CONTINUOUS DOSING OF SOLIDS IN HIGH PRESSURE SYSTEMS

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The substitution of unwanted solvents (CFC's, other organic solvents, water) by supercritical carbon dioxide ($scCO_2$) is still of great interest. The advantages of $scCO_2$ are well known (clean, easy to regenerate and non-toxic), but many promising applications fail to enter the industrial production level because of high investment costs and the inflexibility of the technique bound on the batch process. In many cases the ability of a continuous mass transport of solids from ambient to high pressure would make the processes faster, easier to control and with less energy demand for pressurization.

A good example is the admission of dyestuff (disperse dye as powder/particles) in a high pressure vessel, for the dyeing of textiles or synthetic fibers in $scCO_2$. Today, the whole amount of needed dyestuff has to be put as a batch in a pressure vessel, prior to the beginning of the process. Other applications are the admission of valuable solid substances inside high pressure vessels for the production of pharmaceutical or chemical products.

A technical solution for powdery solids has been invented by the Technical University of Hamburg-Harburg (Prof. R. Eggers). Its name is "FES" (**F**eststoff-**E**intrag-**S**ystem = Solids admission system). Powdery material (e.g. dyestuff), which is stored in a small container, can be quasi-continuously transported from ambient pressure (storage container) into the supercritical fluid (inside the high pressure vessel). This is done by small transport-holes in an shaft, which is horizontally moved through a vertically mounted pressure vessel.

In a cooperation of the TUHH (Prof. R. Eggers) and Siegfried Kempe GmbH (Germany) the FES has been constructed, build and successfully tested at industrial scale. It was integrated in a pilot plant for industrial dyeing of polyester fibers. The main advantages are a homogeneous loading of the $scCO_2$, a better control of the dyeing process and, as a result of these effects, shorter process times. Additionally the invention can save 30 to 50% of dyestuff due to a better utilization of the solid material.

INTRODUCTION

Since the high pressure extraction with supercritical CO_2 has been investigated, it has always been a goal to develop a system for solid materials to be continuously transported into vessels under high pressure [1]. An investigation on this topic has started at the middle of the 80s, at the Technical University of Hamburg-Harburg (TUHH), department of Process Engineering/Heat and Mass Transfer (Prof. R. Eggers). The project included the development of a pilot plant for continuous extraction of natural material with $scCO_2$ [2]. Round about 10 years later, in the end of the 90s, a similar questions appeared: during the development of an industrial process for the dyeing of polyester fibers with scCO_2. This time the challenge was to develop a continuous method of dosing the solid dyestuff (powder/small particles) into the high pressure system.

The process of dyeing textiles or synthetic fibers in scCO_2 has been developed in lab and industrial scale [3] - [7]. Until today, the dyestuff is put into a storage vessel ("**F**arb-**A**nsatz-**B**ehälter" = FAB) prior to the pressurization of the plant. This leads to inhomogeneous uptake of the dye in the solvent (CO_2) and a pour control of the process. For example, the current method does not allow an additional dosing of dyestuff during the process. Further more, another problem occurs by placing the dyestuff as a fixed bed in a pressure vessel: the small particles stick together after being under pressure for a certain period of time. Thus, the ability of the CO_2 to solve the dye decreases with increasing process time, which results in the fact that after reasonable process times (30 min to 2 h) there will always be a residue of unsolved dyestuff left over in the pressure vessel. For most of the dyes which have been investigated at industrial scale [6], a residue of about 30 to 50% of the amount at the beginning, remains at the end of the process (Figure 1).

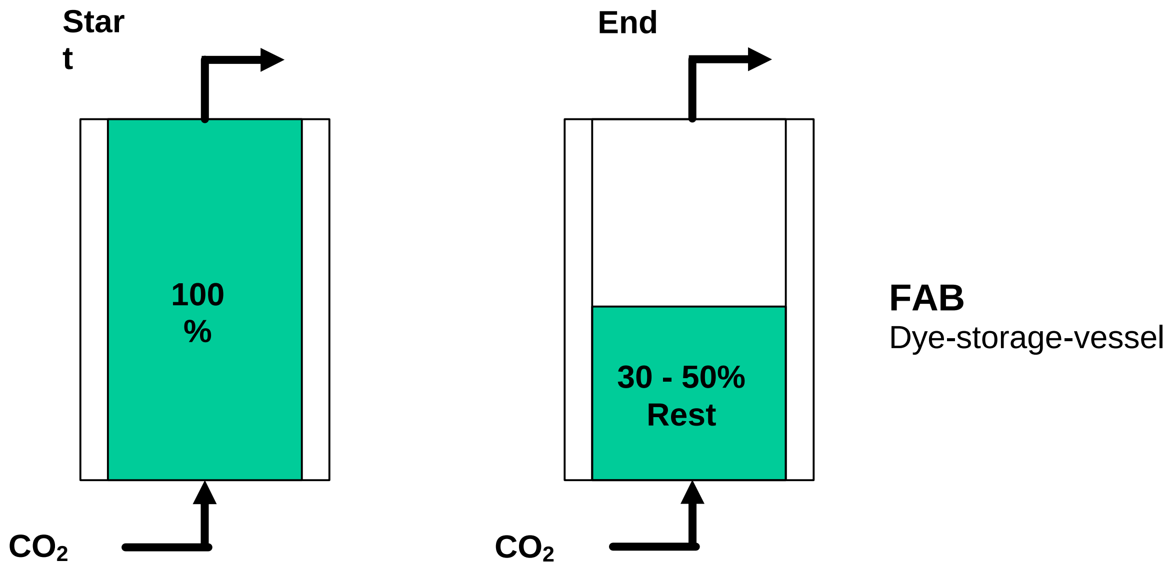

Figure 1: Dye-uptake from a fixed-bed (FAB)

To solve these problems, a new apparatus has been developed, which enables a quasi-continuous dosing of powders and small particles (up to 2 mm in diameter) from ambient pressure into a high pressure system. This technique, which was invented by Prof. R. Eggers [8], has been constructed and built by Siegfried Kempe GmbH (manufacturer of high pressure equipment and plants, Germany). It allows the dosing of the exact amount of valuable material (e.g. disperse dye) which can be solved by the CO_2 (circulating solvent stream).

MATERIALS AND METHODS

The principles of the new apparatus (FES) are shown in Figure 2: At the bottom of a vertically mounted pressure vessel, a shaft with transport holes is horizontally driven by a motor. At the two end-positions of the shaft movement, the transport holes can be filled with particles, coming from two storage containers. The speed of the shaft can be varied from 1 to 30 strokes per minute (1 stroke = back and forth).

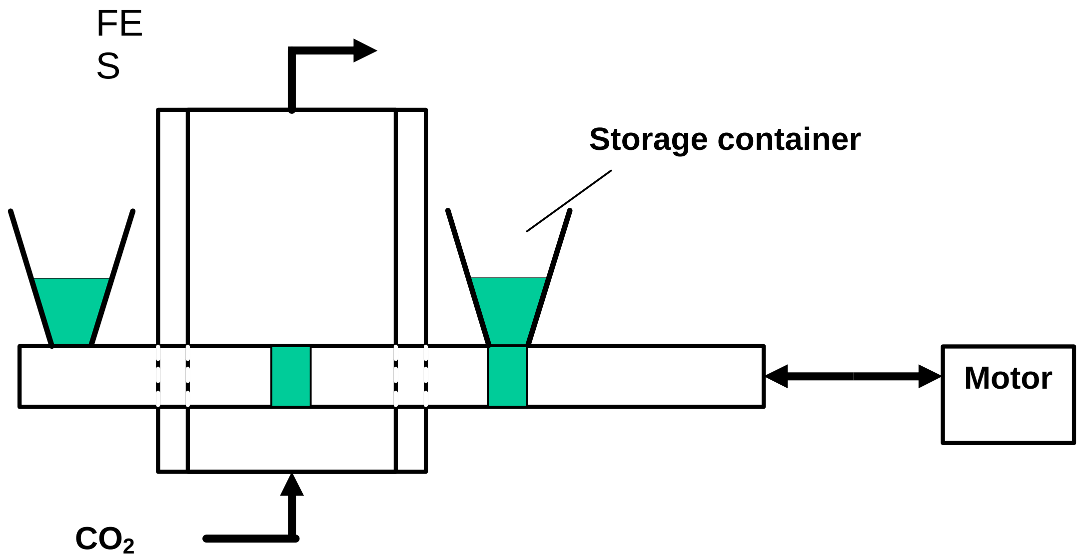

Figure 2: Principles of the new FES

The technical details are summarized in Table 1.

Topic	*Specification*
Max. pressure	500 bar
Max. temperature	150 °C
Solvent	CO_2
Inner volume	ca. 3,5 l
Average solubility of a disperse dye in CO_2	10^{-4} g/g
Shaft movement	1-30 strokes/min
Bulk density of the particles/powder	500 g/l
Volume of a single transport hole	0,2-0,6 ml
Diameter of a transport hole	4-6 mm
Heating system	Fluid (double jacket)

Table 1: Technical data of the FES

GASKET SYSTEM FOR THE SHAFT

One of the main difficulties during the development of the apparatus has been the development of a reliable gasket system for the shaft. All different kinds of standard gasket materials have been tested. The result was a combination of different materials. The developed systems withstands the abrasive effect of the movement of the shaft, especially as the transport holes pass across the gasket.

To investigate the durability of the gaskets, many long-time tests have been performed until a single gasket withstands more than 10000 strokes (back and forth) without showing an increase in leakage.

TESTS AT THE PILOT PLANT FOR DYEING OF POLYESTER FIBERS

The new apparatus (FES) has been combined with an existing pilot plant for dyeing of polyester fibers (Figure 3). The pilot plant has a main pressure vessel of about 70 l inner volume, with the ability to load up to 4 bobbins of fibers (max. 8 kg).

Figure 3: FES mounted at the pilot plant

To investigate the efficiency of the dye uptake in the supercritical CO_2, a photometer has been integrated at the pilot plant. It is a single channel photometer which has been calibrated for all the investigated disperse dyes [9]. The method is an inline measurement, where the photometer is mounted between the dye-uptake (FAB or FES) and the pressure vessel containing the fibers. Two examples of these measurements are displayed in Figure 4: the curve of open circles shows the results of the existing fixed-bed system (FAB) and the triangles show the results of the new dosing system (FES). Both measured at the same conditions and with the same dye. It can be seen that for the fixed-bed system, the dye-uptake reaches a maximum after round about 10 min, but it is decreasing after that maximum for the rest of the process time (50 min). With the new dosing system the dye-uptake reaches the same amount within 10 min, but the concentration can be hold at a constant level until the end of the process. This leads to a more homogeneous dyeing and shorter process times. Additionally the utilization of the dye increases: the amount of unused dye at the end of the process can be reduced to zero.

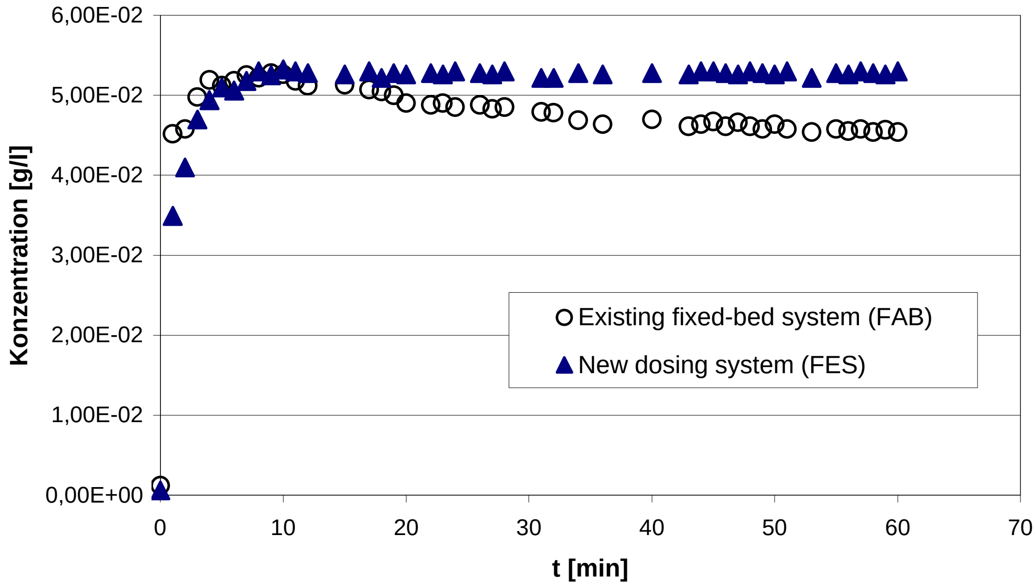

Figure 4: Inline measurements with a single-channel photometer, for a disperse dye at 300 bar/120 °C

CONCLUSION

The new technique of continuous dosing of small solid particles in high pressure systems (FES) can improve an existing process significantly. For the dyeing of polyester fibers it could be shown that it reduced process times and the amount of unused residual dyestuff at the end of the process. This advantages come together with a better control of the process, especially if the new technique is combined with a photometer, as described in this article.

Other applications can be found in pharmaceutical and food industry. For example for the extraction of high valuable substances from natural sources (carotinoids from marigold, natural dye and oil from paprika) [10].

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