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How to monitor the CO_2 purity in the brewery?

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Introduction

Carbon dioxide in the brewery is generated by the yeast during fermentation, together with heat and alcohol. Because CO_2 is required at the end of the manufacturing process to add the fizzy effect to the final beer, it reduces costs by recovering it during fermentation. Nevertheless, great care needs to be taken to avoid contamination of the final beer by air. Oxygen in final beer reduces the product shelf life and contributes to off tastes known as stall or cardboard.

Additionally, a maximum CO_2 recovery yield is expected from this process. In this paper, oxygen impact on CO_2 purity is presented as well as Hach Lange solutions for reliable oxygen measurement. Today purities of around 99.998% can be achieved with the latest CO_2 recovery plants.

How pure should the CO_2 be (considering only the oxygen presence)?

To quantify the oxygen effect into the beer we will identify the scenario taken.

Process

In this case we suppose that carbonation is generated by dissolving the required number of volumes of CO_2 into the beer. Let the oxygen impurity content be x ppmV, and let y volumes of CO_2 be dissolved in one volume of beer. Then the resulting dissolved oxygen concentration will be:

$$DO_2 = x.10^{-6}\frac{literO_2}{literCO_2}.y\frac{literCO_2}{literBeer}.\frac{1}{22.4}\frac{mol}{literO_2}.32.10^6\frac{\mu gO_2}{mol}$$

$$= 1.42xy\mu g / liter$$

Concentration of O_2 in CO_2 (ppmV)	5	10	50	200
Vol. CO_2 dissolved per vol. beer	**Dissolved O_2 ppb in the beer**			
0.5 v/v	4	7	35	142
1.0 v/v	7	14	71	284
2.0 v/v	14	28	142	567

Table 1. CO_2 purity and dissolved O_2 impact, scenario 1

The unexpected result here is that a very small impurity of oxygen in the carbon dioxide can produce a damagingly high dissolved concentration.

The explanation of these phenomena is as follows. In this process equilibrium does not exist, the total gas pressure must exceed the equilibrium pressure corresponding to the desired CO_2 concentration of y volumes per volume, and as CO_2 is dissolved out of the bubbles the partial pressure of oxygen can rise to high values. Hence the means is available to force all oxygen present in the system into the beer.

The purification process [1]

In this system (Figure 1), CO_2 is drawn off the storage tank and flows through a counter-flow water washer where water-soluble compounds are dissolved.

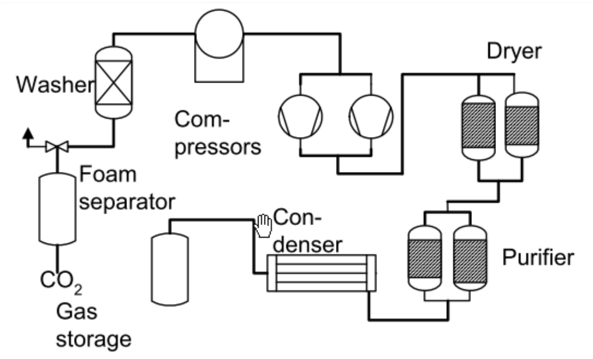

Figure 1. The standard method for CO_2 recovery.

Next, the compressors increase the pressure up to the water condensation level and separate any remaining water from the gas. The next step is to dry and purify the gas. Most of the permanent gases, oxygen and nitrogen, are separated in the condenser following a purification step after which the condensed gas is stored. Inefficient separation of the permanent gases is the main drawback with this traditional CO_2 recovery system. Only about 50 % of the CO_2 released from fermentation can be recovered by means of this configuration due to the difficulty of separating the initially high concentrations of nitrogen and oxygen. Therefore, CO_2 recovery normally begins 24 hours after the start of fermentation to assure that the incoming fermentation gas has a minimum CO_2 concentration of 99.5 Vol.%.

This is the reason why most of the newly installed recovery systems use a rectification column for separating the permanent gases. Here, the dried CO_2 gas is liquefied and afterwards cleaned CO_2 is led in counter flow to boil out the permanent gases (Figure 2).

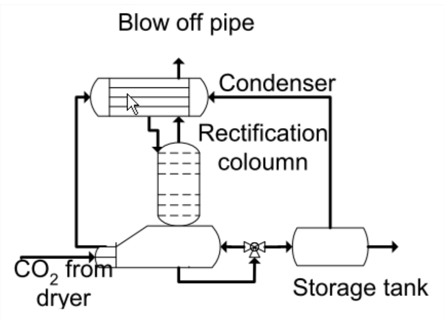

Figure 2. CO_2 rectification.

Measuring technologies

Electrochemical technology

Basically the EC sensor receives a voltage and provides a current proportional to the oxygen partial pressure. Over the years this technology has been proved and provides unsurpassed sensitivity and accuracy for oxygen trace monitoring. As the CO_2 measured is dry, early generation EC sensors had electrolyte depletion which meant having to refill the sensor with electrolyte on a regular basis.

Luminescent technology

In this technology a sensitive dye will have optical properties changed (luminescence) when in contact with oxygen. As with all optical devices, and contrary to historical EC technology, the huge benefit provided is a much lower dependence on calibration and service operations. On the other side the LOD[1] is 15 ppmV when it is about 2 ppmV for the EC sensor. Accuracies are of the same magnitude.

Sampling and setup

Two main sampling solutions exist: off line and in line. Each variant will be described first and evaluated using EC and LDO sensors.

Off line with EC sensor

This variant requires an Orbisphere model 32001.XXX flow chamber (Fig. 1) where the oxygen sensor is attached. A 6mm or ¼" pipe draws the sample from the main CO_2 line. This was historically the first setup described below (Fig. 2).

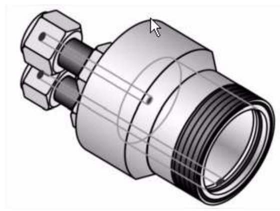

Fig. 1 Flow cell 32001.XXX

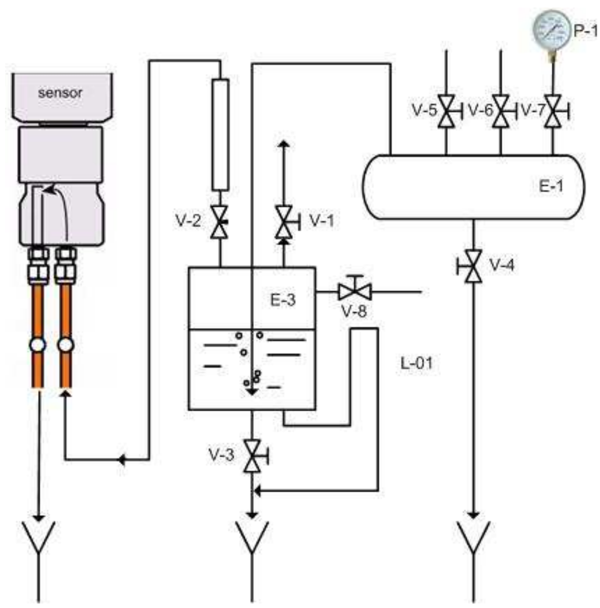

Fig. 2 CO_2 sampling setup

[1] Limit Of Detection

Principle: CO_2 coming from several fermenters first goes in the collector E-1. Valves V-5 to V-7 allows choosing the feeding line, or to connect the water inlet or an oxygen analyzer for validation or calibration purposes. A pressure gauge P-1 indicates the gas pressure. The valve V-4 allows purging the collector of foam and other residues. The collected CO_2 goes to the vessel E-3 where it is saturated with water in order to reduce the electrochemical sensor drying effect when measuring in dry gases. When opened the valve V-1 purges the vessel. Water enters through V-8 and the pipe L-01 acts as a spillway in order to maintain the water at a given level when refilling the vessel. V-3 is the vessel water purge. The needle valve V-2 adjusts the flow that is indicated in the flowmeter (rotameter type). Note that the flowmeter should never be installed at the flow chamber outlet. The reason is because the correct O_2 concentration is shown when the sensor works at ambient pressure, after the needle valve. Typical sample flow of 1-5 ml/min is very low and does not generate any health or safety issues. The optimal sensor configuration is with the 2956A membrane together with the protection cap model 29106 for measurement in dry gases.

This configuration is optional and with the new generation A1100 sensor the humidification step can be removed.

Fig. 3 CO_2 sampling for flow cell 32001.XXX and EC sensor

Fig. 4 Another configuration of CO_2 sampling

Off line with LDO sensor

Dry gas measurement is not an issue with LDO sensors. For this reason the previous setup can be simplified by removing the humidifier vessel.

In line

The direct in-line sampling is facilitated using the ORBISPHERE self-sealing “ProAcc” valve, combined with the Varivent™ housing (Fig 5).

Fig. 5 Principle of the ProAcc self-sealing valve

Inserting any LDO or EC sensor opens a chamber where part of the main stream will flow. The opposite happens when removing the sensor, with the main benefit being to avoid a process interruption as the line always remains with the gas flow inside (Fig. 6).

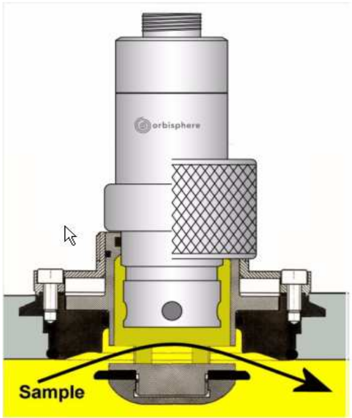

Fig. 6 The ProAcc valve fitted into a Varivent™

Nevertheless, the consequence is that the sensor is measuring the total oxygen pressure and therefore needs to be compensated by the total pressure of the line. This is done by installing a pressure sensor fitted into a model 33078 adapter (Fig. 7). Note that today (May 2012) there is no LDO system available with an external pressure sensor.

Fig. 7 Adapter 33058 with flow chamber for pressure sensor

Variant comparisons and conclusion

3 variants are available today for oxygen measurement in CO_2 recovery by combining sampling and detection technologies. They are described in table below. None of the presented solutions shows exclusive benefits.

While off line variants offer flexibility for service allows different CO_2 source connections, the in-line variant has less complexity.
For the sensor technology, the LDO requires less maintenance but has an LOD of 17 ppmV against 2 ppmV for the EC sensor. This means that the EC technology is therefore more appropriate for high CO_2 purity monitoring or for validation tasks with an external analyzer used as reference.

	Off line		In line	
Criteria	EC	LDO	EC	LDO
Lowest detection level [ppmV]	2	20	2	n/a
Accuracy [ppmV]	±2	±17	±2	
No additional pressure sensor	+ + +	+ + +	---	
Long term stability	+	+ +	-	
Sensor extraction without process interruption	+ + +	+ + +	+ + +	
Validation with external reference	+ + +	+ + +	-	
Response time after service	-+	+ + +	-+	
Maintenance frequency	+	+ +	-	
Complexity	+	+ +	+ + +	
Cost	+	+	+	

Table 2 Sampling variants comparison

Bibliography

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