

## Scalable Production of Carbonaceous Nanomaterials in Supercritical Fluids

### Abstract

When fluids are operated above critical point, Supercritical fluids (SCFs) are obtained which are the short-lived states of matter. It may be applied as substitute media in chromatography, energy production, drug development and food processing. It is now well acknowledged in materials processing. The mainly used SCFs are the supercritical CO<sub>2</sub> (SCC) and supercritical H<sub>2</sub>O (SCW). SCC guides a series of exceptional way of manufacture of carbonaceous nanomaterials. Demonstration of the science of supercritical fluids, and its probable application in industries in progress and amendment of carbonaceous nanomaterials has been undertaken in the current programme.

**Keywords:** Carbonaceous nanomaterials, Critical point, Density, Fluid Phase Equilibrium, nanocomposites

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Received on 25.01.2021

Accepted on 02.02.2021

### Introduction

SCF are inexpensive, non toxic, non flammable media with pressure tunable density, viscosity, diffusivity and surface tension. Solvent properties of SCFs were first reported over by Hannay and Hogarth around 1879. Density, viscosity and diffusivity are the common physical characteristics of SCFs that they share with liquids. High penetrating power of SCFs is due to their 100 to 1000 times greater densities over liquids, 10 to 100 times reduced viscosities over gases and high rate of diffusion @  $10^{-3}$  to  $10^{-4}$  cm<sup>2</sup>/s times over liquids. Such unique combinations of physical behavior SCFs are effused across solids leading to swelling or solubilization (Skerget M., et al. 2011). Judicious variations in temperature and pressure equalizes the densities of liquid and gas phases, restricting phase transitions in SCFs regardless to applied pressure (Vansant J., et al. 2019; Noyori. R. et al. 1999; Abdullah I., et al 2019). Among SCF, the most investigated

are the SCC and SCW (Kenz Z., et al 2014; Qian Z., et al 2019; Styring P., et al, 2014). The preference to these SCF is due to the prominent abundance of their precursors, viz; carbon dioxide and water in nature. These naturally existing precursors are easily transformed into their respective supercritical states either under ambient temperature or ambient pressure (Vansant J., et al. 2019; Noyori. R. et al. 1999; Abdullah I., et al 2019; Caputo,G, et al 2013; Aymonier C., et al. 2013; Johnston KP., et al 2004; Zhao J. et al.2019; Bhamidipati M. et al, 2013; Grignard B, et al. 2019; Tomasko D, et al 2003; Manjare SD, et al. 2019; Goutam SP, et al 2019; Elmaaty TA, et al 2017; Fifield LS, et al 2004).

Fig.2. demonstrates the low pressure phase diagrams of carbon dioxide (left) and water (right). The diagrams are consist of well defined areas that represent the physical parameters under which carbon dioxide or water represents their solid states (A,D), liquid (B) and gaseous (C,E,F) states.

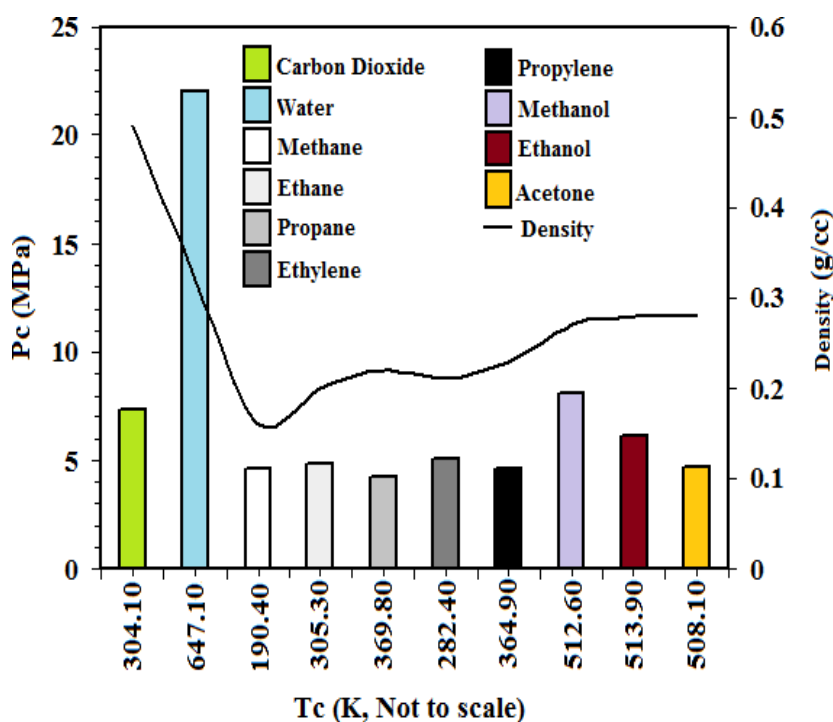


Fig.1. Critical Point and Density Variation in SCF

Solid lines represent the phases transitions between two phase. The heavy dashed lines represent effect of temperature and pressure on phase states of the matter. The point representing co - existence of all the three phases is defined triple point of phase diagram. For carbon dioxide the triple point falls, around  $-56.6^{\circ}\text{C}$  and  $5.1\text{atm}$  whereas for water it falls around of  $0.0099^{\circ}\text{C}$  at pressure of about  $1/166$  times the pressure of Earth's environment at sea level. At A, carbon dioxide condenses directly into dry ice. Increase in pressure from 'E' at constant temperatures renders solid-gas transitions in carbon dioxide to reached into dry ice. Whereas, increase

in pressure imparts solid-liquid transition that leads to solidification of carbon dioxide at point H. However, at G, increase in pressure does not impart additional changes in the phase state of carbon dioxide (Fig.2a).

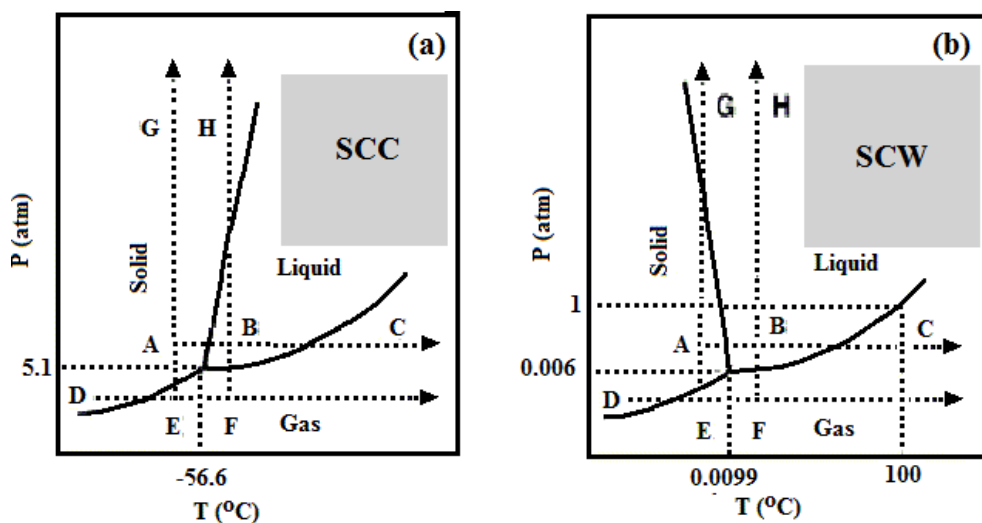


Fig.2. Fluid Phase Equilibrium of SCC (a) and SCW (b)

From point A, at constant pressure, increase in temperature imparts solid liquid transitions at melting point of ice. Further increase in temperature imparts liquid gas transitions in water at B, that induce evaporation at C. At D, increase in temperature imparts solid-gas transitions to water system where in ice evaporate directly into the gas phase through sublimation. The temperature of gases from additional heating warms the resulting gases ('E' and 'F'). At G, increase in pressure allows solid-liquid transition where ice melts (Fig.2b).

### Industrial Importance of SCF

SCF finds their prominent industrial status as environmentally benign media for processing of wide range of materials with diverse properties and applications (Kenz Z, et al 2014, Qian Z, et al 2019). Since, SCF are operated above their critical points, they are referred as dense gases (Styring P, et al, 2014). Academic and industrial significance of SCFs was well established since 1980's. Presently, more than two dozen SCF are well investigated for various industrial applications. SCFs finds their place as an alternative solvent in industrial and laboratory operations involving extraction of bioactive molecules from living resources, carrier medium for chromatography, food processing and solvent for disposal of organic waste (Noyori. R. et al. 1999; Abdullah I. et al. 2019; Caputo G. et al. 2013).

The ease of abundance, non flammable, non toxic nature of CO<sub>2</sub> makes this more viable for production of SCF for variety of industrial processes (Skerget M., et al. 2011, Kenz Z., et al 2014; Qian Z., et al 2019; Caputo,G, et al 2013). Because of gas similar to diffusion and liquid resembling density of SCC facilitates the swelling or partial dissolution of inorganic (Aymonier C., et al. 2013), carbonaceous (Johnston KP., et al 2004) and soft materials like polymers (Zhao J. et al.2019; Bhamidipati M. et al, 2013; Grignard B, et al. 2019; Tomasko D, et al 2003). Such potential of SCC has opened the avenues of transforming inorganic (Aymonier C., et al. 2013) and carbonaceous materials from macro size into their highly dispersed nano sized analogues (Johnston KP., et al 2004). Polymerizations in SCC imparts improved control over molecular mass of polymers (Zhao J. et al.2019).

Exposure of SCC to soft materials like polymers imparts reduction in their T<sub>g</sub>, making them processable into foam, scaffolds (Bhamidipati M. et al, 2013), composites, blends (Grignard B, et al. 2019; Tomasko D, et al 2003) and functional nanostructures ((Johnston KP., et al 2004; Grignard B, et al. 2019; Tomasko D, et al 2003), purification and separation of materials, high quality leather (Goutam SP, et al 2019) and fabrics in attractive shades with improved color and light fastness under ambient temperatures (Elmaaty TA, et al 2017). SCC has been exclusively used as medium for noncovalent functionalization of CNT (Fifield LS, et al 2004), nanofluids (Wang XB, et al. 2005), patterning on one-dimensionals carbon nanomaterials (Xiao LZ, et al 2010), synthesis (Ye S, et al 2009), growth (Li Z, et al. 2007),purification of CNT (Wang JS, et al. 2007; Bertoncini M, et al. 2011), coating polymers over CNT (Wang J, et al. 2005), polymer functionalized CNT and related polymer nanocomposites (Yue B, et al. 2007; Hao J, et al. 2011; Liu Z, et al. 2009; Nguyen VH, et al. 2004), polymer nanocomposites involving graphene (Li L, et al. 2013; Li M, et al. 2015), graphene derived NHs (Wei J, et al. 2019), C60 functionalized with polyvinyl pyridine (Bhullar N, et al. 2007; Zaidi MGH, et al. 2011) vinyl monomers (Agarwal V, et al. 2009; Agrawal V et al. 2010).

Fig.3 demonstrates the dispersion of MWCNT into epoxy resin under pressure of SCC ranging 1200-1800 psi.

Owing to gas similar to diffusion and liquid resembling density, SCC introduce into the *van der Waals* stacking zones of nanotube that on depressurization exfoliate them into fully dispersed structures. Curing of such nanotube epoxy formulations results highly durable polymer nanocomposites with improved dispersion of nanotube into epoxy matrix (Table 1)

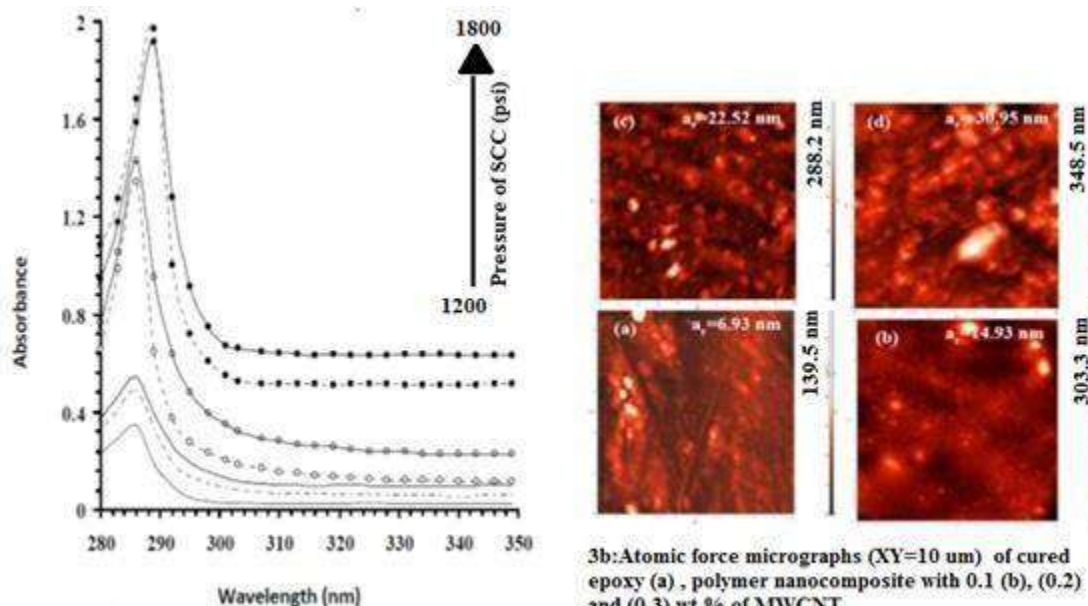


Fig.3a;Dispersion of MWCNT into epoxy resin with pressure of SCC

3b:Atomic force micrographs (XY=10 um) of cured epoxy (a) , polymer nanocomposite with 0.1 (b), (0.2) and (0.3) wt % of MWCNT

**Table 1:Mechanical properties of supercritically synthesized nanocomposites**

	Cured epoxy	Polymer Nanocomposites		
	[MWCNT] (phr) <sup>A</sup> 0.00	0.10	0.20	0.30
<b>Mechanical Properties</b>				
Tensile strength (MPa) <sup>A</sup>	30.36	36.44	47.73	49.36
Young's modulus (MPa)	384.89	389.18	375.32	369.95
Impact strength (KJ/m <sup>2</sup> ) <sup>B</sup>	17.16	21.48	29.98	31.01
Compressive strength(MPa) <sup>C</sup>	131.80	126.90	117.30	110.70

ASTM D 638 (a), 256 (b) & 695 (c)

### Conclusions:

Supercritical fluids, particularly SCC offers wide scope of applications in modification and scalable production of a variety of carbonaceous nanomaterials. Production methods involving SCC are highly scalable, clean and environmentally benign. Process involving SCC leads in the absence or at a low

concentration of toxic and flammable solvents with ease of separation of products through venting off carbon dioxide without expense of power or energy..Liberated carbon dioxide may further be recycled and used , that make the overall process to be industrially continuous in nature.

### Acknowledgements

Research funding from various resources of DBT, DRDO & UGC acknowledged.

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