THE SAME TWO PRINCIPLES

All vapour recovery systems are based on the same two basic chemical principles – chemical equilibrium and filtration.

In this context, the term vapour recovery refers to the vapours being emitted from trucks, railcars, barges, ships and storage tanks when they are filled with volatile petroleum products such as gasoline or crude oil. The vapours consist of air, mixed with VOC (volatile organic compound). In some cases, air is substituted by an inert gas such as nitrogen or CO_2.

CHEMICAL EQUILIBRIUM AND FILTRATION

All vapour recovery systems are based on the use of the basic physical principle of chemical equilibrium in some way. Most vapour recovery systems also use some type of filtration.

Chemical equilibrium is the state in a chemical reaction in which the involved components are present in concentrations which have no further tendency to change with time.

If, for instance, two chemicals (products) react with each other, a chemical equilibrium will develop like in figure 1.

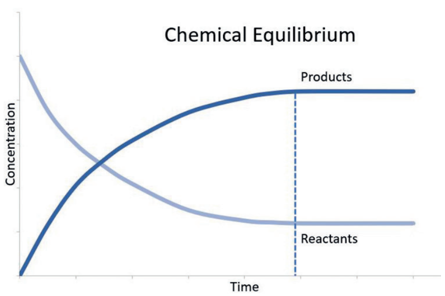

Figure 1 – A chemical equilibrium

The chemical reaction can be as simple as a phase change, such as condensation as a result of changed temperature and/or pressure. For example, a typical summer gasoline in Europe with an RVP (reid vapour pressure) of 70 kPa can hold up to around 50% VOC at 25˚C but only 2,5% VOC at minus 45˚C. So, by cooling the vapours sufficiently, the VOC will condense.

Indeed, some of the very earliest vapour recovery systems where based on pure condensation, achieved from cooling the vapours to -60˚C. These systems were short-lived due to their enormous energy requirement, but that's a different story.

Another and more relevant example of chemical equilibrium is absorption of one product into another.

As an example, diesel oil, which has a low vapour pressure and thereby a low volatility, can be used to absorb most of the VOC's from a flow of gasoline in a scrubber.

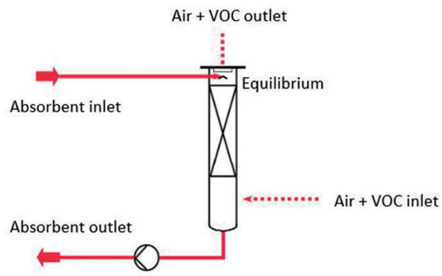

Figure 2 – Diagram of a scrubber

With an efficient scrubber design and correct flow ratios, there will be an equilibrium between the diesel oil and the VOC at the top of the scrubber column. In other words, the air out of the column will be saturated with diesel oil vapours. Since diesel has a typical RVP of around 1 kPa, this corresponds to 1 vol% at 20˚C to which again can be converted to around 25 g VOC/m . This would in fact be an acceptable emission in most countries.

The scrubber diagram is only used to illustrate the principle of an absorption process. In practice, the absorber flow would become extremely high and after having been used as absorbent for more volatile components, the diesel would very soon go out of spec.

It is important to realise that the gas flow out of the top of the absorber will contain all the components, which cannot be absorbed (mainly nitrogen, oxygen and carbon dioxide) along with fully saturated VOC in equilibrium with the conditions at the top of the absorber. Whether the concentration of VOC in the inlet gas was high or low is irrelevant for the concentration in the outlet gas.

Absorption is used in most vapour recovery systems. The main parameters in an absorption process are:

- Chemical compatibility – The willingness of the absorbent to absorb the VOC's in the vapour (water for instance is not good at absorbing VOC)
- The ratio of absorbent versus the VOC's in the vapour (process design)
- The vapour pressure of the absorbent (lower vapour pressure gives lower equilibrium)
- The time and mixing of the absorption process (process design)
- The temperature (lower temperature gives lower vapour pressure)
- The pressure (a given absorbent has a given partial pressure. Increasing the surrounding pressure in the scrubber increases the drive proportionally)

Filtration in the context of vapour recovery means a system where one group of gas molecules can pass, and another group of gas molecules is retained. This way, the feed stream (air with VOC) is divided into two streams – one with high VOC concentration and one with low VOC concentration.

No filter system is 100% efficient, but combining filtration with absorption and using recirculation, the final result can be that the low concentration stream is indeed with a very, very low VOC concentration

Two very different filter systems have been applied for Air with VOC's – namely membranes and activated carbon. Those two types of filters have very different working principles, each with their advantages and drawbacks.

In a typical membrane system, the incoming feed stream is separated into two components: permeate and retentate. Permeate is the gas that travels across the membrane (rich on VOC) and the retentate is what is left of the feed (lean on VOC). A driving force for the gas molecules to pass through the membrane is maintained by a compressor on the feed side and a vacuum system on the permeate side. The VOC-rich permeate side is routed to an absorber system.

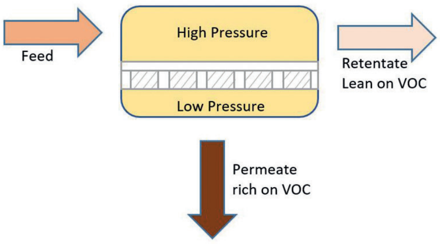

Figure 3 – Principle of membrane system

In a typical system, based on activated carbon, the incoming feed stream is routed through a layer of activated carbon at ambient pressure. The activated carbon can be considered as a 'molecular sponge' where the VOC components adhere to the walls of the pores by weak forces, known as Van der Waals forces, resulting from intermolecular attraction.

In this adsorption process, there is no chemical change to the activated carbon or the VOC molecules. After a certain time, the stream is diverted to another carbon filter and a vacuum system reduces the pressure to near-absolute vacuum. The low pressure causes a shift in equilibrium that breaks the weak forces between the VOC and activated carbon and makes the VOC molecules leave the bed through the vacuum pump in a highly concentrated stream (95 vol% VOC in 5 vol% air), which is routed to an absorber system.

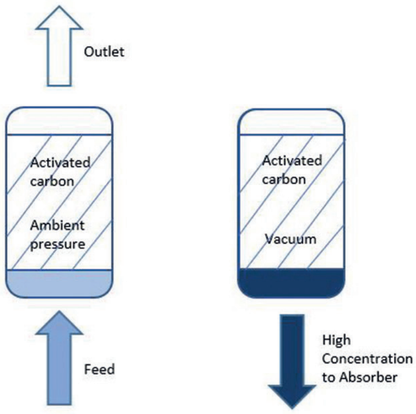

Figure 4 – Principle of activated carbon system

COMBINING CHEMICAL EQUILIBRIUM AND FILTRATION

There are countless ways in which the two basic chemical principles can be combined and converted in to practical technological solutions. Over the past 20 years, a few different principles have emerged as the most widely applied.

Around 90% of all new vapour recovery installations are based on filtration by activated carbon followed by absorption of the recovered VOC in a stream of absorbent.

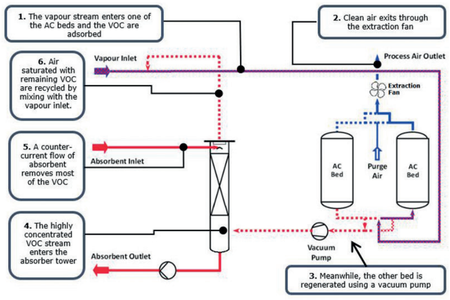

Figure 5 – Principle for VRU based on activated carbon and absorption

The process is simple, reliable, economical and can handle a large turn-down in terms of vapour flow (typically 0 -140% of the continuous design capacity). Most emission requirements can be handled in a single stage system.

size the rest of the system and increase the flexibility of the system.

Another variation is to replace the absorber system with a compressor and a cooler. This allows the recovered product to be collected without the use of absorbent but the system is somewhat less economical from both an investment and operational perspective.

In a few cases where space is extremely limited, a simple pressurised absorption process (PLA) can also be a viable solution.

The efficiency is typically only 60-70%. Which would not be acceptable for any land-based installation, but for on-board ship system it is much better than nothing.

Systems based on membranes are also used for various applications. They have proven reliable and are especially well suited for chemical products such as solvents. But a membrane system has an inherent need for a

Figure 6 – Vapour recovery unit based on activated carbon and absorption. Cool Sorption, 2019

In some cases – for instance where the inlet vapours can be extremely concentrated – a pre-scrubber with pressurisation and/or cooling can be added as an economical way to down-

strong driving force through the membranes and therefore a high energy consumption. It is also more difficult to regulate the flow through the system and typically the turn-down is so limited that some type of vapour buffer is required.

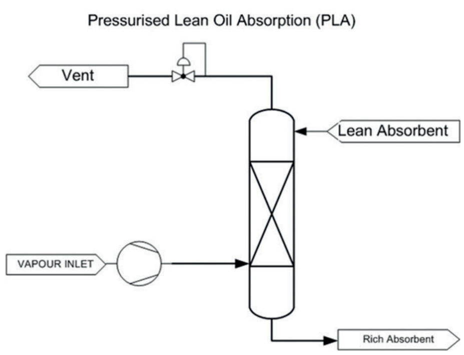

Figure 7 – Pressurised lean oil absorption

FOR MORE INFORMATION

This article was written by Ben Barker, sales manager, Cool Sorption.
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