

BPI REPORT

BANGLADESH PETROLEUM INSTITUTE



A Study on Optimum Ratio of Propane and Butane Mixture in LPG and Effects of Impurities for Different Usages

Dhaka, May, 2022.

Declaration

This is to certify that the work of BPI report entitled "A Study on Optimum Ratio of Propane and Butane Mixture in LPG and Effects of Impurities for Different Usages" has been carried out by Bangladesh Petroleum Institute (BPI) Research Team. The above work or any part of this work has not been submitted anywhere for the award of any degree or diploma.

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BPI Research Team

Abstract

The Liquefied Petroleum Gas (LPG) market in Bangladesh is expanding at a rapid pace. People and industries are attempting to use LPG as a clean fuel. Due to the weather in Bangladesh, the Propane-Butane ratio should be kept within the range of 60:40-70:30 and it was found in this study that the LPG samples are well within this range. In addition, LPG is used in automobiles as Autogas. As an automobile fuel, LPG with more branched hydrocarbons performs better. It was found that LPG samples contained a significant percentage (30-32%) of branched hydrocarbon, which is beneficial to internal combustion (IC) engines. Moreover, impurities or compounds other than propane and butane constitute less than 1% of the total. As a result, the impact of impurities on various applications and environments is minimal. It was also found that the Sulphur content in LPG is very less (<40 ppm) which is good for environment.

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Abbreviations

LPG	Liquefied Petroleum Gas
BD	Bangladesh
RMG	Ready-Made Garments
GDP	Gross Domestic Product
UN	United Nation
LDC	Least Developed Countries
MMcfd	Million Cubic Feet per Day
BCF	Billion Cubic Feet
NG	Natural Gas
JICA	Japan International Cooperation Agency
CNG	Compressed Natural Gas
BTU	British Thermal Unit
MON	Motor Octane Number
RON	Research Octane Number
ASTM	American Society for Testing and Materials
IC	Internal Combustion
PSI	Pound Per Square Inch
SI	Spark Ignition
PPM	Parts Per Million
Sp	Specimen

1. Introduction

Bangladesh has a long history of progress and prosperity. Due to a demographic dividend, substantial ready-made garment (RMG) exports, remittances, and stable macroeconomic conditions, it has been one of the world's fastest expanding economies over the previous decade. The country's economy quickly rebounded after the COVID-19 pandemic. For the last few years, it has maintained a remarkable Gross Domestic Product (GDP) growth. According to the World Bank [1], poverty decreased from 43.5 percent in 1991 to 14.3 percent in 2016 (Based on the international poverty line of \$1.90 per day) which led the country to gain the status of lower-middle income country in 2015. In 2026, the country is expected to upgrade from the United Nation's (UN) list of Least Developed Countries (LDCs). To uphold the growth and development it is essential to make the best use of its energy and mineral resources.

Bangladesh having a population over 164 Million [2] used to depend mostly on natural gas and wood for household cooking. Bangladesh is the world's 32nd largest [3] natural gas consumer, with a per capita consumption of 6531 cubic feet per year. With the ever-increasing demand for gas, the current natural gas supply is insufficient to assure adequate gas delivery to all households and companies. Currently the average natural gas production is about 2978 Million Cubic Feet per Day (MMcfd). In 2020-21 A total 892.76 Billion Cubic Feet (BCF) of natural gas was produced [5].

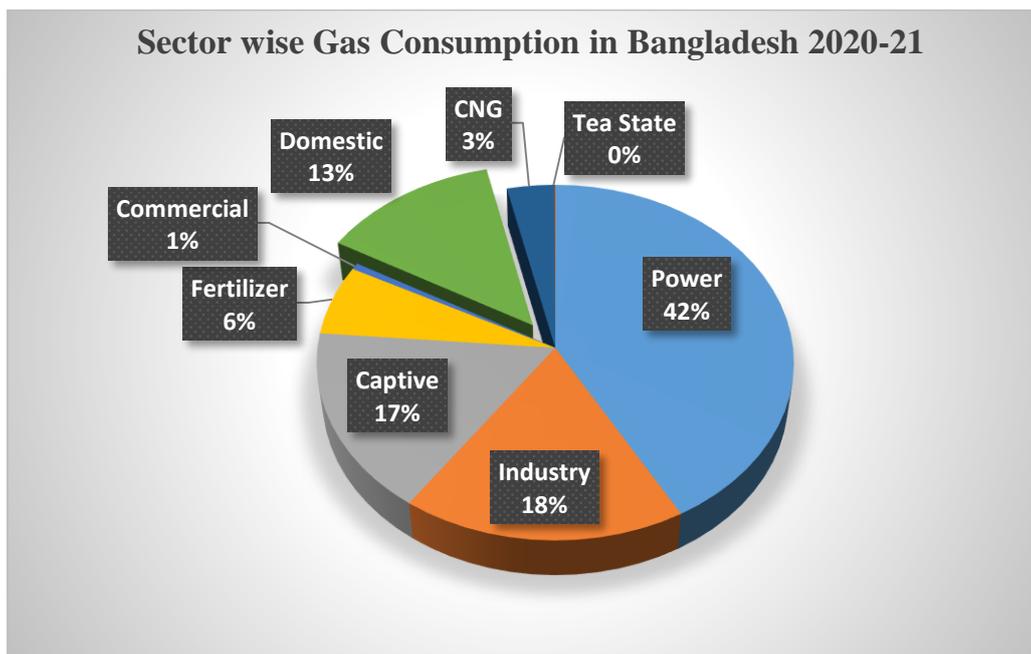


Figure 1: Gas consumption in different sectors of Bangladesh.

The above Fig. 1 shows sector wise gas consumption in Bangladesh 2020-21. As a result of depleting Natural Gas (NG) resources and the Government's decision to put a stopper on new household connections, Liquefied Petroleum Gas (LPG) has seen a remarkable growth in the last few years.

LPG is a pressurized fuel gas that contains a mixture of hydrocarbon gases, most commonly propane (C_3H_8) and butane (C_4H_{10}). It is pressurized in the form of liquid and preserved within a steel container or cylinder for sale or commercial use. Varieties of LPG which are sold and bought over the world include mostly either propane (C_3H_8) or butane (C_4H_{10}). In the northern hemisphere, during winter, the mixture comprises greater propane, while in summer season, they incorporate more butane [4].

According to the report "Energy Scenario of Bangladesh 2020-21" by Hydrocarbon Unit [5], a total of 1.44 Million Metric Ton of LPG was produced and imported by the public and private sector consecutively in the year 2020-21. Above 99% of the total LPG was imported by the private sector whereas the contribution of the public sector was very little. It is evident from the report that the LPG market has seen a growth ranging from 21-71% for the past few years. In the year 2016-17 LPG had a market of 323,382 Metric Ton whereas it reached 1,441,287 Metric Ton by the year 2020-21. The most common use of LPG is domestic but recently LPG has started to be used as automotive fuel named 'Autogas'.

The Japan International Cooperation Agency (JICA) survey team made various assumptions, such as, except for existing natural gas pipeline connections, all new apartments will be forced to use LPG, the demand for gasoline will expand at a faster rate, which will be partially met by LPG, the demand was anticipated to climb dramatically at a 35 percent growth rate and 15 times greater in 2041 than in 2016 [6]. However, this may greatly vary with decision making. LPG is more popular as an alternative fuel because of a number of factors. People can still use kerosene, wood charcoal, gasoline, and other fuels in addition to LPG.

LPG has a variety of characteristics that make it more desirable as a substitute fuel. Apart from LPG, there are still many other fuels available, such as kerosene, wood charcoal, gasoline, and so on. However, in terms of long-term use, LPG's practical properties make it superior to other solutions. The good response of LPG customers and its widespread appeal is increasing business interest in rapidly expanding the LPG

market in Bangladesh. In the context of Bangladesh, some key characteristics like low transportation cost, high efficiency as cooking fuel and power generation, clean fuel clearly show that LPG is far superior to any other option. The proper ratio or composition of propane and butane mixture has a direct effect on the heating facilities. This study focuses on composition of LPG (mostly propane, butane) available in the market of Bangladesh and their effects.



Source: EUROGAZ LPG

Figure 2: LPG storage and bottling plant.

2. Literature Review

LPG production did not begin until around 1904, nearly 40 years after North American crude oil and natural gas production began around 1860 [4]. By 1900, natural gas (methane) cooking and lighting appliances were ubiquitous, but the gaseous fuel was difficult to transport. Compressed natural gas (CNG) could not be transported or stored in the large pressure vessels of the time. For mobile and remote gas applications, LPG is the best fuel. At average ambient temperatures and mild (250 psig) pressures, it is a liquid with a high BTU content that is easy to store and carry. Once vaporized, it can be utilized in natural gas appliances converted to gaseous LPG mixtures with minor air/fuel ratio adjustments. Without any standardization or regulatory restrictions, the early years of the industry were defined by the need to tackle immediate problems. One of the first consumer items to be shipped and sold in pressure vessels was LPG. Producing, transporting, and finally selling it to the general population presented numerous economic and technical obstacles. The industry was at the forefront of several fields of research and development, from manufacturing techniques, equipment, and appliances to composition and property analytical test methods. The outcomes were predictable (in retrospect), and there were plenty of excesses. However, marketing and regulatory forces drove the new business to flourish in a short period of time.

LPG is made by refining petroleum (crude oil) or extracting petroleum or natural gas streams as they emerge from the ground. Walter O. Snelling created it in 1910, and the first commercial goods appeared in 1912. It presently produces about 3% of total energy consumption and burns relatively cleanly, emitting no soot and very little sulfur. It does not pollute the ground or the water because it is a gas, but it can pollute the air. LPG has a 46.1 MJ/kg specific calorific value, compared to 42.5 MJ/kg for fuel oil and 43.5 MJ/kg for premium quality gasoline [7].

However, because of its lower relative density (approximately 0.5–0.58 kg/L, compared to 0.71–0.77 kg/L for gasoline/petrol), its energy density per volume unit of 26 MJ/L is lower than either gasoline or fuel oil. Because the density and vapor pressure of LPG (or its components) change significantly with temperature, this fact must be taken into account whenever the application is linked to safety or custody transfer operations [8], for example, when the typical cutoff level option for LPG reservoir is 85 percent. LPG is a viable feedstock in the chemical industry for the synthesis of olefins such as

ethylene, propylene [9-11], butane [12], and acrylic acid [13-15], in addition to being used as an energy carrier.

LPG is a great cooking fuel because of its higher heating value, good stove efficiency, low cost, and environmentally beneficial properties. The LPG stove's simple and accurate regulation not only makes cooking easier, but it also saves time. Both urban and rural communities have become more reliant on LPG as a result of rising urbanization. In urban areas, reliance on piped natural gas, firewood, and kerosene is decreasing dramatically, probably due to shortages, low pressure, and unpredictability in supply of piped natural gas, gradual shrinking of firewood accessibility, and kerosene price hikes. Given all of these factors, LPG's popularity is rapidly growing. According to market research, a household of four uses 1 to 1.5 cylinders of gas in a month [16]. Since it is highly expensive to expand gas distribution networks to remote areas, LPG is a perfect choice for household cooking [17]. A comparison of the calorific values of LPG and various cooking fuels is shown in the table [18].

Table 1: Calorific values of various fuels.

Name of the Fuel	Calorific value (KJ/kg)
Wood	14400-17400
Charcoal	29600
Kerosene Oil	41000
LPG	45750

The Autogas (LPG) cylinder could be a profitable solution for public and private transportation in the face of increased CNG demand [19]. The fact that torque is accessible at high engine revolutions in LPG-powered vehicles improves drivability, especially in stop-start city driving, which is significant in cities like Dhaka where vehicles are utilized for short trips. Another benefit is that it significantly decreases engine wear [20].

In some ways, Autogas is less expensive and easier to use than CNG. For example, a sedan automobile may go 60-70 kilometers on a full 60-kg CNG cylinder, but a sedan car can travel 400 kilometers with a similar capacity auto-gas cylinder. Auto-gas is also less expensive to convert than CNG, which costs around Tk 20,000 for three-wheelers and Tk 30,000 for vehicles [21]. In addition, LPG has a higher calorific value than oil and gasoline. Petroleum gas is compressed and liquefied before being used as a fuel,

but the energy used to pressurize and liquefy it is not recovered. When you expand it in an evaporator, it will evaporate and absorb heat, resulting in cooling. This property is employed for refrigeration and air conditioning in the form that the liquid form of LPG can be used for cooling and the expanded gas (LPG) may be used for combustion as a fuel [22]. Because of its high refrigeration properties, LPG can be used to cool water jackets or improve inter-cooling within compressor stages. The cooling effect decreases the overall intake charge temperature in a high-output turbo-charged piston engine, improving power output and reducing the potential for knock and pre-ignition [23]. Furthermore, because LPG has a higher research and motor octane number than most other fuels, it can withstand more compression before igniting, preventing knocking in internal combustion engines.

The average Motor octane number (MON)s found for each constituent are well within the 95 percent confidence limits of Boldt's experimental values published in 1967 using data acquired from twelve different laboratories, according to a study on this case. The Research octane number (RON)s and MONs of each ingredient exceed the Australian minimum criteria of 91.0 and 81.0, respectively [24]. Furthermore, because of its high octane number and ease of maintenance, LPG might be employed as an engine fuel for aircraft and ships. Again, its superior antiknock properties allow it to run at a higher compression than petrol inside the engine without early igniting of the fuel/air mixture, as LNG does [23]. At 25°C, liquid propane has an energy density of 495 kg/m³ and liquid butane has an energy density of 601.26 kg/m³ [25], compared to 175 kg/m³ for CNG at 200 bar and 435 kg/m³ for LNG. This means a LPG (propane) powered car can drive up to 2.8 and 1.1 times the distance that a CNG or LNG powered car. In other words, a LPG powered vehicle requires up to 2.8 and 1.1 times less fuel tank capacity than a CNG or LNG driven vehicle for a given vehicle range. Similar to CNG and LNG, an LPG (butane) driven vehicle may travel up to 3.4 and 1.4 times the distance [23].

In many regions of the world, LPG has become the most popular alternative fuel for transportation. Its widespread use even prevents it from being classed as an alternative fuel in some areas. Nearly 20% of light duty vehicles in Turkey run on LPG, while Korea, Poland, and Turkey each have over 2 million vehicles [24]. Following its superiority, the government issued a circular for LPG, the creation of refueling stations and conversion workshops, and its operation and maintenance policy-2016, without defining the pricing formula for car gas. Because natural gas reserves are depleting, a

program has been implemented to replace CNG with LPG as a vehicular fuel. Many gas stations have indeed installed LPG units in recent years. Moreover, the Sulphur content in LPG has an adverse effect on environment. In this study, we have determined the composition of LPG and the effect of impurities for different usages.

3. Methodology

A random sampling method was adopted for laboratory testing and primary data collection. Three LPG cylinders from different brands/companies (available in Bangladesh) were collected on the same day from the local market. All of the three samples were 12kg LPG cylinders. The samples were produced in the laboratory on the same day and went through the following specification/method for testing and data procurement.

Table 2: Testing method for primary data collection.

Serial no.	Description of Test	Method
01.	LPG Composition (C ₁ -C ₆)	ASTM D2163
02.	Density	ASTM D1657
03.	Vapor Pressure	ASTM D1267
04.	Inside Pressure	Laboratory Instrumentation
05.	Volume & Net Weight	Laboratory Instrumentation

Gas chromatography was used to determine hydrocarbons in LP gases and propane/propene mixtures with ASTM D2163 (the official designation for this standard). This test method applies to the determination of the amount of individual hydrocarbons in LPG and propane-propene mixtures, with the exception of high-purity propene in the C₁ to C₅ range. The concentrations of components were measured in the range of 0.01 to 100% [26]. To properly characterize an LPG sample additional tests were required due to the inability of this test analysis to identify hydrocarbons heavier than C₅ as well as non-hydrocarbon components.

The ASTM D1657 is a standard test method for measuring density or relative density of Light Hydrocarbons by Pressure Hydrometer. This test method is used to determine the density or relative density of light hydrocarbons, such as liquefied petroleum gases (LPG), with Reid vapor pressures greater than 101.325 kPa (14.696 psi). At the test temperature, materials with vapor pressures more than 1.4 MPa (200 psi) were not allowed to be employed with the authorized apparatus. Other equipment designs were subjected to higher pressures. The initial readings by pressure hydrometer were not density measurements, but rather uncorrected hydrometer readings. Readings were taken on a hydrometer at the reference temperature of 15°C, and then corrected for the meniscus effect, thermal glass expansion effect, alternate calibration temperature effects, and to the reference temperature using calculations and Adjunct to D1250

Guide for Petroleum Measurement Tables (API MPMS Chapter 11.1) or API MPMS Chapter 11.2.4 (GPA TP-27), as applicable [27].

ASTM D1267 applies to the determination of gauge vapor pressures of LPG products at temperatures ranging from 37.8 °C (100 °F) to 70 °C (158 °F) [28]. In this case, 37.8 °C (100 °F) was considered as a reference for measuring vapor pressure. Furthermore, inside pressure volume and net weight were determined by laboratory instrumentation. The following properties [29] were considered for analysis and calculation of calorific value of the samples.

Table 3: Chemical properties of Propane, n-Butane and Isobutane.

Sl. No.	Chemical Property	Propane (C₃H₈)	n-Butane (C₄H₁₀)	Isobutane (C₄H₁₀)
01.	Energy Content (MJ/kg)	49.58	47.39	45.59
02.	Boiling Temp: °C	-42	-0.4	-11.75
03.	Flame Temp: °C	1967	1970	1975
04.	Gas Volume: m ³ /kg	0.540	0.405	0.402
05.	Relative Density: H ₂ O	0.51	0.58	0.60
06.	Relative Density: air	1.53	2.00	2.07
07.	L per kg	1.96	1.724	1.669
08.	Density @ 15°C: kg/m ³	1.899	2.544	2.533

Since constituents other than C₃ and C₄ contribute a very small amount in the composition of LPG (less than 1%), they were omitted in the calculation of calorific values for the samples.

For secondary data, analytical reports of LPG were collected from different LPG companies available in BD and their supplier. This quality reports are mandatory for the shipment of LPG which are produced by foreign laboratories.

4. Result and Discussion

Currently, there are 60 companies (approx.) who got licenses for LPG business. Among them approximately 30 companies are in operation. The business is mostly run by the private sector which holds approximately 99% of the share. Their plants are mostly located near Chattogram port or Mongla port. Very few of the companies produce LPG locally. They mostly rely on imports. LPG is imported from countries like Kuwait, UAE, USA, Singapore, Malaysia, Indonesia, India etc. They arrive mostly in premixed condition. Later on, LPG is bottled in the available plants located in Bangladesh. From laboratory test of three samples using the method ASTM D2163, the following composition was found.

Table 4: Composition of LPG from primary samples

Sl. No.	Name/Composition	Sample 1	Sample 2	Sample 3
Composition, mol%				
01.	C ₁ , Methane	0.044	0.039	0.020
02.	C ₂ , Ethane	0.152	0.141	0.139
03.	C ₃ , Propane	40.511	40.330	32.771
04.	C ₄ , Isobutane	30.793	30.040	31.945
05.	C ₄ , n-butane	28.354	29.288	35.022
06.	C ₅ , Isopentane	0.122	0.152	0.099
07.	C ₅ , n-Pentane	0.006	0.004	0.004
08.	C ₆	0.018	0.005	0.000
Total		100.00	100.00	100.00

From secondary source, the following data in Table 5 and 6 was obtained.

Table 5: Composition of LPG from secondary samples (1-3)

Test Items	Unit	Method	Sp1	Sp2	Sp3
C ₂ , Ethane	wt%	ASTM D2163	0.37	0.37	0.20
C ₃ , Propane	wt%	ASTM D2163	29.64	29.63	34.68
C ₄ , Butane	wt%	ASTM D2163	69.66	69.67	64.83
C ₅ , Pentane	wt%	ASTM D2163	0.33	0.33	0.29
Total Sulphur	ppm	ASTM D6667	8	8	15

Table 6: Composition of LPG from secondary samples (4-7)

Test Items	Unit	Method	Sp4	Sp5	Sp6	Sp7
C ₂ , Ethane	wt%	ASTM D2163	0.20	0.28	0.29	-
C ₃ , Propane	wt%	ASTM D2163	34.67	34.59	34.69	33.67
C ₄ , Butane	wt%	ASTM D2163	64.84	64.86	64.89	66.24
C ₅ , Pentane	wt%	ASTM D2163	0.29	0.27	0.13	-
Total Sulphur	ppm	ASTM D6667	15	5	16.97	12.60

Table 4 shows that LPG is composed of propane, isobutane and n-butane mostly. The three components contribute above 99% of the total mixture. The following Figure 2 shows the comparison of percent composition among the three samples. It shows two of them contain propane by 40% approximately whereas sample 3 contains about 33%. From Table 3 it is evident that propane has a higher energy content by weight than n-butane or isobutane. In comparison with butane (-0.4 °C), propane's boiling point (-42°C) is lower. This property makes propane a suitable choice for colder climate. Though it contains more energy, only propane as LPG is not suitable for Bangladesh. Based on the climate of BD, LPG mixture containing more butane is preferred.

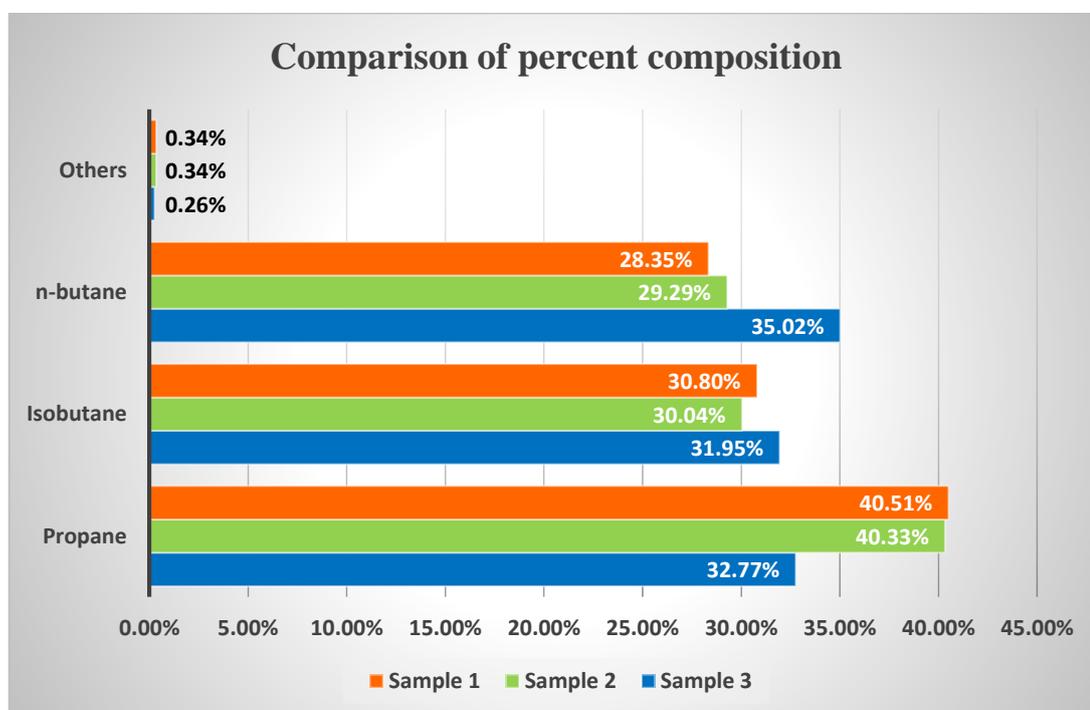


Figure 3: Comparison of percent composition of LPG primary samples.

In Figure 3, a comparison of percentage of propane in secondary samples is shown. In Fig 4, percentage of Butane in secondary samples is shown.

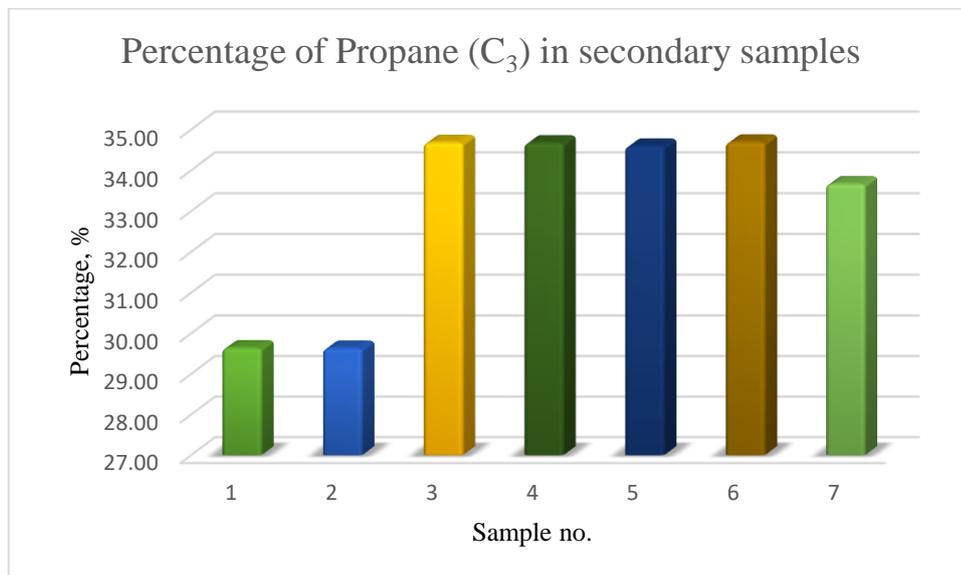


Figure 4: Percentage of Propane (C_3) in secondary samples.

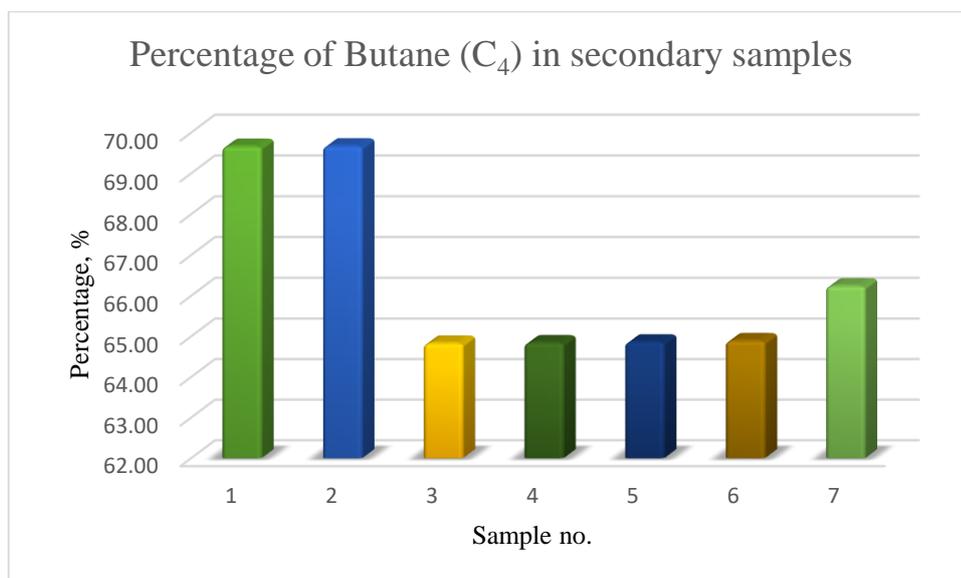


Figure 5: Percentage of Butane (C_4) in secondary samples

Analyzing the data provided by the companies and supplier of LPG in BD it is seen that the mixture contains propane within a range of 29-35% and Butane by 64-70%. The Propane-Butane ratio for the primary samples are shown in the following Table 7. It is observed that sample 1 and sample 2 are very close whereas sample 3 contains more butane with a ratio of 32.77:66.96.

Table 7: Propane Butane ratio of LPG primary samples.

Sl. No.	Name	Propane : Butane
01.	Sample 1	40.51 : 59.14
02.	Sample 2	40.33 : 59.33
03.	Sample 3	32.77 : 66.96

In Table 8, propane butane ratio from secondary samples are shown. It is seen that the propane butane ratio tends to maintain 35:65 excluding others.

Table 8: Propane Butane ratio of LPG secondary samples.

Sl. No.	Name	Propane : Butane
01.	Sample 1	29.64 : 69.66
02.	Sample 2	29.63 : 69.67
03.	Sample 3	34.68 : 64.83
04.	Sample 4	34.67 : 64.84
05.	Sample 5	34.59 : 64.86
06.	Sample 6	34.69 : 64.89
07.	Sample 7	33.67 : 66.24

The price of propane and butane plays a key role here. The price is set by Saudi Aramco which fluctuates on a regular basis. Since our LPG industry is almost import based, a price hike provokes the consumers to an alternative. Calculating the energy content of the primary samples, we can see from the following Figure 3, sample 1 and 2 contains approximately 47.56 KJ/Kg whereas sample 3 contains 47.41 KJ/Kg.

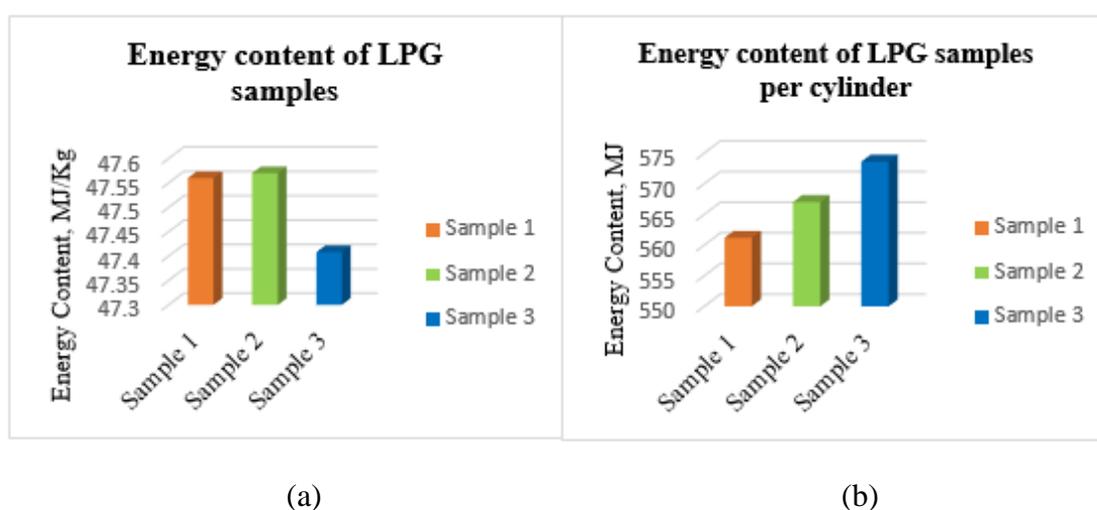


Figure 6: Comparison of energy content of LPG primary samples.

Though energy content per Kg of fuel in Figure 5(a) is less for sample 3, it is much greater in Net energy content in Figure 5(b). This is because Sample 3 had more LPG by weight in the cylinder. It was found sample 1 and 2 (12 kg cylinders) were carrying slightly less amount of LPG. So, it is required to make sure they carry the proper amount.

Moreover, LPG is used as automotive fuel now a days and its use is increasing day by day. LPG containing branched hydrocarbons show better performance as a fuel. From Table 9 it is seen that the primary sample 1 contains 30.915%, sample 2 – 30.192% and sample 3- 32.044% of branched hydrocarbons. So, sample 3 is containing more branched hydrocarbons than the other two.

Table 9: LPG (primary) mixtures containing branched hydrocarbons.

Name	Sample 1	Sample 2	Sample 3
C₄, Isobutane	30.793%	30.040%	31.945%
C₅, Isopentane	0.122%	0.152%	0.099%
Total	30.915%	30.192%	32.044%

Moreover, the research octane number (RON) is relatively higher for isobutane and isopentane which is a key indicator for anti-knock ability for a SI engine. Thus the LPG richer in branched hydrocarbons will perform much better.

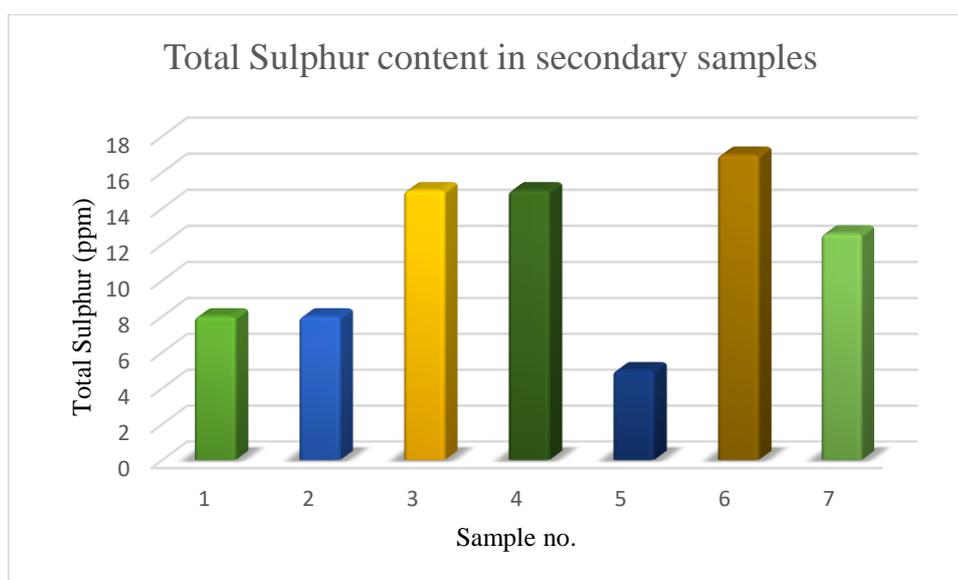


Figure 7: Total Sulphur content in LPG secondary samples

In Fig. 6 total Sulphur content in LPG secondary samples are shown. For Automobile uses the Sulphur content should be below 40 ppm. From the figure it is seen that the amount of Sulphur is well below the margin and very less in the samples.

Along with these, from laboratory testing the following data in Table 10 was found.

Table 10: Various chemical properties of LPG primary samples.

Sl. No.	Description	Sample 1	Sample 2	Sample 3
01.	Density @ 15 °C, Kg/L	0.550	0.549	0.551
02.	Vapor Pressure @ 37.5 °C, psi	84	87	79
03.	Inside Pressure, psi	63	65	60
04.	Inside Temperature, °C	29.1	29.2	29.2
05.	Volume, L	21.45	21.68	21.96

From Table 10 it is seen that all the properties are very close to each other for respective primary samples. Very minute variation is observed among the samples tested. Moreover, from the above data it is seen that impurities or chemicals other than propane and butane constitute a very less amount in LPG which is below 1%. So, the effect of impurities is minimum for different usages and environment.

5. Conclusion and Recommendations

In the context of Bangladesh, LPG market is growing day by day. Since LPG is a clean fuel, people/industries are trying to adopt this fuel. Considering the weather of Bangladesh, the Propane-Butane ratio should be kept within the range of 60:40-70:30 and in this study it is found that the LPG samples are maintaining propane-butane ratio within the range. Moreover, LPG is being used as Autogas for automobiles. LPG enriched in branched hydrocarbons performs better as automobile fuel. A considerable amount of branched hydrocarbon is found in LPG samples which is good for IC engines. It was found that impurities or substances other than propane and butane make up a very small percentage of the total, less than 1%. As a result, they have a minimal impact on various applications and environments.

Since, natural gas resource is depleting in Bangladesh and a clean fuel like LPG is an alternative choice for household purpose, an introduction of reticulated gas system or piped gas system for LPG can be a subject of future study. This system may reduce LPG transportation cost and related hazards.

In addition, LPG market in BD is almost import based and above 99% of the share is controlled by private sector. Since the price is regulated by International market and it has a tendency to fluctuate within a short span of time, it will be a challenge to introduce such facility and consider LPG as a primary fuel for household.

Again, due to unavailability of a deep sea port, larger vessels or ships cannot come to the shore. If a deep sea port is provided, transport cost will reduce and it may help keeping LPG price stable in the market. Considering all these, the following recommendations can be made-

- To increase the amount of branched hydrocarbon which will improve the quality of the LPG fuel.
- To consider reticulated gas system or piped gas system for LPG which will reduce transportation cost and hazards.
- To keep the impurities at minimum level especially Sulphur.
- To increase the facility for LPG production.

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Study on the Physiochemical Properties of Liquefied Petroleum Gas Available by Cylinders in Bangladesh

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Abstract: The work analyzed the composition and other physiochemical properties of liquefied petroleum gas (LPG mixture available in Bangladesh by cylinder. LPG Composition (C₂-C₆), Butadiene, Total Sulfur, Cu Corrosion, Relative Density and Vapor Pressure were determined by respective ASTM methods. Free water content was measured visually and odour tested by smell detection. Data from nine samples were used to compare with ASTM and Indian Standards. The results of this analysis revealed that the LPG contains propane and butane with a certain range of ratio. But that has no free water content. The total Sulfur content is within the permissible limit according to ASTM Standards. The samples do not have corrosive hydrogen sulfide. The vapor pressure is lower than the maximum limit and have very low linear relationship with relative density. The calorific value is highly dependent on the propane and butane content and moderately related to the relative density. Compared to ASTM and Indian standards, the examined LPG mixtures are found to be safe for the tropical country.

Keywords: LPG mixture, physiochemical properties, propane-butane ratio, calorific value of LPG.

I. Introduction

Liquefied petroleum gas (LPG) is a valuable energy source used worldwide for numerous business applications in industry and transportation. The largest market for LPG is the residential/commercial market, followed by the chemical industry, where it is used as a petrochemical feedstock and agriculture [1]. LPG is a pressurized fuel gas that contains a mixture of hydrocarbon gases, most commonly propane (C₃H₈) and butane (C₄H₁₀). It is pressurized in the form of a liquid and stored in a steel container or cylinder for sale or commercial use. The types of LPG sold and purchased worldwide mainly include propane (C₃H₈) or butane (C₄H₁₀). In the polar climate region of Northern Hemisphere, the mixture contains more propane in winter, while it contains more butane in summer since propane has a lower boiling point of -42°C compared to -0.4°C for butane [2].

The demand for liquefied petroleum gas (LPG) in Bangladesh is very high. The JICA survey team made various assumptions, such as all the new housing except existing natural gas pipeline connections will be forced to use LPG, the demand for gasoline will grow faster, and the demand will be partially met by LPG. The growth rate in 2041 is increasing dramatically and is 15 times higher than in 2016 [3]. In the public sector, 12,361 tonnes have been produced in the financial year 2021-22, while 1,531,231 tonnes imported by private companies. Therefore, the public and private sectors together market 1.54 million tonnes of LPG, which meets a certain part of the country's LPG demand [4]. But according to the LPG Operators Association of Bangladesh (LOAB), the country's annual LPG consumption has been reached about 1.8 million tonnes. To meet this demand, about 27 LPG operators are presently catering in Bangladesh [5]. Different operators distribute LPG with different limits of certain specification. In this study, the LPG specifications of different operators have been compared with ASTM Standards and the respective calorific values and propane and butane ratios were examined to acquire knowledge regarding the LPG available in Bangladeshi market. The ASTM Standard Specification covers the products commonly referred to as liquefied gases, consisting of propane, propene (propylene), butane and mixtures of these materials. To cover common areas of application, four basic types of liquid gases are available. This specification applies to products intended for use as residential, commercial and industrial heating and fuels [2].

This article examines the composition and other physiochemical properties of LPG available in Bangladesh and compares with the ASTM and Indian Standards. The aim is to collect information about the LPG available in Bangladeshi market as there is no or very few studies on this topic. The study was also conducted for the validation and future reference.

II. Literature Review

LPG production did not begin until around 1904, almost 40 years after oil and gas production began in North America around 1860. By 1900, natural gas (methane) cooking and lighting appliances were ubiquitous, but the gaseous fuel was difficult to transport [2]. Compressed natural gas (CNG) could neither be transported nor stored in the large pressure vessels of the time. For mobile and remote gas applications, LPG is the best fuel. At average ambient temperatures and mild pressures (250 psig), it is a fluid of high calorific value (BTU) that is easy to store and transport. Once vaporized, it can be used in natural gas appliances that convert into gaseous LPG mixtures with minor adjustments to the air/fuel ratio. Without any standardization or regulatory

restrictions, the industry's early years were characterized by the need to address immediate problems. One of the first consumer goods to be transported and sold in pressure vessels, was liquefied natural gas. Manufacturing, transporting and ultimately selling to the general population presented numerous economic and technical obstacles. The industry has been a leader in several areas of research and development, from manufacturing techniques, equipment and devices to analytical testing methods for composition and properties. The results were (in hindsight) predictable and there were many excesses. However, marketing and regulatory constraints ensured that the new business flourished in a short period of time [2].

LPG is produced by refining petroleum (crude oil) or extracting streams of petroleum or natural gas that emerge from the ground. Walter O. Snelling created it in 1910 and the first commercial goods hit the market in 1912. It currently produces about 3% of total energy consumption and burns relatively cleanly, with no soot and very little sulfur. Because it is a gas, it does not pollute the soil or water, but it can pollute the air. LPG (propane) has a specific calorific value of 46.1 MJ/kg, compared to 42.5 MJ/kg for heating oil and 43.5 MJ/kg for premium grade gasoline [6].

However, its energy density per unit volume is lower than that of gasoline or heating oil at 26 MJ/L due to its lower relative density (approximately 0.50 - 58 kg/L compared to 0.71 - 0.77 kg/L for gasoline/gasoline). Since the density and vapor pressure of LPG (or its components) change significantly with temperature, this fact must be taken into account whenever the application involves safety or custody transfer operations [7].

LPG is an excellent fuel for cooking due to its higher calorific value, good stove efficiency, low cost and environmentally friendly properties. The simple and precise control of the liquid gas stove not only makes cooking easier, but also saves time. Due to increasing urbanization, both urban and rural communities are increasingly reliant on LPG. Since it is very costly to extend gas distribution networks to remote areas, LPG is the perfect choice for household cooking [8]. A comparison of the calorific values of LPG and various cooking fuels [9] is shown in table -1.

Table 1 Calorific values of various fuels [9].

Name of the Fuel	Calorific value (KJ/kg)
Wood	14400-17400
Charcoal	29600
Kerosene Oil	41000
LPG	45750

III. Sampling and Analytical Procedures

A random sampling method was used for laboratory testing and primary data collection. Three LPG cylinders of different brands/companies (available in Bangladesh) were collected from the local market on the same day. All of the three samples (named S1, S2 and S3) were 12kg LPG cylinders. The samples were prepared in the laboratory on the same day and went through the specification/method (table 2) for testing and data collection. In this study, secondary data for six samples (named S4, S5, S6, S7, S8 and S9) were used which were collected from different LPG companies available in Bangladesh and their supplier. They have supplied their analytical reports which were also done by the same analytical procedures.

Table 2 Testing methods for data collection.

Serial no.	Description of Test	Method
01	LPG Composition (C ₂ -C ₆)	ASTM D2163
02	Butadiene	ASTM D2163
03	Total Sulfur	ASTM D6667
04	Free Water	Visual
05	Cu Corrosion	ASTM D1838
06	Relative Density	ASTM D1657
07	Vapor Pressure	ASTM D1267
08	Odour	Smell

Gas chromatography was used to determine hydrocarbons in liquid gases and propane/butane mixtures according to ASTM D2163 (the official designation for this standard). This method applies to the determination of the number of individual hydrocarbons in liquefied petroleum gas and propane-propene/butane mixtures, with the exception of high-purity propene in the range C₂ to C₅. The concentrations of the components are measured in the range from 0.01 to 100% [10]. To properly characterize the LPG sample, additional testing like infrared (IR) spectroscopy, gravimetry, gas chromatography with flame ionization detection etc. are required as the test conducted is unable to identify hydrocarbons heavier than C₅ as well as non-hydrocarbon components.

ASTM D1657 is a standard test method for measuring the density or specific gravity of light hydrocarbons using a pressure hydrometer. This test method is used to determine the density or specific gravity of light hydrocarbons such as liquefied petroleum gases (LPG) with the vapor pressures greater than 101.325 kPa (14,696 psi). At the test temperature, materials with a vapor pressure greater than 1.4 MPa (200 psi) must not be used with the approved device. Higher pressures can apply to other equipment designs for measuring the density of Castor oil, silicon oil, propylene glycol, ethylene glycol, and ethanol etc. [11]. The initial readings from the pressure hydrometer are not density measurements, but rather uncorrected readings from the hydrometer. Readings are taken with a hydrometer at a reference temperature of 15°C and then corrected to the reference temperature using calculations and the addition to the D1250 Guide to Petroleum Measurement Tables (API MPMS) for the meniscus effect, thermal glass expansion effect, alternative calibration temperature effects and Chapter 11.1 or API MPMS Chapter 11.2.4 (GPA TP-27), if applicable [12]. ASTM D1267 applies to the determination of gauge vapor pressure of LPG products at temperatures from 37.8°C (100°F) to 70°C (158°F) [13]. In this case, 37.8 °C (100 °F) was considered as a reference for measuring vapor pressure. In addition, the internal pressure volume and net weight were determined by laboratory instruments.

ASTM D1838 is the standard method for copper corrosion testing to determine compounds in liquid gases with a vapor pressure greater than 124 kPa at 37.8 °C that may be corrosive to copper. Copper corrosion limits provide assurance that problems will not occur with deterioration of the copper and copper alloy fittings and connections of equipment commonly used in production, treatment, processing, storage and transportation operations in the oil industry. For the ASTM D1838 copper corrosion test method, a polished copper strip is immersed in approximately 100 mL of the sample and exposed to a temperature of 37.8 °C (100 °F) for 1 hour in a cylinder capable of withstanding a hydrostatic pressure of at least 6900 kPa or 1000 psig [14]. The copper strip is cleaned and inspected for signs of deterioration. The results are evaluated by comparing the spots on the copper strip to the ASTM color match scale of 1A to 4C. A rating of 1A is given for the appearance of freshly polished copper coupons with slight but barely noticeable discoloration. The 1B rating indicates a slight haze, and the ratings go further down the scale as the corrosion discoloration of the test piece increases, with 4C being the worst and typically appearing as a heavily corroded, blackened and pitted specimen.

Propane has a lower boiling point of -42°C compared to -0.4°C for butane. Therefore, propane will continue to evaporate in colder climates [15]. The calorific value of LPG refers to the amount of thermal energy released from a given volume of fuel. Liquefied gas consists of the main components propane and butane, which have a calorific value of around 46 MJ/kg and 49 MJ/kg respectively [16]. Hence the calorific values of LPG mixtures of samples were calculated as $CV = (46 \times \text{Propane } \%) + (49 \times \text{Butane } \%) \text{ MJ/kg (1)}$

Since constituents other than C₃ and C₄ contribute a very small amount in the composition of LPG (less than 1%), they are omitted in the calculation of calorific values for the samples.

IV. Results and Discussion

The results from laboratory test and secondary data sheets are depicted here in the following tables. Table -3 shows the composition of LPG of the analyzed samples. Table-4 shows other physiochemical properties of the analyzed samples. Table 3 shows that LPG is mostly composed of propane and butane. These two components contribute more than 99% of the total mixture. The propane and butane ratio of the analyzed samples ranges from 29.63:69.67 to 40.511:59.147. The primary data reflects that the propane content ranges from 32.771 to 40.511 mol percent. Sulphur content ranges from 13 to 15 ppm. The minimum vapor pressure is 544.69 and maximum vapor pressure is 599.84 KPa. Relative density ranges from 0.549 to 0.551 kg/L. Calorific value ranges from 47.62 to 47.89 MJ/kg. The secondary data reflects that the propane content ranges from 29.63 to 34.69 mol percent. Sulphur content ranges from 5 to 16.97 ppm. The minimum vapor pressure is 583.49 and maximum vapor pressure is 667.8 KPa. Relative density ranges from 0.5506 to 0.5535 kg/L. Calorific value ranges from 47.6928 to 47.7681 MJ/kg. The free water content is null for both primary and secondary samples. All the primary and secondary data show that the butadiene is less than 0.01 of mol percent, residue on evaporation is less than 0.05 ml/100 ml. The cu corrosion reflects 1A for all the samples.

There are ASTM D1835 and Gas Processors Association GPA 2140 specifications for commercial propane-butane blends, but these are rarely used for consumer applications in North America. There is no current Canadian General Standards Board (CGSB) specification for propane-butane blends because winter temperatures are too cold and butane demand for winter gasoline production is high. In polar climates, propane must be used year-round to ensure low temperature operation. Tropical climates (no winter temperatures, no winter gasoline) tend to use propane-butane blends year-round to utilize the butane. In temperate climates with large seasonal temperature fluctuations, propane could be used in winter and propane-butane mixtures in summer [17].

Some countries have either 100% propane (Australia & USA). An LPG gas mixture of 60:40 propane: butane is used in New Zealand & Belgium. The percentage of propane and butane (propane : butane) in LPG around 35:65 is used in India, Spain & Hungary [15]

Table 3 Composition of LPG of analyzed samples.

Sl. No.	Test Parameter	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6	Sample 7	Sample 8	Sample 9
1	C ₂ , Ethane (mol%)	0.152	0.141	0.139	0.2	0.2	0.28	0.37	0.37	0.29
2	C ₃ , Propane (mol%)	40.511	40.33	32.771	34.68	34.67	34.59	29.64	29.63	34.69
3	C ₄ , Butane (mol%)	59.147	59.328	66.967	64.83	64.84	64.86	69.66	69.67	64.89
4	Pentane (mol%)	0.128	0.156	0.103	0.29	0.29	0.27	0.33	0.33	0.13
5	Propane : Butane	40.511 : 59.147	40.33 : 59.328	32.771 : 66.967	34.68 : 64.83	34.67 : 64.84	34.59 : 64.86	29.64 : 69.66	29.63 : 69.67	34.69 : 64.89
6	Total Sulfur (ppm)	14	15	13	15	15	5	8	8	16.97
7	Butadiene (mol%)	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
8	Residue on Evap. @ 38 Deg C (ml/100ml)	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05

Table 4 Physio Chemical Properties of Analyzed Samples.

Sl. No.	Test Parameter	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6	Sample 7	Sample 8	Sample 9
1	Vapor Pressure @ 37.8 Deg C (KPA)	579.16	599.84	544.69	620.02	620.02	620.85	583.49	583.49	667.8
2	Relative Density @ 37.8 Deg C (kg/L)	0.55	0.549	0.551	0.5524	0.5526	0.5506	0.5552	0.5535	0.5507
3	Free water	Nil								
4	Cu Corrosion, 1H@37.8	1A								

	Deg C									
5	Odour	Detectable								
6	Calorific value MJ/kg	47.61709	47.62252	47.88849	47.7195	47.7198	47.6928	47.7678	47.7681	47.7535

In comparison with butane (-0.4 °C), propane’s boiling point (-42°C) is lower. This property makes propane a suitable choice for colder climate. Only propane as LPG is not suitable for Bangladesh considering heating value, price and safety issue and climatic condition. Being a tropical country, LPG mixture containing more butane is preferred in Bangladesh. A simple comparison among propane and butane ratio of analyzed samples and commonly used ratio in India, Spain and Hungary is depicted in figure 1. Figure 1 reflects that propane and butane ratio of the samples named S4, S5, S6 and S9 are very close to the commonly used ratio in India, Spain and Hungary. The samples S1 and S2 contain more propane but samples S3, S7 and S8 contain more butane.

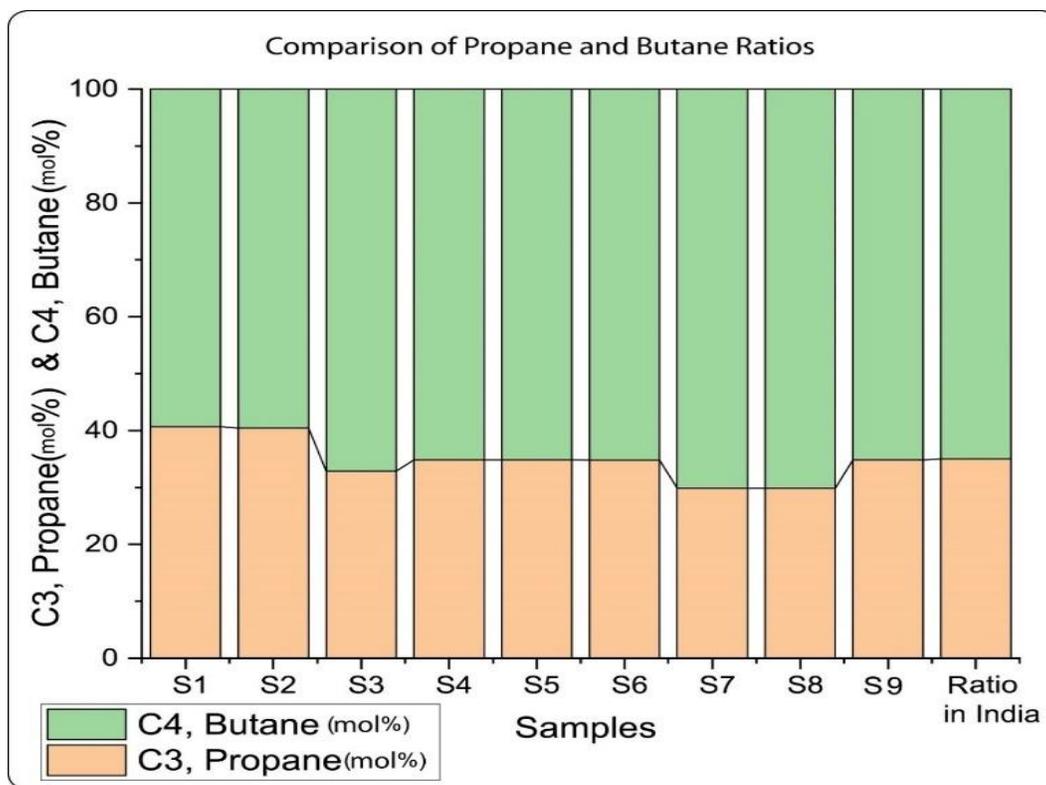


Fig. 1 A simple comparison of propane and butane ratios among the analyzed samples and referenced ratio used in India.

Sulfur can be present in liquid gas in the form of hydrogen sulfide, carbonyl sulfide, carbon disulfide and mercaptan. All forms can be present in the same liquid. Sulfur contamination not only leads to odour problems, but can also form unwanted oxides during combustion and pollute the environment [1], [18]. As per the ASTM standards the permissible sulfur content in LPG mixture is 140 ppm [19] and The Indian Standard limits the sulfur content up to 150 ppm [20]. But Automotive LPG fuel standards in Korea permit maximum 40 ppm which was 100 ppm before 2009 [21]. Table-3 shows that sample 9 contains maximum level of sulfur as 16.97 ppm. The sulfur contents of LPG mixtures available in Bangladesh compared to ASTM, Korea and Indian standards are shown in figure-2. Figure-2 shows there are very low sulfur content in the LPG mixtures available in Bangladesh.

Pentane and heavier hydrocarbons (C₅ + , condensate) are liquids at ambient temperature and pressure [22]. According to ASTM standards the maximum permissible limit of pentane and heavier hydrocarbons in LPG mixture is 2.0% [23]. But in Indian standards it is about 2.5% [20]. Pentane and heavier hydrocarbons content ranges from 0.103 to 0.33 percent (figure-3) which is far less than the ASTM, Korean and Indian standards.

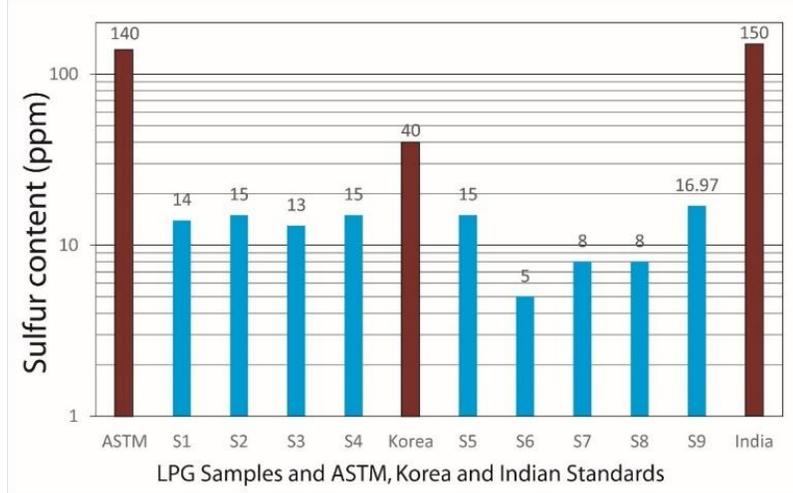


Fig. 2 The sulfur contents of LPG mixtures available in Bangladesh compared to ASTM, Korea and Indian standards

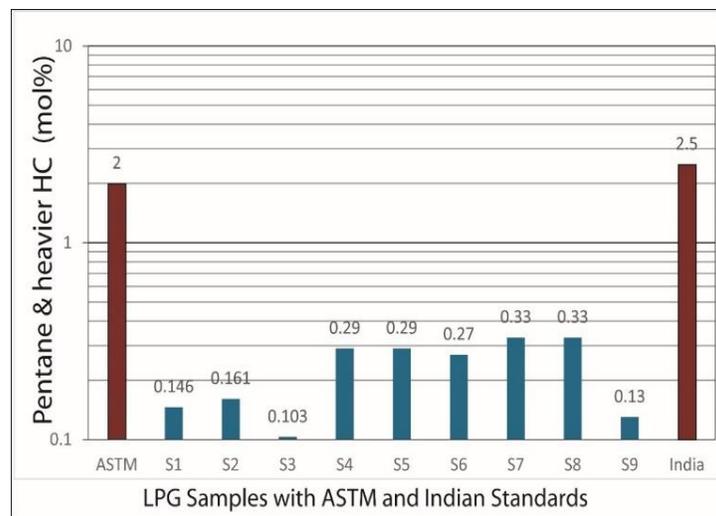


Fig. 3 The pentane contents of LPG mixtures available in Bangladesh compared to ASTM and Indian standards.

The butadiene is a minor component of the LPG product. Butadiene is a dangerous chemical that can cause cancer and genetic defects when inhaled [24] - [26]. The LPG plant operator are facing problem that imports LPG compositions from external sources containing quantities of butadiene that exceed the legal limit of 0.5%. LPG compositions containing a butadiene content of more than 0.5% are considered out of specification, while butadiene contents of less than 0.5% are considered to be on specification [27]. Another reason for limiting the butadiene content in LPG is that butadiene has a higher explosion limit than propane and butane. The higher the butadiene concentration in the liquid gas, the higher the explosion limit [28]. Table-3 shows that the concentrations of butadiene in all samples are less than 0.01% (mole) which are within the safe limit.

According to ASTM and Indian Standards, the LPG mixtures should have no free water content. The examined samples have no free water content as shown in table-3.

The composition of the LPG residue varies with the variation of the LPG composition, especially its impurities and their content[29]. According to ASTM standards, the maximum limit the residue on evaporation of 100 mL LPG at 38 degree Celsius is 0.05 mL. All the samples show the residue on mentioned condition remains below 0.05 mL (table-3).

LPG has a distinct smell that warns of leaks. Generally, LPG is odourized by adding mercaptans. Its odour is detectable in the air at concentrations up to one fifth of the lower flammability limit. In other words, it can be smelled enough before it becomes dangerous enough to catch fire [30]. All the samples had the detectable odour.

The copper corrosion limits are designed to ensure that there are no problems with deterioration of copper and copper alloy fittings and connections commonly used in many types of utility, storage and transportation equipment. The copper corrosion test detects the presence of hydrogen sulfide, which is highly corrosive. However, the result of copper corrosion has no connection with the total sulfur content. The copper corrosion limits also provide assurance that the LPG does not contain H₂S in quantities such that it poses a health and safety risk when the product is known not to contain corrosion inhibitors or other chemicals that reduce the reaction with the copper strip [23]. According to ASTM and Indian standards, the Copper strip corrosion at 38°C for 1

hour should not worse than rating No. 1. All the samples show rating No. 1A for the copper corrosion test at 38°C for 1 hour. The samples don't have H₂S in quantities such that it poses a health and safety risk.

Although there are no specific requirements for density or relative density, it may be needed for other purposes and should be reported. In addition, the specific gravity of the propane and butane mixture is needed to determine the allowable maximum vapor pressure [23]. The relative density @37.8 Deg C (kg/L) have been reported for all the samples with a range from 0.549 to 0.555 kg/L (table 4).

Vapor pressure is an indirect measure of the most extreme low temperature conditions under which initial vaporization is expected. It can be viewed as a semi-quantitative measure of the amount of the most volatile material present in the product. It can also be used as a means of predicting the maximum pressures that may occur at LPG cylinder temperatures. The maximum standards of vapor pressure at 37.8 °C (100 °F) in LPG mixture is about 1435 kPa [23]. The analyzed samples had the vapor pressure at 37.8 °C (100 °F) in the range between 544.69 and 667.8 kPa. A diagram of vapor pressure vs relative density of the analyzed samples is illustrated in figure 4 which shows very low linear relationship between them.

The calorific value (sometimes called as heating value) is the quantity of heat produced by its combustion at constant pressure and under normal temperature and pressure. Figure 5 shows that the calorific values against the butane content of the examined samples have the Pearson's ratio 0.78 which indicates there is high positive linear correlation among them. While the propane content has high negative linear relationship with calorific values (figure 6). The calorific values against the relative density of the tested samples show moderate positive linear relationship (figure 7).

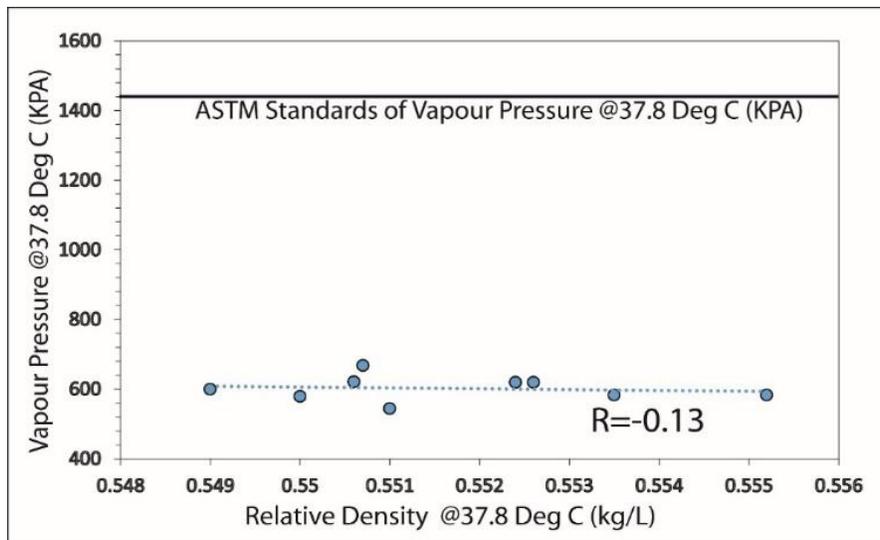


Fig. 4 The vapor pressure against relative density of the examined LPG mixture.

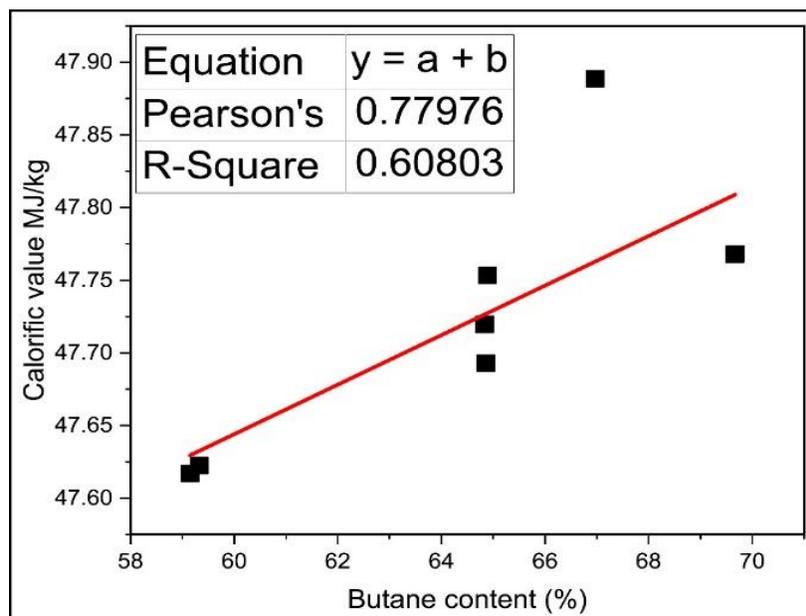


Fig. 5 The calorific value of the examined LPG against butane content.

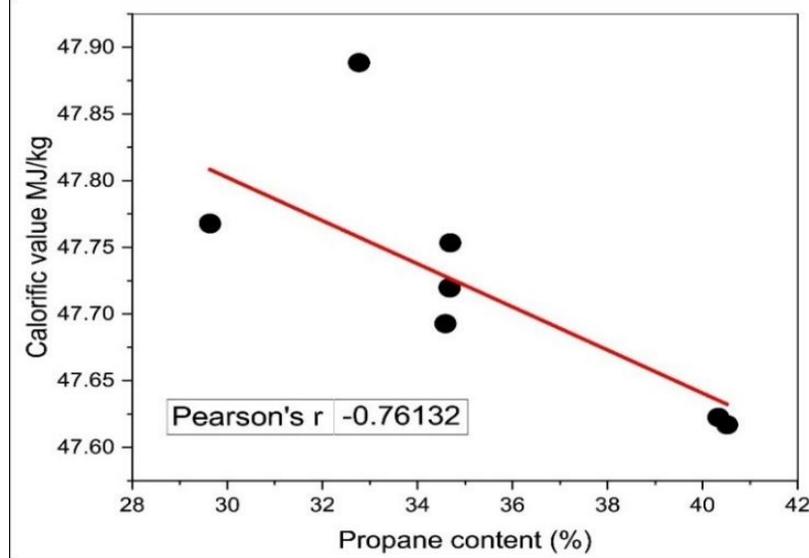


Fig. 6 The calorific value of the examined LPG against propane content.

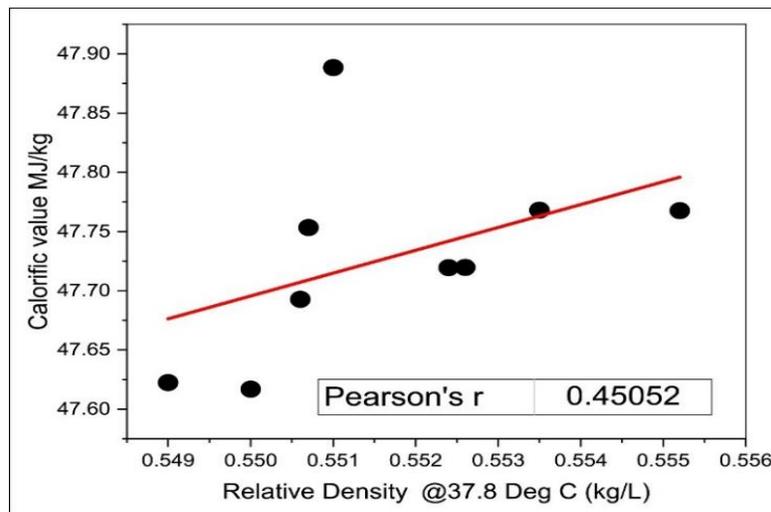


Fig. 7 The calorific value of the examined LPG against relative density.

V. Conclusion

Considering the weather of Bangladesh, the propane-butane ratio of LPG is kept within the range of 40:60-30:70 which is nearly similar to Indian tradition of using propane-butane ratio. There is no free water content. There is very low sulfur content in the LPG mixtures in comparison to the ASTM, Korea and Indian standards. The pentane and heavier hydrocarbon content are much lower than the Indian and ASTM standards. The butadiene has been detected very less than its tolerable limit. The distinct smell of the LPG is easily detectable. The residue on evaporation is within the permissible limit. The LPG does not contain highly corrosive H_2S in quantities such that it poses a health and safety risk. The vapor pressure exerts within the permissible limit and has very low linear relationship with the relative density. But the relative density has moderate positive linear relationship with the calorific value of the tested LPG mixture. The calorific value is also highly correlated positively with butane content and negatively with propane content. Comparison of standard value and existing value of composition and other physicochemical properties of LPG available in cylinders in Bangladesh shows that the LPG mixtures are within safe limit.

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