

# Pressure-Temperature Diagram Analysis of Liquefied Petroleum Gas and Inspection of Retrograde Phenomenon

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**Abstract** – The study on P-T (Pressure-Temperature) diagram of liquefied petroleum gas (LPG) is an important thermodynamic characteristic regarding LPG storage, retrograde phenomena, vapour liquid equilibrium, heating value and BLEVE (Boiling Liquid Expanding Vapour Explosion) phenomena. Nevertheless, the quantitative and detail study on the P-T diagrams for various compositions of LPG is still in great scarcity. Hence, the P-T diagram of LPG is analyzed extensively in the present study. Aspen-Hysys process simulator is used to generate the P-T diagram of LPG. From these P-T diagrams retrograde phenomenon is analyzed extensively for different temperature and pressure which is a very important criterion for LPG storage and maintaining proper vapour pressure in the storage tank and in the supplied bottle. Explanations of the observed effects are also provided in this study. The present study will help the researchers, manufacturers, bottlers, and distributors of LPG to a great extent

**Keywords** –P-T Diagram, Retrograde Phenomenon, Cricondentherm, Cricondentherm, Aspen HYSYS.

## 1. Introduction

Fuel crisis is a major problem in Bangladesh. Natural gas is the prime source of energy in our country. Since it is being used in the sectors of power, industrial, commercial, domestic, automobile, etc largely, the reserve of natural gas is reducing rapidly. As exploration of new gas fields in Bangladesh is not going as expected, it will not be possible for natural gas to fulfil the demand of energy solely after a decade <sup>[1]</sup>. From this scenario the necessity of finding new source of energy is felt. Liquefied petroleum gas, LPG, is a mixture primarily of propane and butane with a negligible addition of pentene, hexen and mercaptan derivatives. LPG has already been proved as an effective alternative domestic fuel in Bangladesh. To popularize the uses of LPG, fundamentals research on various aspects is required. P-T diagram is very important thermodynamic aspect of any combustion-fuel indicating the fuel quality. There are no quantitative and detail research based study on the P-T diagram of LPG available in our literature to provide accurate data to LPG manufacturer, importer, distributor and supplier. Therefore, the objective of the present study is to study the P-T diagram of LPG. Aspen-HYSYS process simulator is used to generate P-T data..

## 2. Literature Review

LPG is getting popular day by day as a domestic fuel. Among the various thermodynamics data, P-T diagram of LPG is very important for storage purpose. Cricondentherm, Cricondenbar and Retrograde Phenomenon are very important tools to analyze P-T diagram of LPG. Unfortunately there are no such extensive works done on these topics previously by the researchers. So this work will help the manufacturers, importers and bottlers to get a complete analysis on P-T behavior of LPG. Eventually this work will be very useful to maintain proper vapor pressure and avoid BLEVE in bottling and storage plant of LPG. The definition of Cricondentherm, Cricondenbar and Retrograde Phenomenon will be discussed in findings and discussion section.

## 3. Methodology

Study of P-T (Pressure-Temperature) diagram of LPG is an experimental procedure but pure experimental setup to generate data to generate P-T diagram for LPG is rarely available and very tough procedure. Hence the simulation method, which is comparatively easier and accurate, is adopted to produce pressure and temperature data to generate P-T diagram. A LPG stream is created in Aspen-HYSYS 7.1 process simulator. The simulation and P-T diagram preparation is briefly stated here. A new

file in aspen-hysys is opened and a package unit is chosen from preference tab. The primary components (e. g. propane, butane etc.) are selected from the component tab. Subsequently, a fluid package which is essential to calculate various physical and process data is selected. In this case Peng-Robinson is selected from the fluid package tab because this fluid package is specially designed to handle hydrocarbons. After entering into the simulation environment a material stream is taken from object pellet. In the condition tab desired temperature and pressure are entered (e.g. 25°C and 1 atm). Then in the composition tab various compositions of propane and butane are entered to generate P-T diagrams for different compositions. From tool menu “Utilities” is selected. An available utilities window is appeared. Then Envelope Utility-1 is selected. By clicking on view utility a window is appeared. By clicking on performance tab and next in PT tab we get a window to prepare P-T diagram for a certain composition <sup>[2]</sup>. From these curves Cricondetherm, Cricondenbar and Retrograde Phenomenon are analyzed

#### 4. Results and Discussion

The P-T diagrams of LPG for different compositions are presented and discussed in the following sub-sections. The composition of most commercial LPG lies between 50-90% propane and 10-50% butane. Hence, P-T diagrams for 50% propane 50% butane, 60% propane 40% butane, 70% propane 30% butane, 80% propane 20% butane, 90% propane 10% butane is our topic of interest . So P-T diagrams are prepared for these compositions only. Cricondetherm, Cricondenbar and Retrograde Phenomenon are very important criterions to analyze P-T diagram of multicomponent systems. So in this section P-T diagram of commercial LPG will be discussed and analyzed in light of Cricondetherm, Cricondenbar and Retrograde Phenomenon, extensively.

##### 4.1. Cricondetherm Observation

In P-T diagram of multicomponent system liquid can exist above the critical temperature (a temperature above which a vapor cannot be liquefied, regardless of the applied pressure and above which there are no difference between liquid and vapor). The highest temperature at which liquid can exist is known as Cricondetherm and is given by the temperature which is tangent to the two phase loop at highest temperature. In Fig 1, Fig 2, Fig 3, Fig 4 and Fig 5 upper lines are bubble point lines, lower lines are dew point lines and the black dots on top of the curves are critical points. From the figures we observe that the temperature belongs to critical point is the highest temperature in the

whole plot. So it can be said that in commercial LPG, no Cricondetherm points are observed.

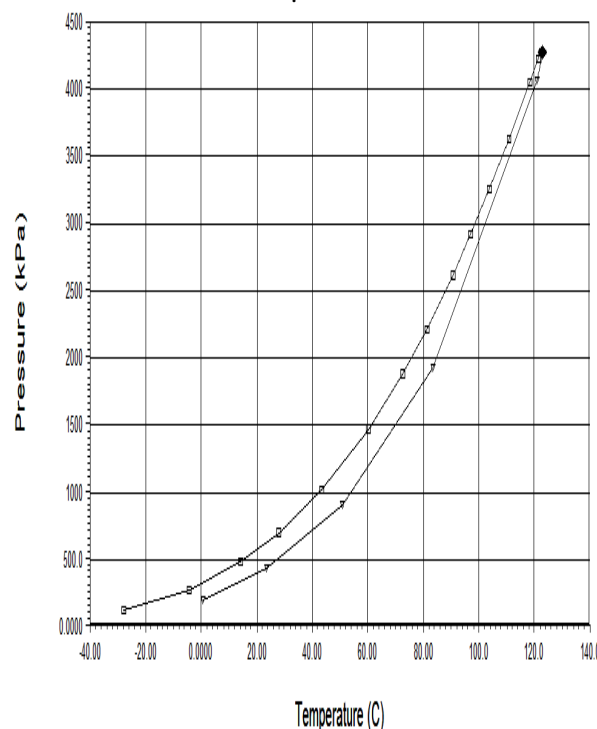


Figure1. P-T diagram of 50-50 LPG

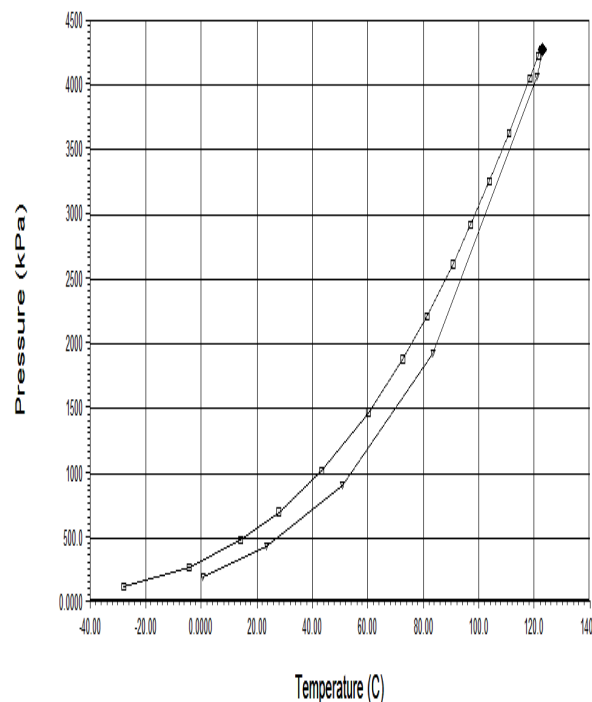
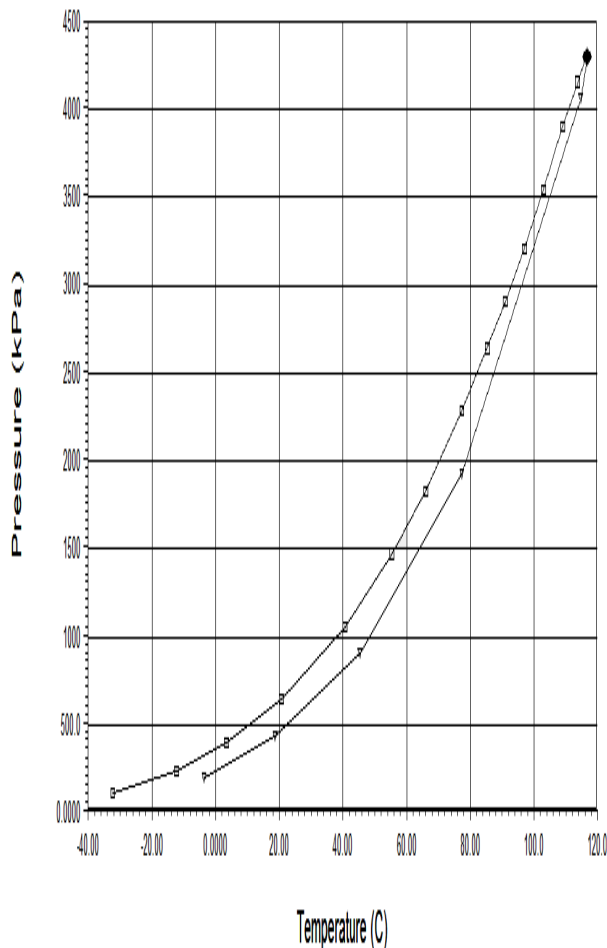
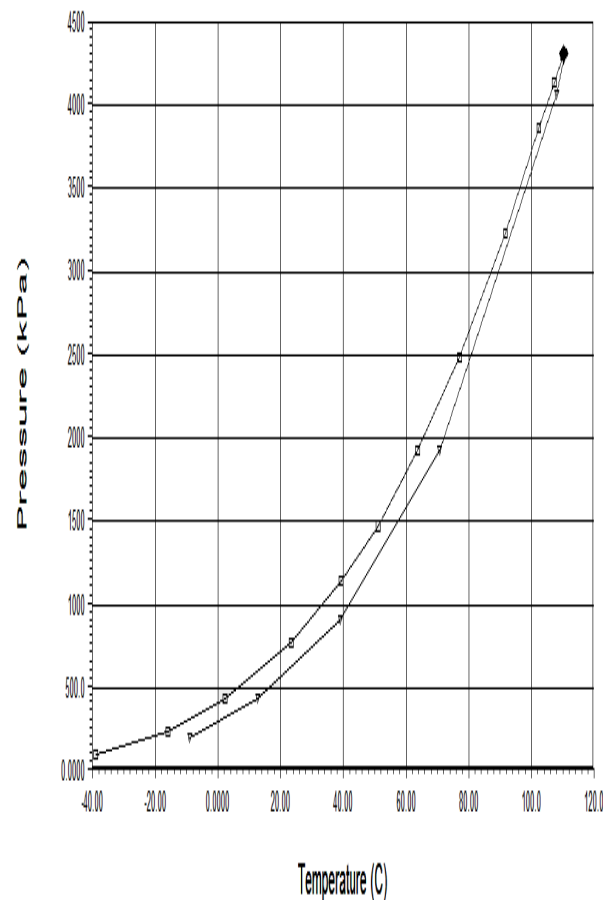


Figure2. P-T diagram of 60-40 LPG



**Figure3.** P-T diagram of 70-30 LPG



**Figure4.** P-T diagram of 80-20 LPG

## 4.2. Cricondenbar Observation

In P-T diagram of multicomponent system vapour can exist above the critical pressure (a pressure below which a vapour cannot be liquefied, regardless of the reduced temperature and above which there are no difference between liquid and vapour). The highest pressure at which vapour can exist is known as Cricondentherm and is given by the pressure which is tangent to the two phase loop at highest pressure. Similar to Cricondentherm, the highest pressure of Fig 1, Fig 2, Fig 3, Fig 4 and Fig 5 corresponds to the critical points. So it can be said that in commercial LPG, no Cricondenbar points are observed. Cricondentherm and Cricondenbar are very important criteria to analyze whether Retrograde Phenomenon is going to take place or not in a certain region of P-T diagram. Some other factors are also responsible for the occurrence of Retrograde Phenomenon. These factors are also described in the following sub-section regarding Retrograde Phenomenon

## 4.3. Retrograde Phenomenon Observation

With the increase of temperature of a system the usual phenomenon is, liquid becomes vapor. But in P-T diagram there is a region where liquid becomes vapor when temperature decreases. This unusual phenomenon is observed only in multicomponent P-T diagrams. This phenomenon is called Isothermal Retrograde Vaporization. The reverse phenomenon is known as Isothermal Retrograde Condensation. In other words, retrograde condensation is defined as the formation of liquid by an isothermal decrease in pressure or an isobaric increase in temperature. Similarly, retrograde vaporization is the formation of vapor by an isothermal compression or an isobaric decrease in temperature. Retrograde phenomena only occurred in a certain region of a multicomponent P-T diagram. Obviously these phenomena occur only at a pressure between critical pressure and Cricondenbar or at a temperature between critical temperature and the Cricondentherm. One may think of these phenomena as being abnormal but in reality this behavior is characteristic of almost all systems composed of two or more components. Indeed, this behavior was predicted by early investigators before it was observed experimentally. However, this

behavior need not be general since retrograde phenomena would not occur in a system whose dew point curve and bubble point curve meet in an acute angle at the critical point so that the Cricondetherm and the Cricondenbar are equal to critical temperature and critical pressure respectively<sup>[3]</sup>. The reverse phenomenon is known as Isothermal Retrograde Condensation. In other words, retrograde condensation is defined as the formation of liquid by an isothermal decrease in pressure or an isobaric increase in temperature. Similarly, retrograde vaporization is the formation of vapor by an isothermal compression or an isobaric decrease in temperature. Retrograde phenomena only occurred in a certain region of a multicomponent P-T diagram. Obviously these phenomena occur only at a pressure between critical pressure and Cricondenbar or at a temperature between critical temperature and the Cricondetherm. One may think of these phenomena as being abnormal but in reality this behavior is characteristic of almost all systems composed of two or more components. Indeed, this behavior was predicted by early investigators before it was observed experimentally. However, this behavior need not be general since retrograde phenomena would not occur in a system whose dew point curve and bubble point curve meet in an acute angle at the critical point so that the Cricondetherm and the Cricondenbar are equal to critical temperature and critical pressure respectively. From the P-T diagram of LPG of different compositions of LPG (e.g. 50% propane 50% butane, 60% propane 40% butane, 70% propane 30% butane, 80% propane 20% butane and 90% propane 10% butane) we observed that that dew point line and the bubble point line do not meet at an acute angle. Also no Cricondetherm and Cricondenbar are observed in these diagrams. So from these observations we can say that Retrograde Phenomenon is not observed in commercial LPG. The possible explanation of these phenomena may be, as molecular weight of propane and butane is low compared to the other hydrocarbons so it is more volatile than other heavy hydrocarbon. As a result volatility of propane and butane will be higher than other heavy hydrocarbon. Due to increased volatility, the dew point pressure and bubble point pressure of propane and butane mixture (LPG) will always remain high and adjacent at a given temperature. So P-T diagram of LPG become narrower. As a result bubble point curve and dew point curve meet at an acute angle and no Cricondetherm and Cricondenbar is observed. This is the possible reason why LPG does not show retrograde phenomenon.

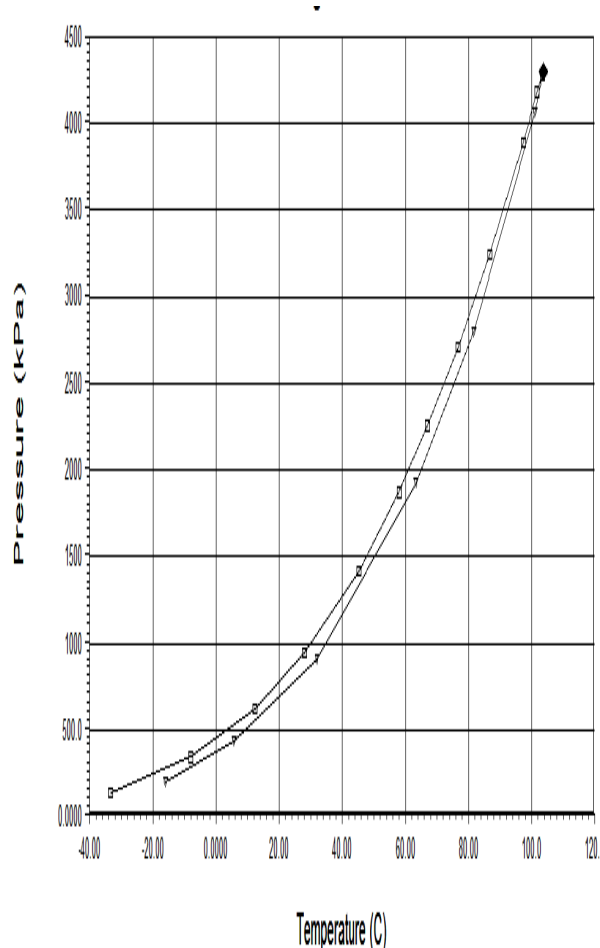


Figure5. P-T diagram of 90-10 LPG

## 5. Conclusions

The P-T (Pressure-Temperature) diagram, Cricondetherm, Cricondenbar and Retrograde Phenomenon of LPG are extensively studied in this study. It is found that different compositions of commercial LPG do not show Cricondetherm point, Cricondenbar point. Hence, no Retrograde Phenomenon is observed in commercial LPG having compositions 50% propane 50% butane, 60% propane 40% butane, 70% propane 30% butane, 80% propane 20% butane, 90% propane 10% butane. Higher volatility of propane and butane mixture is the possible reason of not showing Cricondetherm, Cricondenbar and Retrograde Phenomena. This result will be exceptionally useful to prevent BLEVE incident in the LPG manufacturing, storage, bottling and distribution plant<sup>[4]</sup>. So those who are involved with the research, manufacturer, bottling, and distribution of LPG are expected to be benefited immensely by the results of this study.

## Acknowledgements

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## Vitae

Include a short biography for each author along with a frontal photograph.



Mr. Niaz Bahar Chowdhury was born in Chittagong, Bangladesh. He obtained a B. Sc degree in 2012 in Chemical Engineering department from Bangladesh University of Engineering in Technology.

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