BULETINUL Universităţii Petrol – Gaze din Ploieşti	Vol. LX No. 4A/2008	149 - 154	Seria Tehnică

Liquefied Petroleum Gases Utilization: an Assessment

Tudora Cristescu, Maria Stoicescu, Doru Stoianovici

Universitatea Petrol-Gaze din Ploieşti, Bd. Bucureşti 39, Ploieşti
e-mail: tcristescu@upg-ploiesti.ro

Abstract

We present some aspects on the combustion content and properties of liquefied petroleum gases. We also discuss advantages and disadvantages of the use of these fuels in various settings.

Keywords: *liquefied oil gases, content, combustion*

The Content of Liquefied Oil Gases

Liquefied petroleum gases (LPG) originate from natural or refinery gases and mainly consist of butane C_4H_{10}, propane C_3H_8 and their mixtures. In addition, LPG also contain small fractions of light and heavier hydrocarbons and sulfur compounds. Methane is usually quasi absent, there are traces of ethane, and the fraction of pentanes is smaller than 1%. STAS 66-78 states that LPG (aragaz) is a mixture of hydrocarbons in which the pressurized C_4 fraction (butane) is predominant. LPG are usually enriched with ethyl mercaptane in order to confer the product a specific smell for the purpose of easy detection in case of gas leakage. LPG are used as industrial and residential fuel, and sometimes as solvents; there is a current trend of excessive use of LPG as vehicle fuel (*autogas*).

As per ISCIR's standardization, LPG are classified as 'group B, liquefied gases'; propane and butane are classified as 'category 3b, pure inflammable gases', and their mixtures are classified as 'category 4b, mixtures of inflammable gases'.

There are the following standardized hydrocarbon mixtures:

Mixture A, with vapor tension not exceeding 1.1 MPa (11bar) at 70 ^{0}C and volume mass not smaller than 0,525 kg/l at 50^{0}C;

Mixture AO, with vapor tension not exceeding 1.6 MPa (16bar) at 70 ^{0}C and volume mass not smaller than 0,495 kg/l at 50^{0}C;

Mixture A1, with vapor tension not exceeding 2.1 MPa (21bar) at 70 ^{0}C and volume mass not smaller than 0,485 kg/l at 50^{0}C;

Mixture B, with vapor tension not exceeding 2.6 MPa (26bar) at 70 ^{0}C and volume mass not smaller than 0,450 kg/l at 50^{0}C;

Mixture C, with vapor tension not exceeding 3.1 MPa (31bar) at 70 ^{0}C and volume mass not smaller than 0,440 kg/l at 50^{0}C.

The following commercial denominations are admitted for the aforementioned mixtures: 4b mixture Commercial denomination, Mixture A, mixture AO butane, Mixture C propane.

In addition to hydrocarbons, LPG may contain sulfur, nitrogen and oxygen compounds, which may cause corrosion. LPG obtained from sulfurous oil contains hydrogen sulfide which is an important agent for corroding. It is recommended that liquefied gases for household use do not contain unsaturated hydrocarbons, in order to avoid deposition, and that they are odorized with a strong agent, for signaling gas presence in the atmosphere at concentrations up to under a fifth of the lower explosion bound.

Autogas is a mixture of highly volatile liquefied hydrocarbons, stored at around 13 bar pressure, which when vaporized is introduced in a classic spark engine. GPL is used for engines adapted to work both with gasoline and LPG. Autogas is produced in Romania under proprietary standards (e.g. PETROM); the expiration date for such a fuel is 3 months after its production, under the assumption that all packaging, transport and storage conditions are fulfilled.

Table 1 shows the content of autogas.

Table 1. Autogas content

Property	Value	
	Fuel A Butane	Fuel A Propane
Content:		
- hydrocarbons C_3, %, v/v	28.0-32.0	83,0-87,0
- hydrocarbons C_4, %, v/v	equilibrium	equilibrium
- hydrocarbons C^3+C^{4+}, %, v/v, max	2	2
- olefines total, of which butadienes, %, v/v, max	9.0±3.0 (0.5)	12.0±3.0 (0.5)
Octane rating, COM, min	89.0	89.0

It is worth mentioning that normal butane, isobutane and propane are additionally refrigeration fluids of III-rd group (fluids that are highly flammable when mixed with air, with volume concentrations under 3.5 %).

Combustion Properties of LPG

Caloric power is the heat resulting from complete combustion of the unit quantity of fuel, using air in the minimally necessary quantity; inferior caloric power H_i is the corresponding value when combustion gases are evacuated such that their water vapor content is in a gaseous state.

Theoretical combustion temperature is the maximum temperature of gases resulting from complete combustion of fuel, using air in the minimally necessary quantity, $\alpha = 1$, and no heat dissipation takes place.

Self-ignition temperature is the temperature at which the fuel ignites spontaneously when mixed with air, without requiring the presence of a flame.

Table 2 contains a list of combustion properties of LPG gases.

Table 2. Combustion properties for gases composing LPG

Gas	Density	Theoretical combustion temperature	Self-ignition temperature	Inferior caloric power	
	ρ [kg/m^3_N]	t_t [°C]	t_a [°C]	H_i [kJ/kg]	H_i [kJ/m^3_N]
Ethane	1.356	2050	510	47436	64351
i- butane	2.668	2117	430	45594	121627
n- butane	2.703	2117	430	45720	123552
Propane	2.019	2107	466	46348	93575

For a mixture of homogenous fuels, the caloric power of the mixture is given by:

$$H_{am} = \sum_{i=1}^{n} g_i H_i \tag{1}$$

Table 3 presents values for the caloric power of propane and n-butane mixtures.

Table 3. Caloric power for propane-butane mixtures

Nr. crt.	Propane	n-Butane	$H_{i,\,am}$ [kJ/kg]
	g_i [%]	g_i [%]	
1	0	100	45720
2	10	90	45782.8
3	20	80	45845.6
4	30	70	45908.4
5	40	60	45971.2
6	50	50	46034
7	60	40	46096.8
8	70	30	46159.6
9	80	20	46222.4
10	90	10	46285.2
11	100	0	46348

Flammability limits (explosion limits) define the range in which the explosion of a flammable gas can take place; the lower and upper limits are expressed in percentage of gas in a mixture with air at which combustion takes place.

Table 4 presents the limits of flammability, in mixtures with air, of gaseous fuels contained in LPG.

Table 4. Explosion limits (in air) of gaseous fuels in a LPG mixture

Gas	Flammable limit (in air)	
	min., %	max. , %
Etane	3.2	12.5
Propane	2.37	9.5
Butane	1.86	8.4
Pentane	1.4	7.8

The following relation can be used for the approximate computation of lower and upper limits of explosion of gaseous and vapor mixtures:

$$L = \frac{100}{\sum_{i=1}^{n} \frac{r_i}{L_i}} \tag{2}$$

Table 5 shows the results of using (2) for computation of the lower and upper limits of explosion for propane-butane mixtures.

Flammability temperature (or point of flammability) is the lowest temperature at which a product yields, under standard conditions, a sufficient vapor quantity to form together with air a combustive mixture which ignites in the presence of a flame. The flammability point indicates the level of explosion or fire danger.

Natural gases do not form explosive mixtures at pressures below 50mmHg. The explosion limits are tighter in the presence of inert gases (nitrogen or carbon dioxide). When the concentration of the inert gas is above a certain threshold, an explosion fails to take place. Therefore, inert gases are widely used for purging of industrial installations before going live.

Combustion, self-ignition and flammability temperatures are not physical-chemical constants characterizing light hydrocarbons, as they depend on the shape, volume and level of wear of the storage recipient where their estimation is performed, as well as on the nature of the recipient material and other factors.

Table 5. Explosion limits (in air) for LPG

Nr. crt	Propane		Butane		Explosion limit LPG	
	Mass fraction	Volume fraction	Mass fraction	Mass fraction	min	max
1	0	0	100	100	1.86	8.4
2	10	12.8	90	87.2	1.91	8.53
3	20	24.8	80	75.2	1.96	8.65
4	30	36.1	70	63.9	2.02	8.77
5	40	46.8	60	53.2	2.07	8.88
6	50	56.9	50	43.1	2.12	8.99
7	60	66.4	40	33.6	2.17	9.09
8	70	75.4	30	24.5	2.22	9.21
9	80	84.1	20	15.9	2.27	9.31
10	90	92.2	10	7.8	2.32	9.40
11	100	100	0	0	2.37	9.,5

Arguments for the Utilization of LPG

Worldwide, the use of autogas represents a relatively low fraction of the total LPG production; these liquefied gases are in fact mainly used in the petrochemical industry and largely as household fuel.

For gases that exhibit a critical temperature larger than the temperature of the environment $t_{cr} > t_{atm}$, liquefying can take place only by isothermal compression. The critical parameters of propane are critical temperature $t_{cr} =$ 96,8 ^{0}C, critical pressure $p_{cr} = 42{,}46$ bar; for i-butane $t_{cr} =$ 133,7 ^{0}C, $p_{cr} = 36{,}97$ bar; and for n-butane $t_{cr} =$ 153,2 ^{0}C, $p_{cr} = 36{,}48$ bar. Consequently, liquefaction of propane and butane can be achieved relatively easy.

Following liquefaction, the gas volume decreases considerably. Thus, the volume occupied by the unit of mass at saturation (saturation temperature and 1atm pressure, i.e. liquid state) is considerably smaller than the corresponding volume under standard conditions ($t_0 =$ 15^{0}C and 1atm pressure, i.e. gaseous state): 242.18 times for i-butane, 245.18 times for n-butane, 315.29 times for propane.

The theoretical combustion temperature for propane (2107^{0}C) and butane (2117 ^{0}C) are significantly higher than the corresponding temperature for methane (2040^{0}C). The self-ignition temperature of gases in LPG, i.e. propane (466 ^{0}C), and butane (430 ^{0}C) are larger than the corresponding temperatures of gasoline (245 ^{0}C) and diesel (250 ^{0}C), but they are smaller than the self-ignition temperature of methane (537 ^{0}C). The explosion limits in air mixtures of LPG (1.86...9.5)% are smaller than the same limits for methane (5...15)%.

The flammability points of petroleum fractions lie in the following ranges: under 10^{0}C for gasoline, 30...40^{0}C for petroleum, 55...65^{0}C for diesel, 170...250^{0}C for oil; 90...150^{0}C for black oil.

The inferior caloric power of LPG ranges in the interval 45 720…46 348 kJ/kg, while for diesel (with density ρ = 870 kg/m^3) it is 41 843 kJ/kg, and for gasoline (density ρ = 760 kg/m^3) it is 42 035 kJ/kg. Thus, the inferior caloric power of LPG is larger than for other vehicle fuels.

The main advantage of using LPG is that, in general, autogas is less polluting than diesel and gasoline, since LPG is a mixture of simple hydrocarbons with 3 or 4 carbon atoms and lacking significant impurities (small quantities of sulfur and no additives, thus no lead).

From the combustion balance it results that following the combustion of a propane-butane mixture, the volume fraction of carbon dioxide in combustion gases ranges between 10.64…10.95 % , while for gasoline that fraction is 11.7%, and for diesel it is 12.1…12.8 %.

As a result, burning LPG pollutes less the environment. The transportation of LPG is usually done on rail tank cars, auto tanks and via pipelines. The storage of large quantities of LPG is done in saline cavities, abandoned mines or spherical isothermal ground reservoirs; medium quantities are stored at special pumps at gas stations; small quantities are stored in gas cylinders.

When small quantities of LPG are used, there is no need for a vaporization installation of liquefied gases. Finally, the production, transportation, storage, distribution and use of LPG are generally less difficult than LNG (liquefied natural gas).

Arguments against the Utilization of LPG

Although LPG is often called an ‘eco fuel’, that is improper, since it actually contains carbon; burning LPG produces carbon dioxide which is a polluter. Similarly to the combustion of diesel or gasoline, burning LPG also produces carbon monoxide, sulfur dioxide and nitrogen oxides, which are polluters and additionally contribute to the formation of tropospheric ozone.

The sulfur content of LPG needs to be controlled when the fuel is burnt in household settings, and hydrogen sulfide must not exceed 50 ppm to prevent corrosion.

The explosion limits in air mixtures of LPG (1.86...9.5 %) are higher than for gasoline (1.3...6 %) and oil (1.16...6 %). The storage, transport and use of LPG require, as in the case of any other fuel, the following of a set of special operational procedures, regarding feasibility, work hazard protection, fire preventing and extinguishing. Accidents in installations that use such a fuel can occur as a result of mechanical faults, exploitation faults, design errors, process changes, natural hazards, sabotage etc.

Conclusions

Although it is a relatively cheap fuel, LPG is not widely used even in developed countries, some due to motorists mistrust, but mainly because the 3-4 carbon fractions are used as ingredients in petrochemical processes.

LPG are an alternative for heating fuel; they can also replace other combustion fuels, but nevertheless they are polluting fuels. The amenability to transportation and storage of these fuels offers good import opportunities, such that LPG would represent a fuel source in an energy balance. Additionally, LPG can provide back-up fuel, together with natural gases and other fuels, the need should arise.

Notation List

g_i – mass fraction of component i in a mixture	
H – caloric power	J/kg; J/m^3_N; J/kmol
L – explosion limit	%
p – pressure	Pa, bar
r_i – volume fraction of component i in a mixture	
t – temperature in Celsius	^oC

α – air excess coefficient -
ρ – density (volume mass) kg/m^3

References

1. Anghelache, I., *New auto fuels*, Editura Tehnică, Bucureşti, 1993.
2. Cristescu, T., *Termotehnica*, Editura UPG, Ploieşti, 2004.
3. Cristescu, T., *Properties of hydrocarbon reservoirs,* Editura Universal Cartfil, Ploieşti, 1998.
4. Cristescu, T., Pătărlăgeanu, M., Suditu, S., *The ecological impact of the combustion of some auto fuels– a XV-a Conferinţă Naţională de Termotehnică*, Craiova, 2005.
5. Ionel, I., *Thermoenergy and the environment – measures for reducing the environment pollution by burning classic fuels,* Editura Tehnică, Bucureşti, 1996.
6. Kuzman, Ražnjević, *Thermodynamic tables and diagrams,* Editura Tennică, Bucureşti, 1978.
7. Marinescu, M., Ştefănescu, D., *Combustion installations – exercises for engineers,* Editura Tehnică, Bucureşti, 1985.
8. Onuţu, I., *Environment protection,* Editura UPG, Ploieşti, 2003.
9. Onuţu, I., *The production of ecological oil products, refinery schematics,* Editura UPG, Ploieşti, 2001.
10. Stirimin, Şt., *Gaseous and liquefied hydrocarbons*, Editura Tennică, Bucureşti, 1994.
11. * * * Technical standards C27-85 for tank reservoirs, container reservoirs and gas cylinders for compressed, liquefied or pressure-soluble gases.
12. * * * The law on environment protection published in the Romanian Government Monitor, 304/30 December 1995 and consequent government directives 91/20 June 2002 and 294/27 June 2003

Utilizarea gazelor petroliere lichefiate: o evaluare

Rezumat

Lucrarea cuprinde o serie de aspecte privind compoziţia şi unele proprietăţi legate de ardere ale gazelor petroliere lichefiate. De asemenea sunt prezentate avantajele şi dezavantajele utilizării, în diverse domenii, a acestor combustibili.