor in air and creates a rising white vapor cloud. LNG is colorless, odorless, non-toxic and noncorrosive and has ~625 times the energy density as NG at 60 °F and 14.695 psia. This large increase in energy density is why LNG is so important for storage, transport, and delivery of natural gas. A gallon of LNG contains ~82.6 scf of natural gas, weighs ~3.45 lbs, and contains ~82,990 Btu of energy (depending on high or low heating value, and pressure, temperature, composition). The flammability range of NG is between ~5% and ~15% in air at ambient conditions. NG has a very high auto-ignition temperature of ~1004°F and has higher ignition energy than many other fuels. Methane burns but does not explode in an unconfined environment. Natural gas vaporized from LNG can cause asphyxiation in an unventilated confinement, and cryogenic temperature of LNG cause well-known cryogenic liquid hazards. Methane with one carbon molecule is the cleanest fossil fuel (gasoline has ~8 carbon molecules, while diesel has ~14). Combustion of natural gas emits ~25 % less CO_2/equivalent energy than gasoline/diesel and ~50 % less CO_2/equivalent energy than combustion of coal. It produces significantly lower emissions, e.g. ~87 % reduction of NO_x, ~95+ % reduction of PM, and much lower amounts of SO_x than diesel or gasoline fuels.

2. Sources of Natural Gas

Methane comes from many sources with long-term supply including some renewable/sustainable sources. U.S. sources of methane include:

- Natural gas wells –wells without any oil co-production.
- Associated gas wells –wells with oil co-production.
- Coal seam or coal mine gas –methane gas released by drilling pinnate patterns of horizon wells into coal seams. Coal mines sealed after coal extraction capture methane released from remaining coal.
- Shale gas – sometimes referred to as ‘unconventional gas’, the development of precision horizontal drilling at great depths (~10,000 ft. vertically and ~3,000-5,000 ft. horizontally) followed with high-pressure hydraulic fracturing of tight shale formations.
- Biogas from landfills –naturally occurring methanogenic bacteria convert the complex carbohydrates, lipids/fats, and proteins into a mixture of CH_4 and CO_2 with lesser amounts about 100 other compounds.
- Biogas from anaerobic digesters – waste stream such as municipal solid wastes and other biomass stream such algae biomass can be converted to biogas that is ~65% methane and ~32% CO_2. This is a renewable/sustainable source of methane that can be readily converted to LNG.
- Methane hydrates –DOE reported several years ago that proven reserves of methane hydrates in deep U.S. waters in the Artic and Gulf of Mexico are large enough to provide U.S. energy needs for ~2,000 years!

3. Uses of Natural Gas

The Energy Industry

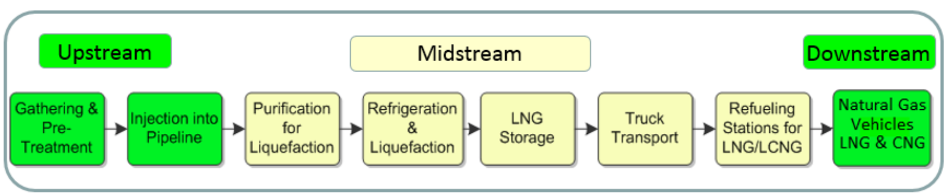
The huge surplus of NG in the U.S. has created numerous new entrepreneurial companies of various sizes and business models across the entire energy supply chain. Several well-known large energy companies have also formed consortia to invest billions of dollars in development of large NG export projects at several U.S. coastal locations. These businesses will make LNG from pipeline gas, transport it to customers via large cryogenic tankers carrying up to ~50 million gallons of LNG per load, and sell it to long-term customers (e.g., Tokyo Gas in Japan) on the world market.

Another major force of change for LNG came in ~2010 when International Maritime Organization members approved large reductions of sulfur and other noxious emissions from crude-based ship fuels. To meet these requirements, ship owners had to convert to low-sulfur distillate or some other alternative to meet emissions limits if the ships want to enter ports in countries such as Norway, Sweden, the EU, U.S. or Canada. Low-priced LNG was a superior fuel choice that catalyzed development of LNG-fueled ships (e.g., Wartsila) about 2012. Many sizes of LNG-fueled ships are being commissioned presently which has driven establishment of bunkering (refueling) infrastructure in ports that safely and reliably provide LNG fuel to such vessels (e.g., Linde).

The U.S. energy industry is big business. Recent U.S. annual energy expenditure among five sectors[1] was $2 trillion[2] and of this, the transportation sector fuel demand was $675 billion. The average price of energy in the U.S. is ~$20/MMBtu with the transportation sector paying the highest price. Natural gas supplies ~18-32 % of each sector <u>except</u> the transportation sector which is ~0.1 %. Vehicle fuels continue to be dominated by petroleum products. However, the U.S. transportation sector fuel choice is changing as explained in section 7 of this article.

The Natural Gas Energy Supply Chain

LNG liquefiers come in many sizes for supply infrastructure: i) global baseload facilities producing 1-10 million gpd of LNG; ii) U.S. peak-shaver facilities making 100,000-200,000 gpd of LNG; iii) small-scale facilities producing 15,000-60,000 gpd of LNG; iv) distributed, refueling station plants making 500-10,000 gpd of LNG; and v) micro-scale plants that make 5-50 gpd. The unit operations required to produce LNG from methane-containing sources of any scale have some unique features depending on location, size, feedstock source, and end use but all of them have common modules illustrated by this energy supply chain for conversion of pipeline natural gas to LNG/CNG fuels in NG vehicles.



4. LNG Purification, Liquefaction, Storage, and Delivery

Purification

Concentrations of carbon dioxide, water, and odorants such as methyl mercaptan in PNG must be reduced below their solubility level in LNG before liquefaction to avoid freezing such impurities out in high-performance Al-brazed plate-fin cryogenic heat exchangers use to cool and liquefy the process stream. Typical concentrations are ~50 ppm CO_2, 1 ppm H_2O, and 100 ppb sulfur compounds which can be obtained by molecular sieve adsorbents such as zeolite type 4A operating in a temperature swing or pressure swing cycle. Methane/PNG purification techniques are very well known[3].

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[1] Industrial, commercial, residential, electricity generation, and transportation are commonly-used sectors of U.S. energy use

[2] U.S. Energy Information Administration website and reports; 2013ff

[3] <u>Engineering Data Book, Vols. I & II</u>; Gas Processors Suppliers Association; 12th ed., (2004)

Liquefaction

Liquefaction of different gases requires different specific energy to produce cryogenic liquid. The ideal (minimum) rate of work to cool and liquefy NG can be calculated by specifying the composition, pressure and temperature of the inlet process stream and the final pressure of the LNG. As an example for pure methane at 288.7 K and 0.1013 MPa (standard conditions) and assuming no pressure drop in the cryogenic heat exchanger, the enthalpy and entropy of the initial (labeled H for hot) and final (labeled f for final) states can be calculated[4] using isothermal compression of and isentropic expansion to LNG using validated codes (Refprops from NIST). Under these conditions the values are:

$$s_H := 6.6031\cdot\frac{kJ}{kg\cdot K} \quad s_f := -0.00009391\cdot\frac{kJ}{kg\cdot K} \quad h_H := 888.96\cdot\frac{kJ}{kg} \quad h_f := -0.010466\cdot\frac{kJ}{kg}$$

$$W_{dotCH4ideal} := massrate_{CH4}\cdot\left[T_H\cdot\left(s_H - s_f\right) + \left(h_f - h_H\right)\right]$$

$$W_{dotCH4} := \frac{W_{dotCH4ideal}}{massrate_{CH4}} \qquad W_{dotCH4} = 1.026\times 10^{3}\cdot\frac{kJ}{kg}$$

There are several cycles used to liquefy natural gas. These include a Linde cycle, a Cascade cycle, a Brayton cycle, Liquid Nitrogen, a Mixed Refrigerant cycle, and developing Active Magnetic Regenerative Liquefier cycles. The real work input in liquefiers based on these cycles is significantly larger because of effects including non-isothermal compression efficiency, heat exchanger approaches, pressure drops, expansion losses, and parasitic heat leaks. Actual work rates are at least 3 times larger than the ideal work rate in most liquefier designs. The thermodynamic performance of a liquefier is given by the Figure of Merit (FOM) defined as the ratio of the ideal to real work rate for liquefaction. A FOM of 0.33 is excellent. Examples of companies involved in design, manufacture, and operation of small-scale LNG plants with conventional designs includes the Lisbon Group; GE Oil & Gas; Linde: Stabilis Energy; and Prometheus Energy Group[5]. Emerald Energy NW is investigating efficient active magnetic regenerative liquefaction.

Storage and Delivery

LNG is usually stored in well-insulated cryogenic tanks near atmospheric pressure such as ~35 psia. It is transported in cryogenic tankers that contain ~10,000 gallons fully loaded. LNG Is delivered via different means depending upon the scale of operation.

5. Adoption of Natural Gas

Robert Bryce of the Manhattan Institute wrote an excellent, well-documented report in April, 2011 entitled **"Ten Reasons why Natural Gas will fuel the Future."**[6] He discusses the impressive changes in the U.S. natural gas business that we call a convergence of factors that are creating a paradigm shift in transportation fuels. Some of R. Bryce's ten reasons are:

- Natural gas saves consumers money.

[4] R. F. Barron, Cryogenic Systems, 2nd edition, Oxford University Press (1985)
[5] Please see web sites of these companies for more information.
[6] www.manhattan-institute.org R. Bryce; Energy Policy & the Environment Report 8, April 5, 2011.

- If it's not going to be nuclear, it's got to be gas.
- Natural gas is abundant and the globalization of the gas market is accelerating.
- Unconventional gas is driving unconventional oil production.
- Unconventional oil production is stimulating the U.S. petrochemical sector and global oil production.
- The U.S.' huge gas production capability and its vast gas infrastructure, make it uniquely well positioned to take advantage of the shift to natural gas.

6. Transportation sector

Early adoption of natural gas as a fuel (CNG and LNG) is happening now! Natural Gas Vehicles are being manufactured by OEM suppliers for heavy duty trucks, medium duty trucks, and light duty vehicles. An increasing number of trucks are running on natural gas today in a variety of applications, including port drayage, bulk hauling, intermodal, goods movement, local pickup and delivery. New developments are regularly announced by well-known companies, e.g., UPS increasing its fleet by 700 LNG-fueled class-8 trucks. As of last year UPS ran 112 LNG tractors and 1,000 CNG delivery vans. The BNSF freight trains announced they are considering conversion of some engines to LNG. The first LNG-fueled ship on the St. Lawrence Seaway was recently commissioned.

About 150,000 gasoline refueling stations operate in the U.S., of which ~127,500 are convenience stores that sell ~80% of all vehicle fuel purchased in the U.S. In addition, there are ~7,000 U.S. truck stops with the vast majority owned by independent operators[7]. In contrast, even though the number is increasing, the U.S. has ~1,500 CNG refueling stations, (~800 open to the public) and ~100 LNG refueling stations, (~70 open to the public)[8]. The Energy Information Administration (EIA) predicts that by 2020 ~5% of the U.S. transportation fuels will be natural gas (50 times what it is today, or $33.8 billion/year). In five years, ~7,500 LNG/CNG refueling stations will be needed to supply this 5% to all classes of vehicles. By 2040 the LNG/CNG vehicle-fuel demand will be 200 times what it is today or $135 billion/year.

The major barrier impeding the transition to natural gas fuels is lack of inexpensive local supply and refueling infrastructure. The high cost of building out the natural gas infrastructure is a key barrier. Average-sized LNG or CNG refueling stations alone cost between $1-$2 million dollars[9] each. We believe innovative advanced technology is needed to provide lower cost, highly-efficient and innovative regenerative purifier/liquefiers to help remove the refueling infrastructure barrier. Large upstream supplies of low-price PNG are available throughout the U.S. in the extensive pipeline network; and downstream natural gas vehicles (NGVs) of all sizes are increasingly available. What is needed is the midstream portion of the energy supply chain; i.e., small-scale purification and liquefaction plants to locally make LNG from PNG plus LNG storage, transport, delivery, and integrated LNG/CNG refueling stations located where vehicle owners have ready access. **Filling this need presents an excellent opportunity for cryotechnology experts who understand today's purification and liquefaction technology, plus a desire to invest in innovative new technology that is less expensive to purchase and operate.**

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[7] www.dieselboss.com/directory_DC.htm

[8] DOE, Alternative Fuels Data Center

[9] Fleet-size LNG/CNG refueling stations, supplied from an increasing number of large distributed-scale LNG plants exploiting the low-cost shale gas, are steadily being funded, built, installed in the U.S. by well-known energy companies such as Clean Energy, Shell U.S.A., G.E. Oil & Gas, Linde at a cost of between $1 million and $2 million dollars per refueling station.