Supercritical Carbon Dioxide and the Pillars of Extraction

As the botanical oil extraction industry grows, so too will the debate over different extraction methods, solvents and technology. With so many options available, it's wise to gain an understanding of the processes involved so that it becomes easier to make an informed decision.

As a low-cost option, supercritical fluid extraction (SFE) using CO_2 is a perfect choice. As a safe alternative to many hydrocarbon solvents, and boasting exceptional opportunities for tuneability, carbon dioxide has become one of the most widely used supercritical solvents in the industry. It's far less hazardous to employees and the environment, and it creates a superior product in comparison to oils obtained though hydrocarbon or ethanol extraction.

Carbon dioxide has fantastic solvency power as a supercritical fluid, retaining the high solvent potency of a liquid, but also holding the lower viscosity and faster diffusion rates of a gas. By taking its gaseous form at standard temperature and pressure, it also provides the opportunity for extractant removal through depressurization, thus acquiring the solutes in a cleaner, more efficient manner. With a reputation as a "residual free" solvent, extracts obtained through CO_2 SFE hold a closer profile to the original natural botanical and have exceptional shelf life.

Two Principles

For successful extraction efforts it's wise to understand the physical profile of both the materials intended for extraction, and the matrix within which they exist. In supercritical fluid extraction, there are two general forces at work– *mass transfer* and *solvency*.

Mass transfer is the net movement of mass from one phase (the matrix) to another (the solvent). In liquid CO_2 extractions, the SCO_2 (solvent) comes in contact with the plant matter (the matrix) and diffuses through it's pores. Within the matrix, the extractants will dissolve into the solvent, and be transported to the surface of the particle. At the surface, the extractants are transferred into the "bulk fluid" or solvent flow. To achieve the most efficient extraction rate, it's important to consider mass transfer resistances presented due to the matrix structure, the extractant location within that matrix, and the available working area for the mass transfer to occur.

The **solvency** of Supercritical CO_2 is based on its density at a given set of conditions, and facilitates the ability of extractants to move from the matrix into the bulk fluid. The greater the solvation power for an extractant of interest, the faster mass transfer will occur. Solvency and corresponding solute volatility are both manipulated by changing temperature and pressure parameters. In this way, extraction yield is related to extraction rate, as the selectivity and solvency of SCO_2 can be manipulated based on the desired compound for extraction.

The Pillars of Extraction

In industrial applications, an ideal extraction would be one that produces the highest amount of target compounds – with minimal co-extraction of undesirables – in the shortest period of time. To achieve this, the extraction parameters that affect mass transfer and solvency can be experimented with. These parameters include extraction time, flow rate, temperature and pressure.

EXTRACTION TIME

In industrial botanical oil extraction, the goal is to achieve a fast extraction rate, maximize oil production, and increase profits. The tuneability of CO2 as a solvent, and the technology within the extraction equipment give ample opportunities to tweak the extraction parameters, and meet this goal. In SFE, extraction time is related to the time it takes to reach mass transfer equilibrium between the solvent and matrix in the extraction chamber.

As mentioned before, the location of the solute within the matrix can contribute to mass transfer resistance. Extractants that are closer to the surface of the matrix will be extracted quickly, those found further away will need more time in contact with the solvent and take longer for the solvent to penetrate deeper.

The graph below illustrates how extraction yields reach an asymptotic value over time.
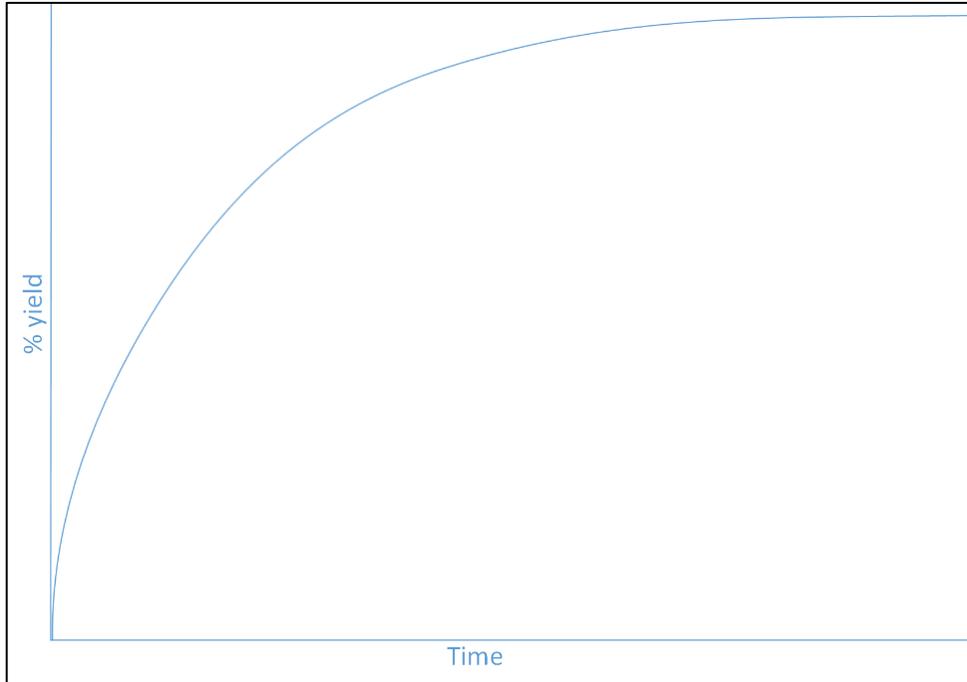
At the beginning of the reaction, the extractants closest to the surface are removed, resulting in a higher rate of yield.

As time continues, the solvent has time to penetrate deeper into the matrix, reaching solutes that were not available at the surface. This is represented in the leveling out of the yield %.

Standing time refers to a period where the supercritical solvent is held in the extraction chamber allowing it to penetrate through the matrix before the flow is introduced. For compounds existing further from the matrix surface – and thus having a higher mass transfer resistance – introducing a period of standing time can be highly beneficial.

FLOW RATE

In industrial practice, when trying to maximize output in shorter time, including periods of standing time is not efficient. In this case, extraction time can be managed through both flow rates and particle size.

Flow rate is the quantity of solvent feed delivered through the extraction chamber over time. If the extraction process is controlled by mass transfer resistance, the measure of solvent feed will help determine the extraction rate.

With a higher flow rate, more solvent comes in contact with the solute. The benefit of this in a closed SFE system is that a large quantity of solvent will constantly pass over the botanical matrix, allowing mass transfer to occur continually. Despite the speed at which the solvent flows, there is a surplus that continues to penetrate the matrix throughout the process. In effect, this allows for solutes deeper in the matrix to be captured, and results in a total extraction of recoverable material. Though a slower flow rate can yield the same results, it needs a far greater amount of time, making higher flow rates a necessity in industrial scale operations.

In an ideal extraction with greatest yield, the *working surface area* will be maximized. This is the quantity of the sample's surface that is available for the solvent to act upon. Compared to larger particles, small particles have a larger surface area in comparison to their volume and therefore, have a higher concentration of extractants closer to the surface. This creates less mass-transfer resistance as there is shorter extraction length.

In extraction, it is best to experiment with a combination of particle size and flow rate to find the best process and avoid solvent channeling. As solvent will always travel the path of least resistance, and smaller particles can pack together more tightly, if the extraction parameters aren't right a less effective result can occur. With the right combination of particle size and flow rate, it is possible to achieve the highest yield in the shortest amount of time.

TEMPERATURE & PRESSURE

The solvency power of SCO2 is proportional to its density, which is connected to temperature and pressure. In this respect, the fastest, high-quality extraction will occur at pressures and temperatures that maximize solvent density and solubility while not destroying the desired extractants.

Essential oils get their strength in flavour and scent from terpenes, flavonoids, and their oxygenated derivatives. These compounds are delicate, and sensitive to degradation through heat or hydrolysis reactions. To preserve these compounds, SCO2 is a fantastic choice as it can be effective at temperatures that will not induce thermal degradation.

If the melting point of the solute is known, the extraction temperature should be set just above that point. Above it, forces that bind the solute together and to the matrix break down, increasing diffusion rate and extraction time. When working at supercritical conditions with thermolabile solutes, it is a good practice to set the extraction temperature just above the critical temperature while still as low as possible to avoid degradation. Between 35 and 60 degrees C is considered a safe range.

When looking to maximize output, high pressures with higher temperature levels should be used to maximize both volatility and density. While higher temperature in extraction can increase the

volatility of the extractants and facilitate mass transfer, it also *reduces* solvent density and solvency strength. However, as pressure is directly proportional to solvent density under isothermal conditions, higher extraction pressures can *increase* them. As extraction temperature increases – thereby increasing volatility, a coincidental increase in extraction pressure will maintain solvent density and solvency strength, resulting in greater, more efficient extractions.

CROSSOVER PRESSURE

There exists a complex relationship between the temperature and pressure of an extraction. Increasing pressure has a positive effect on density but a negative effect on solute volatility, while increasing temperature has a negative effect on density but a positive effect on solute volatility. The balance between the dominance of density and volatility is referred to as the 'crossover pressure'.

Below the crossover pressure, higher extract yield will be obtained by using lower temperatures. Here, the effects of density on solubility are dominant, and higher temperatures at isobaric conditions will decrease solvent density and solubility.

Above the crossover pressure, the effects of volatility become more prominent. An isobaric rise in temperature above this point will increase the vapour pressure of the extractants more than it will decrease the solvent density, and thus provide better yields.

The crossover pressure differs between extractants depending on their physical properties, and is not a standard measurement. The best way to properly optimize an extraction for shortest time and maximum output is to experiment on all possible extraction variables, and measure the results.

To achieve the shortest extraction time, increasing the quantity of working solvent feed and the surface area of the extraction particles is the best course of action. In order to maximize extraction outputs within that period, the solvent strength should be maximized by increasing its density and increasing solute volatility through changes to temperature and pressure.