perfumer & flavorist®

The Expanding Supercritical Fluid CO_2 Extract Universe

Pierre-Jean Hellivan

Opening the door to a wealth of new materials for everything from flavor to fine fragrance

Pierre-Jean Hellivan, Vigon International

"Galbanum SFE and cardamom SFE (pictured) helped me deliver a more vibrant top note and juicier midsection to [06 Amanu]," says perfumer Kevin Verspoor (drom fragrances). "I am a big believer in CO_2 extracts. For the first time, this cold extraction method delivers three-dimensional extracts that smell more like the original plant."

Has the holy grail of extraction technology been found? Is supercritical CO_2 the supreme vessel for the extraction of naturals? Are supercritical fluid CO_2 extracts (SFE) simply surfing the momentum of a fashionable wave within the perfumer and flavorist palette, or do they provide long-term solutions to an ever-more demanding and regulated industry?

CO_2 extracts have been all the rage lately: The technology is trendy, eco-friendly, efficient, highly selective and flexible. CO_2 extracts shine a new light of naturalness on the palette for delivering a sparkling fresh aroma. They are truest to the botanical starting material due to the gentle temperatures of the process. SFEs leave behind zero residual solvent and boast exceptional shelf life, thanks to the inert atmosphere of the process. The technology has the ability to yield incredibly selective fine fractionation of aroma profiles. Supercritical CO_2 performs admirably not only on solid starting materials (such as spices and herbs), but also uniquely well on liquids such as fruit juices or nut oils—thereby opening the door to a wealth of new starting materials.

A Brief History

The pursuit of an industrial application of CO_2 extraction started in the 1960s and 1970s. In France, Pfizer took the first baby steps in SFE research. That company's offshoot, Camilli, and later Calchauvet, first developed supercritical carbon dioxide extraction to duplicate extracts for fragrance originally made with Freon, which had been subsequently banned.

Alain Misitano, a 25-year veteran of the technology, is now responsible for CO_2 development at Firmenich. He recalls, "In 1986, we were extracting florals from concretes, mainly rose and jasmine. Calchauvet was also processing other botanicals, mainly rosemary, ginger and sage." The company assumed leadership in SFE developments for the flavor and fragrance industry. Misitano explains that additional products such as vanillas were introduced. "Pink pepper SFE eventually became our best seller in 1998, [and] our first blockbuster win [occurred] when it was formulated in Estée Lauder *Pleasures*." This CO_2 extraction innovation was eventually acquired by Firmenich, which recently cut the ribbon of its latest CO_2 extraction facility in Grasse.

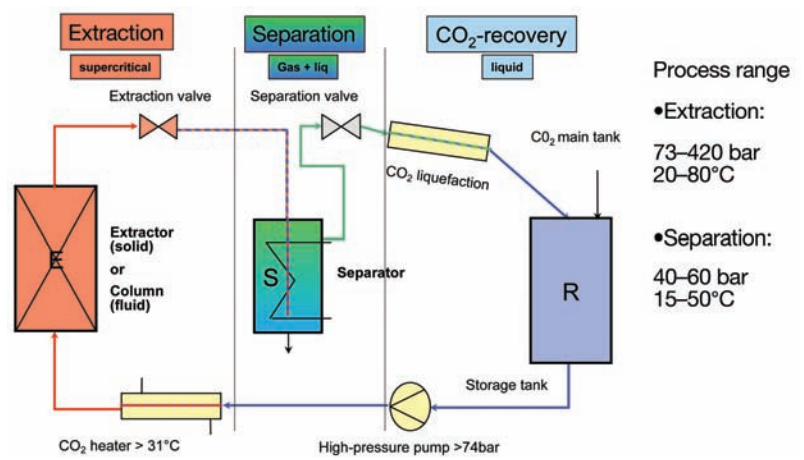
Meanwhile, in the 1980s in Germany, industrial-scale development of CO_2 extraction for the decaffeination of coffee and tea was developed by SKW (now Evonik). This process remains to this day the only efficient non-chemical path to decaffeination (avoiding the chemical process of involving ethyl acetate and methylene chloride). SFE plants started to flourish in the 1980s; large-scale high-pressure units were aimed at the decaffeination market. In parallel, other applications were found. Supercritical CO_2 performed most effectively in the extraction of hops flavor and bitter compounds for the beer industry and was applied beginning in 1984. Similar to decaffeination, a process was engineered for the removal of nicotine in tobacco. Soon, large-scale CO_2 extraction facilities were operating in Germany, Italy, England and the United States. Today, just about any liquid or solid botanical bearing volatile aroma compounds can be extracted successfully with CO_2.

Supercritical vs. Liquid CO_2

CO_2 acquires solvent properties under two physical states: liquid and supercritical. Liquid CO_2 extraction is rarely used today in the flavor and fragrance industry. The scope of aroma molecules that can be extracted by liquid CO_2 remains somewhat narrow, and extraction accuracy somewhat crude.

This article will focus on the more advanced supercritical stage—a puzzling physical form in which CO_2 is not solid, liquid or gaseous. In its supercritical state, CO_2 retains the high solvent potency of its liquid state, but benefits from the lower viscosity and much higher diffusion of its gaseous form. The SFE process

F-1. SFE general flow chart



Courtesy of Evonik

(**F-1**) consists of exposing starting material and carbon dioxide to very precise pressure and temperature settings. The botanical raw material is first loaded in a vessel, while temperature is brought to a minimum of 31°C (90°F) and pressure increased to a minimum threshold of 74 bars (3,600 psi), allowing the CO_2 to reach supercritical stage. The supercritical CO_2 flows freely through the raw material and accurately targets and captures soluble aroma molecules. Its accuracy can be adjusted by dialing in specific pressures. The flow moves on to a separator where pressure and temperature are brought back to conditions where the supercritical CO_2 reverts back to its gaseous state, thereby separating from the extracted liquid. The spent CO_2 gas is recovered and stored in a condenser where its temperature is lowered further to its liquefaction point for storage. This recovered CO_2 can then be used in future batches.

Cost considerations appear to be very favorable to this technology. A study comparing the cost of extracting a vegetable oil with CO_2 versus hexane was presented at the 2010 International Federation of Essential Oils and Aroma Trades event in Morocco.[2] Calculations were based on variables such as solvent cost, maximum solubility, solvent throughput, energy input and operating cost, yields, temperatures and other production parameters. CO_2 extraction was proven to be considerably more advantageous for this specific raw material.[2] Caution must be exercised, however, as this may be true for a given vegetable oil, but does not necessarily apply all other botanicals.

Pinpoint Accuracy in Extraction

Selectivity and solvent power depend on gas density and vapor pressure of substances: Gas density is adjusted by tweaking temperature and pressure, while vapor pressure is adjusted by setting temperature. Control of extraction not only comes from pressure and temperature, but also solvent-to-feed ratio (calculated in kg of CO_2 used per kg raw material) and time allowed. The extract recovery itself can be achieved through three processes, each

First Person: Harry Fremont, Perfumer, Firmenich

In the late 1970s I was incredibly excited when I discovered the fragrance industry and the job of a perfumer. My passion for this business as a whole and of course for trying to create fragrances that people would wear, started at this time and has never stopped since. However, something was bothering me. I had the feeling that everything had already been done. With my lack of experience I could not imagine how different the future could be for this profession. I was wrong on so many levels. Through the new molecules created by research, the discovery of headspace technology and finally the incredible revolution that CO_2 supercritical fluid extraction (SFE) made with natural products, the possibility of newness for a perfumer today is endless.

SFE is a fascinating technique that enables us to extract natural products in a revolutionary way, adding vibrant, new colors to the perfumer's palette and increasing our creative possibilities. As a perfumer I was always frustrated to see the difference between the beauty of some natural products and the roughness of their extracts. SFE has been able to fix this. With this extraction technique, the perfumer is able to choose which fractions of an extract he or she wants to keep for the best rendition. As I always say, SFE has allowed us to create the natural raw material extracts that perfumers have long been dreaming of.

The best example of this for me is Firmenich's vetiver SFE. When one compares regular vetiver oil with that of the SFE extraction, there is truly no comparison. One is a bit musty/mushroom/potatolike, while the other smells like the true vetiver roots. This made a huge difference for me while creating Tom Ford *Grey Vetiver*. I could use more of this vetiver SFE and create this amazing impression of quality and refinement. For me vetiver SFE is a beautiful woody note with subliminal earthy undertone; it is almost like a primal scent like fire, and it grounds people, making the fragrance more addictive.

SFE products are easier to use because they are more precise and intense. Sometimes you don't need a lot to create the effect you want. Galbanum SFE is a good example of this. Again, it is the galbanum of the perfumer's dream, capturing the actual beauty of the green note without having the turpentine/resinous effect that you find in other extractions.

Every time I have a client visit in Firmenich's Grasse facility with Alain Misitano, the person in charge of the SFE, I am always taken aback by the incredibly high-tech installation. I have the feeling that we have made a leap into the future and are finally able to find the best optimal conditions to extract all the beautiful products that nature has created.

Some people have been predicting the demise of natural products for many years. Nothing can be farther from the truth. Naturals will always be a part of great fragrances for the character and complexity they bring, and SFE will definitely be a part of their continuing presence and success in our formulas.

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> —Harry Fremont, Firmenich

tailored to target specific compounds :

- ***Pressure reduction (lowered CO_2 and density):*** This is the classic process for volatile aroma compounds, sometimes performed as fractional pressure reduction in order to increase selectivity.
- ***Isobaric adsorption (constant CO_2 density + adsorbent):*** This process was developed for the decaffeination of tea, adsorbing the caffeine in a bed of activated charcoal.
- ***CO_2-washing (constant CO_2 and density + solvent):*** The addition of lipophilic or hydrophilic food-grade solvents enhances the solubility of polar compounds.

Ralf Kahleyss, who heads up R&D and quality assurance at Evonik, explains that the solubility of CO_2 is perfectly tailored for application in the extraction of molecules relevant to flavor applications.

"Its solubility decreases with increasing polarity and or molecular weight," he says. "Relatively light, small lipophilic molecules (300–400 mw) like volatile aroma compounds (monoterpenes, sesqueterpenes, esters, ketones, lactones and most essential oil components) are easily soluble in supercritical CO_2 (1–10%) at 300 bar. Heavier substances (up to ~2,000 mw) like fatty oils, waxes, resins, alkaloids, carotinoids and water are moderately soluble in supercritical CO_2 (0.1–1%). Insoluble are all polar substances—oligo elements and polymers (salts, proteins, amino acids, polysaccharides, polyterpenes, saponones, tannins, phosholipids, glycosides)."

Kahleyss, an expert in precisely tuning the extraction to target specific compounds, has the opportunity to use the technology for a wide range of applications, noting, "Evonik finds CO_2 has a most effective tool for six niche markets—of course aroma extraction mainly for the flavor market; hop extraction for the brewery industry; pesticide removal from liquids and solids; sterilization; phyto de-oiling for the removal of polyunsaturated fatty acids, carotinoids, sterols and phospholipids; and decaffeination."

F&F Advantages of CO_2

In the F&F industry, supercritical extraction is trendy, efficient, selective and flexible. It boasts a performance or yield edge over conventional solvent extraction methods, mainly for extraction of relatively non-polar aromatic compounds—all the while leaving no residual solvent behind. Other advantages include:

- Generally recognized as safe
- Free of impurities and residual solvent
- Highly selective and flexible extraction
- High recovery rates
- Odor and flavor most genuine to the raw material
- No-heat process delivers unprecedented quality
- Extreme shelf life

First Person: Cathianne Leonardi, Flavorist, Allen Flavors

Flavorists often seek opportunities to provoke original ideas and transform them into sensations of taste and aroma. There are many ways that creativity can be stirred and imagination tangibly expressed to share with the world. We form or observe art, find comfort in interior design, learn languages, play music, compete in sports, perform research, read novels, travel, and of course prepare, taste and appreciate culturally diverse food. Flavorists are placed in a perpetual state of active envisioning given that nourishment is a common denominator of the human experience and taste is pervasive in its delivery.

Natural products indulge the mental state of creative flavorists. We smell, taste and try them in flavors for their major component contributions and unique whispers of minor items. Many flavorists caringly fit together natural products with singular chemicals to craft a cohesive sensorial experience. We each have old favorites that convincingly result in transcendence of flavors. These are held dear in our aroma palettes while we search for items worthy of addition.

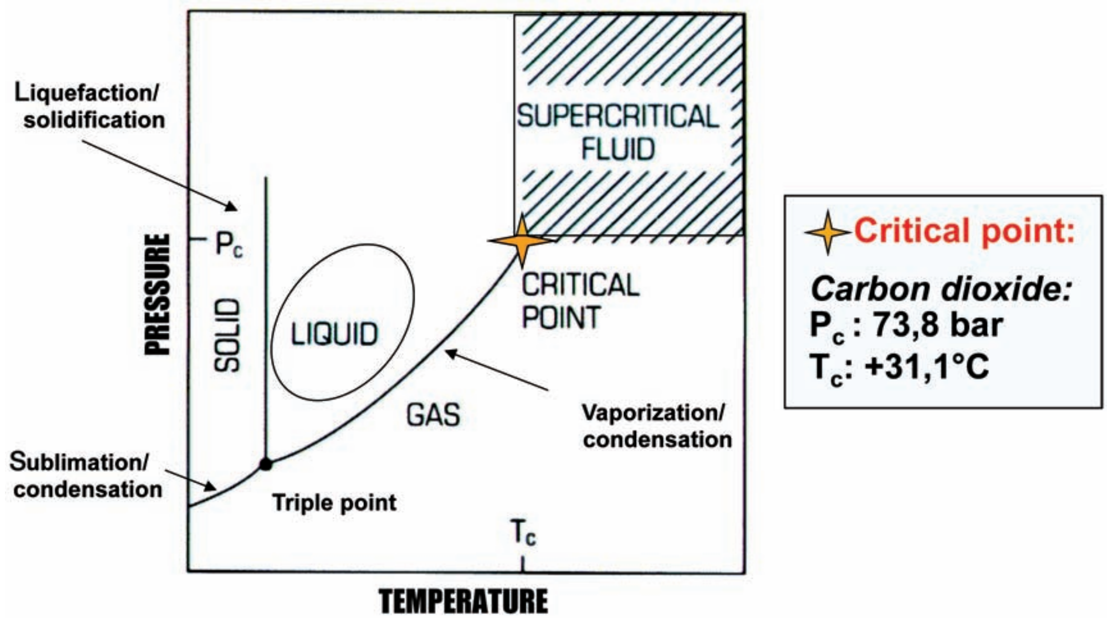
Excitement wells when new naturals are introduced. Opportunities to expand our cherished palettes are embraced. In the present times of organic demands, where some extract solvents are not welcome, interest is piqued with CO_2 extraction. CO_2 supercritical fluid extraction occurs at low temperatures, allowing for finer aromas to be captured while employing an organic-friendly solvent.

Recent introductions in CO_2 extracts by Evonik include an array of tea varietals. The naturally occurring tastes and aromas range from woody to nutty, heavy and waxy to delicately floral. Their uniqueness and potential for complimentary collaboration with an assortment of flavor types make them prime candidates for stimulating imagination and fueling flavor distinction.

The profile of the honeybush tea varietal contains hay, herbal, honey, rose, dried fruit and woody characters with hints of damson. Thoughts of a walk among cedars in fresh autumn air may be conjured along with mental visualizations of pairing it with apple, pear and berry notes.

Rooibos CO_2 extract conveys sensual dried fruit, tobacco, sweaty, caramellic characters and fusel whiskey notes. It is not an ordinary tea and may motivate the flavor type's exploration beyond the usual beverage category. Considering the prominent aromas, it could be a compliment for popular flavors often found in the dairy category. The pai mu tan extract is initially heavy and waxy with floral hay notes. Its slightly nutty and dried fungal, earthy undertones add surprise and intricacy to the taste. Combined with peach and mango, these sensations could deliver uncommon tea experiences. An absolutely beautiful taste and aroma can be discovered in the floral, jasmine, berry, waxy and herbal combination that defines the jasmine type. Impressions of lavender may pop into one's mind, possibly perceived through intertwining of floral and herbal notes. Its pleasing character can easily enhance the appeal of a dozen flavor types.

F-2. Phase diagram of a pure component



Courtesy of Evonik

- Bactericide
- Completely non-reactive
- 100 % FTNS natural flavors
- No stabilizer (or technical adjuvant) necessary
- Organic-compliant
- Clean label

As E.S. Carbonell summarized in a 1991 article:[2]

> Extraction with supercritical CO_2 is an ideal process for the food and flavor industry because physiologically, CO_2 is harmless; there are no problems with residues for the producer customer or authorities; and the low temperatures used usually do not exceed the temperatures during its normal growth cycle. Because the extraction process is conducted in an inert atmosphere, the extracted substance is protected from oxidation and the possibility of off flavors. The selection of specific aroma fractions is also possible."

Supercritical Extraction Equipment

SFE extractors require higher investment cost than a basic liquid CO_2 extractor, mainly due to the higher pressures that must be managed. Its extraction performance is considered much higher, in terms of yield-specific output and selectivity. One illustrative example is Firmenich's Grasse-based equipment.

Misitano explains, "Firmenich CO_2 development and operations teams rely on three extractors: A bench-top unit is relied upon for product development; a small-batch extractor assures fine-tuning of industrialization scale up; a third unit is Firmenich's workhorse, a state-of-the-art extractor that is perfectly suited for our production requirements and batch sizes." The preparation of the raw material is the first key step to a successful, high-yield extraction, he notes: "Starting botanicals are ground to a specific mesh size to increase supercritical CO_2 penetration through the biomass matrix."

For floral concretes of rose jasmine and tuberose, and for the extraction of vanillas, Misitano emphasizes that special safety precautions are now standard operating procedures. Naturally occurring waxes and fatty substances can clog pipes and filters, and so a processing aid is used to secure the flow thru the stainless 200 mm filters.

For application in fragrance, this unit delivers CO_2 extracts covering key olfactory families such as woody (patchouli, pine needles, vetiver), gourmand (ambrette, celery, coffee, green tea, vanillas), floral (jasmine SFE, rose, ylang-ylang), spicy (bay, cardamom, clove, elemi, ginger, white pepper, pink pepper), and green and ambery (cistus, labdanum, olibanum, benzoin). For flavor application, brown notes (vanilla, coffee), spice (white pepper, cardamom, cinnamon, clove) and spirits (rum) notes dominate the available palette.

The SFE process consists of exposing starting material and carbon dioxide to very precise pressure and temperature settings; the botanical raw material is first loaded in a vessel (pictured in two views), while temperature and pressure is increased, allowing the CO_2 to reach supercritical stage; photos courtesy of Evonik.

The CO_2 Extraction of Liquids

The ability to perform CO_2 extractions on aqueous or fatty liquids opens the door to a wealth of new botanical ingredients such as essential oils, fruit juices or nut oils, and therefore new innovative extracts. Two processes are used today to extract liquids.

Firmenich relies on encapsulating the liquid starting material. Misitano explains that "a powder support base works best for essential oils." The substance is then loaded onto the extractor in a powder, and undergoes batch extraction just like any solid ground raw material. This process is particularly efficient for the refined extraction of essential oils for fine fragrance, such as patchouli, vetiver or cedarwood.

Evonik has opted for a continuous countercurrent process for larger volume extractions for flavor. For the extraction of liquid raw materials such as hazelnut oil or banana juice, the company has developed a very specific column at its Trostberg, Germany facility. Inspired by modern molecular distillation techniques, but using high pressure instead of best vacuum, the continuous process was fine-tuned. The liquid raw material is filtered before entering the column to remove any impurities that may clog pumps and pipes. The liquid is introduced in the extractor, pouring down into the distillation column at supercritical conditions above 74 bars. The liquid is allowed to trickle down by gravity through a series of horizontal rods all the way down the column. As the liquid drips down, it disperses over these rods, maximizing surface of exposure. The supercritical CO_2 flows in a countercurrent fashion from the bottom up. The extractive follows the CO_2 flow and exits the distillation column toward the separator, while the spent liquid (called residual oil) is collected by gravity at the bottom of the tower. The end product is a portfolio focused on flavor application, filled with FTNF fruit and nut extracts including strawberry, black currant, cherry, peach, peanut and hazelnut.

Beginning in the 1980s, large-scale high-pressure SFE units—three of which are shown here—were aimed at the decaffeination market; in parallel, other applications were found, including the extraction of hops flavor and bitter compounds for the beer industry; photo courtesy of Evonik.

CO_2s in Fine Fragrance

The beating heart of fine fragrances is increasingly attributed to CO_2 extracts, including pink pepper SFE in Estée Lauder *Pleasures* (1998), vetiver SFE in Tom Ford *Grey Vetiver* (2009; see **First Person: Harry Fremont**) and petitgrain bigaradier SFE in the Richard Fraysse-formulated Caron *Yuzu Man*. (2011).

Most recently, the 2012 FiFi Indie winner Odin New York *06 Amanu* owes its unique character to galbanum SFE and cardamom SFE. Its perfumer, Kevin Verspoor (Drom), says, "Galbanum SFE and cardamom SFE helped me deliver a more vibrant top note and juicier midsection to the fragrance. I am a big believer in CO_2 extracts. For the first time, this cold extraction method delivers three-dimensional extracts that smell more like the original plant. CO_2s

First Person: Brigitte Pellen, Flavorist, Firmenich

When I started my job as a flavorist early 1990s, the CO_2 process was starting to be known.

It was a very new technique, and as a junior flavorist it was exciting to learn flavor creation with new types of extracts and also difficult to realize the full potential of CO_2 extraction. The first product that I met on my shelf was a vanilla CO_2. It was already clear that this type of vanilla produced by CO_2 was bringing an edge to the vanilla portfolio of extracts.

My attraction to natural extracts and fractions has always played an important role in my job of flavorist. Learning the story and background of natural ingredients has always attracted me and I got the chance to play a role in the creation of some in-house extracts. Now at Firmenich … I got to know a large palette of CO_2 extracts outside of vanilla and ginger.

There are specific items that I believe are real winners for flavor creation and would like to highlight. Juniper berry SFE is a must-have in the palette of a flavorist. There is clearly no comparison to the traditional juniper berry essential oil. It is more fruity, rich and fresh without the terpenic/resinous aspects of the oil. It contributes to tropical fruity notes in a juicy, refreshing way. It also brings a differentiation to citrus, is a freshness booster, and is thirst-quenching and fruity.

Rum SFE … made of Caribbean rum, is fruity. The extraction recovers the fully fruity fraction without the alcohol and without the fusel notes. This SFE is so concentrated and strong that a trace in brown notes such as vanilla is feasible.

For flavorists, the CO_2 extracts have a reputation of being expensive … but learning them and trying them, you'll learn that their concentration can be often more concentrated than standard oils. And some materials give a fully different profile, so it is a truly different new extract. For flavor creation, another attractive point to CO_2 is the advantage of residual-solvent-free compared to other solvent extractions. This is coming up more and more as a key point for the food industry.

What is also exciting is to see that there are still progress possible to develop new CO_2 extracts, adjusting the conditions of extractions to new materials. The innovation people still have room and challenge to develop new products. CO_2 extracts have their place in success for new creation, innovative profiles and legislation advantage. I believe that naturals, and specifically CO_2 extracts, will grow in their use in creation.

provide more depth of character compared to essential oils and absolutes, even at lower use levels; their improved identity enhances the natural character and really helps enhance my repertoire."

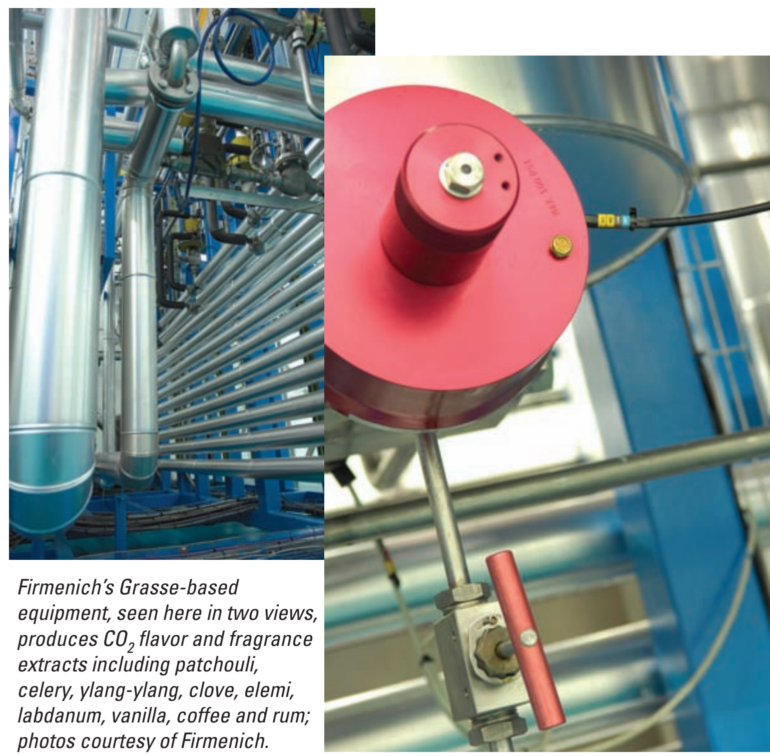
Evaluating Firmenich's juniper berry and ginger SFEs, Verspoor says, "What a difference in vibrancy through the entire construction, from the top note through the middle and the bottom. The juniper is refreshingly sparkling green, whereas its essential oil would be very terpenic." Moving onto to four-day-old blotters of Firmenich's jasmine rose and orris SFEs, he says, "These are well-rounded, full bodied. The orris still has an intense irone note. The rose and jasmine remain tenacious after four days, smelling like the fresh flower." He adds, "dosage should be done with care." CO_2 can afford a wide range of use levels, with profound impact throughout the top, middle and bottom of the fragrance.

Ralf Kahleyss, who heads up R&D and quality assurance at Evonik, says that the solubility of CO_2 is perfectly tailored for application in the extraction of molecules relevant to flavor applications.

Perfumer Fabrice Pellegrin evaluating a product in a CO_2 pilot workshop; photo courtesy of Firmenich.

CO_2s in Flavor Formulations

CO_2 extracts are also an important addition to the flavorist's palette. The low temperature of the extraction process allows for notes not seen in a more conventional toolbox. Interestingly, in flavor applications CO_2 extracts are most useful not necessarily for their fresh true-to-fruit advantage, but rather for their uncanny ability to provide body to a conventional formula. The rule of thumb is to formulate a CO_2 at around 20 ppm. That is all that is needed to deliver a significant difference in body and enhanced natural character of the taste and aroma. A good example is Evonik's banana CO_2 extract FTNF derived from 200-fold banana aroma water. The ingredient is standardized with ethanol and water. Its aroma is genuine, incredibly true to the fruit, extremely ripe, with body and long lastingness. In a classic 11-ingredient banana flavor formula, it fills in the gaps isoamyl acetate cannot fill; the impact of banana CO_2 extract at just 10 ppm delivers a significant increase in body.



Firmenich's Grasse-based equipment, seen here in two views, produces CO_2 flavor and fragrance extracts including patchouli, celery, ylang-ylang, clove, elemi, labdanum, vanilla, coffee and rum; photos courtesy of Firmenich.

Conclusion

Defined by Verspoor as the "literal portrait of the starting material they are extracted from," SFEs represent the next generation of flavor and fragrance materials. They increasingly adorn the palette of creative teams with innovative sensory, technical and regulatory attributes. Whether extracted from solid or liquid starting materials, whether designed for fine fragrance or flavors, SFEs are solidly planted to become the secret ingredient to many winning formulas.

Acknowledgements

The author is grateful to the creators of flavors and fragrances, who shared their passion and volunteered their contributions: Cathianne Leonardi (Allen Flavors), Brigitte Pellen (Firmenich), Harry Fremont (Firmenich) and Kevin Verspoor (Drom); the CO_2 technical experts for unveiling some secrets of their craft: Alain Misitano (Firmenich) and Ralf Kahleyss (Evonik); the marketing teams, for facilitating research and collection of testimonies: Virginie Gervason (Firmenich) and Cynthia Thomas (Evonik); and the team at Vigon International, and especially president Stephen Somers Sr. for supporting the time, effort and resources required for this contribution.

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