

LPG – A Viable Fuel Alternative

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Abstract

The present paper describes the composition, characteristics, properties and technological flow of liquefied petroleum gas operation for motor vehicles, an increasingly economical and environmentally friendly alternative to petrol and diesel. The technological flow of liquefied petroleum gas may involve phase transition. A computing relation is established on the basis of the correlation between pressure-temperature liquefaction and regasification, respectively, at constant pressure, in the case of propane, a relation that is easy to apply.

Keywords: LPG, propane, fuel, linear regression

Introducere

LPG is a mixture of hydrocarbons, mainly propane and butane. The technological flow of LPG exploitation is comprised of the following stages: LPG production (in petrochemical refineries or crude oil treatment plants) → manufacturer warehousing → transport by pipeline/truck/railway/maritime vessel tankers → delivery station warehousing → filler line for cylinders or tanker trucks → transport to the user → user. The stages of LPG logistics involve a series of thermodynamic processes (liquefying/vaporization, heating/cooling, isenthalpic/isentropic expansion, isothermal expansion). LPG is comprised of hydrocarbons containing mainly carbon and hydrogen; in particular, they are used as fuel in industry or households in order to obtain heat. In petrochemical plants they represent the raw material for obtaining other chemicals. The current trend is to use these hydrocarbons extensively, especially for fuel in the auto industry [1].

Liquefied petroleum gas composition

Liquefied petroleum gases originate from natural or refinery gas and mainly contain butane, C_4H_{10} , (C_4), propane, C_3H_8 , (C_3) or mixtures of the two. They also contain small proportions of light and/or heavier hydrocarbons, and sulfur compounds. Usually, methane is virtually absent, and ethanol – in the form of traces – is less than 1%. It is worth mentioning that normal butane, isobutene and propane are also refrigeration fluids of the Third Group (fluids that ignite easily in mixtures with air, with specific concentrations of less than 3.5%).

Liquefied petroleum gases are mainly obtained from:

- fractionation of crude gasoline that leads to natural gas degasification;

- refinery gas as a result of processing and separation.

Figure 1 shows the workflow diagram of processing natural or associated gas (representing the gaseous part from the extracted oil).

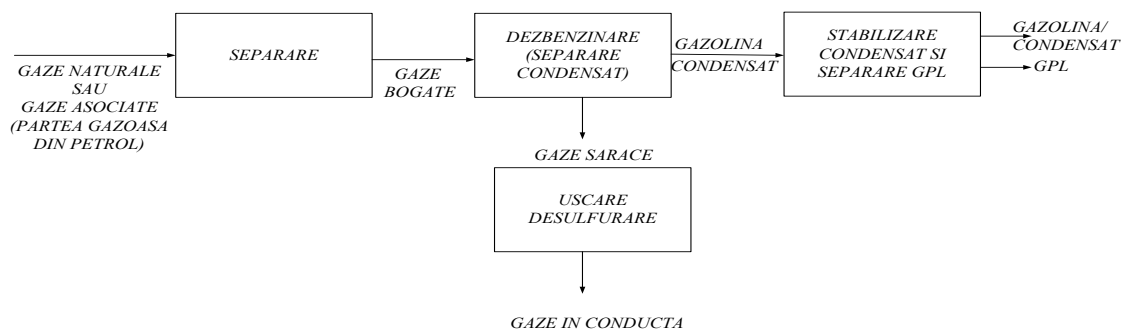


Fig.1 Natural or associated gas processing diagram [1]

Hydrocarbons have the property to form explosive mixtures when combined with air. As a result, measurements must be taken to hastily detect any “oversight” of gas in the atmosphere, before it reaches the explosion lower limit. Gas leakage may occur, for example, at the location where hydrocarbons are used as fuel. To this end, it is compulsory that they be odorized at the intake of distribution networks and the bottling of gas intended for domestic use. The odoriferous substances must fulfil the following conditions:

- be determinable in very low concentrations;
- have a characteristic smell, distinct from other odors.

Table 1 describes technical characteristics of propane.

Table 1. Technical characteristics of propane [3]

Characteristic	Value	
	Type I	Type II
1. Chemical composition %, mass:		
– propane, min.	92	93.5
– hydrocarbons, (C ₂) total, max	5	2.5
– propylene, max.	2	2
– hydrocarbons, (C ₄) total, max	2	2
2. Total sulfur, mg/m ³ _N , max	100	100
3. Water %, max	0.05	0.05

Auto liquefied petroleum gas composition

Auto liquefied petroleum gas is a mixture of highly volatile liquid hydrocarbons that are kept under a pressure of about 13 bar; subsequently, it is introduced as a vaporized state in standard spark ignition engines. Its use as automobile fuel is applicable for engines that are adapted to work with both gasoline and LPG.

In Romania, auto LPG is produced to meet company standards (for example: Petrom, Rompetrol, etc. standards); the validity of such a gaseous fuel is 3 months from manufacture date provided that all the requirements regarding packing, transport and storage have been met. An important advantage of using LPG consists mainly in the fact that it is less polluting, being a mixture of simple hydrocarbons with 3 and 4 carbon atoms (fig. 2) which does not contain many impurities (small amount of sulfur, no lead, no odors) [1].

Table 2 describes several quality conditions of liquefied petroleum gas as an automobile fuel type.

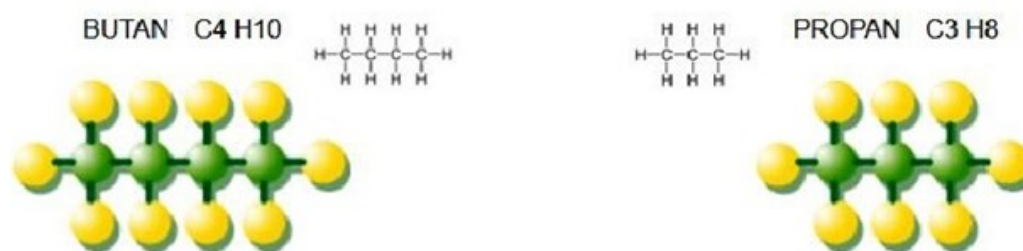


Fig. 2 Auto LPG composition

Table 2. Quality conditions of liquefied petroleum gas as an automobile fuel type.

Feature	Value	
	Fuel A Butane	Fuel B Propane
1. Composition:		
- hydrocarbons C ₃ , %, v/v	28.0-32.0	83.0-87.0
- hydrocarbons C ₄ , %, v/v	Balance	Balance
- hydrocarbons C ³ +C ⁴⁺ , %, v/v, max	2	2
- total olefins, from which butadiene, %, v/v, max	9.0 ± 3.0	12.0±3.0 (0.5)
2. Evaporation residue, ppm, max.	50	50
3. Water content.	None	None
4. Total sulfur content, ppm, max.	50	50
5. Mercaptanic sulfur content, ppm, min	25	25
6. Content of hydrogen sulfide	None	None
7. Copper corrosion (1 h at 40°C), classification	Class I	Class I
8. Vapor pressure at 40°C, kPa, max	1550	1550
9. Odor	characteristic	characteristic
10. Engine Octane, COM, min	89	89

Worldwide, LPG use as automobile fuel represents no more than 5% of the LPG produced, the rest being used in petrochemistry – 25% and as household fuel – 70%.

Thermodynamic characteristics of liquefied petroleum gas

In the case of gas which is characterized by the fact that its critical temperature is higher than ambient temperature, $t_{cr} > t_{atm}$, liquefaction can even be achieved just by isothermal compression. Given that the critical parameters of propane are: $t_{cr} = 96.8$ °C; $p_{cr} = 42.463$ bar; i-butane $t_{cr} = 133.7$ °C; $p_{cr} = 36.971$ bar, n-butane $t_{cr} = 153.2$ °C, $p_{cr} = 36.481$ bar, it is safe to say that propane and butane liquefaction is achieved quite easily. When liquefied, the volume of gas decreases considerably. Hence, the volume occupied by the unit of mass, under its saturation state, at a saturation temperature corresponding to a pressure of 1 atm, versus the volume occupied at standard state, characterized by the same pressure, but having a temperature $t_0 = 15$ °C, i.e., liquid state versus gas state, under the specified thermodynamic conditions, is 242.18 times lower in the case of i-butane, 245.18 times lower for n-butane and 315.29 times lower for propane.

The theoretical combustion temperature of propane is 2107°C, of butane is 2117 °C, and of methane is 2040°C.

The auto-ignition temperature of the gases that compose LPG, i.e., 466 °C for propane and 430°C for butane, is higher than that of petrol – 245 °C, and diesel, respectively – 250 °C, but is lower compared to that of methane, 537 °C.

In air mixtures, the explosion limits of LPG (1.86...9.5) are lower than those of methane, where they range between 5% and 15% but are higher than those of petrol, where they range from 1.3% to 6%, and, respectively, those of oil, which range from 1.16% to 6%.

The lower calorific value of LPG ranges from 45 720 to 46 348 kJ/kg; diesel, with a density $\rho = 870 \text{ kg/m}^3$, has an inferior calorific value of 41843 kJ/kg. Furthermore, petrol, with a density $\rho = 760 \text{ kg/m}^3$, has a calorific value of 42035 kJ/kg. Thus, the lower calorific value of LPG is higher than that of the other fuels used as automobile propellants. The material combustion balance shows that, post propane-butane mixture combustion, the volumetric fraction of carbon dioxide in the combusted gases ranges from 10.64 to 10.95%, whereas in the case of gas it is 11.7%, and in the case of diesel it ranges approximately between 12.1 and 12.8 %. Consequently, environmental pollution is considerably lower when burning LPG. Sometimes LPG is referred to as being an eco-friendly fuel; this is improper because, in reality, it is part of the category of propellants that make use of carbon; its combustion leads to the release of carbon dioxide, which is a pollutant. Similarly to the combustion of diesel fuel or petrol, there will also result carbon monoxide, sulfur dioxide and nitrogen oxides, which are pollutants; moreover, they favor the formation of tropospheric ozone.

Liquefied Petroleum Gas Storage

Liquefied gaseous hydrocarbon deposits are designed to work either at ambient temperatures, under pressure, or at low temperatures, but at pressures that are higher than atmospheric pressure (table 3).

LPG storage requires compliance with specific operational procedures relating to reliability, safety, prevention and firefighting. Accidents in installations that use or handle this fuel may occur due to mechanical faults, operating mistakes, human errors, design changes, natural disasters, sabotage, etc. [10]

Table 3. Storage conditions for liquefied gaseous hydrocarbons [6]

Temperature and storage pressure	Main hydrocarbons to be deposited
At ambient temperature and vapor pressure corresponding to the stored hydrocarbons From 0°C to -50°C at a pressure of 1 bar abs. From -50°C to -150°C at a pressure of 1 bar abs.	Butane, propane, propylene Butane, LPG, propane, propylene Ethylene, ethane, acetylene

Depending on their position relative to the ground surface, the storage means of gaseous hydrocarbons are classified into the following categories:

- aboveground tanks (i.e., metallic or reinforced concrete tanks) of different types installed directly on the ground or over the ground level;
- semi-underground tanks, i.e., vertical cylindrical tanks having the lower part below the ground and the upper part above it; underground storage facilities such as natural caverns or salt caverns, as well as some reinforced or metallic tanks installed in caves or in natural or custom-built caverns;
- underground storage facilities, such as reinforced concrete tanks and tanks buried in frozen ground.

Logistics and Distribution of Liquefied Petroleum Products

The notion of logistics encompasses all activities aimed at achieving a time and space harmonization with goods and people through their appropriate grouping. Therefore, logistics is defined as the integrated planning, organization and control of all commodity and material flows, along with related information flows, from suppliers – through value creation steps – to product delivery to customers, including waste recycling and disposal. [8]

Loading petroleum products

a) *Loading petroleum products at railway ramps:* Loading and unloading petroleum products from rail tank wagons is a high-risk operation. Flammable mixtures may occur both inside the tanks, when filling and emptying them, and around the tanks, pits and sewers.

b) *Loading petroleum products into tankers:* When filling tankers with petroleum products, the fire hazard may occur as a result of the release of flammable vapors from the transferred liquid and the occurrence of explosive mixtures both inside the container and near the exit point of the displaced air. Ignition can arise from static loads caused by the friction of the product by the air layer during loading. [9]

Pressure - temperature correlation for propane liquefaction or regasification at constant pressure

Liquefied petroleum gas technology is likely to involve phase transition, i.e., the LPG conversion from one aggregation state into another.

A phase is defined as a region of space occupied by certain substances and which is homogeneous, i.e., it has the same physico-chemical properties in all its points. As a result, a phase comprises all the parts of a thermodynamic system subjected to the same state equation. According to the Gibbs phase law, in a polycomponent system consisting of NC constituents and NF phases, the number of phases that may exist simultaneously in equilibrium is at most $NC + 2$, which leads to a number of degrees of freedom:

$$NG = NC + 2 - NF \quad (1)$$

The degree of freedom of a system, NG , is defined as the number of independent variables (pressure, temperature) that characterize the system at equilibrium. In the case of certain substances there are several possibilities when in solid state, varying upon their crystalline structure. For a monocomponent system $NC = 1$, the maximum number of phases that may coexist is $NF = 3$ (provided that there is no variation of any parameter the equilibrium state depends on), therefore $NG = 0$ (the triple point); if the number of phases is $NF = 2$, then $NG = 1$; in the equilibrium state two phases co-exist, which leads to the following relation between pressure and temperature:

$$p = f(T_s) \quad (2)$$

The thermodynamic equilibrium between the two phases is achieved when the three thermal, mechanical and chemical equilibria are achieved, being expressed by the equation of temperature, pressure and chemical potential, respectively, as follows:

$$T_1 = T_2; \quad p_1 = p_2; \quad g_1(p, T) = g_2(p, T) \quad (3)$$

For pure substances, the chemical potential is equal to free enthalpy, g , also called isobaric-isothermal potential or Gibbs' function. If the system states are graphically represented by points in a pressure-temperature diagram, then relation 2 is the equation of a curve in that plane, called the *phase equilibrium* or *saturation curve*. The points on this curve represent states in which the two phases can coexist in equilibrium. As regards a biphasic monocomponent system,

the dependence between temperature and vapor pressure $p = f(T_s)$ is given by the vapor pressure curve and depends only on the nature of the fluid. For conventional objects, the phase transformation temperature increases with pressure along the three equilibrium curves, except for water, where the melting curve is characterized by a drop in the melting temperature (solidification) as the pressure increases. *Phase transformation* can only take place at the state parameters correlated to the phase equilibrium curve.

The equilibrium curve of the liquid and gaseous phases begins at the triple point, tr , and ends at the critical point, cr . The critical point is characterized by the *critical state parameters* p_{cr} and t_{cr} . The coordinates of the critical point are constant for a given substance, but depend on the nature of the substance. The curve $p = f(T_s)$ divides the diagram into two areas, namely: to the left hand side of the curve and above it the fluid is in liquid state, whereas to the right of the curve and below it the fluid is in gaseous state. Figure 3 shows the pressure curve of a number of pure substances as a function of temperature, at saturation.

When pressure is p_{cr} and temperature is t_{cr} , the density of the liquid is equal to the vapor density of the respective substance ($\rho_l = \rho_v$). There is no significant difference between the liquid phase and the vapor phase, which is why liquids and gases are generically dubbed *fluids*. The existence of point cr shows that a gas cannot be liquefied by isothermal compression unless it is brought below critical temperature. [1] [2]

Establishing a computation relation for propane pressure variation as a function of temperature by using the linear regression method.

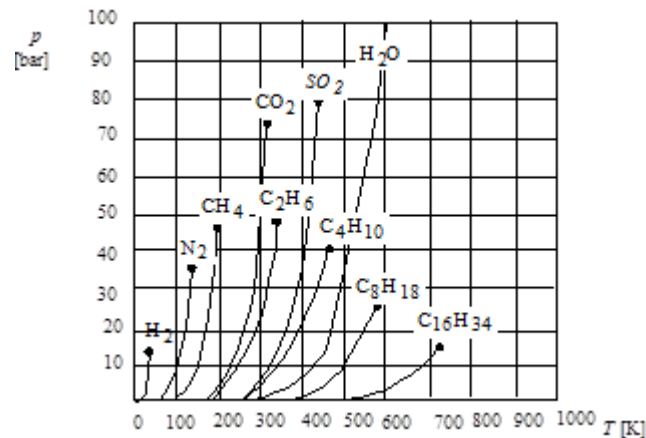


Fig. 3 The pressure curve of a number of pure substances as a function of temperature, at saturation. [7]

For the right selection of the regression function, the distribution series are represented by a correlation graph which makes it clear whether the link between the two variables is rectilinear or curvilinear.

The regression function expresses the manner in which the dependent variable (y) changes if it is only the explanatory variable (x) that varies, while the other factors remain constant. If the graphical representation indicates a linear trend, then the corresponding *regression equation* is the following:

$$y_i = b \cdot x_i + a \quad (4)$$

Parameter a is the intercept and indicates the level variable y would have reached if all the factors, except for the registered one, had had a steady effect on it.

Parameter b is also called a regression coefficient and is geometrically represented as the slope of the regression line. [5]

The regression equation obtained is as follows: $p = 0.1204 * T - 26.152$. The graphic representation is in fig 4.

The proposed relationship is simple and easy to use for calculating propane pressure as a function of temperature.

If all the necessary data are provided, an equation can be created for any hydrocarbon by using the same method. [4]

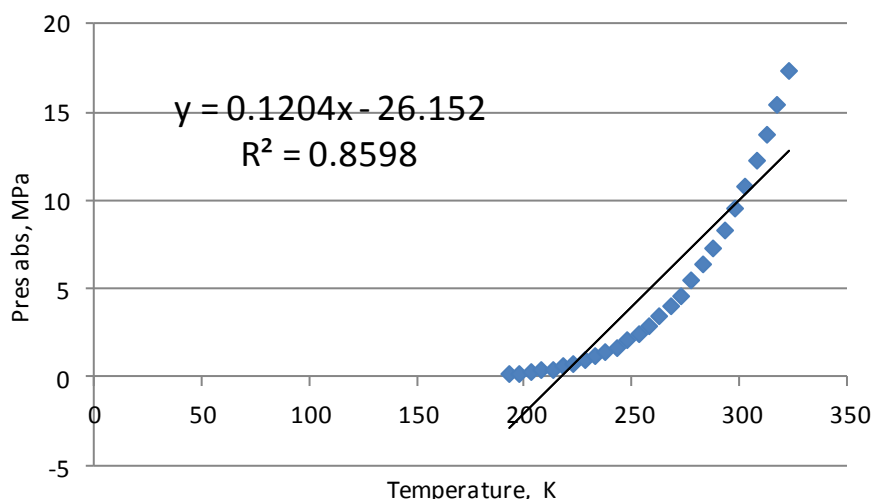


Fig. 4. Linear regression propane [11]

Conclusions

As regards the energy balance of a system, LPG may be an eligible fuel, relatively easy to produce, and the cost of heat is currently competitive on the energy market.

The pressure-temperature correlation when liquefaction and regasification, respectively, take place at constant pressure provides a simple and easy-to-use calculation relationship for propane pressure variation as a function of temperature by means of the linear regression method.

The major advantage of using liquefied petroleum gas is that it is less polluting than diesel and gasoline because LPG is a mixture of simple hydrocarbons that contain few impurities (little sulfur, no additives, no lead). Therefore, LPG is an environmentally friendly option.

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LPG – o alternativă viabilă de combustibil

Rezumat

În lucrare se prezintă compoziția, caracteristicile, proprietățile și fluxul tehnologic de exploatare a Gazelor petroliere lichefiate pentru autovehicule, o alternativă tot mai economică și ecologică a benzinei și motorinei. În fluxul tehnologic al gazelor petroliere lichefiate sunt posibil implicate transformări de fază. Se stabilește o relație de calcul pe baza corelației presiune – temperatură la lichefierea, respectiv regazeificarea, la presiune constantă, în cazul propanului, relație care este ușor de aplicat