

Supercritical Fluid technology impact on environment

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Abstract:

From the very beginning of industrial applications of supercritical fluid technology, it has been asserted that it is *definitely* a “green” technology, as perfect example of processes compatible with a sustainable development. At a moment when environment preservation is becoming a worldwide major issue for any significant industrial project, it is time to revisit this SCF technology – that is spreading in many domains - to honestly evaluate the environment impact of emissions of potential harmful gaseous effluents: Green-house effect gases, volatile organic compounds, ozone-depletion gases, etc.

It is also interesting to consider means to reduce these emission impacts by optimised choice of fluid nature (CO₂, Water, Alkanes, CFCs and HFCs, Dimethyl ether, etc.) and composition when a co-solvent is used (alcohols, esters, hydrocarbons, etc.) and designing collection systems for co-solvents to limit VOC emissions.

Introduction

No need to say that *any* technology is presently subjected to environmental impact analysis, including, even with more attention, any “alleged-green” one. After decades of positive acceptation, supercritical fluid technology cannot be an exception, especially as it is now spreading on a worldwide basis in many different applications involving “green” and “not green” products and processes. So, I consider it is now time to stress on various aspects of this SCF technology, even if most of these things may appear obvious to those skilled-in-the-art.

At first, I will consider the impact of SCF and co-solvents emission, as many fluids may be used although carbon dioxide and water are by far the most common SCFs. Finally, I will come to the most acute issues related to particle emission.

Environmental impact of supercritical fluid and co-solvent emissions

As supercritical fluid operations generally end in venting part of the gaseous fluid, possibly added with a co-solvent, impact of SCF emission in atmosphere must be evaluated on several aspects: Toxicity, flammability, atmosphere pollution related to VOC release (especially tropospheric ozone photosynthesis), long-term effects (green-house effect, stratosphere ozone depletion). Disposal of SCFs that are liquid at room conditions (water, some hydrocarbons and alcohols) will not be considered in this paper as it is generally managed classically.

In Table 1 is presented a list of compounds that are used in subcritical or supercritical conditions with their critical properties (name, molecular mass Mw, critical pressure Pc, critical temperature Tc, critical specific gravity ρ_c) and the hazards related to their use. Moreover, many SCF plants uses co-solvents added to carbon dioxide: These co-solvents are chosen as polar solvents, and in most cases, Ethanol is preferred, especially when “organic-labelled” products are processed; other GRAS solvents are also used, like Isopropanol, Butanol or esters like Ethyl acetate; in some cases, Methanol or non-polar hydrocarbons (like Hexane) are required.

Table1 : SCF solvents and co-solvents (in bold, the usual ones).
(Quantitative data from [1] except * from [2])

Compound	Mw	Pc (MPa)	Tc (K)	ρ_c (kg.m ⁻³)	HAZARDS
Carbon dioxide	44.01	7.38	304.1	468.7	NF GW
Nitrous oxide N ₂ O	44.01	7.24	309.6	451.9	C GW
Xenon	131.3	5.84	289.7	1,109	None
Ammonia	17.03	11.35	405.5	234.9	F Toxic VOC
Water	18.015	22.12	647.3	315.5	None
Methane	16.04	4.60	190.4	161.7	F VOC GW
Ethane	30.07	4.88	305.4	202.8	F VOC GW
Ethylene	28.05	5.04	282.4	215.1	F VOC GW
Propane	44.09	4.25	369.8	217.2	F VOC GW
Propene	42.08	4.60	364.9	232.5	F VOC GW
n-Butane	58.12	3.8	425.2	227.9	F VOC GW
Isobutane	58.12	3.65	408.2	221.0	F VOC GW
n-pentane	72.15	3.37	469.7	237.3	F VOC GW
n-hexane	86.18	3.01	507.5	232.9	F VOC GW
Benzene	78.11	4.89	562.2	301.6	F Toxic VOC GW
Toluene	92.14	4.10	591.8	291.6	F Toxic VOC GW
Dimethylether	46.07	5.24	400.0	255.8	F VOC GW
Diethylether	74.12	3.64	466.7	264.7	F Toxic VOC
Methanol	32.04	8.09	512.6	271.5	F Toxic VOC
Ethanol	46.07	6.14	513.9	275.7	F VOC
Isopropanol	60.10	4.76	508.3	273.2	F VOC
n-Butanol	74.12	4.42	563.1	269.5	F VOC
Fluoromethane R41	34.03	5.6	315	300.6	F GW
Difluoromethane R32	52.02	5.83	351.6	430.7	NF GW
Trifluoromethane R23	70.01	4.86	299.3	527.6	NF GW
Tetrafluoromethane R14	88.01	3.74	227.6	630.4	NF GW
CF₃ - CH₂F R134a *	102.00	4.06	374.2	515.0	NF GW
Perfluoroethane R116	138.01	3.06	293.0	621.7	NF GW
Perfluoropropane R218	188.02	2.68	345.1	627.2	NF GW
Sulfur hexafluoride	146.05	3.76	318.7	734.7	NF GW

The hazards generated by a SCF process, as listed in Table 1 (with **bold** characters when acute) can be summarised as follows:

- **Flammability (F or NF or C):** Most of these compounds are flammable and may lead to potentially-explosive mixtures with air, requiring very strict safety rules (explosion-proof equipment). Moreover, nitrous oxide N₂O is suspected to behave as a comburant (C) that may lead to explosion when mixed with flammable gases or liquids: this hazard must be considered prior to using it in any high-pressure system. All fluoro-compounds may also decompose into highly-toxic products when exposed to a flame.
- **VOC release (VOC):** All organic compounds rejected into atmosphere in gaseous form are considered as Volatile Organic Compounds and subjected to strict regulations. Beyond their own toxicity to plants and animals, they are considered as pollutants inducing various photochemical reactions leading to toxic compounds like ozone and

nitric oxides. Moreover, they are sometimes released as aerosols much more dangerous (potential explosive) and aggressive to environment than diluted gases.

- **Toxicity (Toxic):** Some SCFs or co-solvents present an acute toxicity, explaining that they are very rarely utilised, especially aromatic hydrocarbons, and to a much lower extend hexane; chlorinated co-solvents are no longer acceptable in spite of their attractive properties. Due to its moderate toxicity, Methanol is more accepted. Ammonia is both flammable and toxic but presents a chemical activity that cannot be avoided in many cases. However, I would stress on the fact that any SCF can lead to *asphyxia* when released in a close area due to oxygen depletion, demanding oxygen-monitoring systems in all rooms where a SCF plant is operated (and in connected rooms).

- **Long-term effects:** The long-term effects of SCFs concerns stratospheric ozone depletion and global warming by the so-called “Green-House” effect:

- *Ozone-depletion gases* being banned or being progressively abandoned, all chlorine and bromine-containing molecules (CFCs and HCFCs) are no longer to be considered and only HFCs are presently used or studied as SCFs.

- *Global Warming (GW)* is induced by release of some SCFs: The Global Warming Potential (GWP) of each compound depends on both the molecule efficiency characterised by its absorption of infrared radiations and absorption spectrum, and its atmospheric lifetime. GWP is estimated relatively to the same mass of CO₂ (chosen as reference) and for a given timescale. When a gas has a high GWP but a short lifetime, it will have a large GWP on a short time but a small one on a long time. On the contrary, if a molecule has a longer atmospheric lifetime than CO₂, its GWP will increase with the timescale considered. Information gathered from various documents mostly based on IPCC data (Intergovernmental Panel on Climate Change) and [3] are presented in Table 2; these data are to be considered as orders of magnitude rather than precise values. These data clearly show that all fluorinated fluids exhibit a large GWP in comparison with CO₂, the more for perfluoro-compounds that are extremely stable in atmosphere.

Table 2: Global Warming Potential evaluated on a period of 100 years and estimated atmospheric lifetime of some gases [3]

Compound	GWP	Atm. Lifetime Years	Comments
Carbon dioxide	1	>10,000	GWP reference
Nitrous oxide	300	114	
Ammonia	<1	0.01	
Methane	25	12 ± 3	GWP decreases in time as hydrocarbons degrade to CO ₂ and water (GWP = 72 for Methane on 20 years)
Propane	20	0.04	
Butane	20	0.02	
Dimethyl ether	<20	short	
Fluoromethane R41	92	2.4	
Difluoromethane R32	675	4.9	
Trifluoromethane R23	14,800	270	
Tetrafluoromethane R14	7,400	50,000	
CF₃ - CH₂F R134a *	1,430	14	
Perfluoroethane R116	12,200	10,000	
Perfluoropropane R218	8,830	2,600	
Sulfur hexafluoride	22,800	3,200	

Limitation of SCF emissions

• **Global Warming gases:** First of all, CO₂ must be considered as *the* SCF ! As it is abundant and very inexpensive, there is no real economic incentive to reduce consumption and ... emission, except on special locations (islands, remote sites) or specific applications requiring high-purity gas. In fact, as CO₂ used as SCF represents only a very small part of CO₂ available from petrochemical sources where it is a fatal by-product (mainly in ammonia synthesis plants), it is true to consider that emissions from SCF plants do not contribute to Global Warming, as this gas would have been released anyway to atmosphere, knowing that the CO₂ market is very limited in comparison to fatal production. Nevertheless, it is sometimes valuable to reduce CO₂ consumption, especially on specific applications and in large-scale plants. For example, most CO₂ extraction plants are designed to recycle CO₂ from the separation zone at a pressure near 50 bar. This means that, at the end of each extraction batch, the extractors are depressurised from 50 bar to atmosphere by venting; the resulting CO₂ consumption can be estimated at 120 kg/m³; moreover, some CO₂ is also lost within the extract; so, when a dry plant material is treated with a specific gravity of 400 kg/m³, the CO₂ losses can be estimated around 0.4 kg per kg of raw material. For large production units, it is valuable to recompress the gas from ~10 bar to 50 bar, reducing the consumption down to ~0.1 kg CO₂/kg feed, at the cost of a compressor (investment and operating costs).

When another fluid than CO₂ or water is used, the context is completely different requiring to reduce as completely as possible any fluid loss for economic, safety and environmental reasons. Obviously, when one HFC is used as solvent, all must be done to reduce emissions both for economic reasons - as they are much more expensive than CO₂ - and for environment hazards as their GWP are very high. This demands a complete recovery of the gas by recompression after extraction completion, down to as low a pressure as possible. In spite of the significant advantage related to the possibility to run extraction at a much lower pressure than with CO₂, this explains why industrial development of HFC extraction has remained so limited.

• **Limitation of VOC emissions:** When an organic compound (like alkanes) is used or when a co-solvent is added to CO₂, VOC reduction must be implemented both for economic, safety and environmental reasons. The simplest method required for organic solvent collection consists in gas effluent depressurisation inducing a temperature decrease and liquid condensation that permits liquid recovery in a flash drum. For example, emission of an organic compound (Molar mass M_O g/mole) used as co-solvent in a CO₂ stream (flow rate U in kg/h) can be easily calculated by considering the depressurised mixture (at P and T) as a perfect gas. The solvent vapour pressure P_V is estimated from any available data in literature, for example Antoine's law, the coefficients being available for all classical co-solvents in most handbooks :

$$\text{Log}_{10} P_V = A - B/(T+C)$$

The VOC mass emission Q (kg/h) is given by :

$$Q = U * P_V / P * M_O / 44$$

This calculation supposes that no liquid phase is entrained in form of an aerosol; a metallic fibre mat is commonly used as demister in flash drums to stop such fine droplets.

When a very high VOC capture is required, two complementary processes are to be considered:

- *Adsorption* on a selective adsorbent, generally activated carbon: This route warrants a high efficiency of capture of organic compound, but requires a rather large consumption of adsorbent to warranty a high efficiency of capture, with handling, disposal and cost issues (and possibly hazards related to fire);
- *Scrubbing*: A second route for cutting down VOC emission consists in scrubbing the gaseous effluent with water, when the organic compound is water-soluble (the most common co-solvent is Ethanol). This is simple and inexpensive, and leads to an aqueous waste easy to dispose of without handling issues. Scrubbing may also be efficient to cut emissions of volatile reactants or products in SCF reaction systems.

● **Particle emission control:** As a very important effort is presently dedicated to manufacturing innovative “nano-structured” materials and especially nano-particles that seem to offer unlimited applications in many domains, there is no doubt that particle emission control is the most acute challenge for SCF process development and industrialisation. The issues are both related to “normal” conditions emissions in gas effluents and accidental release from high pressure equipment that may, at any moment, suffer of a leakage. We are currently dealing with these issues when designing and/or operating particle design processes in two main domains:

- *Pharmaceutical formulation* of active ingredients (API) requires a complete isolation of the equipment with simultaneous protection of the product itself in compliance with GMP, of operators that must be protected from any adverse event (including powder or aerosol emission due to a leakage), and of environment from any release of API, especially when high-potent ingredients are processed (steroids, antibiotics, anti-cancer, etc.). This implies to operate equipment designed for avoiding any particle release when harvesting as shown in Figure 1 presenting a GMP-compliant unit, with complete protection of the operator (with individual respiratory systems) who is recovering the API particles in a safe container from the atomisation chamber after SCF micronisation. Such unit is installed in a clean room with complete filtration of air. When high-potent APIs are processed, the fluid is not directly released to atmosphere after batch completion, but is either scrubbed in a liquid or micro-filtered (Figure 2) prior to venting or even, in extreme cases, recompressed and stored for disposal by incineration.



Figure 1: Safe particle harvesting



Figure 2: Effluent filtering system

○ *Inorganic or composite micro-/nano-particles manufacture or treatment* for ceramics, refractory materials, metallic pigments, etc. is also under scrutiny due to potential hazards related to particle inhalation. Even if the compound(s) are not toxic, nanoparticles may have presently unknown biological activity as illustrated by the tragedy of asbestos contamination. So, drastic rules are to be enforced when manufacturing such materials, similarly of what is done for pharmaceutical ingredients regarding operator and environment protection, but protection of the product itself may be significantly different (i.e. protection against moisture or oxidation that may lead to unwanted reactions). In Figure 3 and 4 we present a pilot plant designed for hydrothermal preparation of nanoparticles of oxides, with a safe collection system permitting harvesting without any particle release.

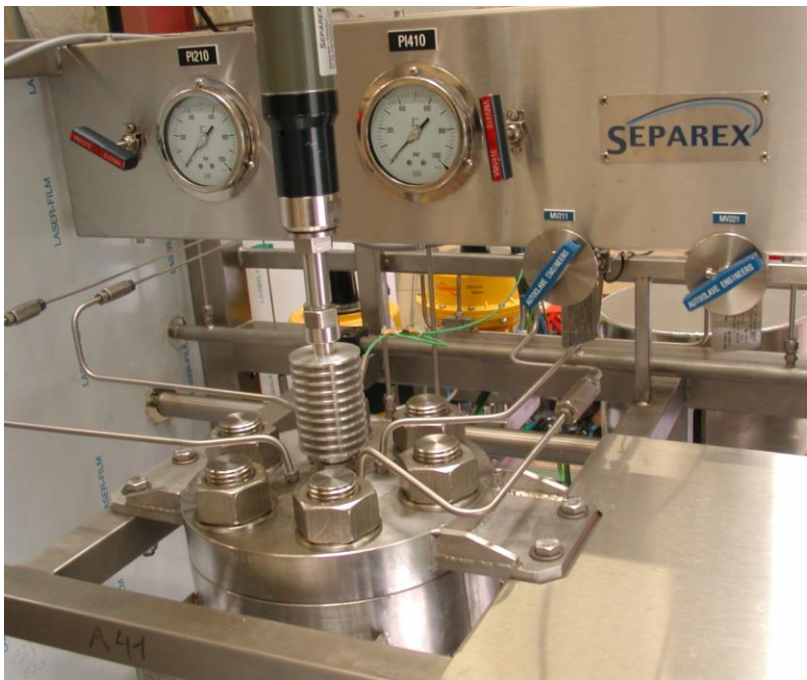


Figure 3: High-pressure (500 bar) high-temperature (450°C) Stirred Reactor for particle design **Figure 4: Safe particle harvesting**

References

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