



Analysing CO₂ in the gases industry

By **Sam A. Rushing** on Jun 01, 2017

Carbon dioxide (CO₂) quality begins with the raw feedstock, and even the ingredients and agents which go into this feedgas or feedstock – these agents can be substances such as the natural gas or coal which is combusted for flue gas, then downstream liquefaction and purification occurs.

The lion's share of CO₂ source types are chemical by-product in nature, most of which are a handful of source types, including a highly-concentrated by-product from reformer operations in oil refineries and by-product from anhydrous ammonia operations. There is also an ever-important number of fermentation by-product plants in the US, distilled ethanol from (usually) corn and grain.

Then we have natural sources from mother nature; which are wells dating back before the dawn of man. These major sources are often the cleanest and easiest to recover and refine, and typically these sources are very high in raw CO₂ content, in a water-saturated stream. Once the water is knocked out, then the CO₂ content alone can be up to or beyond 99% by volume. In some cases, as with the natural sources, impurities are a challenge; for example, there have been cases containing high levels of hydrocarbons, including methane and heavier hydrocarbons, too much sulfur content, and of course the case of benzene, which is particularly difficult.

Beyond these potential problems with some natural sources, the wells can be the cheapest method of producing CO₂, if they are high pressure (thus eliminating the feed compression component in the plant and very pure – many of these sources are extremely pure. In such cases, little more than carbon is required for purification, plus the usual liquefaction in a CO₂ plant. These chemical by-product sources are also relatively easy to purify, and often do not require additional hardware such as Lo -Cat operations for sulfur removal, or catalytic oxidation for the removal of higher levels of impurities. In the end, when operating a CO₂ plant, to accomplish the desired food and/or beverage-grade quality, in-line gas chromatographs (GC) are used to monitor a continuous flow of quality. GC is a standard analysis measure today.

Other source types such as titanium dioxide and ethylene oxide are less common. In the case of ethylene oxide, this is a bit more difficult to refine, due to chlorides in the raw stream, and the requirement for some more expensive metals used in the construction of the CO₂ plant. The metallurgical issue requires more capital investment in an ethylene oxide by-product operation. However, food and beverage quality is fully achievable from these sources, in any event.

Next, flue gas and natural gas processing operations are found in some markets, albeit few in number, however, the common amine solvent MEA (monoethanolamine) is the basis behind recovering CO₂ from a lean stream, with CO₂ content down to 3% from natural gas-fired cogeneration exhaust (once found in a New England plant). More commonly, CO₂ content in the teens or above, on a percentage basis, is recovered and concentrated in the MEA plant. Downstream is the traditional CO₂ plant, which liquefies and purifies the CO₂, which is readily achieved. In the end, an excellent quality product is available from this form of raw feedstock, and the ingredients used in producing the flue gas – that being natural gas, and even coal in some cases – such as with AES cogeneration plants in Maryland and Oklahoma (US).

What is important, in reviewing the most common plant types found in the US and in many global markets, is to mention that food and beverage grade is well produced from these traditional source types.

Quality perception

In the world of chemistry and chemical processes, much can be done in terms of taking a rather 'nasty' product (or a product which is perceived to be offensive) and turning it into something desirable. With the 'nasty' perception taken into context, many consumers would be less than pleased to know their product is coming from various chemical sources, like ammonia or ethylene oxide, as well as their view of waste-related sources per sé.

On the other hand, some of this thinking is changing, with respect to the sources themselves, as well as the refiners, and ultimately the consumers. It is entirely feasible to turn some waste-borne streams into something chemically pure, meeting all the demands surrounding the chemical, physical, odour, and taste elements laid down by organisations including the CGA (Compressed Gas Association), ISBT (International Society of Beverage Technologists), and like organisations which set standards, as well as the gas companies.

In the end, as the world requires more recycling and reclamation of otherwise wasted raw feedstocks, particularly when chemical purity is fully achievable, and a desire to reduce emissions becomes a matter of fact on a global level, the sources for CO₂ refinement will become more diverse – and ultimately reduce the carbon footprint, and become acceptable. It is interesting to see some of the major soft drink firms starting to recycle materials to produce plastic containers, where this recycling will eventually morph into raw ingredients, including CO₂ supplies, which are chemically pure and strategically located. With improvement in strategic location of sources, this would impact the bottom line of both the supplier and consumer very favourably. Commercial labs test the product along the supply chain from the source to the gas company, to the customer, in many cases; all dependent upon need and set protocols.

Then, sources are known for their ease or difficulty to produce a quality product for industry; and ongoing testing and monitoring of quality is a directive in the industry today. From this point forward, the next steps from distribution to storage, and then the application in industry have their input on, and interpretation of, quality and testing.

Organisations that set the bar

In the US, many years ago, the USP (US Pharmacopoeia) was a simple guide as to standards, and even certain independents in the US used this very basic standard for quality at one time. On the other hand, in part, what prompted the stringent standards for quality in the beverage market, were a few cases of contamination, as I recall a few incidents in Europe, and additional cases elsewhere.

For example, in the US, an independent producer owned and operated a CO₂ plant sourced from Eastman Chemical, a coal gasification source which (probably) was never tested properly, perhaps as not required at the time. After years of operation, it was discovered the CO₂ product sold from this plant contained higher than acceptable levels of hydrogen cyanide. Subsequently, the company closed the operation, and eventually went out of business. Many of the cases of testing or contamination included operator misunderstandings or error as well.

Today, organisations which are relied upon include the CGA, the ISBT, and EIGA (European Industrial Gases Association), among others. Within the CGA, grade 'I' generally defines beverage grade; the 'H' grade covers food applications in industry. There are other organisations and standards used for quality guidelines, by large food processors such as Tyson Foods, which probably has more meat and poultry operations combined than any other US processor. As a footnote, the USP grade 'G' corresponds to commercial use for the product.

Net effects of quality and downstream testing

The bottom line, with respect to testing and retesting product, is the assurance that quality and chemical purity will be met; however, other features of the CO₂ will be in line, such as definitions surrounding taste and odour. For example, we don't want our food products to taste like the feedstock or ingredients contained in the sources where CO₂ is derived, do we?

When thinking of beverage applications, it is well known this sector is the most highly tested of all sectors of the industry, beyond USP, even though it probably represents 20% of US demand for CO₂ in the merchant market, with relatively flat growth. Due to a history of a few accidents in sourcing, processing and handling, representing cases of contamination (whether this be plant operator error or feedstock contamination, for example), it is the stringently tested line of CO₂ for a given product, that being soft drinks (primarily) and beer production.

In some markets, many of the large breweries use merchant (beverage-grade) CO₂ to back-pressure the system, and not for actual carbonation. In the beer arena, smaller breweries more commonly use merchant CO₂ to supplement their carbonation needs, unlike some of the largest breweries.

Once again, in the case of soft drink manufacturing, the demands for CO₂ are very stringent, to the point of testing every load of product delivered to the soft drink manufacturing plants; not just what the gas manufacturer is already testing, and all the care already taken. The major beverage firms have their list of requirements and standards from quality and assurance perspectives, and further requirements for tours of new plants which produce CO₂. Then, a regimen of testing occurs with many of these firms, such as quality specifications covering both limiting characteristics and specific test methodology, and of course testing every delivered load of product. These standards are supported by definitions set by the trade organisations.

For the CO₂ producer and suppliers, it is critical to follow the requirements defined by the beverage customers and the trade associations; and even work with the trade associations and beverage majors to initiate change and further acceptance of source types for the merchant CO₂ market.

Even though it is often not apparent for the consumers of food and beverage products, which are scrutinised rather strongly for taste, odour, and quality, it remains key to producing a viable product to serve the desired markets. This is an industry which is constantly evolving, and developing new applications, which is truly interesting.

About the author

Sam A. Rushing is President of Advanced Cryogenics, Ltd, a chemist, and a global consultant to all sectors of the CO₂ industry, as well as cryogenic gases. If you have a CO₂-related or cryogenic project, and need expertise, please call upon the company. Advanced Cryogenics also supplies a full menu of CO₂ and cryogenic equipment, new and used.

+001 305 825 2597,

rushing@terranova.net

www.carbondioxideconsultants.com