

**CHARACTERISTICS OF LIQUEFIED PETROLEUM GAS IN STORAGE  
DURING EXHAUSTION PROCESS**

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CHARACTERISTICS OF LIQUEFIED PETROLEUM GAS IN STORAGE  
DURING EXHAUSTION PROCESS

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requirements for the award of the degree of  
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## ABSTRACT

Liquefied Petroleum Gas (LPG) has been regarded as a cleaner fuel because it has less impact on air quality. The study conducted opened up a more realistic solution to predict the actual usage of LPG. This is to minimize the problem related to the residue amount since there was no single method capable to empty the cylinder. Residue problem was still unsolved since at the early stage of LPG usage in Malaysia, therefore, it was considered as one of the national interest projects. The objective of this study is to obtain detailed understanding of LPG characteristics in cylinder during the continuous exhaustion process via modification of the existing operation design. The parameters affecting the evaporation process such as the surrounding temperature, composition, initial flow rate and filling weight of LPG were observed through experimental works on the rig set up. The experimental data was compared with the model that was developed based on fundamentals of material and energy balance under dynamic condition using MathCAD 2000. A rather good agreement between the model and experimental data was obtained. The propane content of minimum of 60%, the quantity filling of minimum and maximum of 62.5% and 84.0% and the surrounding temperature of minimum of 25°C must be considered in the planning of the composition and filling percentage design as well as selection of the installation method. Additionally, based on scaled-up factor the maximum discharging flow rate is approximately 18.0 m<sup>3</sup>/hr. The distributions of heat in cylinder showed that the sensible heat used for evaporation process is taken mainly at the internal wall. With that, the dominant heat derived for the evaporation process is through the axial direction than the radial direction. Finally, the study indicates that with proper selection of operating parameters the LPG residue in a cylinder could be reduced to less than 10%.

## ABSTRAK

Gas Petroleum Cecair (GPC) dipertimbangkan sebagai satu bahanapi yang bersih kerana hanya memberi sedikit kesan pencemaran kepada kualiti udara. Kajian yang dibuat mengemukakan penyelesaian secara realistik dalam meramal penggunaan sebenar GPC. Ini untuk mengatasi masalah berkaitan dengan baki kerana tidak ada satu kaedahpun yang mampu mengosongkan silinder secara lengkap. Masalah baki masih lagi belum dapat diselesaikan sejak dari awal penggunaan GPC di Malaysia, maka ia dipertimbangkan sebagai kajian yang mempunyai kepentingan negara. Objektif kajian ini adalah untuk memperolehi pemahaman yang terperinci mengenai ciri-ciri GPC di dalam silinder semasa proses pengeluaran berterusan seterusnya mengubahsuai rekabentuk operasi sedia ada. Parameter-parameter yang mempengaruhi proses peruwapan GPC seperti suhu persekitaran, komposisi, berat dan kadar alir diramal melalui ujikaji makmal ke atas rig yang dibangunkan. Data daripada ujikaji makmal dibandingkan dengan data dari model ringkas yang dibangun menggunakan perisian MathCAD 2000 berdasarkan hukum asas keseimbangan bahan dan tenaga pada keadaan dinamik. Keputusan yang hampir sama telah diperolehi antara kedua-dua kaedah yang digunakan. Kandungan propana minimum 60%, kuantiti pengisian minimum dan maksimum 62.5% dan 84.0% dan suhu persekitaran minimum 25°C perlu dipertimbangkan dalam sebarang perancangan rekabentuk komposisi dan peratus pengisian serta kaedah pemasangan. Sebagai tambahan, berdasarkan kepada faktor penskalaan kadar alir maksimum ialah dianggarkan setinggi 18.0 m<sup>3</sup>/jam. Agihan haba dalam silinder menunjukkan majoriti haba deria yang diambil semasa proses peruwapan adalah pada dinding dalam silinder. Oleh itu, haba diambil secara dominan untuk proses peruwapan menerusi arah paksian berbanding arah jejarian. Akhir sekali, kajian menunjukkan pemilihan parameter-parameter operasi dengan betul boleh mengurangkan baki GPC kepada kurang daripada 10 peratus.

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**LIST OF ABBREVIATIONS**

<b>ABBREVIATIONS</b>	<b>DESCRIPTIONS</b>
a	constant
A	surface area
AAA	Australian Automobile Association
B	chemical species, constant
c	heat capacity
d	diameter
D, E, F	constant
dX	distance difference
dr	distance difference
dT	temperature difference
E(t)	energy at time t
f	fugacity
GPSA	Gas Processor Supplier Association
Gr	Grashof number
h	convection heat transfer coefficient
$\Delta H$	latent heat of vaporization
H	enthalpy of vapor, height
k	thermal conductivity
L	length
LFTB	Liquid Fuels Trust Board
LPG	Liquefied Petroleum Gas
MW	molecular weight
m	mass
n	mole
N	number
Nu	Nusselt number
P	pressure

Pr	Prandtl number
Q	flow rate, heat flux
r	radius
R	resistance of heat transfer, gas constant
t	time
T	temperature, total
V	volume, molar volume
x	liquid mole fraction, wetted
y	gas mole fraction
Z	gas compressibility factor

### *Superscripts*

ig	ideal gas
m	constant
L	liquid
sat	saturation

### *Subscripts*

Axi	axial
Acc	accumulation
b	boiling
B	bulk
c	critical, convective
Cons	consumption
conv	convection
C3	propane
C4	butane
C3L	liquid propane
D	discharge
Eq	equivalent
f	film
i	internal or component
j	component
ij	molecular pair

ice	ice layer
Gen	Generation
L	liquid
Max	maximum
Min	minimum
o	external
out	outside
p	pressure
r	pseudo reduced, radiative
rad	radiation
ref	reference
s	system
v	vapor
vap	vapor
vapMax	maximum vapor
vapMin	minimum vapor
vapC3	vapor of propane
vapC4	vapor of butane
W	wall
1	higher region
2	lower regions

*Greek symbols*

$\beta$	expansion constant
$\delta$	empirical interaction
$\varepsilon$	emissivity
$\phi$	fugacity coefficient
$\gamma$	activity coefficient
$\Phi$	gamma/phi fugacity coefficient
$\rho$	density
$\omega$	acentric factor
$\mu$	viscosity

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## CHAPTER 1

### INTRODUCTION

#### 1.1 Research Background

Liquefied petroleum gas (LPG) has become more popular compared to other liquid fuels based on several factors i.e. easy to handle, less pollution, minimum storage space and can produce a high quality product (Australian Automobile Association , 2001 & Jaimes and Sandoval, 2002). Four percent of the energy demand of the world is met with LPG (Karamangil, 2006). At present, in certain countries, the increase in LPG consumption rate is equal to the rate of the population growth. In the latest development, LPG seems to be the appropriate long term candidate to replace refrigerants in the existing refrigerator (Fatouh and Khafafy, 2006) since it will provide energy saving up to six percent and environmental protection (Maclaine and Leoardi, 1995 & Liu *et al.*, 1995). There are a few concepts of LPG distribution to the customer and it depends on the categories of customer i.e. whether it is domestic, commercial or industrial. LPG will be delivered to the customer using cylinder, bulk storage and pipeline.

LPG is a group of hydrocarbons derived from crude petroleum processes or natural gas (Karamangil, 2006 & Ceviz and Yuksel, 2006), which are gases at normal temperatures and atmospheric pressures but which become liquid with either a moderate drop in temperature or pressure, or both. With that characteristic, sometimes LPG is known as a 'hydrocarbon borderline product' (Leary, 1980). LPG is a mixture of petroleum hydrocarbons consisting mainly of propane and butane and it can also exist in its individual components such as pure propane or butane (Johnson, 1977 & Purkayastha

and Bansal, 1998). Besides the main components, other minor components, which may exist in LPG, are propylene, butylenes, and butadiene with these minor components mainly depending on its sources (William, 1982). The difference in the LPG produced in crude petroleum processes is that some of the unsaturated hydrocarbons appear together with the LPG such as propylene and butylenes (Beggs, 1984 & Hazzaini, 1998). Statistically, in the market, 75 percent of LPG is derived from natural gas and 25 percent is from crude petroleum processes (Thomas *et al*, 1965). In Malaysia, however, the differential among the two cannot be identified because of the bottling plant design is in such a way that the products from the gas processing plant and the refinery come through a commingle line.

An understanding of the behavior of LPG is necessary to assist in the planning and engineering design of process plant, transportation and storage, safety and other applications (Seeto and Bowen, 1983). LPG can be easily liquefied and vaporized, hence, it is stored under pressure above its boiling point (Park *et al.*, 2006). Propane is liquefied when it is frozen below  $-42^{\circ}\text{C}$  under atmospheric pressure or pressurized at above 7 bar (700 kPa) under constant temperature. Butane is more easily liquefied under the conditions of  $-0.5^{\circ}\text{C}$  and 2 bar (200 kPa). Furthermore, as LPG becomes extremely less voluminous (propane reduced to one over 270, butane one over 240) when liquefied, it is feasible to be safely transported and stored (Loasiripojana and Assabumrungrat, 2005). LPG has a high evaporation heat point, requiring a large quantity of evaporation heat when vaporized. So, the installation of separate vaporization facilities are required when a large quantity of LPG is used such as for industrial purpose.

LPG is colorless, odorless and tasteless in liquid and vapor form, yet liquid leaks are often characterized by foggy conditions at ground level as the cooling effect condenses water vapor in the air, and frost may occur at the point of escape. Only a small quantity of odorant is added in order to detect it when leaking. A liquid, LPG is only half of the weight of water yet in gaseous form is twice as heavy as air, so it is difficult to disperse and tends to hug the ground, sliding downhill to accumulate in lower lying areas (Ditali *et al.*, 2000 & Seeto and Bowen, 1983). It is propane and butane that is the most commonly used and most easily liquefied of these gases. Both have flammability limits between 2 to 4 percent in air, so just 1 liter of split liquid cloud create up to  $12.5\text{ m}^3$  of flammable vapor which could be ignited perhaps 50m downwind from the leak point

(Stawczyk, 2003). It is observed that the flammability range of LPG becomes narrow with the addition of nitrogen gas (Mishara and Rahman, 2003). The information of this limit is very much required for the prevention of explosive hazards (Clay *et al.*, 1988 & Chakraborty *et al.*, 1975). However, the degree of hazards depends on many factors such as the mass of substances released, physico-chemical properties of the substance in the moment of its release, flammability and toxicity of the medium flowing out (Stawczyk, 2003). Any liquid with a flash point greater than 26.7°C is considered a non-flammable substance (Lehr and Beatty, 2004). Even though LPG is not poisonous but after exposure to LPG it will cause death due to asphyxia from hypoxia as a result of the exclusion of oxygen by the gas (Tatsushige *et al.*, 1996) as well as lung damage from breathing cold vapors (Hanlin, 2006).

Commercial LPG in the market normally consists of propane and butane with 30 percent and 70 percent in composition (3070) respectively. However, its composition will vary accordingly and subject to the application, country and surrounding temperatures (Purkayasha and Bansal, 1998, Philip *et al.*, 2004, Leal and Santiago, 2004 & Kwangsam *et al.*, 2004). Generally, the gas industry will follow the agreement with clients or follow the specification fixed by the Gas Processor Supplier Association (GPSA) concerning the composition (Royal Dutch, 1986 & William, 1983). The specification of GPSA is based on the maximum vapor pressure, minimum vaporization rate and the limitation of the components that will cause corrosion such as water and sulfur. This means that the industry will use both of the cases. However, usually LPG contains a certain amount of residue with higher vaporization points falling in the range of lubricant oil. The sources of residue are the LPG processing equipment i.e. pumps, compressors and containers (Quan *et al.*, 2004). In industries, there is a routine need to analyze residues in LPG for quality control. Usually, on specific application, residues concentration of LPG must meet industrial codes. For instance, the Australia LPG Association requires the residue concentration below 20 ppm of mass (Quan *et al.*, 2005).

LPG is economically feasible to be produced, transported, sold, and stored as a liquid fuel (Stawczyk, 2003 & Murillo *et al.*, 2005). The obvious advantage of this liquefied fuel is that its heating energy is highly concentrated compared to other liquefied fuels (Purkayasha and Bansal, 1998 & Murillo *et al.*, 2005). For instance one cubic feet of liquid propane can provide nearly 47 percent more heating value compared to the same



amount of liquid methane (Clifford, 1973 & Karamangil, 2006). LPG, however, provides low combustion velocity at low pressure than gasoline but will increase according to pressure increase (Mohd Kamaluddin, 1984 & Murillo *et al.*, 2005).

LPG has received increasing attention since it was recognized as a reasonable energy resource and commonly used for many applications (Hazzaini, 1998 & Dokupil *et al.*, 2006). LPG supply for industrial and commercial use is available to the consumer in cylinders of larger capacity than the regular domestic household cylinders or in bulk tanks of even larger capacities. Commercial cylinders are generally used for restaurants and bakeries where the LPG consumption and gas delivery rate are high that the vaporization rate of the regular household cylinders cannot support. Commercial cylinders may be linked together to support higher capacities which is through manifold system. LPG offers a great reduction in pollutant emissions (Chang *et al.*, 2001) which is 100 times lower than gasoline (Karamangil, 2006). Because of these reasons, LPG can be utilized in many sectors such as domestic, commercial and industrial sectors. LPG can be transported and stored in liquid form under moderate pressures and at normal temperatures. When released at atmospheric pressure at relatively low temperature it vaporizes and can be handled as a gas (Purkayasha and Bansal, 1998). But this operation cycle included a problem related to the loss due to the residual amount of gas left at exhaustion. This problem has been considered as one of the main drawbacks in LPG cylinders that create unsatisfactory conditions.

This problem occurs when the vapor is consumed through the natural evaporation process at high exhaustion rate (Nor Maizura, 1994). In this process, the temperature of the liquid and the pressure inside the cylinder drop rapidly and may reach a point when the cylinder pressure is insufficient to supply the gas at the required exhaustion rate (Ditali *et al.*, 2000). The required exhaustion pressure is the minimum inlet pressure for a regulator and normally considers being at 7 psi (0.5 bar) for commercial sector (Che Badrul, 1994). At this point the exhaustion rate may approach zero and create residue in the cylinder.

Even though the use of portable cylinder in Malaysia has started since early 1980s, when LPG has made its way to most commercial and residential area to cater for public needs, especially in cooking and heating appliances (Ahmad Fauzi *et al.*, 1991), there is still unsolved residual problem especially in commercial size cylinder. The problem occurs when natural evaporation takes place. During the evaporation temperature and pressure in the cylinder will drop (Raj, 1981, Waite *et al.*, 1983, Vai and Chun, 2004 & Chen *et al.*, 2004) to the point that pressure is not able to push out the LPG from the cylinder at the required level of flow. At that point, normally the pressure inside the cylinder is equal to the atmospheric pressure and some amount of LPG still exists in the cylinder (Dick and Timms, 1970). It is reported that more than 30 percent of residue or 12.6 kg is found in the 50 kg water capacity cylinder (Che Badrul, 1994). The residue of the LPG in the cylinder resulted in the customer paying extra money for the unused fuel. Gas suppliers have received complaints on this problem. The residue consisted of 2.17% of propane and 97.82% of butane by weight respectively (Che Badrul, 1994). Recently, even though there are a number of researchers investigating the residue problem, a complete solution is yet to be found.

The possible methods in reducing the residue problem and thus increasing the evaporation process in liquefied petroleum gas storage are increasing thermal conductivity and heat capacity, installing coil system inside the storage, adding absorbent material inside the storage, applying coating agents on outer vessel wall and changing initial LPG composition. However, based on the results declared by previous researchers there is no single method capable to completely withdraw LPG from storage or in other words to empty the storage but only to minimize the residue (Dick and Timms, 1970).

Since there is no single method or technique capable to empty the cylinder and the residue will vary with the mode of application and yet the dimension of the cylinder is also not the same with different suppliers, then another approach need to be explored. However all methods mentioned above show some potential in improvement of the evaporation process. Nevertheless, the methods lack applicability and practicability to be adopted, and hence are not possible to be commercialized (Muhammad Noorul Anam, 2002).

Therefore, the researcher suggested that it should be better if the overall concept of mass and heat transfer to the LPG cylinder under dynamic condition is carried out in detail. This is because the major factor affecting the residue is the amount of sensible heat required during the evaporation process. By understanding the concept of heat and mass transfer under dynamic conditions, it will lead to the development of a mathematical model. The data gathered from both methods which are mathematical model and experimental rig will be compared. Hence, it will lead to the development of a new design of operation parameters of LPG. Last but not least, it will benefit the customers by gaining more energy corresponding to the price that they paid for as well as to gas suppliers in any designing related to the LPG for the purpose of reducing the loss incurred by the customer through evaluating all these parameters.

## **1.2 Objective and Scopes of Study**

Although much information has been obtained to date, there are remaining technical and theoretical gaps related to the behavior or characteristics of LPG in cylinder during continuous exhaustion process. Therefore, the objective of this study is to obtain the detailed understanding of LPG behavior in the cylinder system during the continuous exhaustion. The research will attempt to overcome the problems of LPG residue in cylinder via modification of the existing operation parameters design.

In LPG storage operations, several main parameters affect the performance of the discharging process such as the surrounding temperature, LPG composition, and discharging flow rate as well as filling weight. Therefore the first objective of this study is to elucidate the inter-related effects of these parameters on bath evaporation process in storage. In order to compare the experimental results, a mathematical model will be developed based on the fundamental theory of material and energy balance under dynamic conditions.

Cylinder thermal behavior holds the key role since it has strong impact on the performance of vaporization process in cylinder. One of the useful methods to analyze heat distribution is based on dimensionless analysis. Therefore, an analysis of heat distribution on the basis of axial and radial flow directions will be the second objective of this study.

Experimental work has been carried out through a small scale cylinder to reduce experimental time and thus allowing more repetitions to confirm data obtained. Based on the results obtained and detailed analysis, the design operation parameters will be proposed and will be the third objective of this study.

All the identified parameters were varied accordingly which were 10°C to 35°C for the surrounding temperature, commercial propane to commercial butane for the LPG composition, 20 liters per minute to 73 liters per minute for the flow rate and 2 kg to 7 kg for the filling weight.

In this study, the parameters that are to be discussed are the profiles of temperature, pressure, vapor and liquid composition, weight, flow rate and liquid level. Thus, by evaluating all these parameters, it will be beneficial in any designing related to the LPG storage for the purpose of reducing the loss incurred due to the residue problem.

### **1.3 Report Outline**

This thesis will discuss on the study of evaporation process of LPG in storage. The study conducted opens up a more realistic solution to predict the actual usage of LPG, which is to overcome or minimize the problems of LPG residue in cylinders via modification of the existing operation design parameters.

The thesis consists of five chapters, which starts with the introduction and ends with conclusions and recommendations. In Chapter 1, the discussion is based on the research background, which highlights on the increasing attention that LPG has received since it was recognized as one of the popular fuels, the problem that occurs when the vapor is consumed through the natural evaporation process and the possible methods in reducing the residue problem. In conjunction with that, the objective and scopes of the study are also highlighted with the focus on experimental.

In Chapter 2, which is a literature study, the highlighted discussion is related to the basic concepts of evaporation process, heat and mass transfer and vapor liquid equilibrium. All discussions are related to the LPG, which is stored in the cylinder under pressure. Apart from that, the overview of the history and usage of LPG in Malaysia is highlighted at the beginning of this chapter.

In Chapter 4, it is about materials and methods used for the experimental study. The schematic diagram of the experimental rig with consists of all equipment is discussed in this chapter. Apart from that, the study procedure is also highlighted in this chapter. Prior to that a simple model for experimental data comparison has been developed as highlighted in Chapter 3. The result gathered from the experimental study which includes temperature profile, pressure profile, vapor and liquid composition, liquid level and weight are discussed in Chapter 5. The discussion is based on the four main categories that have been studied which are the variation in surrounding temperature, variation in initial flow rate, variation in composition and variation in filling weight of LPG. At the end of the Chapter 5, comparison of the experimental results through theoretical model is highlighted.

Chapter 6 is the final part of this thesis, which highlights the conclusions and recommendations that can be achieved from the research work.

#### **1.4 Summary**

In Chapter 1, the researcher tries to highlight the definition and general concepts of LPG storage as well as the problem occurring when the gas is consumed through the natural evaporation process, which is related to the residual problem. It is reported that more than 30 percent of residue is found in cylinder with 50 kg water capacity size. Even though a lot of researches have been done to explore and overcome that problem, there is but no single method capable of doing it. Therefore, through this study, which consists of three main objectives that are related to the characteristics of LPG, it will be able to investigate the actual residue.