DESIGN AND PERFORMANCE OF A TECHNICAL-SCALE MACHINE FOR POLYESTER DYEING IN $SCCO_2$

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A technical-scale textile dyeing machine has been designed, built and tested for the dyeing of polyester cloth in supercritical carbon dioxide ($scCO_2$). To minimise the process cost, a new type of pressure vessel and a new type of centrifugal pump were developed. The dyeing vessel is a stainless steel liner, reinforced with carbon fibres to take up the radial pressure forces. The axial forces, working on the lids of the vessel, are taken up by an external yoke. A low-pressure centrifugal pump, used to circulate the $scCO_2$ through the dye and the polyester, has been designed for service in a $scCO_2$ environment and placed inside the dyeing vessel.

Tests proved that it is possible to dye polyester batches of 2 kg in a two-hour process. Per batch, 95% of the CO_2 was recycled. The polyester was dyed evenly, had good fastness properties, did not exhibit excessive shrinking and it showed no change in tensile strength, indicating that the dyed product was of the same quality as in aqueous dyeing.

INTRODUCTION

In industrial textile dyeing processes, large amounts of water are consumed and heavily polluted. This is obviously an environmental concern, but it also an economical issue, for the textile industry, because of the ever more stringent regulations on wastewater treatment. Furthermore, the current shortage of fresh water, suitable for human consumption, makes the use of water for textile dyeing unattractive.

Dyeing in $scCO_2$ instead of water solves these problems The main advantage of the use of $scCO_2$ is that the dye that remains in the solvent after the process, can easily be removed by precipitation, induced by depressurisation. In this way, the dye powder and the clean gaseous CO_2 can both be collected for recycling. No waste is generated in the process and no fresh water is consumed.

Supercritical textile dyeing has therefore received considerable scientific attention in the last two decades. The present paper describes one of the results from a project carried out by the Delft University of Technology, FeyeCon D&I B.V., Stork Prints B.V. and Ames Europe B.V. [1,2]. Several other research groups have also worked on the dyeing of polyester, cotton, wool, silk and other textiles, as is reviewed by Bach et al. [3]. In most cases, hydrophobic, $scCO_2$-soluble dyes are used. To allow sufficient solubilisation of these molecules, typical dyeing pressures and temperatures of 300 bar and 120ºC are used.

Polyester can be dyed with commercially available, so-called disperse dyes. The dye molecules dissolve in the $scCO_2$ and then diffuse into the polymer, where they are retained by physical (dispersion) forces, because both the polymer and the dye are hydrophobic. The diffusion in the textile fibres is facilitated by the swelling of polyester in $scCO_2$.

Natural fibres like cotton, silk and wool, however, are hydrophilic and exhibit no physical attraction toward $scCO_2$-soluble dyes. The dyes should be bound to these textiles by covalent bonding, i.e. reactive disperse dyes are to be used. Since these dyes are not commercially available and because the need for a chemical reaction complicates the process significantly, the dyeing of natural fibres in $scCO_2$ is more difficult than for polyester.

From the above considerations it is clear that there are two major draw-backs of supercritical fluid dyeing. Firstly, due to the required pressure of 300 bar, the equipment is expensive, relative to aqueous dyeing machines that operate at maximally 3 bar. The second problem with supercritical dyeing is that the technique is readily applicable to polyester, but the dyeing of natural fibres requires more research and development before an implementation is possible.

The present paper focuses on the first issue: the cost of the dyeing machinery. To avoid simultaneous problems with equipment and dye-fibre chemical reactions, natural fibres are left out of consideration here and the equipment is designed solely for polyester dyeing with non-reactive disperse dyes. To test the applicability of the process on a technical scale, a dyeing machine was designed, built and tested.

PROCESS DESIGN

The process and equipment were designed to dye polyester in batches of maximally 10 kg, in a two-hour process. To minimise the volume of the dyeing vessel, relative to the amount of polyester, the so-called beam-dyeing principle was chosen. In this method, known from the aqueous process, the knitted or woven polyester cloth is wound around a perforated pipe (beam). As is shown in figure 1, the pipe is closed at one end, so that the $scCO_2$-dye solution, which is pumped into the other end, is forced through the textile layers.

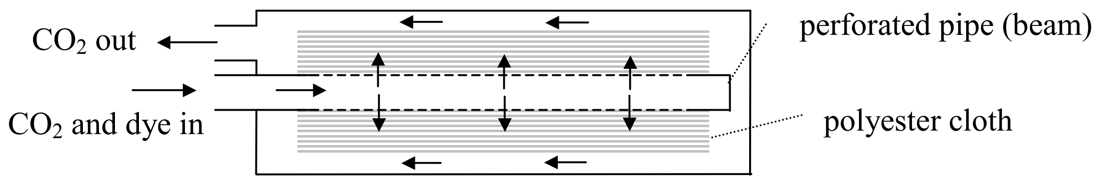

Figure 1. Schematic representation of a beam dyeing process.

The CO_2 is circulated through the textile roll, through a heat exchanger and finally through a vessel containing the dye powder, as is shown in figure 2. During the circulation, dye dissolution and dye diffusion into the fibres take place simultaneously. After this dyeing step, the $scCO_2$ contains residual dye, which has to be rinsed out of the vessel to prevent fouling of the textile and the equipment when the machine is depressurised.

During the rinsing, clean liquid CO_2 is pumped from a storage vessel into the machine, while dye-containing $scCO_2$ is removed through a pressure reducing valve. This way, the pressure and the temperature are kept constant during the rinsing. The CO_2 and the dye exiting the reducing valve, enter a separator vessel, where the CO_2 gasifies and the dye precipitates. The CO_2-gas is then condensed and flows into the storage vessel. The pressure in the storage and separator vessel are kept at 60 bar by regulating the temperature of the condenser.

After the rinsing step, the pressure in the dyeing vessel is lowered to 60 bar. The now remaining CO_2 is forced out of the dyeing vessel and into the condenser by means of a gas booster. When the pressure inside the dyeing vessel has reached 4 bar, the remaining CO_2 is vented to the atmosphere. This corresponds to 95% of the CO_2 being collected in the storage vessel, ready for reuse.

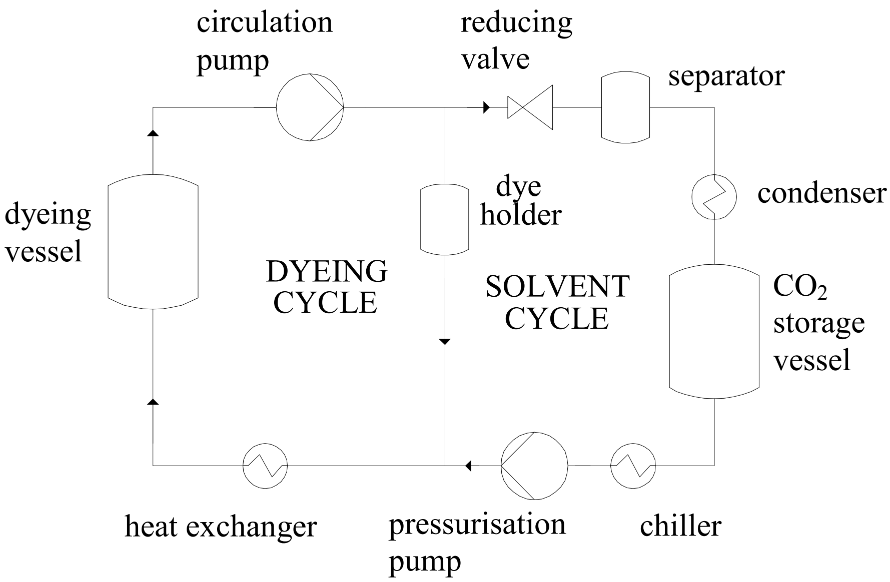

Figure 2. Simplified process flow diagram for the technical-scale dyeing machine.

EQUIPMENT DESIGN

The equipment was designed so, that the different process steps could be carried out in the times mentioned in table 1, resulting in a total batch time of two hours.

Table 1. Process steps and times for polyester beam dyeing in $scCO_2$.

Process step	Time (min)
Loading textile and dye	3
Pressure and temperature rise	15
Dyeing at 120ºC and 300 bar	50
Rinsing step	30
Depressurisation	20
Unloading textile	2
Total batch time	120

When scaling up the dyeing process, the two most costly equipment items are the dyeing vessel and the circulation pump. These were especially designed for this application, resulting in a new type of pressure vessel [4] and a new type of centrifugal pump [5].

dyeing vessel

When using a stainless steel dyeing vessel, the investment cost is be high, especially when it is scaled up to an industrial volume of typically 1000 litre. The large mass of steel that is needed also entails a high operational cost, because of the energy required to heat the dyeing vessel. Therefore, in this work a horizontal stainless steel liner is used with carbon fibres wound around the circumference to take up the radial pressure forces. Two stainless steel lids were used, without any connection to the vessel. To keep the lids in place, i.e. to take up the axial pressure forces, an external carbon steel yoke was placed around the vessel. The energy loss due to heat leakage through the lids, into the yoke, was negligible. The yoke could be moved up and down, to allow loading and unloading of the textile beams. Figure 3 gives an impression of the configuration.

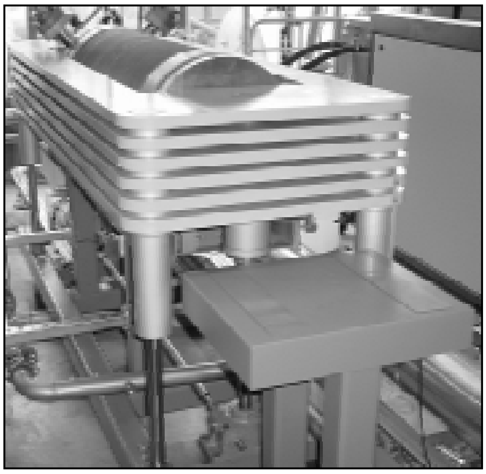

Figure 3. Picture of the carbon fibre-reinforced dyeing vessel, enclosed by a steel yoke.

centrifugal pump

Since the solubility of disperse dyes in $scCO_2$ is low (typically 10^{-5} to 10^{-4} g/g), a high flow (~20 m^3/hour) is required to transport all dye from the dissolution vessel to the textile. The pressure drop of the CO_2-flow is in the order of 3 bar. A centrifugal pump delivers such a combination of flow and pressure. However, if such a device is to be suitable for a static pressure of 300 bars, the cost is high and weighs heavily on the investment. Therefore, a new type of centrifugal pump was designed, essentially a low-pressure pump that was placed inside the dyeing vessel. Special electrical motor spools, special bearings and a special vane were used to allow service in a $scCO_2$-environment. Because the $scCO_2$ flows along the electrical motor, it acts as a coolant for the electrical spools. The pump flow could be regulated with a frequency drive. It should be noted that the pump is drawn outside the dyeing vessel in figure 2, for the sake of a better overview.

The rest of the equipment consists of:

- A chiller, to subcool the liquid CO_2 in order to prevent cavitation in the piston-cylinder pump.
- An air-driven piston-cylinder pump, for pumping liquid CO_2 from the storage vessel into the dyeing vessel.
- A 4-liter stainless steel vessel where the dye powder was introduced prior to pressurisation. In this dye holder, a filter was placed to prevent dye particles from reaching the textile. Contact of solid, undissolved dye with the cloth would lead to stain formation.
- A shell-and-tube heat exchanger for heating the $scCO_2$ and, indirectly, the polyester and the machine. The shell-side was heated with steam.
- A regulating valve, to lower the pressure from the dyeing pressure (300 bar) to the storage pressure (60 bar).

- A 20-liter separator vessel, with a steam jacket to enable vaporisation of the CO_2 entering the vessel. In the separator, a filter is placed to prevent entrainment of dye particles in the direction of the storage vessel.
- An air-driven gas booster. This device is for lowering the pressure in the dyeing vessel to 4 bar, at the end of the process, to recycle as much CO_2 as possible. In figure 2, the gas booster is not shown.
- A cooling machine, to pump a water-glycol mixture through the condenser and through the chiller.
- A combined condenser-storage unit. A pressure vessel was used with a condensation coil placed in the top. Condensation occurred on the outside of the tube coil. The integration of the condenser and the storage vessel lowered the equipment cost.

EXPERIMENTS AND RESULTS

Rolls of 2 kg polyester were used, from Ames Europe (The Netherlands). The polymer was received free of spinning oil and heat-set at 195ºC. The tested dyes were the commercially available Disperse Red 82, Disperse Yellow 211 and Disperse Blue 79. Their purity ranged from 95 to 99%.

It was found that the textile could be dyed evenly and deeply with all 3 dyes, but only when the flow inside and outside the polyester roll was completely rotation-symmetrical.

The quality of the dyed product was tested by Ames Europe, for the case of Disperse Red 82. The results, shown in table 2, give the colour difference in terms of ΔE, a quantity generally used in the textile industry. ΔE is here the difference in colour between the inside and the outside of the roll and it is therefore a measure for the evenness of dyeing. A value of ΔE smaller than 1.2 is not visible to the human eye and is therefore regarded as satisfactory.

The fastness of the colour is expressed in terms of the system of the Society of Dyers and Colourists. This system gives numbers ranging from 1 to 5, an increasing number corresponding with a better fastness of the dye. In industrial practice, 4 and 5 are regarded as good. The standards according to which the fastness tests were carried out are also mentioned in table 2.

The experiments were done at 300 bar and 120ºC, with the process times as given by table 1. The flow through the textile was varied from 10 to 20 m^3/hour.

Table 2. Properties of polyester dyed at 300 bar, 120ºC, in 2 hours, with Disperse Red 82.

		fastness to:			
flow m^3/hour	ΔE	water (ISO105E01)	washing (ISO105C06)	sweat (ISO105E04)	rubbing (ISO105X12)
10	0.82	4.5	4.5	4.5	4.3
20	0.94	4.5	4.5	4.5	4.3

The experiments resulted in dark red polyester. The values of ΔE are smaller than 1.2, indicating an even dyeing throughout the roll. An increase in pump flow gave a darker colouration. The fastness of the colour was sufficient in all cases.

To investigate the influence of the process on the mechanical properties of the polyester fibres, the mass per unit area cloth and the tensile strength were measured, before and after the dyeing process.

Table 3. Mechanical properties of polyester before and after supercritical fluid dyeing.

polyester	specific mass (g/m^2)	tensile strength (N)	
		length	width
untreated	56	323	159
dyed (10 m^3/hour)	64	347	177
dyed (20 m^3/hour)	59	322	174

As is shown in table 3, there is a slight increase in specific mass, corresponding with a small degree of shrinking. This degree, however, is the same in current aqueous dyeing processes and therefore acceptable. Table 3 also shows that the strength of the textile is not affected by the treatment. The two treated polyesters in table 3 are the same as in table 2.

CONCLUSIONS

A technical scale machine was designed, built and tested to dye polyester in supercritical CO_2. A new type of pressure vessel and a new type of centrifugal pump were developed and applied. Both equipment items significantly lower the equipment and process cost and therefore facilitate future industrial application.

Experiments were conducted, dyeing 2 kg rolls of polyester at 300 bar and 120ºC, in a two-hour process. In each batch, 95% of the CO_2 was recycled. The results showed deep and even colouration, throughout the whole roll. The fastness was tested and found to be good. No excessive shrinking occurred and the mechanical strength of the cloth was not changed by the dyeing process.

It can be concluded that the equipment functioned well and that the dyed product was of the same quality as in current industrial processes.

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