Whitepaper

Endress+Hauser
People for Process Automation

Optimizing CO_2 measurement using Coriolis flowmeters

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Executive summary

Cross-industry interest in the measurement of high-pressure carbon dioxide has dramatically increased. Sustainability targets have been intertwined with financial implications, as CO_2 producers and emitters have sought the best solution for measurement. Coriolis flowmeters have emerged as the resounding choice for measurement in these cases. While Coriolis flowmeters do offer premium accuracies, there are certain considerations that must be understood when designing a new CO_2 measurement system. This paper will investigate and provide recommendations to measurement operators who find themselves thrust into CO_2's burgeoning expansion.

1 Introduction

Governmental regulations surrounding carbon dioxide (CO_2) emissions have caused many industrial producers to look for creative solutions to achieve global energy and climate objectives. Many of these solutions fall under the umbrella of CO_2 capture, utilization and storage (CCUS). CCUS entails the retrieval of CO_2 from significant emission sources, such as power plants and industrial facilities utilizing fossil fuels or biomass as their energy source. Captured CO_2 is pressurized and transported through pipelines, ships, railways or trucks to a variety of reuse applications. It can also be injected into deep geological formations, such as depleted oil and gas reservoirs, where it is permanently stored.

The demand for accurate CO_2 measurement at all stages of the CCUS process is motivated by tax policies and government incentives. As an example, Canada's “Greenhouse Gas Pollution Pricing Act” imposes taxes on businesses for every ton of CO_2 emissions until 2030. In the case of a refinery with a daily production capacity of 300.000 barrels, annual CO_2 emissions may reach up to 4 million tons. Given this production scale, even a modest measurement uncertainty of 1.0 % could potentially lead to a financial impact of CAD 6.8 million.

Measuring CO_2 presents a set of unique challenges. Coriolis flowmeters are celebrated for their high accuracy and reliability, making them an attractive choice for various applications, including those within CCUS. However, accurate measurement of CO_2 can be complicated by the variable phases it assumes under different pressure and temperature conditions. CO_2 can exist as a gas, liquid, solid or even a supercritical fluid, each of which has different density and flow characteristics. This variability demands proper process design, flowmeter selection, sizing and commissioning to ensure the desired measuring accuracy across the entire range of conditions encountered in CCUS processes. This paper focuses on how to correctly address these challenges to ensure the successful and reliable measurement of CO_2 in CCUS.

2 Fundamentals of CO_2

2.1 Phase diagram of CO_2

To help create a baseline in understanding the properties of CO_2, we first look at its phase diagram. Phase diagrams provide a visual representation of which state of aggregation is to be expected at a pressure and temperature combination. In Figure 1, the colored lines represent the combinations of pressure and temperature at which both states can coexist in equilibrium and thus initiate a change in state of aggregation. For example, the green line represents a pressure and temperature combination that will cause solid CO_2 to sublimate into vapor. The purple line shows the combination where CO_2 can melt from solid to liquid or freeze from liquid to solid. The yellow line shows the combination of

pressure and temperature which causes a liquid to evaporate into a gas or gas to condensate into a liquid.
The blue dot shows CO_2's triple point. At this pressure and temperature, all states of aggregation can exist at once. For measurement purposes, one important indicator is called the critical point, represented as a red dot. At temperatures and pressures beyond the critical point, CO_2 is in supercritical phase where liquid and gas phases are no longer discernable from one another.

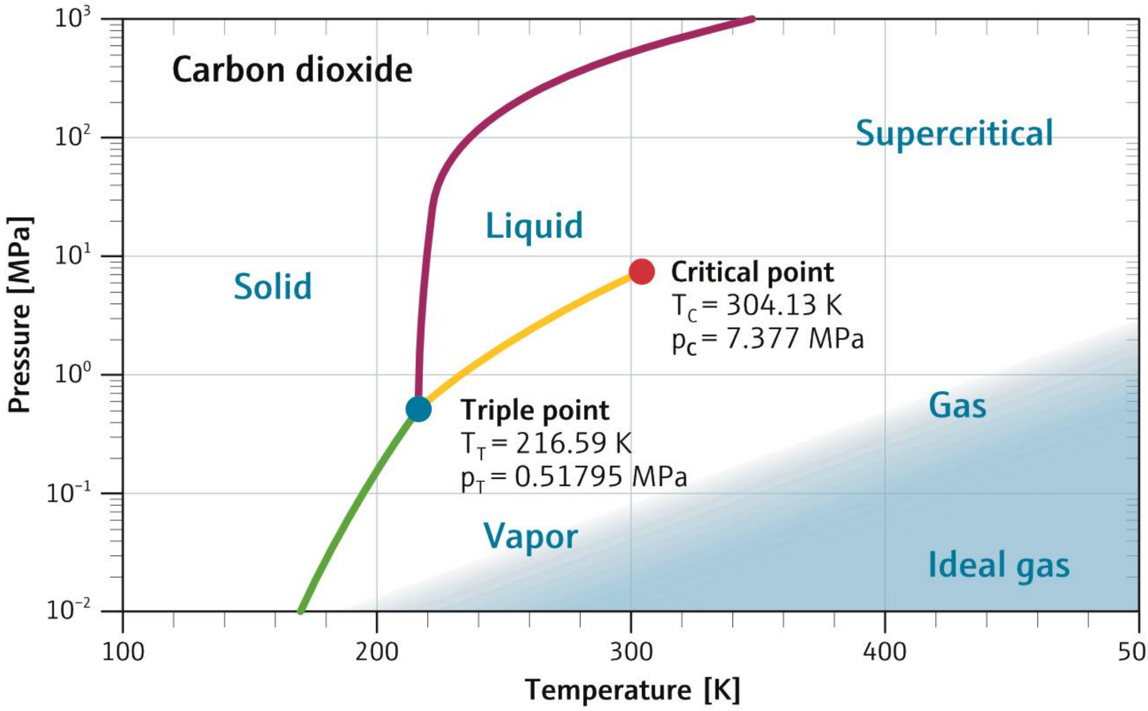


Figure 1: Carbon dioxide phase diagram

Flow measurement of fluids in liquid and gaseous states are well researched and different measuring principles can be used. Further research is currently being carried out to determine the suitability of different technologies for carbon dioxide flow measurement. Because there are fewer applications in the supercritical regime, and only a handful of these require high accuracy flow measurements, there are fewer documented references for CO_2 measurement performance determination. Coriolis mass flowmeters have the advantage that they can be used on all three states of aggregation.

2.2 Description of supercritical state of CO_2 and two-phase region

CO_2 has its critical point at 30.8 °C and 73.7 bar. Above this temperature and pressure, it is in the supercritical state. In this state, it will fill the entire pipe like a gas, have a higher density resembling a liquid and a low viscosity like a gas. It will be highly compressible near and at the critical point and the fluid properties change very rapidly.

In some foreseen operating conditions in CCUS applications, high pressures are required (dense phase liquid), and daily variations in ambient temperature could drive the system to the supercritical regime. In a similar fashion, at lower pressure and temperature, liquid carbon dioxide could evaporate as the temperature increases. In this case, two-phase mixtures could flow in the system. The density of CO_2 in liquid, gas and two-phase mixtures at different pressures and temperatures can be seen in Figure 2. For best performance, Coriolis flowmeters should be operated in single-phase fluids (either liquid or gas). The two-phase region should be avoided using careful process design. The two-phase region is the area at, and under, the bell shape in the plot. Above the critical pressure, the fluid will behave as either a compressible liquid or a very dense gas without a phase transition when ambient temperature changes. The supercritical state is generally considered uniform, although thermal properties seem to be not as uniform and may exhibit liquid-like or gas-like behavior under different conditions as reported by Simeoni et. al. (G. G. Simeoni, 2010) and Bolmatov et. al. (Bolmatov, Brazhkin, & Trachenko, 2013).

A good understanding of the fluid behavior at different process conditions ensures that the selection, sizing and installation of the Coriolis flowmeters will yield the best measurement results.

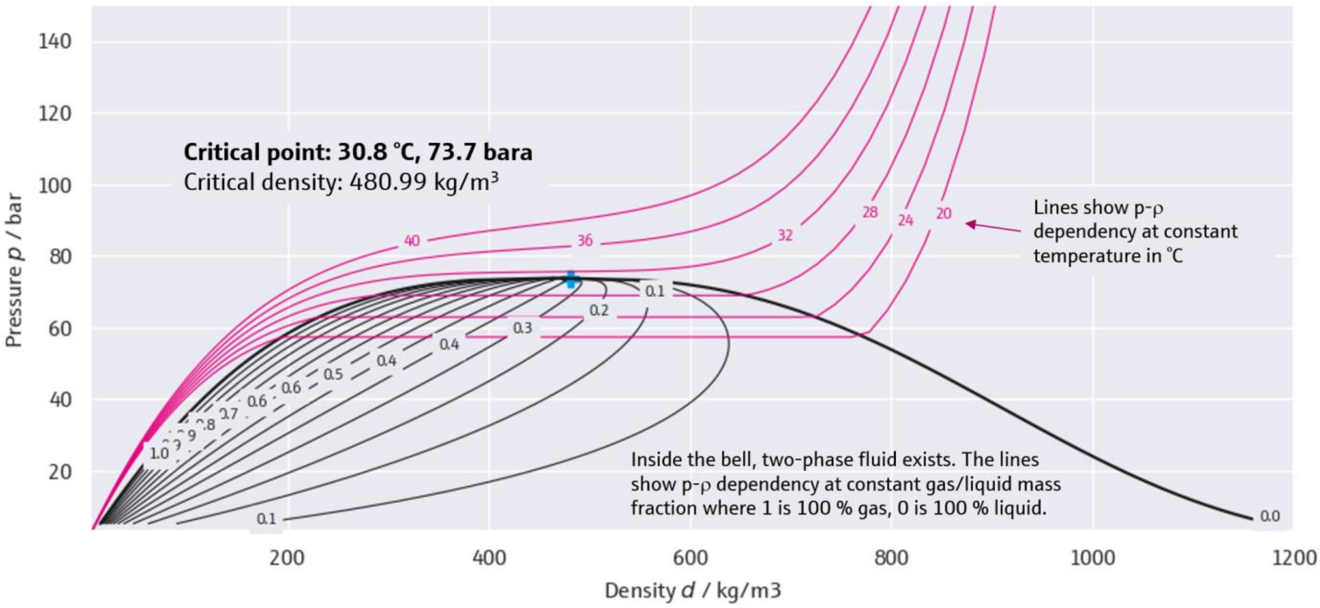
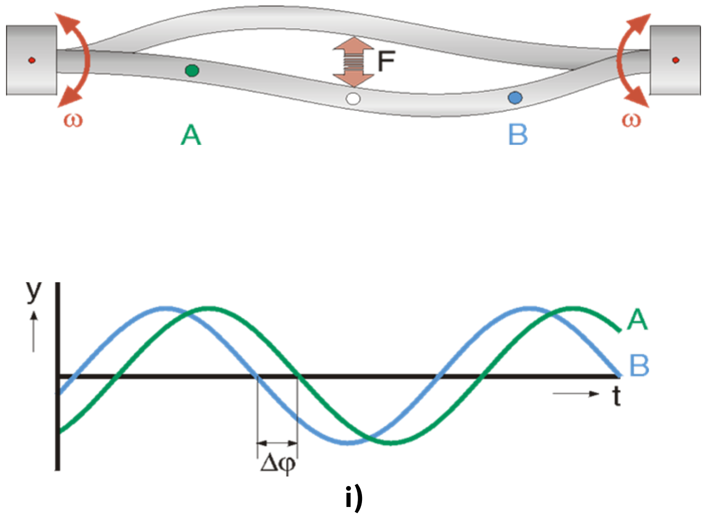


Figure 2: Pressure-density (p-ρ) diagram showing 20 to 40 °C isotherms (magenta). Saturation curves for different quality factors (black) are shown from 0 (only liquid) to 1 (only vapor).

2.3 Coriolis mass flow measuring principle

Coriolis mass flowmeters operate by exciting the measuring tube to oscillate at its resonance frequency. Once mass is flowing, the Coriolis force causes the measuring tubes to ‘twist’. Sensors at the inflow and outflow (see Figure 3: Schematic of Coriolis mass flowmeter tube and pickup coil signals (i). Coriolis mass flow measuring principle and formulas for mass flow and density measurement (ii)., elements A and B) register the difference in time in this movement, in other words they register the phase difference of the two signals. The phase difference of the signal ($\Delta\varphi$) is proportional to the mass flow ($\dot{m}$) in the pipe. The resonance frequency of the system (f_r) is related to the tube's stiffness (K) and its total mass, which is equal to the mass of fluid filling the tube (m_f) plus the empty tube's own mass (m_t). Thus, the resonance frequency is related to the density (ρ) of the fluid filling the tube's volume ($m_f = V_f\,\rho$). Coriolis flowmeters are normally calibrated with water and the mass flow proportionality is determined. Density calibration is typically done using water and air.

As shown, there is no restriction on the state of aggregation of the fluid, thus Coriolis flowmeters can measure substances in any fluid state: liquid, gas or supercritical state. Yet experience and research have shown that under certain conditions, the speed of sound of the fluid could influence the measurement.



$$\Delta\varphi \sim m \times v = \dot{m}$$

$$f_r = \frac{1}{2\pi}\sqrt{\frac{K}{V_f\,\rho + m_t}}$$

ii)

Figure 3: Schematic of Coriolis mass flowmeter tube and pickup coil signals (i). Coriolis mass flow measuring principle and formulas for mass flow and density measurement (ii).

2.4 Speed of sound effect on measuring accuracy

The speed of sound is the distance travelled per unit of time by a sound wave as it propagates through an elastic medium. Sound waves normally travel faster in liquids than they do in gases.

It has been shown that Coriolis mass flowmeters need correction of the calibration factors obtained in water when operated in fluids with low speed of sound, like gases. This correction is systematic and has been determined theoretically and proven experimentally (M. Anklin, 2000). The error mechanism is known as the resonator effect. As the fluid in the tube vibrates, the mechanical vibration travels across the fluid as a compression wave (sound wave). The fluid is compressed and decompressed, effectively decoupling the center of mass of the fluid from the tube's center of mass. This decoupling generates a force against the tube wall in the direction of the Coriolis force, thus the meter overreads. The amount of decoupling depends on the fluid's speed of sound, the vibrating frequency and the diameter of the tube. After the discovery of this phenomenon, Hemp and Kutin (Hemp & Kutin, 2006) proposed a simple approximation for the error due to the resonator effect. Their solution came as the formula $E_{\dot{m}} = \frac{1}{2}\left(\frac{f}{c}r\right)^2$, where c is the speed of sound, r is the tube radius and f the operating frequency. At low speed of sound and high operating frequency, the amount of correction needed is bigger. At high speed of sound, i.e. in liquid application, the effect vanishes and no correction is needed.

In Figure 4, the speed of sound of carbon dioxide is plotted at different pressures and temperatures. At lower temperatures and higher pressures, the speed of sound is much higher. The fluid exhibits liquid-like behavior and no correction is needed in this operating regime. Close to the critical point, the speed of sound of CO_2 changes very rapidly to lower values typical of a gas. Speed of sound compensation is relevant in this region, where the fluid is behaving more like a gas, and careful parametrization of Coriolis flowmeters is needed. At higher temperatures and lower pressures, the speed of sound of CO_2 is much lower and hardly changes with temperature and pressure. In this region, detailed knowledge of the minute changes in sound velocity values associated with pressure and temperature changes is not required to make compensations.

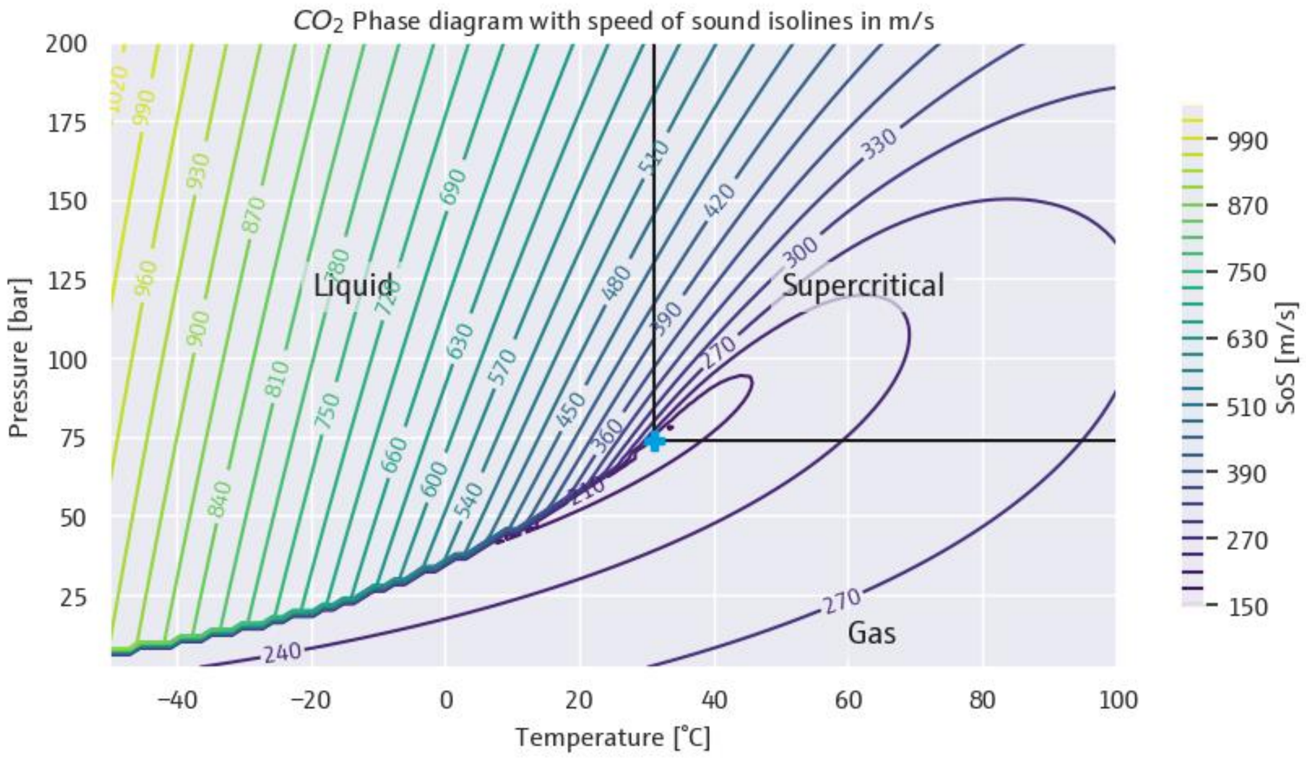


Figure 4. CO_2 phase diagram with lines showing constant speed of sound at different pressure and temperature.

When measuring CO_2 with Coriolis mass flowmeters in CCUS applications, this variation in speed of sound shall be considered. It is very important to follow speed of sound changes when operating in the vicinity of the critical point or, as discussed in the previous section, when temperature swings bring carbon dioxide in and out of the supercritical state of aggregation.

Some manufacturers compensate for the speed of sound error by programming gas mode functions for specific gases. When the fluid has been selected, the flowmeter will apply embedded coefficients to compensate for the error due to the speed of sound effect over many pressure and temperature ranges. This compensation is highly dependent on temperature, which is normally measured directly at the flowmeter, and the pressure value can either be set as a fixed point or brought into the instrument from an external pressure sensor.

2.5 Impact of gas composition

Most discussions about accurate CO_2 measurement happen under the assumption of extremely high purity of CO_2, i.e. 99 % mol. In industrial CO_2 applications like CCUS, the witnessed gas composition can be significantly different. Levels anywhere from 85 to 99 % mol are a common reality. A minor introduction of 4 % mol of another gas component in the mixture composition could produce two-phase flow conditions, as illustrated in Figure 6. In addition, the speed of sound of the fluid is composition-dependent and its variation with process conditions should be considered for proper instrument parametrization to ensure best performance in the application. For most manufacturers, a custom gas mode parametrization is available to adjust to the correct gas composition properties in the application. For example, this can be used to program the reference sound velocity and the speed of sound temperature dependency coefficient. The flowmeter can then apply the correction appropriate to the gas composition.

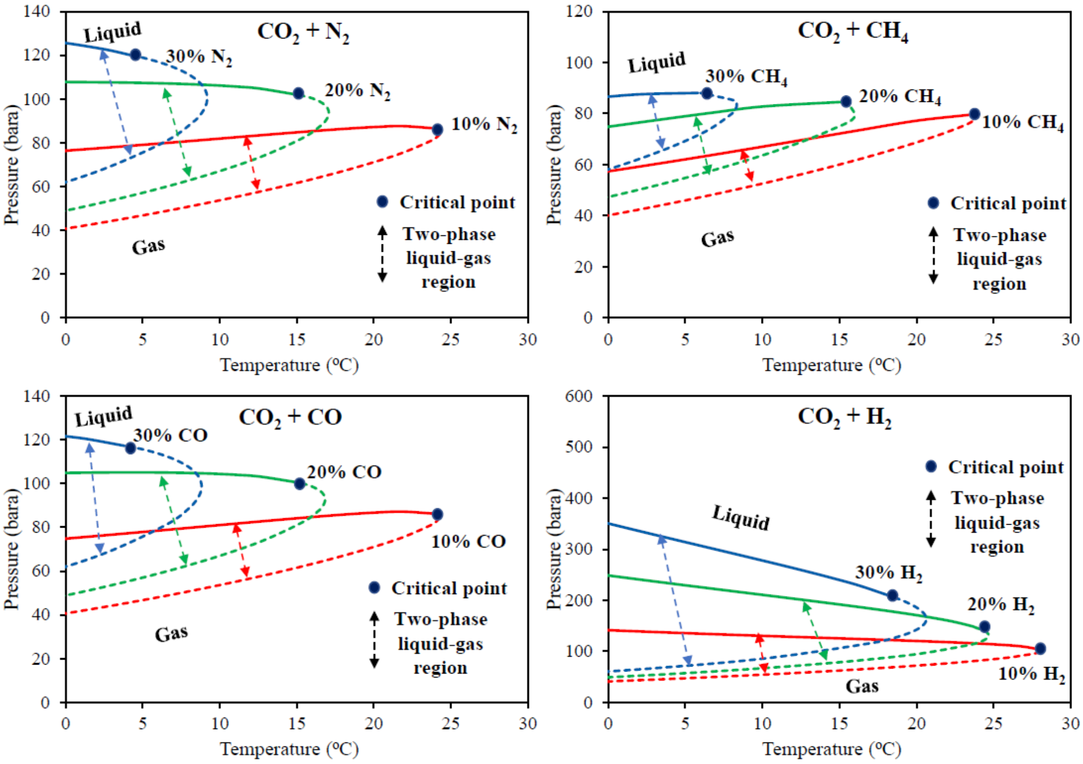


Figure 6: Phase envelopes for different CO_2 mixtures depict the shift in process conditions where two-phase fluid can exist. Reproduced with permission from (Laboratory, TÜV SÜD National Engineering, 2021).

Other notable effects of impure CO_2 can include a shift in the critical point and two-phase locations, previously outlined in the phase diagram of CO_2. This needs to be investigated with increasing attention as CO_2 purity declines. One must also review their process for material compatibility concerns, with varying gas composition. Materials commonly used in Coriolis flowmeters like 316L, 904L, alloy C22 and super duplex materials are all compatible with pure CO_2 processes, regardless of phase. However, in supercritical phase processes where carbon steel pipelines are used, H_2O can turn impurities into acids that will degrade the piping system and flowmeter. If O_2 is also present, the corrosion process of carbon steels is accelerated. Meticulous scrutiny must be paid to material selection and process conditions to mitigate the risks associated with varying gas compositions. In addition to material compatibility, monitoring humidity values is imperative in a CO_2 process with carbon steel. Keeping a value of below 500 ppm will reduce the risk of corrosion (Gan Cuia, 2019).

3 Application, sizing, selection

3.1 Determining point of measurement

Industrial CCUS processes vary greatly in process pressure and temperature design. Figure 7 outlines a typical CCUS value chain. CO_2 is first collected as a gas, then compressed. This compressed gas is transported as a liquid or supercritical fluid by ship, rail or pipeline. Once at its destination, it is either compressed further for sequestration or turned back to a gas phase for utilization in a CO_2 consuming process. At each step of this chain, different phases exist requiring different approaches. The first step for a producer is to determine at which points they need measurement and what phase exists at that point in the process. Regardless of flowmeter accuracy, if the process pressures and temperatures are not stable and two-phase flow is created, measuring accuracy will be greatly affected.

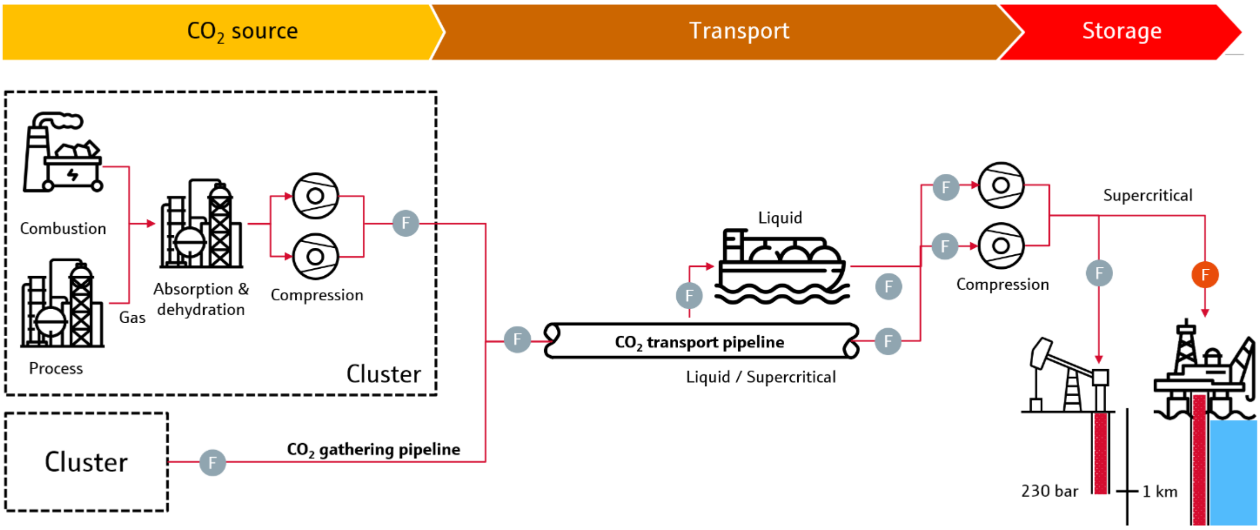


Figure 7: Carbon capture and storage process map showing typical states of aggregation

3.2 Using a sizing tool correctly

Once the measuring points are defined, a fitting device needs to be selected. Flowmeter manufactures often have robust sizing and selection tools to aid customers in picking the best flowmeter for their application. The steps for correct sizing and selection implemented in these tools are listed below.

3.2.1 Determine the CO_2 state from process input data

Figure 8 outlines a decision tree that uses the process conditions to determine the state of aggregation of carbon dioxide. This decision tree is part of the instrument manufacturer's sizing tool but is also useful to reference in CCUS process discussions.

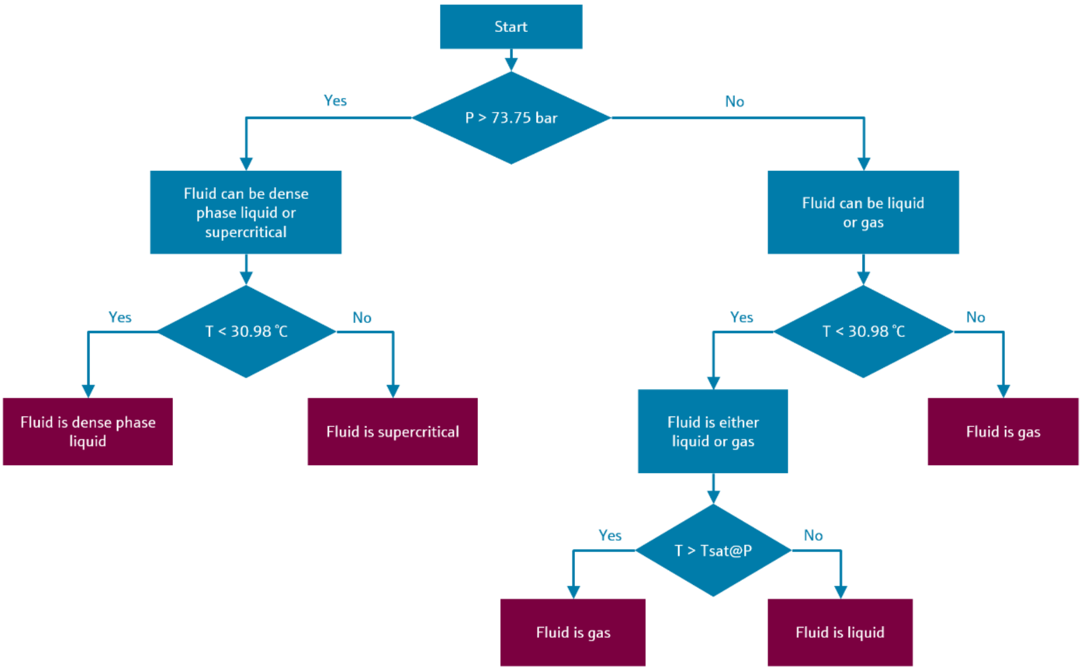


Figure 8: CO_2 state of aggregation decision tree

3.2.2 Select the right fluid model

Flowmeter manufacturers publish sizing applications that emulate the equation of state for various fluids. These applications help to determine a fitting size of flowmeter for each specific application. Figure 9 illustrates another view of the phase diagram, but with suggested fluid models associated to pressure and temperature regions. Selecting the correct fluid model is essential in the sizing stage to ensure that the fluid properties relevant for sizing are correctly determined and that the specified flowmeter operates as expected in the application.

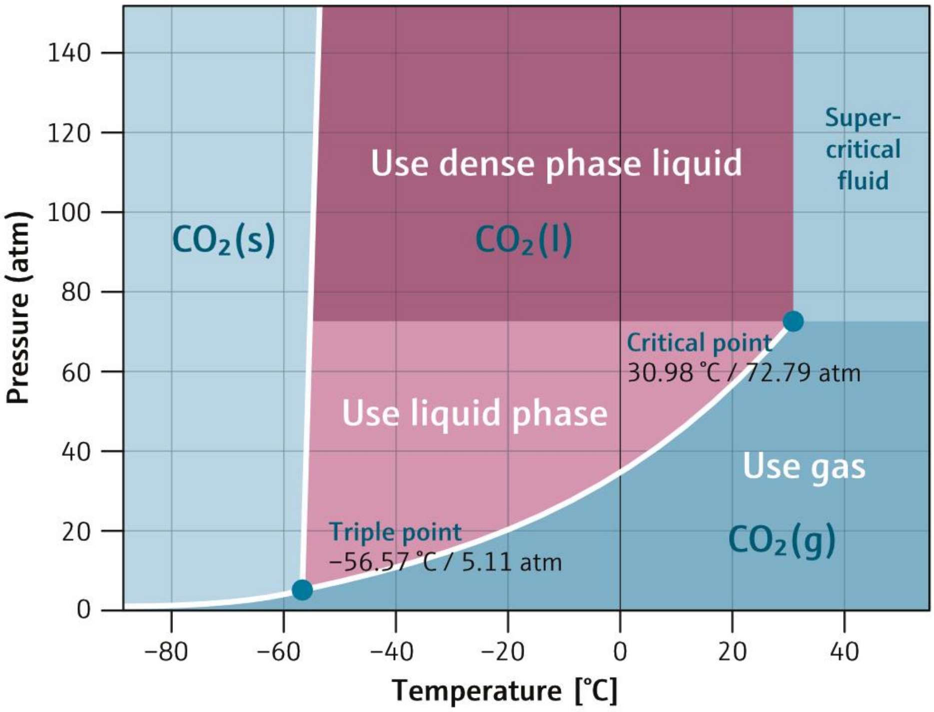


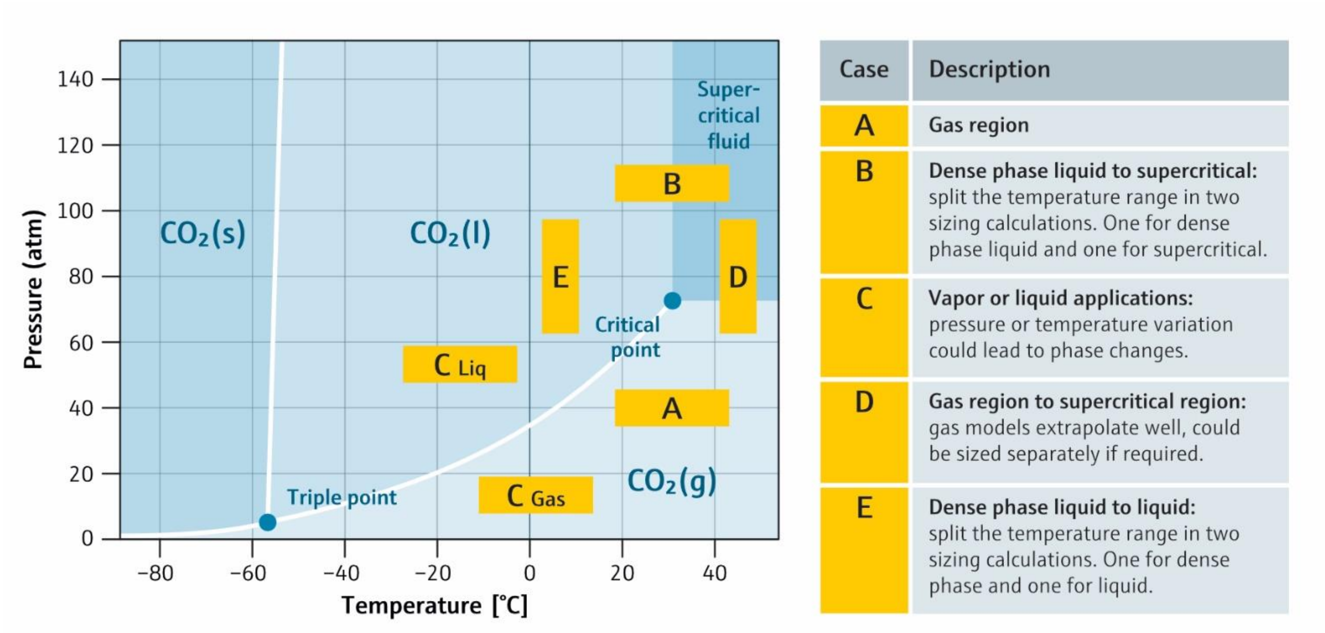
Figure 9: Suggested fluid models according to pressure-temperature region.

3.2.3 Perform sizing

Aided by process data, the manufacturer sizing tool can be used to ensure that the correct flowmeter size is selected for the process at hand. This tool will also ensure that the flowmeter proposed for the process maintains its expected accuracy, visualized with a bell curve graph of flowmeter accuracy across a range of flow rate velocities. Manufacturers and channel partners are always available to support in the evaluation of sizing.

3.2.4 Check for phase changes or violations of assumptions

It is possible that a CCUS measuring point's operating conditions are in a range wide enough that it has the potential to change phases. It is essential that a review be conducted of the process data to ensure single-phase operation of flowmeters. Figure 10 depicts some of these projected situations. One special situation is depicted by case "B", where the process conditions cross the boundary between dense phase liquid and supercritical state. This can be one of the most complex use cases with CO_2 measurement, with the aforementioned variations in fluid properties in different phases. Flowmeter manufacturers validate the calibration of instruments using different reference systems for fluids in liquid and gaseous states. And thus, the reference accuracy is based on the reference systems used, which are different for gases or liquids. For gases, the uncertainty of reference systems is much bigger due to inherent complexity to determine the mass of gases in flowing conditions. In case B, the fluid will move from a liquid regime to a supercritical regime without exhibiting any phase change, only a continuous change in density and speed of sound. So which accuracy specification is valid? This is an area of continuous research in the flow measurement community. Therefore, manufacturers tend to mark a limit in performance and recommend using two accuracy specifications for each region until the consensus is reached. In such cases, the flowmeter shall be sized using both phase possibilities. Once the sizing tool recommends the ideal flowmeter line size using the dense phase data points, the sizing exercise should be performed again in the supercritical possibility of the process. If the line size of the suggested meter differs between phase possibility, operators should choose a flowmeter specific to one line size and judge the negative performance effects of operating that instrument in the other phase. For phase transitions between liquid and gas, some manufacturers offer an advanced diagnostic functionality that can be trended in a control system to flag such a phase change or process upset. Those features are described in greater detail in section 4.4.



Case	Description
A	Gas region
B	**Dense phase liquid to supercritical:** split the temperature range in two sizing calculations. One for dense phase liquid and one for supercritical.
C	**Vapor or liquid applications:** pressure or temperature variation could lead to phase changes.
D	**Gas region to supercritical region:** gas models extrapolate well, could be sized separately if required.
E	**Dense phase liquid to liquid:** split the temperature range in two sizing calculations. One for dense phase and one for liquid.

Figure 10: Use cases of CO_2 measurement in different states of aggregation

3.2.5 Complete sizing

Review previous steps as a final check and proceed to ordering the flowmeter.

4 Commissioning

4.1 Pressure compensation (fixed vs. external)

While fixed pressure remains a viable option, the potential for measurement errors arises if the actual pressure deviates from the predetermined value. Thus, in adherence to best practices, employing an external pressure measurement is recommended. This is the case especially when operating in the vicinity of the critical point of the fluid. Additionally, positioning the pressure measuring point as closely as possible to the flow measuring point is advised. Three line size diameters downstream is a good rule of thumb to ensure the pressure has recovered from the drop due to the area reduction in the Coriolis flowmeter. Integrating this measurement directly into the flowmeter via a process signal not only provides live pressure data but also enables the compensation of flow measurements, thereby guaranteeing the highest level of accuracy.

4.2 Perform as found verification to provide baseline values

Some manufacturers have implemented onboard verification technologies that can be used to determine the condition of flowmeters in situ. Conducting an as-found verification immediately after the installation of the meter is crucial for establishing baseline values in the actual process conditions. This practice, widely adopted across all industries, serves multiple purposes. Firstly, it provides an initial set of condition data against which future measurements can be compared, allowing for the monitoring of the meter’s health over time. Trending capability is essential for identifying any deviations or drifts in measuring accuracy, which could indicate potential issues with the meter or the process conditions.

Moreover, as-found verification demonstrates due diligence by ensuring that the reported readings are both accurate and reliable. This process involves a thorough check of the meter’s performance under actual operating conditions, helping to detect any possible failures or inaccuracies early on. By identifying and addressing these issues promptly, integrity can be maintained in the measurement system.

4.3 Predictive diagnostics

Coriolis mass flowmeters contain a wealth of diagnostic data which can be integrated into a control system. This diagnostic data provides an insight into the operator’s process. Some software suites offer verification reports for increased confidence in measuring performance. In these verification reports, live instrument data is compiled and judged against factory set thresholds on the device. If live data readings exceed predetermined factory thresholds, the verification report will flag the values for operator review. A failed verification report is a key indicator that the instrument should be examined for functional integrity. Depending on which values are beyond set thresholds, a recalibration might be necessary. Conversely, a passed verification report gives operators increased confidence that their flowmeter is performing within factory specifications.

Beyond detailed verification reports, there is an entire landscape of advanced diagnostic functionality that differs depending on which instrument manufacturer is selected by the user. For example, using Endress+Hauser's patented Heartbeat Technology, operators can monitor and trend values like Heartbeat Sensor Integrity (HBSI). Using this test point, detection of critical safety concerns in CO_2 processes like corrosion/abrasion of the inner Coriolis tube wall(s) is possible. With acid drop out being a major concern in industrial CO_2 processes, such monitoring functionality enables predictive maintenance planning. Best practice is to engage the manufacturer with the specific process requirements, for custom application of such tools. A brief introduction of general test points is outlined below.

4.4 Density monitoring

Density monitoring is a key indicator in CCUS applications. As illustrated in the previous phase change diagrams, density values will be greatly affected by which phase CO_2 exhibits. Monitoring and trending of this variable can give the user insight if their process is unstable or changing phase. Control system alarms can then be set to quickly mediate the upset in the process. This proactive approach helps maintain the efficiency and reliability of CCUS processes.

4.5 Excitation current

Excitation current serves as a crucial diagnostic, offering insights into the magnitude of current applied to the exciter coils of the flowmeter. A high excitation current may indicate various process upset conditions, including introduction of liquid in gas applications, substantial percentage of solids in the fluid, process build-up on the measuring tube(s) or defective components in the flowmeter.

4.6 Oscillation damping

Oscillation damping is comprised from the ratio of excitation current to oscillation amplitude and expressed in the engineering unit A/m. Unlike excitation current, oscillation damping serves as a more sophisticated diagnostic tool, allowing for the utilization of a ratio to discern the presence of bubbles (such as inhomogeneous/slug flow or microbubbles), solids, high-viscosity fluids or a combination of process anomalies. It is advisable to trend and monitor this data to distinguish between normal trends and deviations from the established norm.

4.7 Signal asymmetry

Signal asymmetry is the difference in oscillation amplitude at the beginning and the end of the flow measuring tube(s). Detecting variations in the signal asymmetry value can be an indicator of abrasion due to high velocities with solid particles present.

Alternatively, some flowmeters' internal verification test can detect such process impacts so the user doesn't need to be a Coriolis specialist.

5 Conclusion

Accurate CO_2 measurement is critical for industrial producers to meet regulatory requirements and minimize financial liabilities. The stringent regulations on CO_2 emissions necessitate precise measurement throughout the CCUS (Carbon Capture, Utilization and Storage) value chain. Even minor inaccuracies can lead to significant financial impacts, making reliable measurement essential for operational efficiency.

Coriolis flowmeters have proven to be a robust solution for CO_2 measurement due to their high accuracy and reliability across various states of aggregation – liquid, gas, and supercritical. However, the unique challenges posed by CO_2, such as phase changes, variations in speed of sound and the presence of impurities, require careful consideration in the design and implementation of measurement systems.

Key elements for optimizing CO_2 measurement include:

1. **Proper sizing and selection**: Utilizing robust sizing tools to select the appropriate flowmeter based on specific process conditions ensures optimal performance.
2. **Commissioning practices**: Implementing external pressure measurement and predictive diagnostics enhances measuring accuracy and reliability.
3. **Material compatibility**: Ensuring that materials used in flowmeters and pipelines are compatible with the varying compositions of CO_2 to prevent corrosion and degradation.
4. **Advanced diagnostics**: Leveraging diagnostic data from flowmeters to monitor process conditions and detect potential issues early, thereby enabling proactive maintenance.

By adhering to these best practices, industries can achieve accurate CO_2 measurement, which not only supports regulatory compliance but also offers economic benefits through tax incentives and improved operational efficiency. As the global focus on sustainability and climate objectives intensifies, the importance of precise CO_2 measurement will continue to grow, making it a vital aspect of modern industrial operations.

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