Hydrocarbon properties and underground storage

A single body (H_2, CO_2, O_2, alkanes C_nH_{2n+2}) is characterized by an equation of state, for example a relationship between pressure, P, mass volume, v, and absolute temperature, T. For a gas, $Pv = rT$ is a fair approximation of the equation of state and similarly, for a liquid, $v/v_0 = 1 + \alpha(T-T_0) - \beta(P-P_0)$. Along an isothermal line in the plane (v, P), these two states are separated by a transition domain, called biphasic, between the points v_L and v_G of Figure 1. In this domain the pressure is constant and the two phases exist in varying proportions. When the temperature is increased, the segment of the biphasic equilibrium becomes narrower and narrower until it is reduced to a point, defined by pressure, temperature (T_c) and volume **critical**.

The biphasic equilibrium lines (liquid-gas, liquid-solid, solid-gas) can also be drawn in the plane P, T, Figure 1 at the top right. The liquid-gas equilibrium line begins at the triple point (Tr) and ends at the critical point (C). Beyond that is the supercritical domain where the two states no longer differ, we are dealing with a light liquid or a heavy gas.

These physical data determine the economics of hydrocarbon transport and storage. The atmospheric pressure evaporation temperature of alkanes (main components of hydrocarbons) was plotted as a function of their index n, (Figure 1 bottom right). The ratio v_G / v_L of the volumes occupied for the same temperature by the gas phase and the liquid phase is 350 for propane at 15°C and 0.8 MPa, and 600 for methane at -162°C and 0.1 MPa : this is a considerable difference, and the volume required to store hydrocarbons that are liquid ($n > 4$) under normal conditions (0.1 MPa, 15°C) is much smaller. This explains the exceptional success of liquid hydrocarbons in the 20th century, and the difficulty of substituting other forms of energy for them: they are easy to transport, distribute and store, even for the end user (gasoline tank). This also applies to gaseous products under normal but easily liquefied conditions by compressing or cooling them somewhat (propane, $n = 3$ and butane $n = 4$), point A (0.1 MPa, 15°C) in Figure 1: they can be stored in lighters or camp blueberries. Gaseous alkanes, which are more difficult to liquefy (methane in natural gas, $n = 1$ or ethane, $n = 2$) do not have the same advantages, their distribution and storage are necessarily centralised (although natural gas is sometimes stored in two-phase form at 0.1 MPa and -162°C in LNG tankers). The development of their production and use has been slower than that of liquid hydrocarbons and, for their mass storage, the underground solution under high pressure is practically the only one.

Other products can be stored underground in hypercritical form, when their critical temperature is lower than the natural temperature of the land (ethylene, propylene). This is also the case for CO_2, supercritical beyond $T_c = 31°C$ and $P_c = 7.4$ MPa, conditions that occur naturally beyond 800 m depth.

References and notes

Cover image. In a cave, the presence of stalactites and the underground river highlights the continuous exchanges between the solid, liquid and gaseous phases. [Source: pixabay. Royalty-free image]

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