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5.1 Introduction

Chemical processes and products that are environmentally and economically sound are key factors in the development of a sustainable society. Process technology that delivers sustainable products is expected to fulfil a number of requirements. For sustainable products, renewable or recyclable raw materials should be used and all materials involved in the production process have to be evaluated as to their risk and toxicity potential. During processing, raw materials and energy have to be used as efficiently as possible and production of emissions and waste has to be kept to a minimum. The quality of sustainable products must also be high. Commercial competitiveness of the products and the process technology to produce them is another important factor which has to be evaluated (Saling *et al.*, 2002; Rebitzer *et al.*, 2004; Pennington *et al.*, 2004; Stewart and Jolliet, 2004; Anon, 2005a).

Although the product (textile) itself cannot be considered as sustainable, the dyeing process of fibres in supercritical carbon dioxide (scCO₂) is an example of a 'clean' process suitable for fulfilling many of the requirements of sustainability, as listed above. In this process, a recyclable process medium (CO₂) is used together with an efficient and minimum input of chemicals (only dyes, no auxiliaries) and energy (low dyeing times, fusion of processes, no drying) and with minimal emissions and waste production. The quality of the dyed materials is also very high. Economical feasibility has to be determined in the future after industrial scale up of the plant and the process.

5.1.1 Environmental compatibility of CO₂

There are many beneficial environmental effects when scCO₂ is applied as process medium: CO₂ does not contribute to smog, it has no acute ecotoxicity and the ozone layer is not damaged. It is also non-carcinogenic, non-flammable and non-toxic (Jessop and Leitner, 1999); however, air with a CO₂ content of more than 10% can be life-threatening if breathed. Due to its higher specific

gravity of 1.539 (Anon, 2003) compared with air, gaseous CO₂, if released at high concentration in a closed room, at first accumulates on the ground. Therefore, CO₂ defection systems have to be installed. The maximum allowable workplace concentration (MAC) is 5000 ppm (Anon, 1992).

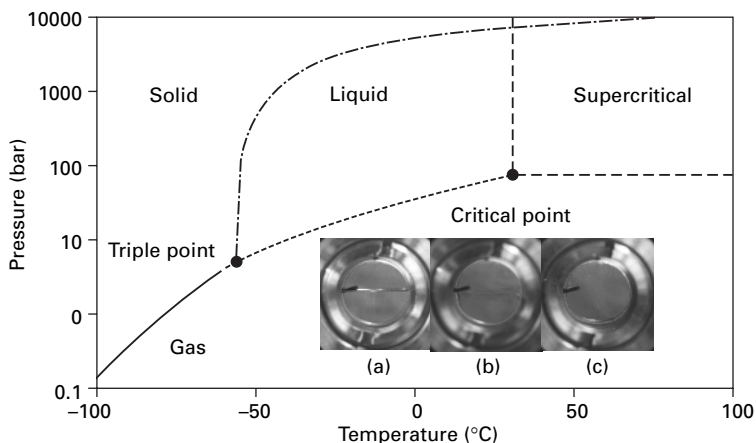
On the other hand, CO₂ is known as a greenhouse gas and there is an international growing concern about global warming and its inter-relationship with levels of CO₂ in the air (Anon, 2003). Around 1800, before the industrial revolution, the CO₂ concentration in the atmosphere was about 280 ppm and, in 1960, it was already 315 ppm. Since the mid-1900s, CO₂ levels have been continually increasing at an average annual rate of slightly more than 1 ppm, due to an increased combustion of fossil fuels and natural processes. At present, the average CO₂ concentration in the atmosphere is about 380 ppm (Anon, 2003).

In this context, processes which do not emit but apply CO₂ as a solvent have also been discussed very critically. Therefore, it is essential to investigate the sources of CO₂ and how it is recovered. Commercial quantities of CO₂ are produced by separating and purifying relatively CO₂-rich gases coming from combustion or biological processes that would otherwise be released directly to the atmosphere. Common sources are hydrogen and ammonia plants, magnesium production from dolomite, limekiln operations and fermentation operations such as the production of beer or the manufacture of ethanol from corn (Anon, 2003). CO₂ may also be recovered from wells (Anon, 2003). That means that processes such as supercritical fluid dyeing do not increase CO₂ emissions, but rather provide an opportunity for recycling of waste CO₂.

5.1.2 Physicochemical properties of CO₂

Generally, a supercritical fluid is defined (Angus *et al.*, 1976; Span and Wagner, 1996; Darr and Poliakoff, 1999) as a 'substance for which the temperature and pressure are above their critical values and which has a density close to or higher than its critical density' (Kemmere, 2005). The supercritical state can also be described (Baldyga *et al.*, 2004) as 'statistical clusters of augmented density with a structure resembling that of a liquid surrounded by less dense and more chaotic regions of compressed gas. The number and dimensions of these clusters vary significantly with pressure and temperature resulting in high compressibility near the critical point' (Kemmere, 2005).

At the critical point, CO₂ has a temperature of 31.1 °C and a pressure of 73.8 bar (Angus *et al.*, 1976; Span and Wagner, 1996). As shown in the photos (from left to right) in the phase diagram in Fig. 5.1, below the critical parameters two distinct phases of liquid and gaseous CO₂ are separated by the phase boundary. As the temperature and pressure rise along the vapour-



5.1 Behaviour of CO₂ along the liquid/gas phase equilibrium line in the phase diagram (Anon, 1992) observing a high pressure view cell (from left to right 20 °C/58 bar, 30 °C/71 bar, 33 °C/75 bar).

liquid coexistence line, liquid CO₂ expands and the two phases become less distinct forming a so-called supercritical phase. Above the critical point, the vapour–liquid line completely disappears.

Supercritical CO₂ can be regarded as a ‘hybrid solvent’ due to the fact that by simply changing the pressure or the temperature, the properties can be tuned from liquid-like to gas-like without crossing a phase boundary (Kemmere, 2005) as presented in Table 5.1.

Generally, the liquid-like high and variable density of supercritical fluids causes a tunable solvating power. The density of CO₂ at the critical point is 468 kg m⁻³ (Anon, 2003). Pressure increase enhances solvent power and solubility due to a higher density of the fluid. When the temperature is raised, fluid density decreases, but solute vapor pressure is increased, resulting in a specific temperature-dependent behaviour of each solute (Arunajatesan, 2002). Viscosity of supercritical fluids is more gas-like resulting in a reduced pressure loss (ΔP) due to lower friction and transport limitations in technical processes. The negligible surface tension leads to excellent ‘wetting’ properties. Moreover, higher diffusivity compared with a liquid can affect the selectivity of chemical reactions (Arunajatesan, 2002) but it can also accelerate scCO₂ processes such as dyeing.

5.1.3 Current environmentally sound applications of CO₂

CO₂ is applied in many industrial processes: in the food industry, for cleaning of surfaces, for neutralization and large quantities are used as a raw material in the chemical process industry, especially for the production of methanol,

Table 5.1 Range of physical properties of gases and liquids compared with supercritical fluids at T_c and P_c and after fourfold ($4P_c$) increase in pressure

Property	Gas	Supercritical fluid		Liquid
		$T_c P_c$	$T_c 4P_c$	
Density ρ^* (kg/m ³)	0.6–2	200–500	400–900	600–1600
Viscosity η^\dagger (Pa·s)	10^{-5}	10^{-4}	–	10^{-3}
Diffusivity* (m ² /s)	1×10^{-5} – 4×10^{-5}	0.7×10^{-7}	0.2×10^{-7}	0.2×10^{-9} – 2×10^{-9}

*Weibel, 1999 and Anon, 2005b.

†Lucien and Foster, 1999.

urea and oil (Anon, 2003). CO₂ is a ‘green’ industrial extraction medium replacing organic solvents for purification of odorants but also for the removal of agrochemicals from ginseng extract, of caffeine from coffee beans, of water from ethanol and of monomers from polymers on an industrial scale (Anon, 2003). CO₂ dry cleaning, as another example of an environmentally sound extraction process, as proved by LCA studies (Flückinger, 1999), has meanwhile become commercialized to replace the carcinogenic perchloroethylene in future (Peterson, 2003). Newer developments are the solvent substitution by CO₂ in lithography (Hoggan *et al.*, 2004) and in polymerization reactions, e.g. in the manufacturing of certain grades of polymers based on tetrafluoroethylene (Teflon™) by DuPont (DeSimone *et al.*, 1992; Romack and DeSimone, 1995; DeSimone, 2002). Moreover, production of fine particles with a narrow spectrum of particle size distribution by rapid expansion of supercritical solutions are of great interest for pharmaceutical applications (Subramaniam *et al.*, 1997). CO₂ can also be used as a coolant in air conditioning of automobiles (Brown *et al.*, 2002) to replace chlorofluorocarbons.

5.2 History of supercritical fluid dyeing

To this day, extraction is the main field of industrial application of CO₂. The first patents on impregnation of thermoplastic polymers with fragrance or pest control agents or pharmaceutical compositions appeared in 1986 (Sand, 1986). One year later in 1987, another patent claimed that ‘polymers can be infused by additives such as UV-stabilizers and sensitizers, antioxidants and dyes (colorants) in supercritical carbon dioxide’. The main field of interest in this patent was the impregnation of PVC and rubber, but as polymer substrates poly(ethylene terephthalate) (PET), polyamide, polyacrylic and polyurethane polymers, and polyolefins are also mentioned (Beres *et al.*, 1987).

In 1988, the first patent focused on dyeing of textile substrates in pure scCO₂ and the application of polar co-solvents such as water, alcohol, and/or salts in order to change the polarity of the supercritical fluid was described (Schollmeyer *et al.*, 1990). It was later on supplemented by other more far-reaching patents on dyeing by DTNW (Schollmeyer and Knittel, 1993; Knittel *et al.*, 1993a; Knittel and Schollmeyer, 1995b) and on dyes suitable for scCO₂ by Ciba Specialty Chemicals Inc. (former Ciba Geigy AG) (Schlenker *et al.*, 1992a, 1992b, 1992c; Schlenker *et al.*, 1993).

5.2.1 Milestones of process and plant development

First experiences of dyeing of PET in scCO₂ were made by DTNW in 1989 on a laboratory scale in close co-operation with Professor G. M. Schneider at the Ruhr University of Bochum, Germany, in a high pressure phase equilibrium plant of 6 ml volume (Poulakis *et al.*, 1991). After the first tests had been successful, in 1990, a static dyeing apparatus consisting of a 400 ml autoclave with a stirrable, perforated dyeing beam was developed by DTNW (Knittel *et al.*, 1993b; Knittel and Schollmeyer, 1995c). Based on the optimum dyeing conditions obtained on a laboratory scale in this plant (Saus *et al.*, 1992, 1993a, 1993b, 1993c; Knittel *et al.*, 1994a, 1994b; Knittel and Schollmeyer, 1995a) in 1991, the first dyeing machine on a semi-technical scale was constructed and built by Josef Jasper GmbH & Co. Velen, Germany, in close cooperation with DTNW (Knittel *et al.*, 1993b; Knittel and Schollmeyer, 1995c). The autoclave had a volume of 67 l for dyeing a maximum of four bobbins with a yarn weight of 2 kg each. Within this co-operation, several patents concerning the machinery equipment and the dyeing plant technology have been published by Jasper (Jasper, 1993a, 1993b, 1993c, 1993d, 1993e).

In 1994, one of the Jasper scCO₂-dyeing machines was installed by Amann & Söhne GmbH & Co. Bönningheim, Germany, for dyeing of PET sewing threads and for testing whether this technology was transferable to the textile industry (Anon, 1995). On this machine, many technical problems arose in the test phase and Jasper gave this technology up after the last presentation of parts of a scCO₂-dyeing machine at the International Textile Machinery Exhibition ITMA 95 in Milan, Italy. In this context, Amann transferred the machine to the faculty of Process Engineering II of the Technical University of Hamburg-Harburg, Germany, for further research and development (von Schnitzler, 2000). Since 2004, JVS Engineering, a start-up of the Technical University of Hamburg-Harburg has been attempting to develop applications in CO₂ with this modified Jasper-plant (von Schnitzler, 2004).

In 1995, a new approach was started by Uhde High Pressure Technologies GmbH Hagen, Germany, and DTNW resulting in a new construction of a scCO₂-dyeing pilot plant with a volume of the autoclave of 30 l. Whereas with the Jasper scCO₂-dyeing machine only impregnation processes were

possible, the new Uhde plant was extended by an extraction cycle for removal and separation of excess dyes and spinning oils during the dyeing process, for cleaning of the plant at colour changes and for recycling of CO₂. Moreover, a separate dye storage vessel and a pump with a much higher flow rate was integrated. The pilot plant was first presented at the ITMA 95 in Milan, Italy, and, in 1996, at the OTEMAS in Osaka, Japan (Bach *et al.*, 2002a).

In 1999, the German producer and finisher of home textiles, Ado Gardinenwerke GmbH & Co. Aschendorf, joined Uhde and DTNW and, after evaluation of the dyeing results within a research project of just under three years (Bach *et al.*, 2002b), it became the objective of the partners in 2003 to push this technology forward together with other textile companies and scale up the scCO₂-plant to an industrial scale.

Since 1995, growing interest has been observed worldwide in this technology, starting in the USA and Asia and later on also in Europe. Besides the numerous publications on results of scCO₂ dyeing of natural and synthetic fibres on a laboratory scale, as summarized by Bach *et al.* (2002b), up to now, three separate major runs have been taken to scale up the scCO₂ dyeing process and the plant to an industrial scale.

Besides the development in Germany, an American consortium of NC State University, North Carolina, Unifi[®] Inc., Ciba-Geigy Corp. (USA), and Praxair Inc. intended to test the scCO₂ technology mainly for dyeing of yarns and fabrics from PET, cotton, polyamide, and PET/cotton blends. According to information from the NC State University website, the project ended in 1999 (Seastrunk, 1999). After that time, no further activities have been published where Unifi[®] Inc. was involved. Meanwhile, it seems that a 'prototype supercritical fluid dyeing system capable of dyeing multiple, commercial-size PET yarn packages has been built' (Montero *et al.*, 2000), but up to now no dyeing results or experience with this machine have been published and no information is available as to in which textile finishing company this machine is placed.

In 2003, an Asian consortium comprising textile-finishing and fibre-producing companies, and researchers from Fukui University started an approach with a budget of five million euro from the Japanese government to develop within three years a plant and processes on an industrial scale for scCO₂ dyeing of fibres that are difficult to dye by conventional water technology. The machine is built by Hisaka Works. Mitsubishi Rayon and Teijin as project partners are working on dyeing of polypropylene and aramide (Stylios, 2004; Aoyama, 2005). Results have not yet been published.

5.3 Current supercritical fluid dyeing technologies

In 2005, world fibre production was 60.8 million tonnes with PET being the leading synthetic fibre. The annual growth of PET production over the last

three years was between 7 and 9% with a market share of 40.6% in 2005 (PET filament fibres 23.7%, PET staple fibres 16.9%). For comparison, polyamide had a share of only 6.4% (3.9 million tonnes) (Anon, 2005c).

Since 1999, production of cellulosic fibres has continuously increased with a slight decline for cotton in 2005. The market share of cotton with 41.2% in world fibre production is very similar to the share of PET. Over recent years, only wool and silk have had minor and stagnant shares of 2.0 and 0.2%, respectively (Anon, 2005c).

Because of the significance of PET and cotton, the development of supercritical fluid dyeing technologies worldwide is mainly focused on these fibres and only to a minor extent on wool, silk, polyamide and other technical fibres. While the dyeing of PET works very well in scCO_2 , dyeing of polar fibres like cotton is still challenging when high fastness properties and colour yields are required. The limitations of dyeing natural fibres in scCO_2 arise from the inability of CO_2 to break hydrogen bonds (Kazarian *et al.*, 1996; Saus *et al.*, 1993d), the low degree of fibre swelling and the low reactivity of the OH-bonds in cellulose in the slightly acidic CO_2 medium (Bach *et al.*, 2002a). Furthermore, disperse dyes only show slight interactions with polar fibres, leading to unacceptably low fastness data, while reactive-, direct-, and acid dyes which are used in conventional water dyeing are nearly insoluble in scCO_2 .

In this way, attempts have been made to increase the dye solubility and the dye uptake of cellulose and protein fibres in scCO_2 by using polar co-solvents. The affinity of disperse dyes to the fibre was increased by impregnation with swelling and crosslinking agents, and by modifications of the surface of the fibre with functional groups, as summarized by Bach *et al.* (2002a). In other scCO_2 experiments, reactive disperse dyes for dyeing of unmodified natural polar fibres and polyamide were used (Bach *et al.*, 2002a; Liao, 2004; Cid *et al.*, 2004; Maeda *et al.*, 2004).

For ecological reasons most of the dyeing experiments on natural fibres described so far lose the main advantages of being a water-free process. For dyeing of cotton, pre- and after-treatment are frequently more water- and energy-consuming than the conventional water-based dyeing process.

In order to obtain convenient high colour depths, substances are permanently fixed on the fibre surface in high concentrations of the modifying agent. This leads to significant changes in the fibre properties (of e.g. cotton) which are unacceptable for most applications (Bach *et al.*, 2002a).

Recently, there have been new developments based on reverse micellar systems for solubilization of conventional basic, acid, direct or reactive dyes from water dyeing for scCO_2 -based dyeing of cotton, wool, silk, acrylics and polyamide (Sawada *et al.*, 2002, 2003, 2004a, 2004b; Sawada and Ueda, 2004; Jun *et al.*, 2004; Lewin-Kretzschmar and Harting, 2004; Jun *et al.*, 2005). In the future it has to be evaluated whether this can be an ecologically

sound alternative for scCO_2 dyeing of cellulose and protein fibres. Currently, many questions concerning dye fixation, suppression of dye fibre repulsion, colour yield and the optimum reverse micellar system remain unanswered.

The most suitable scCO_2 dyeing technology under ecological aspects for natural fibres with all the advantages known from PET dyeing is the application of reactive disperse dyes. However, the dyes that have been applied in scCO_2 dyeing experiments so far are not commercially available yet and were custom-made in the laboratories of the different research groups.

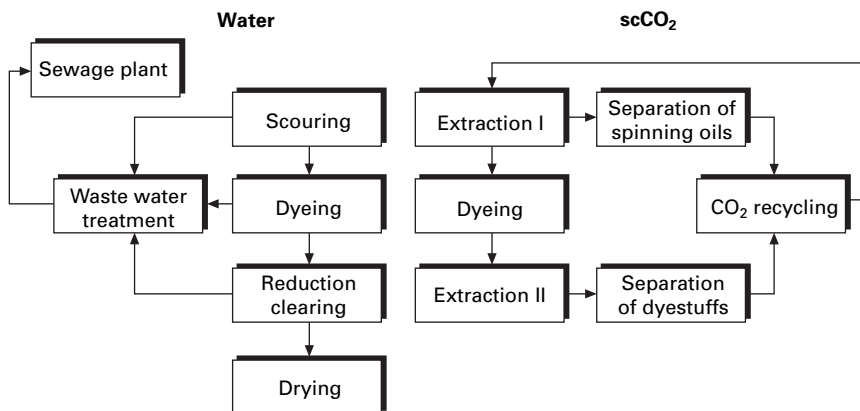
5.3.1 Environmental aspects of PET dyeing in scCO_2

Worldwide, the dyeing of PET in scCO_2 is the most extensively investigated finishing process and, while a convenient number of data sets are accessible to evaluate this process in particular in terms of many ecological aspects, there is a lack of published data for the equivalent water dyeing process which makes it very difficult to compare both processes in detail and to quantify the differences in their environmental impact.

From Fig. 5.2 it is evident that conventional water dyeing is an *end-of-the-pipe* process, whereas with scCO_2 a *quasi-closed loop* process can be accomplished. After precipitation of spinning oils and excess dye in a separator, CO_2 is recycled and can be reused. 'Quasi' means that extraction residues of dyestuffs and spinning oils are not recyclable as well as about 10% of CO_2 which is released into the atmosphere (Bach *et al.*, 1998).

5.3.2 Process steps for PET dyeing in scCO_2

The definite process steps for dyeing of PET in scCO_2 can be seen in Fig. 5.2. In short, the first step (Extraction I) represents the partial extraction

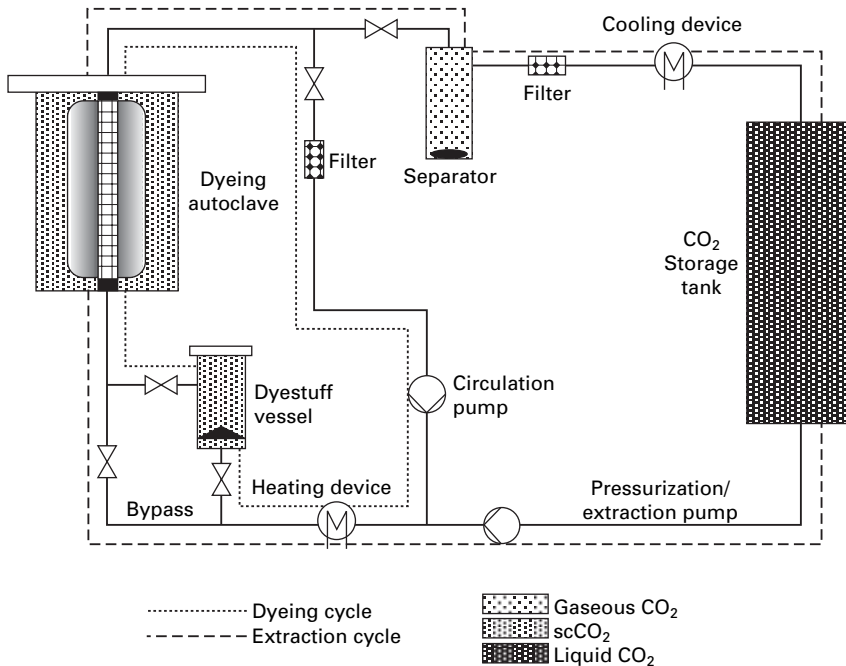


5.2 Comparison of the process steps for dyeing of PET using water and scCO_2 (Bach *et al.*, 2002a, modified).

of spinning oils, followed by dyeing. Then extraction step II is started for removal of adhering dye from the fabric surface and the inner of the plant by rinsing with fresh cold scCO_2 . The temperature in the plant is decreased as fast as possible below the glass transition temperature of the polymer to avoid extraction of dye from the fibre bulk. Extracted dyes and spinning oils are precipitated in a separator. At the end of the dyeing process, CO_2 in the plant is depressurized under liquefaction to the pressure in the CO_2 storage tank of about 50–55 bar. Remaining gaseous CO_2 in the plant is released into the atmosphere. In illustration of the complete process, in Fig. 5.3 extraction and dyeing cycles are drawn in as well as CO_2 phase conditions in the different parts of the Uhde plant (Bach *et al.*, 1998). A flow scheme and a detailed description of the process has been published elsewhere (Bach *et al.*, 1998, 2002a, 2002b).

5.3.3 Scale-up parameters of the scCO_2 dyeing process and the plant

Based on the experience with the Uhde plant on a technical scale, data for an up-scaled process and plant have been published for the dyeing of 120 kg PET fabrics relating to a fabric length of 200 m and a width of 3 m (Bach



5.3 Schematic of the Uhde dyeing plant (Bach *et al.*, 1998, modified).

et al., 2004b). The volume of the whole plant is approximately 950 l and that of the dyeing autoclave 600 l. The up-scaled plant fulfils the process conditions as described in Table 5.2. A schematical drawing of parts of the front and side view of the plant is presented in Fig. 5.4.

In Table 5.2 only the most important parameters are presented. Besides temperature and pressure, the flow rate of the circulation pump in the scCO₂ dyeing cycle has a significant influence on the levelness of the dyed goods which is essential for a high product quality (Bach *et al.*, 2002a).

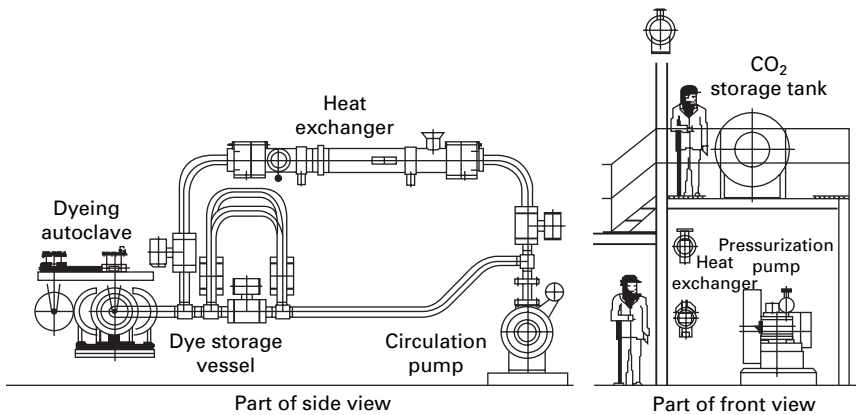
Determination of the process time in scCO₂

In environmentally sound processes, raw materials and energy should be used as efficiently as possible. In this context, the process time for a complete scCO₂ dyeing cycle is one of the key factors in the calculation of energy consumption of an up-scaled plant and has to be evaluated. For estimation of the dyeing time, knowledge of the solubility of dyes in scCO₂ is a very important parameter, but the relationships of solubility and dye distribution between the fibre and CO₂ are highly complex. In the literature, mainly

Table 5.2 Process conditions for dyeing of PET fabrics in scCO₂ based on the Uhde plant*

Parameter	Setting
Working temperature	100–140 °C
Working pressure	250–350 bar
Density of scCO ₂	450–750 kg/m ³
Flow rate of scCO ₂	1800–4200 kg min ⁻¹

*Bach *et al.*, 2004b.



5.4 Schematic of the up-scaled Uhde dyeing plant (Bach *et al.*, 2004b).

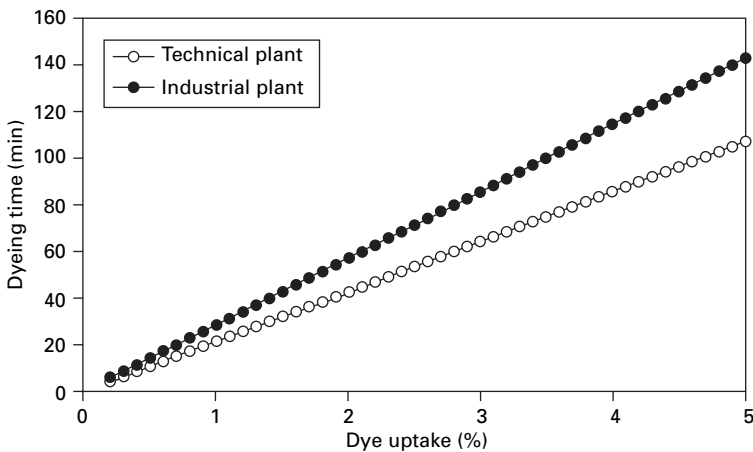
solubility data at equilibrium are available (Özcan *et al.*, 1997; Draper *et al.*, 2000; Lee *et al.*, 2001; Tabata *et al.*, 2001; Bach *et al.*, 2001; Bao and Dai, 2005), but this is scarcely applicable for practical use. Due to the very short contact times between the dyeing medium and the dyes in the dyestuff vessel, saturation of scCO_2 with the dyes is nearly impossible. Therefore, a theoretical model was developed for determination of dye solubility as described elsewhere (Bach *et al.*, 2004b).

Based on the model, dye solubility of several disperse dyes was determined at various flow rates of the circulation pump in the Uhde plant. The data show (not presented here) that doubling of the flow rate decreases the solubility of nearly all dyes tested by 30%, proving that non-equilibrium conditions predominate in the dyestuff vessel at optimum process parameters (Bach *et al.*, 2004b).

For a dye uptake of 2% – relating to 20 g of pure dye per kg of PET – calculated from the non-equilibrium solubility data in scCO_2 , a dyeing time of 40 min in the Uhde plant and 60 min in the up-scaled plant is needed, as presented in Fig. 5.5. The dye uptake of PET in scCO_2 is equivalent to a minimum of 4% in water dyeing, when estimating an amount of auxiliaries in the dye formulation of 50%. Dye content of the disperse dyes used for water dyeing normally varies between 30 and 50% (Bach *et al.*, 2004b).

Energy consumption of the industrial scCO_2 dyeing plant

After evaluation of the dyeing step, which is the most time-consuming one, the total process time can be extrapolated. As schematically shown in

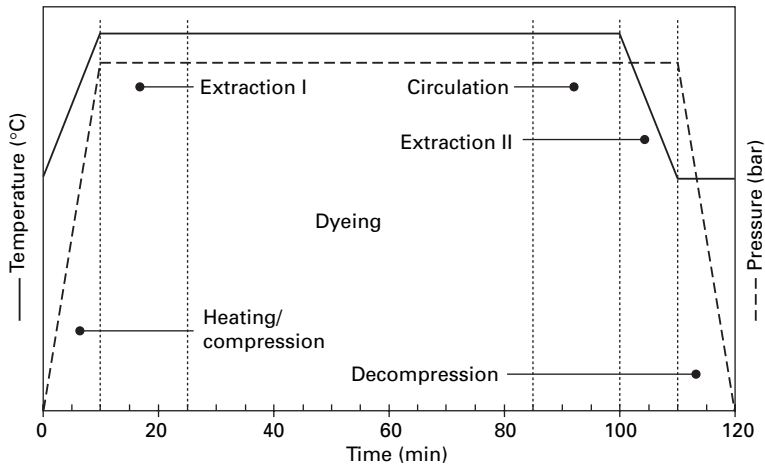


5.5 Theoretically calculated dyeing times for PET in the Uhde plant (technical plant) and in an up-scaled plant (industrial plant) based on the non-equilibrium solubility measurements under optimum dyeing conditions (Bach *et al.*, 2004b).

Fig. 5.6, process time is divided into pressurization/heating and decompression of 10 min each, extraction I and II of 15 and 10 min, respectively, and dyeing within 60 min followed by a level-out phase of 15 min, which can even be left out for many dyes tested (Bach *et al.*, 2004b). All in all, the whole process will take two hours.

Heating and cooling energies of the devices and the energies needed for heating and pressurization of the CO₂ were determined based on the data in Fig. 5.6, as summarized in Table 5.3.

The total specific energy consumption of the scCO₂ process is very close to that as published in 1994 by van Asselt and Klein Woltering from Tebodin B.V. for high-temperature beam dyeing of PET in water including rinsing/washing and drying of the dyed fabric. They obtained a value for the energy consumption of 4.53 kWh kg⁻¹, estimating a dyeing process time of 7.5 h (van Asselt and Klein Woltering, 1994). The calculations also



5.6 Flow scheme of the temperature and pressure programmes during the scCO₂ dyeing process in the up-scaled industrial plant (Bach *et al.*, 2004b).

Table 5.3 Specific energy consumption per kg of textile estimated for the up-scaled plant*

	Specific energy consumption (kWh kg ⁻¹)
Heat	1.5
Electrical energy incl. energy for cooling	3.0
Sum	4.5

*Bach *et al.*, 2002b.

agree to a great extent with the data of Ado Gardinenwerke GmbH & Co. (Schüler, 2002).

Although treatment time in scCO₂ is significantly lower compared with the water dyeing process including drying, the energy consumption of both processes seems to be similar. Probably, one reason could be that warm up before dyeing and cooling in extraction step II (Fig. 5.2 and 5.6) of the thicker steel walls of the scCO₂ plant, which are essential to handle the high pressure of the process, need more energy compared with a water dyeing plant. Another reason is that data of the electrical energy consumption in Table 5.3 also include cooling energy for liquefaction of CO₂ for recycling, which was not considered for the water-based process.

For reduction of energy consumption, it may be possible to keep the scCO₂ plant at a mean temperature during the whole dyeing process, thus avoiding unnecessary heating and cooling of plant parts. A cooling down to room temperature would only be necessary for maintenance work, repair or by a fall in production (Bach *et al.*, 2004c).

In particular, it might be possible to keep the temperature of the autoclave and the dyestuff vessel constant during the complete process cycle. In this case, only the temperature of the dyed goods, the interior of the autoclave and the CO₂ is changed in extraction step II. This would help to minimize the energy consumption of the process and the plant but a final quantification will only be possible after an industrial plant is put into operation (Bach *et al.*, 2004b).

CO₂ consumption of the industrial dyeing plant

For minimization of emissions in scCO₂ dyeing, most of the CO₂ in the process can be recycled, as presented in Table 5.4. The loss in CO₂ from the industrial dyeing plant was estimated by Uhde under consideration of CO₂-recycling under optimum conditions up to the pressure of the storage tank of about 50–55 bar.

Table 5.4 Specific loss in CO₂ of the up-scaled plant*

	CO ₂ -loss (kg)
Dyeing and dyestuff cycle	140
Separator	18
Total	158
Specific loss including separator (per kg textile)	1.23
Specific loss without separator (per kg textile)	1.17

*Bach *et al.*, 2002b.

Emptying of the separator is not needed after each dyeing. Therefore, the lower value of the specific loss of CO₂ is much closer to reality than the higher one (Bach *et al.*, 2002b) relating to a total loss in CO₂ of about 18%.

In order to recycle larger quantities, CO₂ can be evacuated by a compressor from the plant into a pressure vessel. There, the gas is cooled, compressed to 55 bar and returned into the storage tank. An increased recycling rate is also possible by cooling the CO₂ in the storage tank down below room temperature. However, this needs additional energy.

For both methods, a cost–benefit analysis has to be carried out for the rate of CO₂ recycling, on the one hand and costs for energy and machinery equipment needed for compression, liquefaction and storage of CO₂, on the other.

Economization in chemicals compared with water dyeing of PET

When considering minimal waste production as demanded for environmentally sound processes, scCO₂ dyeing of PET is really a ‘clean’ finishing process because only dyes are needed. For comparison, the environmental impact of the analogous water-based process is summarized in Table 5.5, according to the chemical composition of the effluents, to the waste air production during passage through the stenter and a listing of all *additional* chemicals which are essential in water dyeing. The data are calculated on the actual construction parameters of an up-scaled scCO₂ plant for dyeing and finishing of 120 kg of PET fabrics as described at the start of Section 5.3.3.

The data of the water consumption in Table 5.5 take into consideration the water input, wastewater and water for cooling. The effluent contamination is characterized by the chemical oxygen demand (COD), the nitrogen content and the phosphorus content of the wastewater after scouring, dyeing, reductive

*Table 5.5 Ecologically relevant data of industrial finishing of PET fabrics in water**

	per kg PET	per process	per annum
Water consumption (m ³)	0.28	34	7480
Effluent contamination			
COD (kg)	0.26	30.6	6732
Nitrogen (kg)	0.002	0.22	48.62
Phosphorus (kg)	0.002	0.26	56.1
Waste air			
Waste air (m ³)	75	9000	1980000
Total carbon (kg)	0.002	0.21	45.7
Auxiliaries			
Dyeing (l)	0.07	8.6	1892
Reduction clearing (l)	0.06	6.8	1496

*Schüler, 2002.

afterclearing including rinsing after each process, and softening. The waste air results from drying of the PET fabric after the final softening process.

It should be noted that the data on the amount of auxiliaries of dyeing and reduction clearing are not quite exact, because they are all in liquid form and may contain a certain amount of water. The data on the auxiliaries in dyeing represent the input of an antistatic agent, a dispersing agent, a migrating agent and acetic acid. Process chemicals in reduction clearing are an antistatic agent, a reducing agent and sodium hydroxide.

The column '*per annum*' in Table 5.5 shows the data calculated for one dyeing process per day and 220 working days per year.

Generally, a complete finishing operation in water takes about 6 h (Schüler, 2002). Based on the significantly shorter process times, in $scCO_2$ theoretically up to six process cycles could be accomplished per day. That means, when working with one CO_2 dyeing plant, 20.3 m³ of auxiliaries from dyeing and reductive afterclearing and about 45 000 m³ of water and wastewater could be avoided per year.

Product quality after $scCO_2$ dyeing

For the transfer of a new process into industry, it is essential, that the field of application is broad and the quality of the products produced with the new technology must be at least equally as good as from the current technology. Based on the experience with the $scCO_2$ dyeing technology on a technical scale, it is obvious meanwhile that, for PET under optimum dyeing conditions, all shades as in water dyeing but also high colour yields are obtained. As proven by colorimetric measurements after multi-chrome dyeing of PET, no differences in the reflectance spectra at the inside, middle, and outside of the fabric pack were found indicating a high levelness of dyeing. All dyes applied in this technology are approved by the Oecotex Standard 100.

The quality of the dyed material concerning washing, rubbing and sublimation is also very good. Generally, fastness notes of five are obtained even when dye concentrations of 4.5% were applied. Compared with the water dyeing process on an industrial scale, wash fastness of PET when dyed in the same shade is sometimes up to one grade higher (Bach *et al.*, 2004a).

Stress-strain and viscosimetric molecular weight measurements of $scCO_2$ dyed PET show that no fibre damage takes place under optimum dyeing conditions. In fact, the breaking force and breaking elongation is sometimes higher compared with the blank and water-dyed fabric as tested by Ado. If heat-set PET is applied, shrinkage during CO_2 -dyeing is very low: a maximum of 1.5%. In these special cases, shrinkage in CO_2 was generally lower than in water for all PET fibres tested (Bach *et al.*, 2004a).

Finally, it can be concluded that all of the quality standards of textile-finishing companies can be fully met with the $scCO_2$ dyeing technology (Bach *et al.*, 2004a).

5.3.4 Commercial competitiveness of the scCO₂ dyeing process

Another very important parameter for the transfer of this new technology into industry is the estimation of the economic efficiency of the scCO₂ dyeing process compared with water dyeing of PET. In Germany in particular, water and wastewater are very expensive. Related to the costs for energy and auxiliaries in water dyeing of PET and subsequent drying, the costs for water are about 60% of the total process costs (Schüler, 2002).

CO₂ is a relatively cheap gas with high purity grades and it is commercially available worldwide. CO₂ is very easily recyclable and can be reused as a process medium (Jessop and Leitner, 1999; Kemmere, 2005). Consequently, compared with a conventional water dyeing process, the operational costs in scCO₂ are much lower (Bach *et al.*, 2002a, 2002b; Schüler, 2002).

Moreover, by applying CO₂, industry becomes independent from water sources without generation of liquid wastes. While water quality can differ from city to city within the same country depending on the source of water, CO₂ is subject to international quality standards of worldwide validity. Because of the globalization of textile-finishing companies, dyeing recipes will be applicable worldwide, but compatibility of the dyeing plants has also to be checked in the future.

When considering process costs, there is an obvious economic advantage in the scCO₂ process, which is partly compensated by the high investment costs of the plant. It has to be kept in mind that process costs can be further diminished by installing three autoclaves in one plant (van Asselt and Klein Woltering, 1994). For example, in autoclave one, CO₂ is pressurized and the fibre extracted, in the second autoclave impregnation/dyeing takes place and the third one is in the operation mode of decompression, emptying and loading of new textile to be dyed. This parallel processing is possible just by opening and closing certain valves because two different pumps for pressurization/extraction and scCO₂ circulation are used (see Fig. 5.3 and 5.4). Some diagrams and flow schemes of plants using this concept have been presented by van Asselt and Klein Woltering (1994).

5.4 Future trends in supercritical fluid dyeing technologies

5.4.1 Fusion of finishing processes and dyeing of fully fashioned textiles

When there is a requirement for fast colour changes in fashion and fixture design, investigating the fusion of finishing processes such as impregnation of dyes, softeners and flame retardant agents in CO₂ will become more and

more important. This would significantly decrease the process time for finishing of textiles and increase the flexibility of the process due to a make-to-order finishing within very low delivery times and small contingents of stock-keeping.

Flexibility can be further improved if fully fashioned textiles such as curtains, zippers, underwear, brassieres, and sportswear could be dyed in scCO₂ as claimed in a patent by Kerle *et al.* (2004). However, the optimum form of supply of the textiles in the autoclave has to be examined at first.

5.4.2 Dyeing of high-performance fibres in scCO₂

For many years scCO₂ has been regarded as a solvent that has the potential to overcome all of the problems of water dyeing for difficult-to-dye technical fibres such as meta- and para-aramides, poly(ether ether ketone) (PEEK), polybenzimidazole (PBI), polyimide (PI) and liquid-crystal polyesters (Vectran®). Meanwhile, it has become more and more evident that, if a synthetic fibre can hardly be dyed in water, the same will be valid in scCO₂ (Bach *et al.*, 2002a).

In order to improve the dye uptake of many high-performance fibres in scCO₂, application of co-solvents known as carriers from water dyeing such as 1-methyl-2-pyrrolidone, acetophenone, benzylalcohol, benzaldehyde and also water, alcohols and acetone in combination with high temperatures were suggested (Knittel and Schollmeyer, 1997; Bach, 1997; Hatano *et al.*, 2001) but dyeing of high-performance fibres in scCO₂ is still challenging. For the development of dyeing processes for difficult-to-dye technical fibres which are used in the textile industry, a deeper understanding of the CO₂/co-solvent (carrier) dyeing process is needed, suitable dyes have to be selected and removal of the solvent from the fibre by CO₂ extraction has to be determined to avoid an extra drying step. In addition, cleaning of the plant at color changes has to be optimized due to an increased solubility of many disperse dyes in scCO₂ when co-solvents are applied (Bach *et al.*, 2002a).

From the economical point of view, process costs will rise when working with organic co-solvents due to higher investment costs for explosion proof scCO₂ dyeing plants. Sealing rings in the plant have to tolerate the co-solvent and temperatures of up to 150 °C, which may also cause extra costs.

From the environmental point of view, dyeing of high performance fibres in scCO₂ with co-solvents has the advantage that separation of co-solvent and CO₂ is easily feasible due to the 'volatile' solvent properties of CO₂ (Jessop and Leitner, 1999; Kemmere, 2005); however, for recycling of the process medium, separation of dissolved substances from the spinning process and dyes has to be determined in much more detail.

In this way, as opposed to the conventional water-based process, carrier dyeing in scCO₂ has the potential to be a more environmentally sound and

suitable dyeing process for difficult-to-dye technical fibres, but there are some challenges which must first be overcome.

5.4.3 Future of scCO₂ dyeing technology

Although a considerable amount of experience with the scCO₂ dyeing technology worldwide exists on a laboratory or technical scale, it is not possible to speculate about the future of this technology until a plant has been built and validated on industrial scale by a textile-finishing company. Testing and optimization of the process and the plant should be carried out at first with PET as the easiest-to-dye textile material in scCO₂ in order to deal with the questions that can only be answered in an up-scaled plant (Bach *et al.*, 2002a, 2002b, 2004b). Additionally, if this technology has been successfully proven on an industrial scale, this may also push forward the development of other water-free processes in textile finishing such as sizing, scouring, bleaching and dyeing of natural fibres, e.g. cotton, wool and silk. This will need co-operation between research organizations and the chemical industry, because examination and approval of new or modified finishing agents and dyes is very expensive.

5.5 Sources of further information and advice

For a deeper insight into the scientific aspects of scCO₂ dyeing, the possibilities and limitations of the technology for synthetic and natural fibres, dyeing concepts and mechanisms, the thermo-mechanical behaviour of fibres and solubility of dyes and the worldwide state-of-the-art, the review article of Bach *et al.* (2002a), is recommended.

For information about the phase behaviour and the physico-chemical properties of CO₂ and CO₂/co-solvent mixtures, there are two databases which can be used via the internet: <http://webbook.nist.gov/chemistry/> and <http://www.questconsult.com/~jrm/thermot.html>. Comprehensive information about CO₂ can also be obtained from the internet sites of many gas producers.

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