In focus...

Co_2 applications and sourcing alternatives

By: Sam a. Rushing, Advanced Cryogenics, Ltd

On one hand, carbon dioxide (CO_2) is often mentioned in the press as the most abundant greenhouse gas, now in excess of 400 ppm (parts-per-million), according to most measurements, and a serious threat to global warming and a major contributor to climate change.

On the other hand, there have been rather severe shortages in various world merchant markets, primarily due to a lack of by-product carbon dioxide from (sometimes) anhydrous ammonia production, which is a common raw feedstock for many CO_2 liquefaction/purification plants. The reasons for such outages are annual turnarounds of the source plants, reduced source plant operating schedules (due to shorter farming seasons), and natural gas feedstock problems for the ammonia plants, as one troubled source type.

There are also a host of mechanical problems and maintenance schedules, for various source plants, such as ethanol plants in some global markets, which seem to occur all at the same time – which coincidentally leads to dire shortages in these markets. To put this in context, with the dire shortage of CO_2 for traditional uses such as soft drink and beer carbonation, meat processing, and a host of other uses, one could feel that since there is so much CO_2 in excess everywhere, and ever more being vented to the atmosphere all the time (such as with Trump's love of coal), how can we not have the commodity available for our daily traditional needs, such as beverage carbonation?

Of course, this question requires a complex answer, that being, a function of sourcing for the CO_2 plants which acquire the commodity from (usually highly concentrated) by-product streams in the energy and chemical industries, primarily. Diversity of sources is the ultimate solution to the sourcing problem. Much of what has happened in terms of lack of CO_2 supplies in certain global markets, has in part precipitated thoughts surrounding a need to further diversify source types, and perhaps go to non-traditional sources to overcome this, as a long-term fix.

Applications

We are in an era of increased food processing, with developing economies moving further toward processing and preservations techniques which can use cryogenics and specifically carbon dioxide in various forms, to achieve improved value and freshness. Food is the first application mentioned since, in the US, this represents roughly 40% of all merchant usage – and a comparable sum in many developed economies.

In many markets which are studied, there is often an ongoing battle among refrigeration methods, including the use of cryogens, including CO_2 and nitrogen. Mechanical refrigeration and glycol chilling are large in various markets. Long-term, I have noticed among the largest of CO_2 food processors, at one time there was a high use of CO_2 such as major poultry processors, then new management came in and mechanical refrigeration became trendy. Then, over time, some of these plants morphed into combined mechanical and CO_2 utilising operations – such as CO_2 snow used in specific uses for grinding and blending of the poultry products, in this case; and IQF (individually quick frozen) took place mechanically. Individual plants sometimes returned in part or sometimes in full to CO_2, including the predominant IQF (individually quick frozen) use of CO_2 initially, then on to mechanical refrigeration; then eventually returning in part or in full to carbon dioxide.

When CO_2 is taken into context, it is far more resilient, and fully compatible with a wide range of applications compared to mechanical, glycol or nitrogen options. One specific feature of CO_2 is that it is available in three phases (solid as dry ice, gaseous in a vapour form, and liquid), all of which are fully unlike the other refrigeration alternatives.

Conceivably, food and more specifically meat/poultry plants have uses for all three CO_2 phases in-house. This would be the use of CO_2 pellets (3/4" or rice size) for blending, grinding, cooling in shipping and more, then the use of a gaseous CO_2 which can be for MAP (modified atmosphere packaging) use in a packaging process. Then, there is the liquid product which is piped into a plant and used in IQF applications, the production of snow or pellets, and vapour used in MAP applications, all from bulk liquid storage onsite. Even pneumatic applications can be derived from this means. Of course, there is also the common application for CO_2 usage in the more humane 'stunning' of hogs and poultry, for example.

As for the future of food processing, the major gas companies have been the primary factor in developing food applications, along with application improvements and developments within/by the major food processors which consume significant quantities of product. As to equipment suppliers, there are brand named products such as Chart's Chilzilla system, which claims to increase dry ice production and improve food freezing efficiencies via increasing refrigeration capacity up to 24% over traditional bulk storage.

Other claims by gas companies, of a proprietary nature, suggest improved product flow through various types of freezers, improved gas injection and efficiencies, along with improved controls, which ultimately lead to improved quality of a chilled or frozen product, and less CO_2 usage and power consumption producing such results. Some years ago, specific valves were patented and claimed to be the centre of the proprietary food freezer, as one example of claimed improvements toward refrigeration value, refrigeration efficiencies, and reduced CO_2 usage. Other thoughts toward achieving a value-added feature in food processing via various freezers has been residence time in a cryogenic freezer, followed by mechanical refrigeration; or cryo-mechanical freezers as a means of branding certain equipment as proprietary. The ultimate goal is increased sales and a growing customer base for the gas companies of course, however, they are working toward incrementally improving hardware and gaining efficiencies along the way.

Looking at other applications which are moving along in popularity and as new or improved uses for the commodity, it is interesting to note sometimes older applications such as greenhouse growth enhancement via CO_2 are enjoying a renaissance. This sector is enjoying increased usage for certain premium crops, including plans to vent by-product from captive ethanol sources directly into large (premium crop) greenhouse operations. Beyond this, select premium crops are gaining notoriety, and a wide use in more regions and states. In such cases, CO_2 is being used in new and expanded closed greenhouse operations – which is simply more use in the agricultural sector. Beyond this, there are developments, for these premium

> **"As was harshly felt in places such as the UK and Mexico, CO_2 supplies this summer have become extremely unavailable"**

crops, to apply the product in the field. As for applications for outdoor premium crop growth enrichment, the product is piped along the rows of the plants and released to enhance growth. This use of the product in the field, for a high-priced premium crop is particularly interesting; where in the past, a very dilute flue gas was attempted to be used for crop growth enhancement, which was borne from engine exhaust fumes from the pumping stations in the fields. The latter example, as a dilute form of CO_2 from engine exhaust, was in the end reported to not be beneficial.

The application of CO_2 in concrete, which strengthens and sequesters at the same time, via injection into the poured and pre-cast modes, creates more calcium carbonate formation. The dosing companies are entering the picture, which claim to have the dosage of CO_2 developed to a science. This is a growing use; however, in some developed markets, it is largely unknown.

Sourcing

As was harshly felt in places such as the UK and Mexico, CO_2 supplies this summer have become extremely unavailable, largely due to the ammonia sector. Ammonia is probably the second most abundant raw gas to the gas company refining network in the US, behind ethanol as the most abundant.

In Mexico and the UK, a number of problems resulted in rather dire shortages of food and beverage applications for the product, such as a dire lack of CO_2 which is an integral part of British pubs, and fears of the lack of CO_2 as a refrigerant, both in liquid and dry ice states, along with MAP uses brought many to fear for their safety when consuming common meat and dairy products, due to fears of spoilage and bacterial contamination. In Mexico, the beverage sector is likely the largest market for CO_2 and in the heat of summer, the lack of traditional beverages from soft drinks to beer, created a sort of misery for the consuming public.

What happened in these markets, is a series of factors – from ammonia production schedules, to state-owned ammonia plants, along with feedstock supply issues; to mechanical problems, and annual maintenance, among other issues, precipitated a 'perfect storm' behind the practically sheer lack of supplies in some of these markets.

In these markets, the press was reporting on the lack of CO_2 supplies, unlike other times of shortages; and this was in the mainstream press, not only limited to publications in the chemical and gases industry, as other shortages were reported in the past.

The answer to the lack of adequate CO_2 supplies, even at a higher replacement cost, such as shipments from a longer (regional) distance to the demand centre, was often the key problem with these recent shortages. When available from a distant market, the more immediate answer to the problem is replacement CO_2 shipped into these markets from other sources, such as US sources supplementing Mexican CO_2 demands.

However, this is a temporary solution to the problem. On the other hand, ▸

this 'perfect storm' scenario should not repeat itself often again, in my view. The ultimate answer to this problem of the almost sheer lack of supply capabilities, is to expand the portfolio of CO_2 source types – this is largely what exists in the US, a full menu of available sources to the gas companies. It has been argued among experts that perhaps the US is too reliant on ethanol/fermentation as a source type, where over 40% of all US sources are derived from (primarily) fuel-grade ethanol plants. When arguing this point, it is said that both sides of the political isle are in favour of ethanol; and even in the harsh political climate in Washington today, there is strong support in favour of ethanol as a fuel additive. Therefore, it is felt the US fuel grade ethanol plants will be around for a long time ahead.

As it turns out, over time, which can be a week to a few months, or even to years out, various CO_2 sources can have their problems – making CO_2 unavailable, or reduced in availability. Examples of this include a natural gas spike, bankruptcies, and a full reorganisation of the ammonia industry which occurred in the US decades back, making the product unavailable in some regions and creating merchant CO_2 shortages in other US markets. The CO_2 industry survived by the well-developed back-up system which is served by multiple plants and source types within the confines of the gas companies.

In Mexico, it is said by some, alternate sourcing will be sought, such as a return by some companies to CO_2 combustion plants which are then self-sufficient, assuming available hydrocarbon-based feedstocks are available, such as fuel oil, diesel, and natural gas. In the short to even long-term, there will be imports of CO_2 from outside Mexico, including from the US, and longer-term strategies for diversification of by-product source types – beyond ammonia, reformer and other hydrocarbon source types are under consideration. This will need to be the case for places such as the UK too.

Future sourcing

As I touched on earlier, numerous source types outside the realm of the primary so-called traditional options including ammonia, ethanol, natural, gas processing, hydrogen reformer, ethylene oxide, and TiO_2, have been discussed, and may be implemented in various world markets, in the past and present. Reliability and affordability are, however, the principal factors with the non-traditional sources.

> "Advanced biofuels have not moved along as many hoped they would..."

Such non-traditional sources could include flue gas (two of which flue gas plants exist in the US, operated by the AES Corporation), however these are a novelty in a way, since the capital cost is lumped into the power plant cost. If the flue gas plant is fully loaded with costs, the production of CO_2 would be near $100/tonne and, sometimes much more. There are other technologies which are discussing CO_2 from air capture, proprietary in nature, however the cost of production is well beyond what is found among the traditional sources, in places such as the US.

Future planning and sourcing opportunities may in fact come from some of the novel processes and lab-based discoveries in advanced biofuels, chemistry, and engineering. Specific to this, in a biofuels site today, the discussion surrounding seaweed may become a significant feedstock for fermentation; if so, the corn shortages which have been experienced, would then become irrelevant, perhaps.

Further, I believe the ultimate answer for tomorrow's sourcing challenges with CO_2 may be a product of improved processes evolving from what is now uncompetitive in certain markets, such as the developed economies of Europe, Japan, and the US, for example. This could include improved solvents in the recovery of flue gas from power plants, and other combustion by-product processes, as well as large cement manufacturing operations, and even stationary CO_2 capture systems – the latter hoping for ever more active, and reactive processes which can competitively yield a concentrated CO_2 product from direct capture systems, to flue gas sources – all of which are almost unlimited in capacity and location.

When flue gas from cogeneration was becoming the fad in the early 90s, one of the most attractive features of this technology was that power and flue gas sources are more strategically located than many of today's chemical by-products – energy and natural-based sources. On the other hand, this technology cannot stand alone as is, with the MEA-based solvent at the heart of the recovery process – unless it is improved upon significantly with much better or novel alternatives, thus lowering the cost of recovery (upstream) of liquefaction and purification.

In the end, some of the technologies which would represent new types of CO_2 sources are at best, lab scale, or exist as announcements from academia, and are therefore, potentially far off. Others could include better flue gas and direct from air systems, which over time, could become affordable, and competitive with traditional source types.

If future advanced biofuels from corn stover, and non-food crops, such as switchgrass, seaweed, and other organic matter become widespread and competitive with traditional, affordable technologies, this could become a future form of sourcing the industry. Advanced biofuels, per se, have not moved along as many hoped they would.

In the end, the best insurance the gas companies can have is diversification among source types; not just hydrocarbon or fermentation-based, but a wider range of alternatives. GW

ABOUT THE AUTHOR

Sam A. Rushing is President of Advanced Cryogenics, Ltd, a major CO_2 consulting and cryogenic gas consulting firm, working globally for decades.

Email: rushing@terranova.net
Tel. 305 852 2597
www.carbondioxideconsultants.com