Liquefied petroleum gases

Liquefied petroleum gases are products of the refining of crude oil, and are therefore closely related to other petroleum products such as petrol, lubricating oils and fuel oils. They consist of hydrocarbons, which are compounds containing only carbon and hydrogen.

The simplest member of the hydrocarbon family is methane, which has the chemical formula CH_4, indicating that a methane molecule consists of one carbon atom bound to four hydrogen atoms. Methane can only be liquefied at low temperatures and is therefore difficult to handle commercially. Propane (C_3H_8) and butane (C_4H_{10}), however, although gases at normal temperatures, can be liquefied by the application of relatively low pressures and can therefore be stored in pressure storage vessels at ambient temperatures in the liquid state, becoming gases again when the pressure is released. The ratios of gas volume to liquid volume, at standard temperature and pressure, are approximately 274 and 233 to 1 for propane and butane respectively, so that from compact storage large volumes of high calorific value gas are readily available.

The two principal grades of LPG sold in the United Kingdom are commercial propane, consisting mainly of C_3 hydrocarbons, and commercial butane, consisting mainly of C_4 hydrocarbons. These products are marketed by Shell Marketing Ltd and are available either in bulk or in portable cylinders.

All LPG marketed in the UK by Shell Marketing is manufactured within the quality specifications covered by the BS 4250:1968 *Specifications for Commercial Propane and Commercial Butane*.

Commercial propane

This grade of LPG is used for a wide variety of industrial processes and other uses. It is available either in bulk, when it is supplied into static storage vessels, or in portable cylinders, when it is marketed under the trade name 'Propagas'.

Commercial propane is used for steel cutting, the production of controlled atmospheres in metallurgical and other furnaces, and for any process in which a high quality gaseous fuel is required. It is also widely used as Propagas for internal combustion engines on mechanical handling plant, portable pumps, generators and compressors as well as for flood-lighting, heating, brazing, paint stripping, soldering, hand torches for plumbing and many other industrial applications.

Commercial propane specification: BS 4250

The British Standard specifies requirements for the quality of commercial propane as follows:

Commercial propane shall be a hydrocarbon mixture consisting predominantly of propane and/or propylene. It shall not contain harmful quantities of toxic or nauseating substances and shall be free from mechanically entrained water. It shall have the following composition and properties:

1
The total content of C_2 hydrocarbons shall not exceed 5·0 moles per cent as determined by gas chromatography, mass spectrometry or infra-red spectrometry.

2
The total content of ethylene shall not exceed 1·0 moles per cent as determined by gas chromatography, mass spectrometry or infra-red spectrometry.

3
The total content of C_4 and higher hydrocarbons shall not exceed 10 moles per cent as determined by gas chromatography, mass spectrometry or infra-red spectrometry.

4
The total content of C_5 and higher hydrocarbons shall not exceed 2 moles per cent as determined by gas chromatography or mass spectrometry.

5
The vapour pressure at 45°C (113°F) shall not be greater than 17·9 kgf/cm² gauge (255 lbf/in² gauge) when determined by the method described in BS 3324.

6
The total content of sulphur (after stenching) shall not exceed 0·02 per cent by weight as determined by the turbidimetric procedure described in the Institute of Petroleum method IP 107.

7
The content of mercaptan sulphur (after stenching) shall not exceed 92 mg/m³ (4·0 grains/100 ft³) at s.t.p. (saturated) as determined by procedure A described in the Institute of Petroleum method IP 104.

8
The hydrogen sulphide content shall be below that detectable by method 2 (lead sulphide stain method) of BS 3156 (i.e. no visible stain).

9
The total content of acetylenes shall not exceed 2 moles per cent, as determined by gas chromatography or mass spectrometry.

10
The odour of the gas shall be distinctive, unpleasant and non-persistent, and shall indicate the presence of gas down to concentrations in air of one-fifth of the lower limit of flammability. The lower limit of flammability for commercial propane may be taken as 2·4 per cent by volume in air.

Commercial butane

Where large offtakes of LPG are required in industry, butane is generally used because of its price advantage.

There are two main types of butane handling systems in common use:

1
For general factory services, it is distributed as a butane–air mixture which is produced from a gas–air mixing unit. Butane–air is an ideal fuel gas for long or complicated pipework systems, or for plant which has been converted from some other gaseous fuel, since it minimises burner conversion work (see also page 29).

2
For simpler distribution systems, or for supplies to a small number of high-offtake points such as large kilns or furnaces, neat butane vapour can be distributed in heated and lagged pipelines (see page 30).

Commercial butane is also supplied in small cylinders, when it is marketed under the trade name 'Bottogas'. These cylinders are used in caravans, for camping and domestic purposes, and for many other similar applications.

Commercial butane specification: BS 4250

The British Standard specifies requirements for the quality of commercial butane as follows:

Commercial butane shall be a hydrocarbon mixture consisting predominantly of butanes and/or butylenes. It shall not contain harmful quantities of nauseating substances and shall be free from mechanically entrained water.

It shall have the following composition and properties:

1
Ninety-five per cent by volume of the material shall evaporate at a temperature of 2·2°C (36°F) or lower, corrected to a barometric pressure of 760 mmHg (29·92 inHg).

2
The vapour pressure at 45°C (113°F) shall not be greater than 5·9 kgf/cm² gauge (85 lbf/in² gauge) when determined by the method described in BS 3324. Additionally, for the portable container trade only, the vapour pressure at 45°C (113°F) shall be not less than 4·92 kgf/cm² gauge (70 lbf/in² gauge) when determined by the method described in BS 3324.

3
The total content of dienes shall not exceed 10 moles per cent as determined by gas chromatography or mass spectrometry.

4
The total content of sulphur (after stenching) shall not exceed 0·02 per cent by weight as determined by the turbidimetric procedure described in the Institute of Petroleum method IP 107.

5
The content of mercaptan sulphur (after stenching) shall not exceed 92 mg/m³ (4·0 grains/100 ft³) at s.t.p. (saturated) as determined by procedure A described in the Institute of Petroleum method IP 104.

6
The hydrogen sulphide content shall be below that detectable by Method 2 (lead sulphide stain method) of BS 3156 (i.e. no visible stain).

7
The total content of acetylenes shall not exceed 2 moles per cent as determined by gas chromatography or mass spectrometry.

Table 1 Typical properties of commercial LPG grades

					Commercial butane		*Commercial propane*
Relative density of liquid at 60°F (15·6°C)					0·57 to 0·58		0·50 to 0·51
Imperial gallons/ton at 60°F					385 to 393		439 to 448
Litre/tonne at 15·6°C					1 723 to 1 760		1 965 to 2 019
Relative density of gas compared with air at 60°F (15·6°C) and 30 inHg (1015·9 mbar)					1·90 to 2·10		1·40 to 1·55
Volume of gas (ft³) per lb of liquid at 60°F and 30 inHg					6·5 to 6·9		8·6 to 8·7
Volume of gas (litres) per kg of liquid at 15·6°C and 1015·9 mbar					406 to 431		537 to 543
Ratio of gas volume to liquid volume at 60°F (15·6°C) and 30 inHg (1015·9 mbar)					233		274
Boiling point at atmospheric pressure							
	°F approx.				28		−49
	°C approx.				−2		−45
Vapour pressure for products at their maximum specified vapour pressure							
Temp.	*°F*	*°C*	*lbf/in²*	*bars*	*lbf/in²*	*bars*	
	−40	−40	—	—	20	1·38	
	0	−17·8	—	—	45	3·11	
	32	0	28	1·93	80	5·52	
	100	37·8	85	5·86	225	15·5	
	113	45	100	6·89	270	18·6	
Latent heat of vaporisation (Btu/lb) at 60°F					160		154
Latent heat of vaporisation (kJ/kg) at 15·6°C					372·2		358·2
Specific heat of liquid at 60°F (Btu/lb deg F)					0·57		0·60
Specific heat of liquid at 15·6°C (kJ/kg deg C)					2·386		2·512
Sulphur content, per cent. weight					Negligible to 0·02		Negligible to 0·02
Limits of flammability (percentage by volume of gas in a gas-air mixture to form a combustible mixture)					Upper, 9·0 Lower 1·8		Upper 10·0 Lower 2·2
Calorific values:							
Gross	(Btu/ft³) dry				3 270		2 500
	(MJ/m³) dry				121·8		93·1
	(Btu/lb)				21 200		21 500
	(MJ/kg)				49·3		50·0
Net	(Btu/ft³) dry				3 030		2 310
	(MJ/m³) dry				112·9		86·1
	(Btu/lb)				19 700		19 900
	(MJ/kg)				45·8		46·3
Therm/ton (gross CV)					475		482
GJ/tonne					49·3		50·0
Air required for combustion							
(ft³ to burn 1 ft³ of gas)					30		24
(m³ to burn 1 m³ of gas)					30		24

Note: 1 tonne = 1 000 kg

8
The odour of the gas shall be distinctive, unpleasant and non-persistent, and shall indicate the presence of gas down to concentrations in air of one-fifth of the lower limit of flammability. The lower limit of flammability for commercial butane may be taken as 1·9 per cent by volume in air.

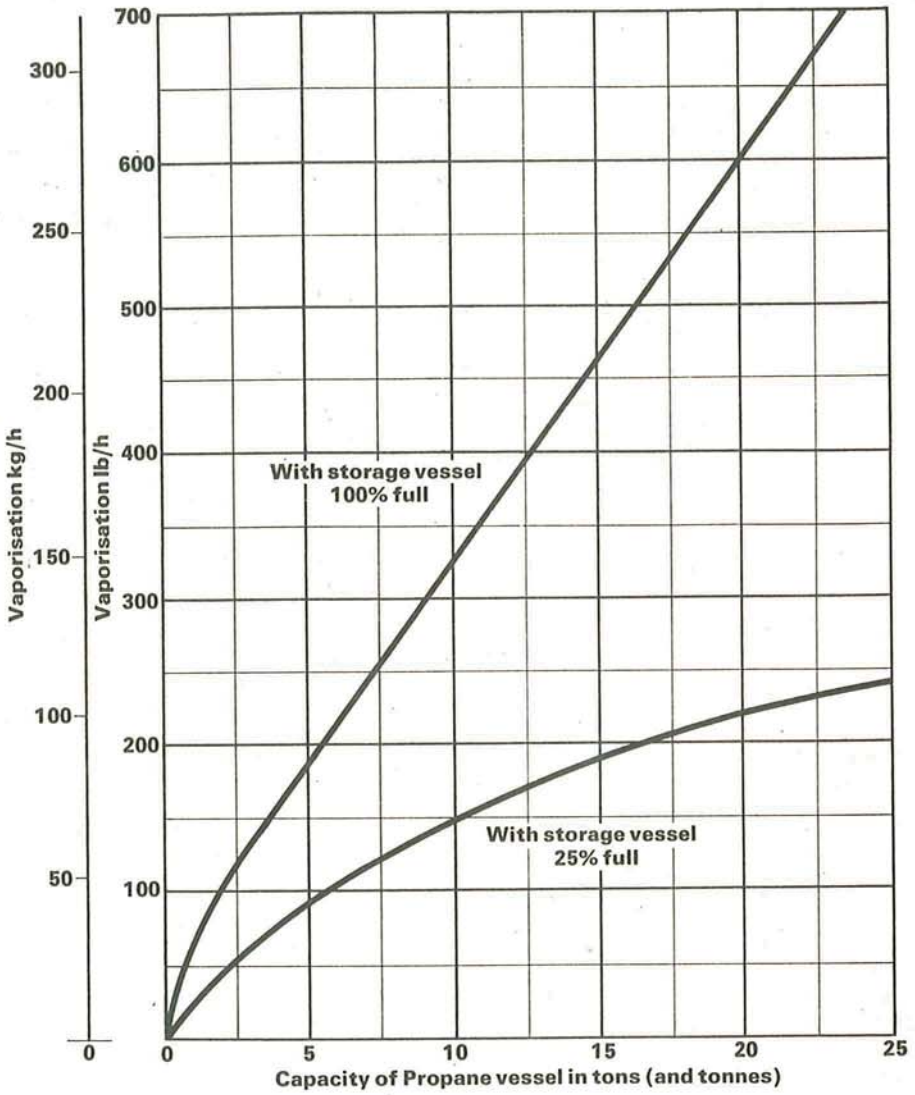
Note: These specifications for commercial propane and commercial butane cover the basic composition of LPG as regards their hydrocarbon content and the amount of sulphur compounds present, and lay down a standard of perceptible odour. The latter is necessary so that gas leaks may be detected by smell, and an odorant is intentionally added to the gas so that it meets the specification.

Characteristics of liquefied petroleum gases

LPG in its gaseous form is characterised by a high specific gravity, a high calorific value and high purity, since it consists entirely of hydrocarbons with a virtual absence of sulphur. In comparison with town gas, LPG has a lower flame velocity and narrower limits of flammability in mixtures with air. These factors influence the design of burners and equipment for LPG, but present no special difficulties. Table 1 shows typical properties of commercial LPG grades.

On a weight basis the latent heats of vaporisation of propane and butane are similar, 154 and 160 Btu/lb (358 and 372 kJ/kg) respectively at 15·6°C, and are equivalent to about 0·75 per cent of the calorific value of each fuel. Unless an artificial source of heat, such as a vaporiser, is used, the heat necessary for vaporisation can only be obtained from the liquid itself or by conduction through the walls of the container. As the storage container empties, the surface area of vessel wall in contact with liquid is reduced, and consequently the rate at which heat can be absorbed from the surrounding atmosphere also decreases. This places a limit on the rate at which gas can be evolved, so that the lower the boiling point (and hence the higher the vapour pressure) of the LPG, the larger the offtake which can be obtained at a given temperature, and the greater the temperature difference across the storage vessel wall that can be tolerated for a given outlet pressure.

Fig. 1 Approximate vaporisation rates from propane vessels



Vaporisation rates based on ambient temperature of 20°F (−6·7°C) and storage vessel pressure of 15 lbf/in² gauge (1·03 bars)

Figure 1 shows the maximum continuous rates of vaporisation that can be obtained from various sizes of propane storage vessels. The rates have been calculated for a storage vessel pressure of 15 lbf/in² gauge (1·03 bars) and an ambient temperature of 20°F (− 6·7°C). These rates are approximate and should not be used for design purposes without reference to Shell Marketing Ltd since there are a number of other factors which also need to be considered. The curves, fo instance, indicate that the rate of vaporisation falls as the level of the liquid propane falls. To ensure continuity of an adequate gas supply the level of storage should not be allowed to fall below the minimum assumed at the design stage. This may be a significant factor in designing the size of storage vessel required.

Vapour pressure

The vapour pressure of a liquid at a given temperature is defined as the pressure

exerted by the liquid in equilibrium with its vapour at a specified temperature. It is one of the most important characteristics of LPG, since it determines the pressure exerted by the gas at ambient temperatures, and therefore affects the handling requirements and the designed working pressures of the storage vessels.

Since the boiling point of a liquid is the temperature at which its vapour pressure is equal to the applied pressure, then the higher the vapour pressure of a liquid at a given temperature, the lower will be its boiling point. The main difference between commercial propane and commercial butane is therefore in their vapour pressures. Commercial propane has the higher vapour pressure of the two LPG at a given temperature, and therefore the lower boiling point, so that it is preferable for high rates of offtakes where natural vaporisation is used.

Fig. 2 shows vapour pressure/temperature curves for commercial propane and commercial butane.

Gross calorific value

This is defined as the amount of heat liberated when unit volume (or unit mass) of a gas is burned at a standard temperature and pressure. It is usually expressed as Btu/ft³ at 60°F (15·6°C) and 30 inHg (i.e. Btu per standard cubic foot), or kJ/m³ at 15·6°C and 1 015·9 mbar, and includes the latent heat of the water vapour produced in the combustion process. Table 2 shows typical calorific values of liquefied petroleum gases and other gaseous fuels, enabling a comparison of heating values to be made. It can be seen that in comparison with other gaseous fuels, the heating values of LPG are high. The table also shows that on a weight basis the calorific values of commercial propane and commercial butane are similar, although volumetrically commercial butane has the greater value.

Sulphur content

In comparison with other fuels, LPG has a very low sulphur content which is limited to a specified minimum, making it a very desirable fuel.

Fig. 2 Vapour pressure / temperature curves for commercial propane and commercial butane

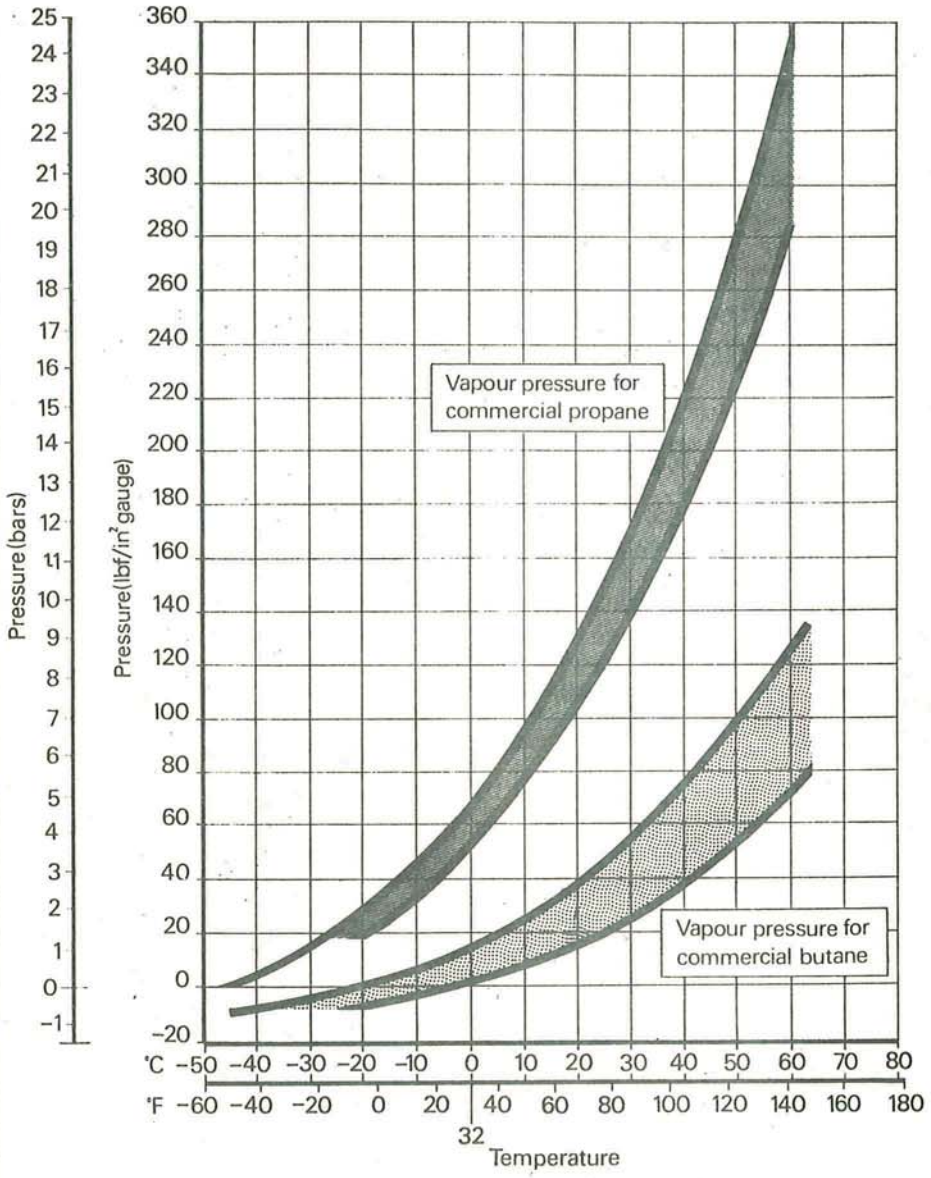


Table 2 Typical gross calorific values of gaseous fuels

Gas	*Btu/std ft³*	*kJ/m³*	*Btu/lb*	*kJ/kg*
Commercial Propane	2 500	93 132	21 500	50 009
Commercial Butane	3 270	121 817	21 200	49 311
Producer gas (cold)	125–165	4 657–6 147	—	—
Town gas	375–550	13 970–20 489	—	—
Natural gas	850–1250	31 665–46 566	—	—
Acetylene	1 500	55 880	21 460	49 916

Relative density

The relative density of a liquid is defined as the ratio of its weight to that of an equal volume of water at the same temperature. The relative densities of both liquid propane and liquid butane are approximately half that of water, and must be taken into account when calculating the maximum weight of product that can be carried in a given storage vessel.

The relative density of a gas is the ratio of its weight to that of an equal volume of air at the same temperature and pressure. Both propane and butane are much heavier than air, so that in the event of a leak both will tend to accumulate at low levels, near floors, and in basements and wells etc. For this reason, adequate ventilation at floor level is necessary, and liquefied petroleum gas should not be used or stored below ground level inside buildings.

Limits of flammability

Gaseous fuels will burn only when mixed with air in certain proportions which lie between two well-defined limits, known as the 'limits of flammability'. As a combustible gas is gradually mixed with air in increasing proportions, a concentration is reached at which the mixture just becomes flammable. This is called the 'lower limit of flammability' of the gas. As the concentration of gas in the mixture is increased further, a point is reached at which the mixture ceases to burn, and the concentration of the gas just before this point is called the 'upper limit of flammability'. Therefore combustion of the gas can only be achieved if the concentration of the gas in the gas–air mixture lies between these two limits. The limits of flammability for propane and butane are, in fact, much narrower than for most other gaseous fuels, making LPG much safer in this respect.

Coefficient of expansion

This is defined as the increase in volume of unit volume of a substance when its temperature is raised by one degree. It is important in that the coefficient of expansion of LPG in its liquid form is relatively high, so that when filling a storage vessel adequate space must always be provided to allow for expansion of the liquid.

Other physical characteristics

Liquefied petroleum gases are colourless and possess anaesthetic properties, but they are not in themselves toxic. However, because they are heavier than air, they will tend to displace it in the event of a leak and if allowed to collect in large quantities, could cause a deficiency of oxygen for normal respiration. Consequently, except for certain specialised applications, all LPG must have a distinctive odour to enable its detection. The British Standard Specification BS 4250 : 1968 therefore requires that the gas be detectable in air at concentrations of one-fifth of its lower limit of flammability.
LPG must not be contaminated with water. Apart from the obvious danger of internal corrosion of the storage vessels, water in the fuel may lead to hydrate formation and so impair the operation of regulators; it is also liable to condense when the gas expands.