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WATERLESS DYEING [REVIEW]

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Abstract: *The textile industry is believed to be one of the biggest consumers of water. Water consumption and exhaustion in dyeing textile materials in conventional methods is an important environmental problem. The cost of waste water treatment will cause a prominent problem in the future as it does today. Increasing consideration of ecologic consequences of industrial processes as well as legislation enforcing the avoidance of environmental problems have caused a reorientation of thinking and promoted projects for replacement of conventional technologies. One of these new technologies is dyeing in supercritical fluids.*
Dyeing with supercritical carbon dioxide is a favourable concept considering the value of water as a natural resource and the cost of waste water treatment. This dyeing method offers many advantages over conventional aqueous dyeing: During this dyeing process no water is used, therefore there is no waste water problem, no other chemicals are required; the carbon dioxide can be recycled; the dystuff which is not adsorbed on the substrate can be collected and reused; The necessary energy consumption in this process is relatively lower than is needed to heat water in conventional methods of dyeing. Due to unnecessary of drying process, it helps to save both energy and time; and dyeing cycle is shorter compared with traditional methods. In addition carbon dioxide is non-toxic and non-flammable.

Key words: *Supercritical fluid, supercritical dyeing, disperse dyestuffs, solid-fluid equilibrium.*

1. INTRODUCTION

As a green, safe and environmentally friendly medium, supercritical carbon dioxide fluid, which was introduced at the first time in textile dyeing as an alternative to traditional water bath by E. Schollmeyer et al., in 1988 (Bach et al., 2002) and further developed by Knittel, has been worldwide investigated and tried for textile dyeing and other applications due to its essential advantages. Dyeing in supercritical carbon dioxide has been applied on synthetic fibers and especially on polyester fabrics. As the method has gained success on polyesters, the other fibers have begun to be applied too. Natural fibers, firstly cotton, than wool and silk fibers have been dyed in supercritical carbon dioxide. Supercritical fluid CO_2 enables polyester to be dyed with modified disperse dyes. It causes the polymer fibre to swell, allowing the disperse dye to diffuse and penetrate the pore and capillary structure of the fibres. The viscosity of the dye solution is lower, making the circulation of the dye solutions easier and less energy intensive [1], [2].

2.WHAT IS SUPERCRITICAL FLUID?

The supercritical state is sometimes referred to as the fourth state of matter. A supercritical fluid can be defined as a substance above its critical temperature and pressure. Under this conditions the fluid has unique properties, in that it does not condense or evaporate to form a liquid or a gas. Referring to the idealized pressure–temperature diagram for a pure substance shown in Figure 1, it is observed that the supercritical state exists at temperature and pressure conditions above the so-called criticalpoint. As the critical point of a substance is approached, its isothermal compressibility tends to infinity. Correspondingly, the specific volume or density of the substance changes dramatically. In the critical region, a substance that is a gas at normal conditions exhibits liquid-like density and a much-increased solvent capacity. This behavior occurs because increase in density decreases mean intermolecular distance resulting in an increase in the number of interactions between the solvent and solute. Even though liquid like densities are observed for supercritical fluids, other properties are similar to those of gases. For example, viscosity values are relatively low while diffusivity values are relatively high. Low viscosity results in supercritical fluids being easier to pump, but also somewhat more easily diverted. High diffusivity generally results in improved mass transfer [3,4].

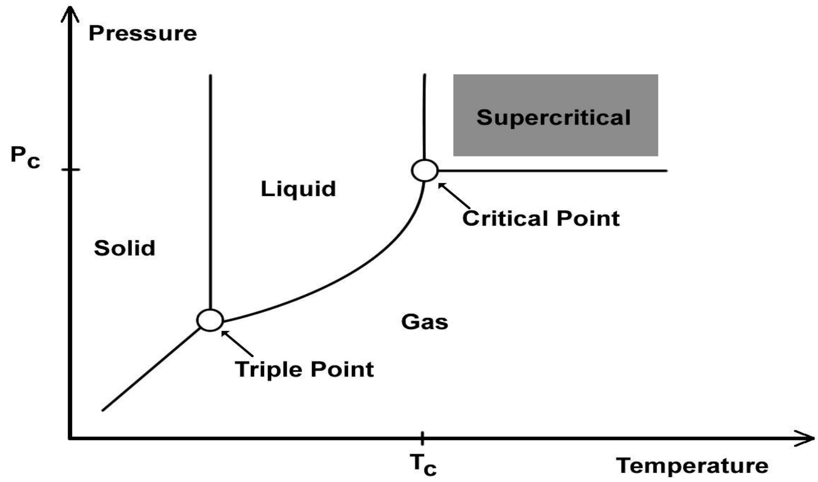

Fig.1. Pressure–Temperature Diagram [5].

3.DYEING IN SUPERCRITICAL CARBON DIOXIDE

The application of SCFs, especially supercritical carbon dioxide (SC-CO_2), in the textile industry has recently become an alternative technology for developing a more environmentally friendly dyeing process. Carbon dioxide, has so far been the most widely used, because of its convenient critical point (Tc=31◦C and Pc=74 bar), cheapness, chemical stability, non-flammability, stability in radioactive applications and non-toxicity. On account of its solvating ability towards non-polar or slightly polar organic molecules in the supercritical phase, CO_2 can be used to transport disperse dyes to polyester fibres, without having to use the traditional aqueous medium, thus avoiding pollution problems. Since polyester fibres typically have a very compact structure and high crystallinity, the choice of dyes for them is limited to the disperse dye range [4,5,6,7].
Table 1 provides an order of magnitude comparison of physical properties typical for gas, liquid and supercritical fluid state. Above the critical point, carbon dioxide has properties of both a liquid and a gas. In this way supercritical CO_2, has liquid-like densities, which is advantageous for dissolving hydrophobic dyes, and gas-like low viscosities and diffusion properties, which can lead to shorter dyeing times compared to water. Compared to water dyeing, the extraction of spinning oils, the dyeing and the removal of excess dye can all be carried out in one plant in the carbon dioxide dyeing process which involves only changing the temperature and pressure conditions; drying is not required because at the end of the process CO_2 is released in the gaseous state. The CO_2 can be recycled easily, up to 90% after precipitation of the extracted [5,8].

Table 1. *Order of magnitude comparison of physical properties substance[3].*

	Gas	**Liquid**	**Supercritical Fluid**
Density(gr/cm^3)	1/1000	1	0.6
Diffusivity(cm^2/sn)	1/10	5/10000	1/1000
Viscosity(gr/cmxsn)	1/10000	1/100	1/10000

The dyestuff/supercritical carbon dioxide/fiber system will in this respect, represent a three-component/ three-phase system. The three components are the gas, the dyestuff and the fiber polymer. In their solid state, dyestuff and polymer are present in the form of three separate phases besides the supercritical mixture. The dyestuff is dissolved in the supercritical fluid, transferred to, absorbed by and diffused into the fiber. Supercritical carbon dioxide is known to reduce considerably the glass transition temperature for many polimers, resulting in an increased mass transfer rate inside the polymeric matrix. In the first approximation the system is described as the distribution equilibrium of the dyestuff between fluid and fibers. A more exact definition of the thermodynamic processes involved in this system will have to consider the solubility of carbon dioxide in the polymer and in the solid dyestuff as well as the solubility of the polymer in the fluid. For the sake of simplification, the dyestuff will be considered as pure component, whereas the solubility of carbon dioxide and polymer in the solid dyestuff can be neglected. The solubility if the polymer in the fluid is so low that it can be neglected as well. All other mixtures can, however, significantly affect the dyeing process[2,5,9].

4. DYEING APPARATUS

A simple apparatus for dyeing in supercritical carbon dioxide is shown in figure 2. It consists of a temperature controller, a vessel heater which surrounds the vessel, a stainless steel dyeing vessel, a manometer, a carbon dioxide pump and a cooler for cooling the head of the carbon dioxide pump. The sample to be dyed is wrapped around a perforated stainless steel tube and mounted inside the autoclave around the stirrer. The apparatus is then sealed and heated to the working temperature and during this time carbon dioxide is pumped into the autoclave. The pressure rises to 350 bar, an isochoric process achieved by heating to 130◦C . Following a dye time the pressure within the autoclave is reduced to atmospheric temperature within about 2-3 minutes, the carbon dioxide being routed through a separating vessel in order to recuperate precipitated residual dye stuff. Dyestuff order is placed in the bottom of the vessel; the apparatus is sealed, purged with gaseous carbon dioxide, and preheated. When it reaches working temperature, carbon dioxide is isothermally compressed to the chosen working pressure under constant stirring. Pressure is maintained for a dyeing period up to 60 minutes and after wards released [2,4,5,10].

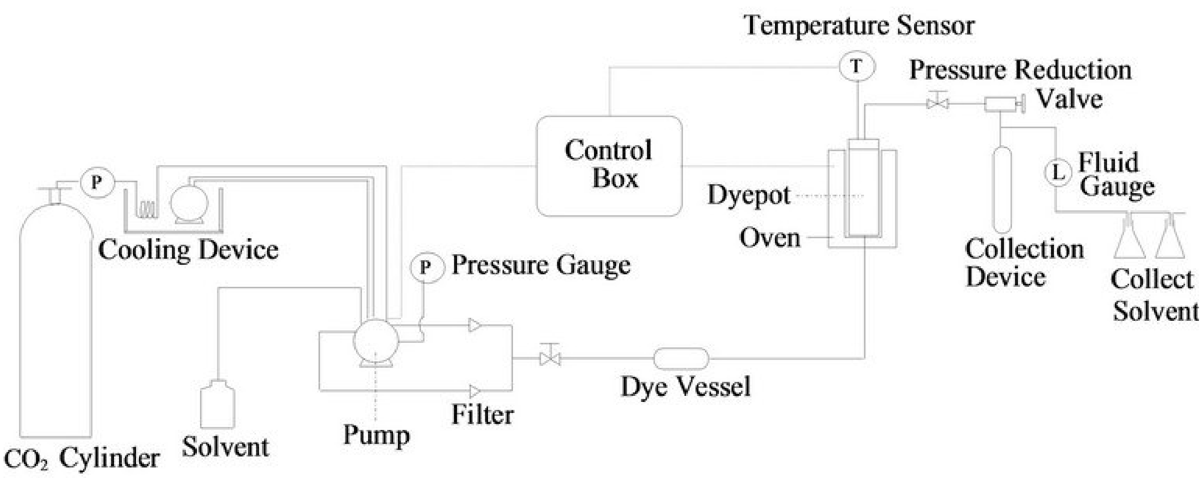

Fig. 2: Supercritical Dyeing Process [2].

5. CONCLUSIONS

Supercritical fluids have smaller densities, less viscosities but greater diffusion properties. Also supercritical fluids have greater penetration properties. Carbon dioxide, has so far been the most widely used, because of its convenient critical point , cheapness, chemical stability, non-flammability, stability in radioactive applications and non-toxicity. Owing to small viscosity of supercritical carbondioxide and to high diffusion coefficient of dyestuff molecules in this condition, disperse dyestuff molecules easily penetrate into fibres and as a result supercritical carbondioxide dyeing provides a better dyestuff transportation compared to dyeing in water [4,5,6,7,12].
Currently, supercritical dyeing requires higher pressures than are currently available in conventional jet dyeing machines. To obtain the required temperature and pressures, autoclaves with large holding capacities must be used in the dyeing process.

Supercritical dyeing has shorter dyeing cycles compared to aqueus dyeing. The major attraction of supercritical CO_2 is that it is a means of saving substantial amounts of water and energy, environmentally friendly, water and effluents free in the dyeing of textiles.

The investigation to study possibilities of using supercritical system for textile dyeing processes have in the first instance been performed with the aim of finding an ecologically acceptable alternative to conventional dyeing. Supercritical dyeing with CO_2 is confined to synthetic fibers. The technology has become a commercially viable system for dyeing polyester, elastane and nylon [11,12]. For natural fibers the diffusion of supercritical CO_2 is hampered by its inability to break the hydrogen bonds present in many natural fibers, including cotton, wool and silk. A further problem is that reactive dyes, direct dyes and acid dyes which are suitable for the dyeing of natural fibers are insoluble in supercritical CO_2. Further studies might be conducted on methods to modify naturel fibers or to develop new fixation mechanism in order to improve dyeing efficiency of natural fibers, as they are not easily dyed in supercritical conditions.

REFERENCES

[1] Jia-Jie Long, Hong-Mei Xu, Chuang-Long Cui, Xiao-Chen Wei, Feng Chen, An-Kuang Cheng, A novel plant for fabric rope dyeing in supercritical carbon dioxide and its cleaner production, Journal of Cleaner Production 65, 574-582, 2014.

[2] Shen-Kung Liao, Pi-Shiun Chang, Literatures on Dyeing Technique of Supercritical Fluid Carbon Dioxide, American Journal of Analytical Chemistry,Vol.3 No.12A Article ID:26157,8 pages, (2012).

[3] Hendrix, W.A., Progress in Supercritical CO_2 Dyeing, Journal of Industrial Textiles, Vol. 31, No.1, 43-55, July 2001.

[4] Ozcan, A.S., Clifford, A.A., Bartle, K.D. and Lewis D.M., Dyeing of Cotton Fibres with Disperse Dyes in Supercritical Carbon Dioxide, Dyes and Pigments, Vol.36, No.2, 103-110, 1998.

[5] Dyeing in Supercritical Carbon Dioxide, (http://www.geocities.com.htm).

[6] Montero, G.A., Smith, C.B., Hendrix, W.A. and Butcher, D.L., Supercritical Fluid Technology in Textile Processing: An Owerview, Ind. Engineering Chemical Research, Vol.39, No.12, 4806-4812, 2000.

[7] De Giorgi, M.R., Cadoni, E., Maricca, D., and Piras, A. Dyeing Polyester Fibres with Disperse Dyes in Supercritical CO_2, Dyes and Pigments, 45, 75-79, 2000.

[8] DyeCoo: Waterless dyeing,(http://dyecoo.com).

[9] Sicardi, S., Manna L. and Banchero, M., Diffusion of Disperse Dyes in PET Films During Impregnation with a Supercritical Fluid, Journal of Supercritical Fluids, 17, 187-194, 2000.

[10] Schmidt, A., Bach, E. und Schollmeyer, E.,The Dyeing of Natural Fibres with Reactive Disperse Dyes in Supercritical Carbon Dioxide, Dyes and Pigments, Volume 56, Issue 1, Pages 27–35, January 2003.

[11] Dyeing Textiles with Supercritical Carbon Dioxide: A Non-Aqueous Dyeing System, (http://www.techexchange.com).

[12] Van der Kraan, M., Fernandez, Cid, M.V., Woerlee, G.F., Veugelers, W.J.T., G.J. Witkamp, Dyeing of natural and synthetic textiles in supercritical carbon dioxide with disperse reactive dyes, The journal of Supercritical Fluids, Volume 40, Issue 3, Pages 470–476, April 2007.