→ White Paper

A Member of The Linde Group

# Understanding behaviours of hydrocarbon mixtures in contact with overpressure gas

## Introduction

The choice between piston and liquid withdrawal overpressure cylinders, otherwise known as traditional cylinders with overpressure for liquid hydrocarbon mixtures, is an important one – with a number of factors to be considered before a decision is made on the most suitable mixture type.

Factors such as precision, maintenance, costs and certification levels should be considered to ensure optimum accuracy and value for money.

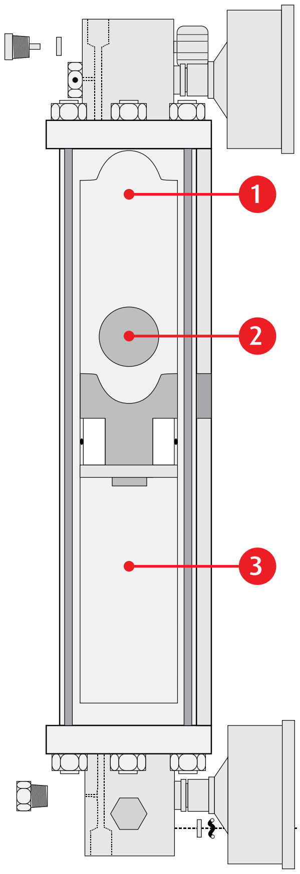
To assist in this decision, BOC conducted a number of simulations to determine the effects of hydrocarbon mixtures in contact with overpressure gas including helium, hydrogen and nitrogen.

The results are important to consider when choosing between a piston cylinder and a traditional cylinder, and when deciding how to use a traditional cylinder. This will help laboratory managers and maintenance teams using piston cylinders or traditional cylinders better understand the benefits and disadvantages of each.

BOC can assist with this by providing detailed composition use charts for your mixture of choice upon request.

# What are piston cylinders and traditional cylinders?

## Piston cylinders




Piston cylinders, also known as constant pressure cylinders, are designed to maintain constant liquid composition by eliminating any headspace above the liquid phase. A piston cylinder contains two chambers separated by a diaphragm. On one side 1 is the hydrocarbon mixture with a mixing ball 2 or paddle and on the other side is the overpressure gas 3. The overpressure gas keeps the hydrocarbon mixture as a liquid throughout use. The actual pressure depends on the mixture but could be anywhere between 10 to 100 bar or more.

Since there is no contact between the hydrocarbon liquid and the overpressure gas in a piston cylinder, mass transfer is not possible. This ensures the hydrocarbon concentrations do not change during use, and there is no dissolution of the overpressure gas into the mixture. This allows the certification level to be higher than for traditional cylinders, with lower analytical uncertainties.

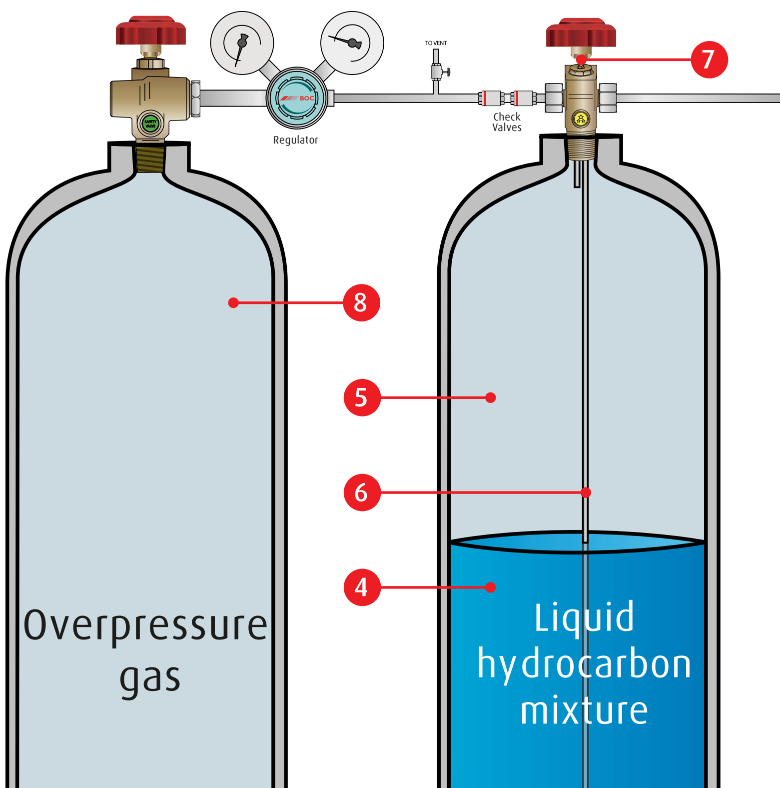
It also allows higher concentrations of methane, ethane and carbon dioxide due to the higher available overpressure. This is useful for customers such as LNG facilities who want to see higher concentrations of these gases to enable an artificial composition closer to the real concentration of gas being analysed. The result is a liquid mixture closer to what they are trying to measure, and therefore reduces uncertainty.

## Traditional cylinders

Liquid withdrawal overpressure cylinders are traditional cylinders that are filled with a liquid mixture 4 that has an inert overpressure gas 5 added to the headspace. A dip tube 6 allows for liquid withdrawal, while the overpressure gas provides motive force and ensures that there is no vaporisation in the sample pipework.

BOC cylinders include a dual port valve 7 connected to gas headspace, to allow for connection of overpressure gas for pressurisation 8. This allows the application of constant overpressure over the life of the cylinder.

The pressure used depends on the bubble point of the liquid but it is generally kept between 10 to 30 bar. However, as will be described later, it is not used for keeping lighter components in the liquid phase. Helium is most commonly used as it dissolves the least in the liquid phase but nitrogen and hydrogen may also be used.



# Piston cylinders and traditional cylinders.
## Factors for consideration.

### Piston cylinders

- Piston cylinders hold significantly less product (usually 400ml or 800ml) than overpressure cylinders which hold around 8L. Yet they require just as much analytical verification and require as much or more filling time and complexity as overpressure cylinders.
- Piston cylinders are significantly more expensive than a standard overpressure cylinder. They have more moving parts and have a complex diaphragm mechanism that standard cylinders do not have. Due to this, the ongoing maintenance costs for piston cylinders are significant.
- Ultimately, the cost of product per unit is higher compared to overpressure cylinders.

### Traditional cylinders

- Traditional cylinders contain a large amount of product in a cost effective and low maintenance cylinder asset.
- They provide a high level of certification with low analytical uncertainties, although not quite as good as piston cylinders.
- Because traditional cylinders have the hydrocarbon mixture in contact with the overpressure gas during use, they come with important effects on mixture properties that need to be understood. To understand this behaviour more accurately, we have conducted a number of simulations.

# Research and findings. How changes in concentration are affected by starting pressure and temperature.

## Research and Findings

BOC conducted several simulations run on a nominal hydrocarbon mixture.

The simulations were run using proprietary software and equations, based on the Peng-Robinson equations of state. They give an estimate of the mixture composition at multiple points during the use of the cylinder.

| Component | Concentration (liquid phase, Mol%) |
|---|---|
| Ethane | 1.46 |
| Propane | 68.3 |
| iso-Butane | 10.1 |
| n-Butane | 15.1 |
| n-Pentane | 5.1 |

# Component concentration in liquid phase. Analysis of component concentration shift in liquid phase.

Figure 1 shows the concentrations of each component in the liquid phase, as liquid is withdrawn and the mixture is used. The concentrations are normalised against the initial concentration in the liquid phase, prior to use. It also assumes no top-up of helium overpressure gas during the usage of the cylinder.

As the liquid mixture is withdrawn and the headspace volume increases, the lighter components with higher vapour pressures start to vapourise into the gas phase. This has the effect of reducing the concentration of the lighter components in the liquid phase, while increasing the concentration of heavier components. The changes in concentration are more pronounced as the mixture gets closer to being emptied. This effect is why overpressure cylinder usage is limited to between 50% to 80% of the liquid used.

For piston mixtures, the composition stays constant through the life of the cylinder. The liquid is not in contact with the gas phase head pressure, so there is no loss of light components and no enriching of heavy components.

## Key finding

In traditional cylinders, higher vapour pressure reduces the concentration of lighter components in the liquid phase and increases the concentration of heavier components. For piston mixtures, the composition stays constant through the life of the cylinder.

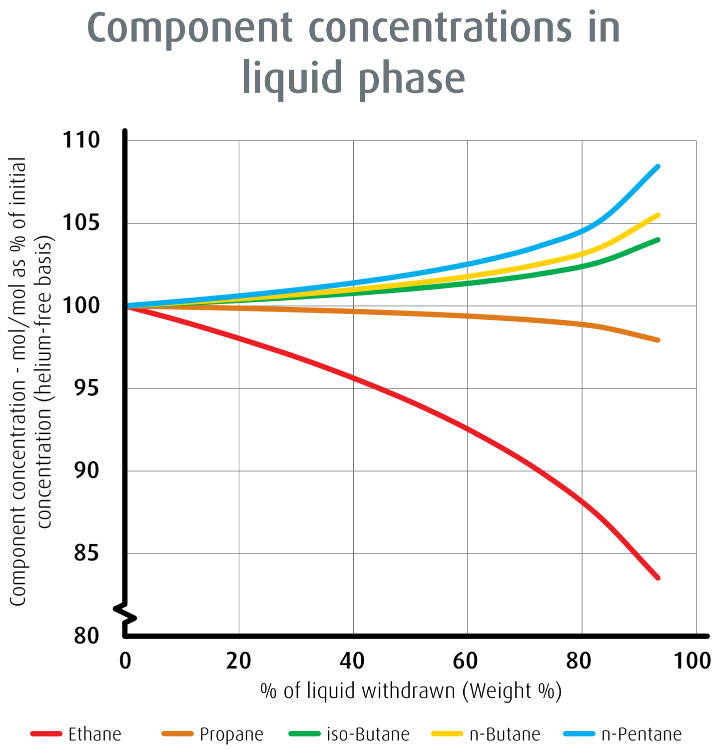



**Figure 1: Liquid phase concentrations during cylinder use**

# Ethane concentration in liquid phase. Investigating how the change in concentration is affected by starting pressure and temperature.

This investigation, as shown in figure 2, demonstrates that reducing the temperature of the mixture reduces the change in concentration, while increasing the temperature increases the change. This is expected, since vapour pressure is reduced as the temperature decreases, and vice versa.

As the vapour pressure decreases, the amount of ethane escaping into the gas phase also decreases. This means that there is less vapourisation of ethane, and the liquid concentration stays more stable during withdrawal of liquid.

The second effect is that increasing the overpressure does not change the ethane concentration. This is because vapour pressure for compounds is not dependent on total pressure, only on temperature. Whether the total pressure is 10 bar, 20 bar or 30 bar, the vapour pressure of ethane stays constant. Therefore, the total amount of ethane escaping into the gas phase stays the same and the liquid phase concentrations are the same no matter the amount of overpressure.

## Key finding

The main consideration in choosing the overpressure is to keep the total cylinder pressure above the mixture bubble point for the full life of the cylinder. However, there may be other considerations not directly due to the composition changes in the cylinder, including matching the cylinder pressure to the sample pressure.

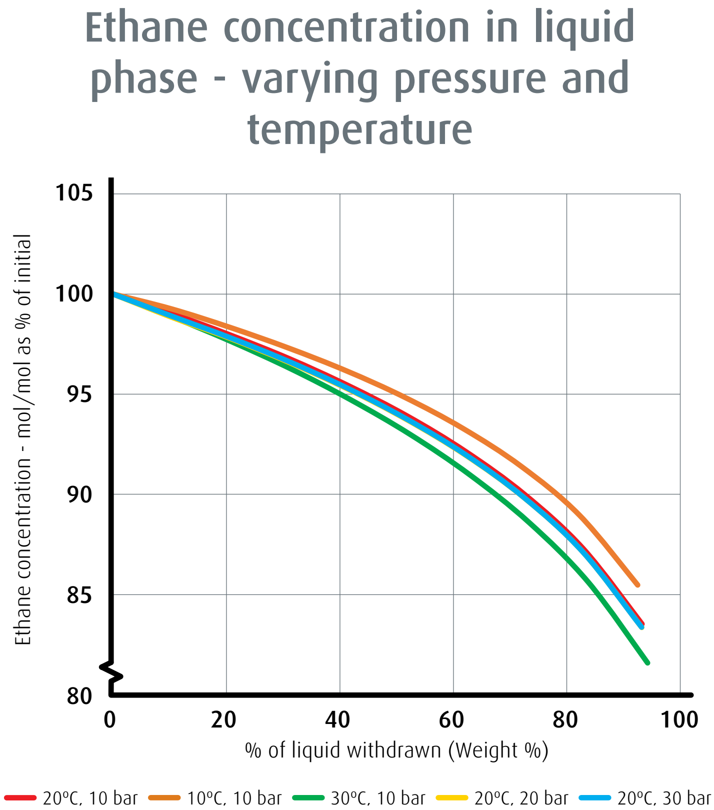



**Figure 2: Ethane liquid phase concentrations during cylinder use – varying pressure and temperature. Ethane has been chosen as it shows the greatest change in concentration over the life of the cylinder.**

# Ethane concentration in liquid phase – top up compared with no top up. Assessing whether keeping constant pressure on the mixture, by topping up the helium during use, has any effect on composition.

Without top up of the overpressure during use, the cylinder pressure will decrease over the life of the cylinder. One option is to top up the overpressure gas during consumption, which keeps the cylinder pressure constant through the life of the cylinder. This is done by connecting a regulated supply of the overpressure gas connected to the gas phase cylinder valve of the mixture cylinder.

However, figure 3 shows that there is no change in ethane concentration with different pressures, either with changing starting pressure, or with modifying the pressure during usage. Again, this is because vapour pressure of each component does not change with total pressure. However, there may be other reasons to maintain constant overpressure during cylinder usage, such as for increased repeatability during gas chromatography (GC) analysis.

## Key finding

Without top up of the overpressure during use, the cylinder pressure will decrease over the life of the cylinder.

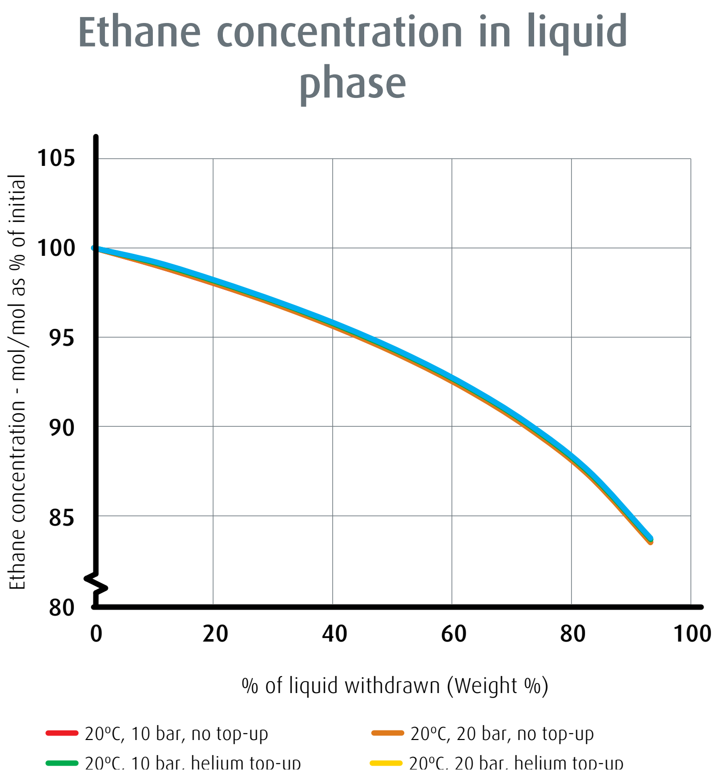



**Figure 3: Ethane liquid phase concentrations during cylinder use – top up of pressure**

# Overpressure gas concentration in liquid phase. Observing how the overpressure dissolves in the liquid phase, for multiple different scenarios.

Figure 4 shows how the overpressure gas dissolves in the liquid phase. All the previous scenarios used helium as the overpressure gas, as it is the most widely used and it is the default for BOC mixtures. However, nitrogen and hydrogen can also be used as the overpressure gas.

Helium dissolves least in the liquid phase for a given pressure. Hydrogen is closely behind, while nitrogen dissolves more than twice as much in the liquid phase. This can affect chromatographic results and needs to be carefully accounted for during analysis. The graph shows that increasing the overpressure greatly increases the amount that is dissolved in the liquid phase. Changing the overpressure from 10 bar to 20 bar increases the rate that helium dissolves by a factor of 3.

Finally, it also shows that when the overpressure gas is not topped up, the liquid phase concentration decreases as the cylinder is used. As the headspace volume increases, more of the overpressure gas comes out of solution and the liquid phase concentration decreases. This effect is not seen if the overpressure gas is topped up during use of the cylinder. The amount dissolved keeps relatively constant over the life of the cylinder, with a slight increase as the lighter hydrocarbon components start to vapourise.

While helium is commonly used as it dissolves least in the liquid phase, nitrogen or hydrogen may be used for other reasons like increasing sensitivity of GC analysis. It is important to consider the amount that the overpressure gas dissolves in the liquid phase when choosing the amount of overpressure.

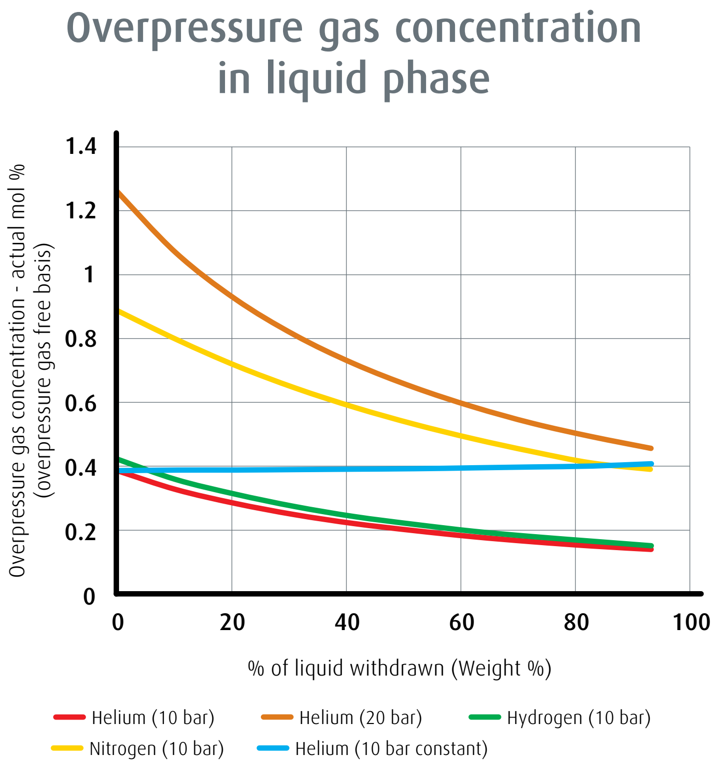



**Figure 4: Overpressure gas concentration in liquid phase – actual Mol %**

## Key finding

Constant overpressure has the advantage of keeping the amount of overpressure gas dissolved in the liquid phase relatively constant through the life of the cylinder.


Setpoint
Actual
Method Storage and Automation

## Conclusion

This paper has weighed up the key factors for consideration when choosing between a piston cylinder and a traditional cylinder with overpressure for liquid hydrocarbon mixtures.

There are four key findings resulting from several simulations run on a nominal hydrocarbon mixture which address considerations around component concentration in the liquid phase, ethane concentration in liquid phase, keeping constant pressure on the mixture by topping up the helium and observing how the overpressure dissolves in the liquid phase.

The findings answer key questions for laboratory managers and maintenance teams using piston cylinders or traditional cylinders and demonstrate the benefits and drawbacks of both.

All of these effects are important to consider, both when choosing between a piston and a traditional cylinder, and when deciding how to use a traditional cylinder. BOC can assist with this by providing detailed composition use charts for your mixture of choice upon request.

To discuss your requirements with one of our technical specialists, contact BOC today.

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# Getting ahead through innovation.

With its innovative concepts, Linde is playing a pioneering role in the global market. As a technology leader, it is our task to constantly raise the bar. Traditionally driven by entrepreneurship, we are working steadily on new high-quality products and innovative processes.

Linde offers more. We create added value, clearly discernible competitive advantages, and greater profitability. Each concept is tailored specifically to meet our customers' requirements – offering standardised as well as customised solutions. This applies to all industries and all companies regardless of their size.

If you want to keep pace with tomorrow's competition, you need a partner by your side for whom top quality, process optimisation, and enhanced productivity are part of daily business. However, we define partnership not merely as being there for you but being with you. After all, joint activities form the core of commercial success.

**Linde – ideas become solutions.**

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