

Textile Dry Cleaning Using Carbon Dioxide: Process, Apparatus and Mechanical Action

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Textile Dry Cleaning Using Carbon Dioxide: Process, Apparatus and Mechanical Action

Proefschrift

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Summary

Fabrics that are sensitive to water, may wrinkle or shrink when washed in regular washing machines and are usually cleaned by professional dry cleaners. Dry cleaning is a process of removing soils from substrate, in this case textile, using a non-aqueous solvent. The most common solvent in conventional dry cleaning is perchloroethylene (PER). Despite its satisfactory cleaning performance, PER has several drawbacks. For instance, PER has many adverse health effects and is classified as probably carcinogenic to humans.

One approach is to develop an alternative solvent for PER. This has led to many studies that investigate the possibility of using other solvents in textile dry cleaning. CO₂ is chosen in this study because it has several advantages compared to the other alternative solvents i.e. it is non-toxic, non-flammable, non-corrosive, safe for the environment, cheap, easily recovered, available on a large scale and no drying step is required. However, several issues remain to be addressed.

Previous studies have shown that particulate soil removal in CO₂ dry cleaning is relatively low. This is due to the high interaction forces between particles and textile, the low density difference between liquid and gas phase of CO₂ (that cause a low level of mechanical action), and the low viscosity of CO₂ (that cause a low momentum transfer). Another issue in some CO₂ dry cleaning machines is the occurrence of redeposition. Redeposition is a process of soil transfer from one textile surface to another, and happens when the released soil is not properly stabilized in or removed from the cleaning medium. Once redeposition happens, it usually cannot be reversed which leads to greying of the fabric and unsatisfying cleaning results. CO₂ dry cleaning also needs substantially higher pressures compared to dry cleaning with other solvents which requires equipment with higher investment costs.

The main objective of this study is to improve the cleaning performance of CO₂ dry cleaning for particulate soils, firstly by studying and solving the redeposition problem, secondly by enhancing the amount of mechanical action applied to the fabric. When the redeposition was studied, each type of particulate soil used in the

experiments showed redeposition while no reduction in redeposition was observed by adding a rinsing step. It was also found that the redeposited particles were more evenly distributed and that the redeposition was more severe by using a longer washing time. Modifying the filtration system and using scavenger textiles as pre-filter materials helped to reduce redeposition significantly. Another method to reduce redeposition was by adding cellulose based chemicals in the cleaning vessel as anti redeposition agent.

Several methods to increase mechanical action have been used: addition of particles, bubble formation, and other actions such as liquid spray. The presence of additional particles has been studied by varying the type, the size, and the amount of particles. It is concluded that particle addition could increase the absolute value of the average CPI from 9% to 15%. The increase was especially high for lipstick and sand soiled materials. No influence of particle diameter or type of particles has been observed. Sand is so far the most suitable extra particle from economical point of view. However, using loose sand particles in commercial scale dry cleaning might not be practical due to the difficulty of cleaning the vessel after the washing process and might eventually cause mechanical attrition in the dry cleaning system. Using Amihope LL as (particulate) surfactant also tends to give a higher CPI than commercial liquid surfactants (ClipCOO and Washpoint).

Since cavitation has been proven to be beneficial in other CO₂ cleaning applications, this study investigated the possibility of improving the performance of CO₂ textile dry cleaning by using ultrasound. However, in experiments with both 1 L and 90 L apparatus, it was found that using ultrasound did not give a significant improvement on particulate soil removal from textile. The effect of other mechanisms of mechanical action, such as rotating drum, CO₂ liquid or bubble spray, and stirring on the cleaning performance have also been investigated. The washing results show that combination of liquid CO₂ spray and rotating drum may be a suitable mechanism to provide textile movement. However, the highest average CPI of the CO₂ machine and process was still 25% lower than the results with PER.

Another objective of this thesis is to achieve more insight in the cleaning process since little information is available regarding the textile movement inside the rotating drum in the CO₂ medium. This has been studied with an endoscopic camera

in the 25 L CO₂ dry cleaning machine. The results with the endoscopic camera show that no plug formation occurs and the textile movement in CO₂ is sluggish, which means that the mechanical movement of textile in CO₂ dry cleaning does not follow the simplified tumbling-movement model which was developed in a previous study, and the mechanical action is much less than was predicted.

Experiments with an observation cell equipped with a mechanical actuator were performed to apply well defined forces on the textile, and these results have been used to perform a quantitative analysis of the mechanical forces. Experimental results show that for certain particulate soils (e.g. lipstick), a more rigorous textile movement leads to higher particle removal. For other particulate soils (e.g. clay) the maximum amount of particles that can be removed by mechanical action alone has been reached with a very small amount of mechanical action. The quantitative analysis of mechanical forces in observation cell for clay particles show that the amount of force that is exerted by the actuator is higher than theoretically required to remove all clay particles from the textile surface and also higher than the available force in a commercial dry cleaning machine. However, without the help of chemical action from a suitable detergent, higher mechanical action does not lead to a higher soil removal for clay particles because of the high interaction forces between the clay and the textile in the CO₂ medium.

Based on the results of the above, an ideal CO₂ dry cleaning machine and process have been designed. This is a combination of best practices, new insights obtained from the results of this study, and the best available technologies. Besides of having a good cleaning performance, a dry cleaning machine should ideally have an affordable investment and operating costs, as well as produce a low amount of chemical waste. The performance and the investment costs of CO₂ dry cleaning are not yet comparable with the conventional solvents or the other alternative solvents. However, we believe that CO₂ is the only real green solvent for textile dry cleaning and our studies have shown that it has a high potential to replace PER in the future. The economy evaluation also showed that the operating costs for dry-cleaning using CO₂ are comparable to the costs of using PER.

Samenvatting

Weefsels die gevoelig zijn voor water kunnen verkreukelen of krimpen als ze worden gewassen in gewone (water) wasmachines en worden daarom doorgaans chemisch gereinigd bij stomerijen. Chemisch reinigen is een proces waarbij vlekken van een substraat, in dit geval textiel, worden verwijderd met een oplosmiddel dat niet op water is gebaseerd. Het meest gebruikte oplosmiddel voor conventioneel chemisch reinigen is perchloorethyleen (PER). Ondanks de goede reinigingsprestaties heeft PER een aantal nadelen; PER heeft bijvoorbeeld nadelige gevolgen voor de gezondheid en het is geclassificeerd als mogelijk carcinogeen voor mensen.

Een alternatief is het gebruik van een ander oplosmiddel ter vervanging van PER. In deze studie is voor CO₂ als alternatief gekozen, omdat het een aantal voordelen heeft in vergelijking met andere oplosmiddelen; het is niet toxisch, niet brandbaar, niet corrosief, veilig voor het milieu, goedkoop, gemakkelijk te recyclen, op grote schaal beschikbaar en er is geen droogstap nodig. Er zijn echter nog een aantal zaken die onderzocht moeten worden.

Eerdere studies hebben laten zien dat er relatief weinig vaste vuildeeltjes worden verwijderd tijdens reinigen met CO₂. Dit komt door de grote vanderwaalskrachten tussen de deeltjes en het textiel, het kleine verschil in dichtheid tussen de vloeibare fase en de gasfase van het CO₂ (wat een lage hoeveelheid mechanische actie tot gevolg heeft) en de lage viscositeit van CO₂ (wat een lage impulsoverdracht tot gevolg heeft). Een ander probleem in sommige CO₂ machines is redepositie. Redepositie is een proces waarbij vuil van één textieloppervlak naar een ander gaat en wat plaatsvindt wanneer het vrijgekomen vuil niet goed gestabiliseerd wordt in of verwijderd wordt uit het reinigingsmedium. Als redepositie plaatsvindt kan het doorgaans niet worden teruggedraaid, wat leidt tot vergrauwing van het weefsel en een onbevredigend reinigingsresultaat. Reinigen met CO₂ heeft ook substantieel hogere drukken nodig, in vergelijking met chemisch reinigen met andere oplosmiddelen, waardoor apparatuur nodig is met hogere investeringskosten.

Het doel van dit proefschrift is het verbeteren van de reinigingsprestatie van CO₂ voor vaste vuildeeltjes, door ten eerste het redepositie probleem te bestuderen en op te lossen en ten tweede de hoeveelheid mechanische actie uitgeoefend op het textiel te verhogen. Tijdens het onderzoeken van de redepositie bleek dat elk type vast vuildeeltje dat werd gebruikt in de experimenten redepositie vertoonde, terwijl er geen reductie in redepositie werd geobserveerd door het toevoegen van een spoelstap. Er werd ook gevonden dat de redepositie van de deeltjes gelijkmatiger was en dat de redepositie toenam bij een langere reinigingstijd. Door het aanpassen van het filtersysteem en het gebruik van textiel als voorfilter werd de redepositie aanzienlijk verminderd. Een andere methode voor het reduceren van de redepositie bleek het toevoegen van chemicaliën, gebaseerd op cellulose, in het reinigingsvat.

Diverse methodes om de hoeveelheid mechanische actie te verhogen zijn onderzocht: toevoegen van vaste deeltjes, vorming van belletjes en andere acties zoals vloeistofspray. De invloed van de aanwezigheid van extra vaste deeltjes is bestudeerd door het type, de grootte en de hoeveelheid vaste deeltjes te variëren. Hieruit volgde dat het toevoegen van vaste deeltjes de absolute waarde van de gemiddelde CPI verhoogt van 9 % naar 15 %. De toename was extra groot voor met lippenstift en zand bevulde materialen. De diameter of het type deeltjes leek geen invloed te hebben op het resultaat. Zand is meest geschikt om toe te voegen vanuit economisch oogpunt. Echter, het gebruik van losse zanddeeltjes op commerciële schaal is wellicht niet praktisch vanwege de moeilijkheden bij het schoonmaken van het reinigingsvat na het wasproces en het kan uiteindelijk mechanische attritie van het reinigingssysteem veroorzaken. Het gebruik van Amihope LL als (vaste) oppervlakte-actieve stof geeft een hogere CPI dan commerciële verkrijgbare vloeibare oppervlakte-actieve stoffen (ClipCOO en Washpoint).

Omdat het gebruik van cavitatie voordelen heeft in andere CO₂ reinigingstoepassingen, is in deze studie de mogelijkheid onderzocht om het reinigen van textiel met CO₂ te verbeteren door ultrageluid toe te passen. In experimenten met zowel 1 L als 90 L apparaten werd echter gevonden dat het gebruik van ultrageluid geen significante verbetering gaf voor het verwijderen van vaste vuildeeltjes van textiel. Het effect van andere mechanismen van mechanische actie, zoals een roterende binnentrommel, vloeibare CO₂ spray of bubbelspray en roeren,

op de reinigingsprestaties is ook onderzocht. De resultaten laten zien dat de combinatie van een vloeibare CO₂ spray en een roterende binnentrommel een geschikt mechanisme kan zijn om textielbeweging te verzorgen. De hoogste gemiddelde CPI van een CO₂ machine en proces was echter nog steeds 25% lager dan de resultaten met PER.

Een ander doel van dit proefschrift is het verkrijgen van meer inzicht in het reinigingsproces. Op dit moment is weinig informatie beschikbaar over de textielbeweging in de roterende binnentrommel. Dit is daarom bestudeerd met een endoscopische camera in een 25 L CO₂ machine. De resultaten laten zien dat er geen formatie van textielproppen plaatsvindt en dat de textielbeweging in CO₂ traag is, wat erop duidt dat de mechanische beweging van textiel in CO₂ niet het versimpelde tuimelbeweging model volgt dat ontwikkeld is in een eerdere studie, en dat de hoeveelheid mechanische actie veel lager is dan voorzien.

Er zijn ook experimenten uitgevoerd met een observatiecel. Deze is uitgerust met een mechanisch drijfwerk om goed gedefinieerde krachten uit te kunnen oefenen op het textiel. De experimenten laten zien dat voor bepaalde vaste vuildeeltjes (bijvoorbeeld lippenstift) een rigoureuzere textielbeweging leidt tot het verwijderen van meer deeltjes. Voor andere vaste vuildeeltjes (bijvoorbeeld klei) wordt de maximale hoeveelheid deeltjes dat kan worden verwijderd door enkel mechanische actie al bereikt bij een zeer lage hoeveelheid mechanische actie. De kwantitatieve analyse van de mechanische krachten in de observatiecel laat zien dat voor kleideeltjes de hoeveelheid kracht uitgeoefend door het drijfwerk hoger is dan theoretisch benodigd is om alle kleideeltjes te verwijderen van het textieloppervlak. In het geval van kleideeltjes is echter chemische actie van een detergent nodig om ervoor te zorgen dat een grotere hoeveelheid mechanische actie leidt tot het verwijderen van meer vuil. Dit vanwege de grote vanderwaalskrachten tussen klei en textiel in CO₂.

Gebaseerd op de bovengenoemde resultaten zijn een ideaal proces en machine voor reinigen met CO₂ ontworpen. Dit ontwerp is een combinatie van de beste op dit moment gebruikte processen, nieuwe inzichten vergaard uit de resultaten van deze studie en de beste beschikbare machines. Naast een goede reinigingsprestatie zou een machine idealiter betaalbare investerings- en

operationele kosten hebben en slechts een kleine hoeveelheid afval moeten produceren. De prestaties en investeringskosten van een proces met CO₂ zijn op dit moment nog niet vergelijkbaar met conventionele oplosmiddelen of met andere alternatieve oplosmiddelen. Wij geloven echter dat CO₂ het enige echte groene oplosmiddel is voor het chemisch reinigen van textiel en onze studies hebben laten zien dat het de potentie heeft om PER in de toekomst te vervangen. De economische evaluatie heeft aangetoond dat de operationele kosten voor chemisch reinigen met CO₂ vergelijkbaar zijn dan de kosten met PER.

Chapter 1

Introduction

1.1. Background

Washing laundry is one of the most basic daily routine in the world. Nowadays, laundry washing is mostly done using washing machines in private households which consumes a substantial amount of water and energy. However, several types of fabric that are sensitive to water, for example wool, may wrinkle or shrink when washed in these regular washing machines. These fabrics are usually cleaned by professional dry cleaners. Dry cleaning is a process of removing soils from substrate, in this case textile, using a non-aqueous solvent.

The most common solvent in conventional dry cleaning is perchloroethylene (PER). Despite its satisfactory cleaning performance, PER has several drawbacks. PER has many adverse health effects such as damage of kidneys and liver, or gastrointestinal irritation. The known LD50s of PER are 4700 mg/kg (ipr-mouse) and 8850 mg/kg (oral-rat) [1]. Studies have shown that repeated exposure of PER by inhalation and mouth causes kidney and liver damage as well as cancer in animals, and likewise in humans. Moreover, PER is classified as probably carcinogenic to humans (IARC Group 2A) [2]. PER is an air pollutant and a groundwater contaminant, and thus harmful for the environment when emitted.

One approach is to minimize PER exposure to below the accepted limits. Nowadays most apparatus are developed as such that the PER recovery rate is larger than 98% [3]. However, because of the toxic nature of PER, this chemical is still regulated in an increasing number of countries and states. For instance, in California PER will be banned by 2023 [4]. It is thus more sustainable to develop an alternative solvent for PER. This has led to many studies that investigate the possibility of using other solvents, such as hydrocarbon solvents, silicon based solvents, and carbon dioxide (CO₂) in textile dry cleaning [5].

1.2. CO₂ dry cleaning

In this study we choose CO₂ because it is the only solvent that fulfills the 12 principles of green chemistry [6]. CO₂ has several advantages compared to the other alternative solvents. It is non-toxic, non-flammable, non-corrosive, safe for the environment, cheap, easily recovered, and available on a large scale. As an additional advantage, a drying step is not necessary because CO₂ evaporates from the fabric when the cleaning chamber is depressurized. However, several issues remain to be addressed for successful commercialization.

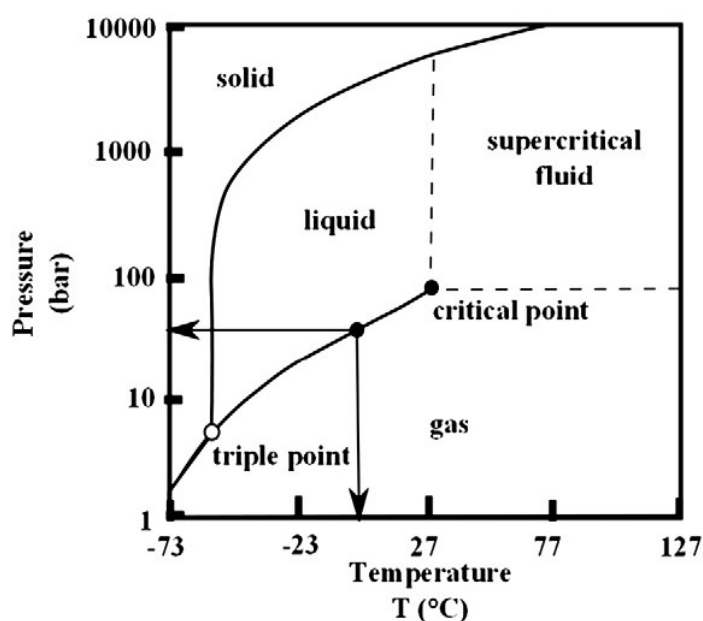


Figure 1.1: The P-T phase diagram of CO₂. The black dot on the gas-liquid boundary line represents a possible condition in dry-cleaning (45 bar and 10°C), adapted from Leitner [8]

An important difference between dry cleaning with CO₂ and other solvents is that CO₂ dry cleaning needs a substantially higher pressure (45-60 bar). This leads to high pressure equipment which requires substantially higher investment costs than those for other solvents. During the cleaning process, the pressure and temperature are maintained as such that the system always stays at to the two-phase boundary line (see Figure 1.1), i.e. the liquid CO₂ stays in equilibrium with the saturated CO₂

gas. The presence of the gas-liquid interface has been reported to be necessary to achieve mechanical action in the washing process in a rotating-drum system [7].

In general, textile has three kinds of dirt (soil) that can be removed:

- Substances that are soluble in the pure solvent
- Substances that are insoluble in the pure solvent, but can be solubilized with the help of additives
- Particulate soil that is attached to/trapped in the textile matrix

Previous studies [9,10] have reported that the performance of CO₂ is comparable to that of PER in non-particulate soil removal (the first two stains). This is because CO₂ is non-polar and thus interacts well with non-polar soil e.g., fat and oil.

For the successful particle removal (the last stain), the forces that keep particles bound to textile have to be overcome. In CO₂ dry cleaning, the low density difference between liquid and gas phase of CO₂ leads to a low level of mechanical action. At the operating conditions, the density difference for CO₂ is around 700 kg/m³ (strongly depending on temperature) while for PER this is 1600 kg/m³ (independent of temperature). Furthermore, CO₂ has a low viscosity of 10⁻⁴ Pa.s resulting in low momentum transfer, while in PER this is 9.10⁻⁴ Pa.s.

Aside from the fact that CO₂ removes significantly less particulate soil than PER, another issue is the occurrence of redeposition. Redeposition is a process of soil transfer from one textile surface to another, and happens when the released soil is not properly stabilized in or removed from the cleaning medium. Once redeposition happens, it usually cannot be reversed which leads to greying of the fabric and unsatisfying cleaning results [11]. This problem has been mentioned in a previous study [12] and is also found by several commercial CO₂ dry cleaners (Porsmose, M. - Kymi Rens, personal communication, 2012).

1.3. Objective

The main objective of this study is to improve the cleaning performance of CO₂ dry cleaning, firstly by studying and solving the redeposition problem, secondly by enhancing the amount of mechanical action applied to the fabric with the objective to increase the particulate soil removal. Several methods to increase mechanical action

have been used: additional particles, bubble formation, and other actions such as jet spray. Besides mechanical action, there are other Sinner's parameters that influence the washing performance: chemical action, washing time and process temperature. The first subject has been investigated by our colleagues at Wageningen University, while the last two subjects have been covered in previous study [13].

Another objective of this thesis is to achieve more insight in the cleaning process. Little information is available regarding the textile movement inside the rotating drum in the CO₂ medium. This has been investigated in this study by installing an endoscopic camera in the pilot plant CO₂ dry cleaning apparatus. Furthermore, the influence of directly-applied mechanical force on the textile has been investigated by using a new observation cell which is equipped with a mechanical actuator. With this apparatus, the influence of different mechanical actions (direction, force, speed) on the cleaning performance can be investigated and the results can be used to perform a quantitative analysis of the mechanical forces. Based on the results of the above, an ideal CO₂ dry cleaning machine and process has been designed. Due to limited time, the modelling of the textile movement is not covered in this study but is highly recommended for future work.

1.4. Outline

Chapter 2 describes the state of the art of CO₂ textile dry cleaning. Chapter 3 describes the redeposition problem in CO₂ dry cleaning and how to reduce its occurrence. Chapter 4-6 describe the tests performed to enhance the cleaning performance of CO₂ dry cleaning: using additional particles (Chapter 4), using bubble formation (Chapter 5) and other mechanical actions such as spraying (Chapter 6). The results of the observation with an endoscopic camera are also given in Chapter 6, while the results from the observation cell will be given in Chapter 7. All of these results are used to make a new machine design and cleaning process for CO₂ textile dry cleaning (Chapter 8). Lastly, the economical evaluation for this process is performed (Chapter 9) and the pictures of the set-ups can be found in Appendix A.

1.5. How to read this book

Each chapter stands independently and thus can be read separately.

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Chapter 2

History and State of the Art of CO₂ Dry Cleaning Process and Equipment

2.1. Introduction

Textile dry cleaning in Europe is conducted in over 50,000 facilities utilizing around 75,000 machines to clean more than 2 million tons of textile each year. Comparable numbers are also found in USA [1]. The majority (95%) of these dry cleaners employ perchloroethylene (PER) as washing fluid/solvent which use is becoming more and more restricted by government or state regulations due to its toxic nature [2]. Several investigations have been conducted by both academia and industrial companies to find suitable alternatives for PER, such as silicon or hydrocarbon based solvents. However, the greenest and most sustainable alternative is CO₂ because it fulfills the basic properties of a green solvent (i.e. low or non-toxic, chemically stable, readily available and easily recyclable).

This chapter documents the development of process and equipment for CO₂ textile dry cleaning. The detergency aspect of this process has been described in [3]. Currently, there are around 20 commercial CO₂ machines in the US (mostly on West Coast) and 10 in Europe (Sweden, Denmark) in operation [4]. This number has significantly decreased from the previous decade because the after-sales service was hardly available for the first generation of dry-cleaning machines, and thus it was very hard to keep these machines running. On the other hand, the competitive nature of the business makes the new dry cleaning owners reluctant to invest substantial initial investments required for high pressure CO₂ machine.

2.2. Inventions and early developments

Research on dry-cleaning with liquid CO₂ replacing the traditionally used harmful and toxic cleaning agent perchloroethylene, started in the early 1970's when the first patent application was filed by Maffei [5]. The principle of this process is given in Figure 2.1. The textile is placed in the cylinder and the liquid CO₂ from refrigerated storage flows through the cylinder and then to the evaporator where the liquid CO₂ is converted to gas to remove the dissolved soil from CO₂. The gas is then condensed and transferred into the storage tank. However, Maffei never built any prototype of his invention and thus no additional detail of the system is available, such as type of mechanical action or surfactant.

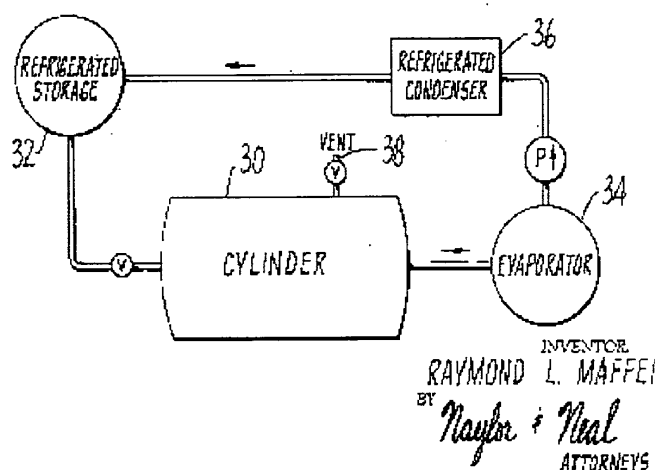


Figure 2.1: Maffei dry cleaning process

Several commercial parties worked on the development of CO₂ dry cleaning equipment in the following decades. During the late 1980's, the Clorox Company filed several patents about this subject [6-10]. These patents claim to decrease polymer damage (due to the pressure difference during depressurization step) by substituting liquid CO₂ by a compressed gas prior to depressurizing of the cleaning vessel. They also claim the use of a sealed magnetically coupled cleaning vessel containing a rotatable drum for holding garments during the cleaning cycle, and increased energy efficiency by channeling heating and cooling effects associated with CO₂ gas condensation and expansion to various parts of the system. However, this company has never commercialized their system.

2.3. Micell

Micell technologies [11, 12] applied for several patents and developed the Micare system which utilizes a MICO₂ machine, as shown in Figure 2.2. The cleaning vessel in the MICO₂ machine is a rotating drum with a sealed drive. The rotating drum is designed to alternate between clockwise and counterclockwise modes so that the textiles do not get wound into a large lump. It was reported that the garments travel upwards via the rotating drum out of the liquid phase to the gas phase and are dropped at the 10 or 11 o'clock position on the counter-clockwise rotation, and 1 or 2 o'clock on the clockwise rotation. As garments are dropped into the liquid CO₂ phase, they would descend to the bottom of the rotating drum until they are picked up by the rotating drum to repeat the cycle. However, due to the lack of sight glass on the machine it was not proven that the garments follow the previously described movement. Furthermore, in Chapter 6 of this thesis it is shown that most of the time the textile rotates along with the drum without the falling action or falls before reaching the desired point of the 10 or 11 o'clock position. It should be noted however, that the size and the amount of the textile might affect the amount of mechanical forces in the system.

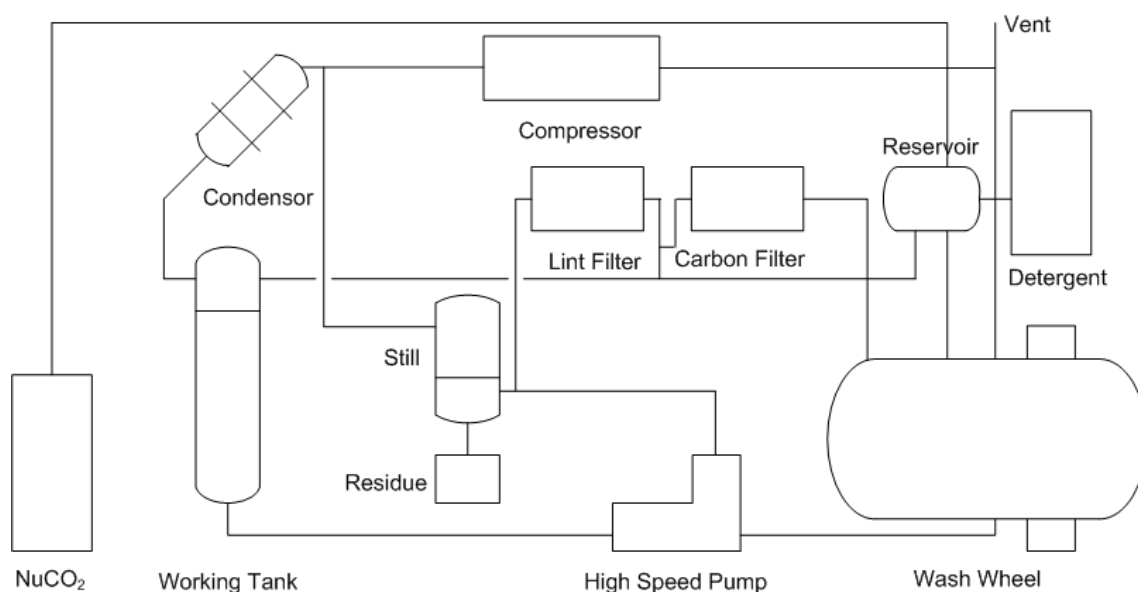


Figure 2.2: MICO process schematic unit [12]

According to Micell, much of the mechanical cleaning on insoluble particles is expected to occur when the garments are forced from gas to liquid phase and vice versa. However, according to our observation, the particle removal is mostly affected by the degree of textile deformation, i.e. how vigorous the textile moves. For instance, a combination of rotating and stretching movements provides a higher cleaning performance than rotating or stretching movement only (Chapter 6). It was also observed that a rotating drum alone does not provide a high degree of textile movement. After the cleaning cycle, the machine transfers both the liquid and gaseous CO₂ to the working tank, a portion of the cleaning fluid is sent to the still, which separates the CO₂ from the residue [13]. A general overview of the process is given in [14].

The first dry cleaning facility to offer the Micare system was Hangers™ Cleaners located in Wilmington, North Carolina. The following machines were subsequently developed by MiCell Technologies:

- MiCO2 G200
- MiCO2 G300

Micell exited the dry cleaning business in 2001. The Hangers license was sold to Aga (DryWash Consortium) in 2002, who then started a franchise organization in Europe while Cool Clean Technologies acquired the machine technology.

2.4. DryWash

Hughes Aircraft Company applied for a series of patents during the 1990's [15-18]. Together with Global Technologies and Los Alamos National Laboratory, they developed DryWash, a commercial machine and process that uses CO₂ as a cleaning solvent for fabrics. A prototype CO₂ dry-cleaning machine was demonstrated at a trade show in 1995. The DryWash process is shown schematically in Figure 2.3.

In the DryWash system, the garments are held in a perforated basket inside the cleaning vessel. DryWash Fluid (pre-mixture of liquid CO₂ and additives) is pumped from a storage tank into the cleaning vessel, and a recirculating loop is established. It was described that the mechanical action is provided by using a

rotating drum with or without a hydrodynamic agitation, in which nozzles located on the wall of the basket spray high-speed jets of liquid CO₂. It has been reported that the jets create a vortex that causes the clothes to spin around inside the basket which requires a lot of power. As the garments pass through the fluid jets, they would momentarily stretch slightly, and once they have moved away from the jets, they would relax to their original size. This stretch-relax cycle is reported to dislodge particles. Due to the lack of sight glass on the machines equipped with jet spray, it is not known if the textile moves as described.

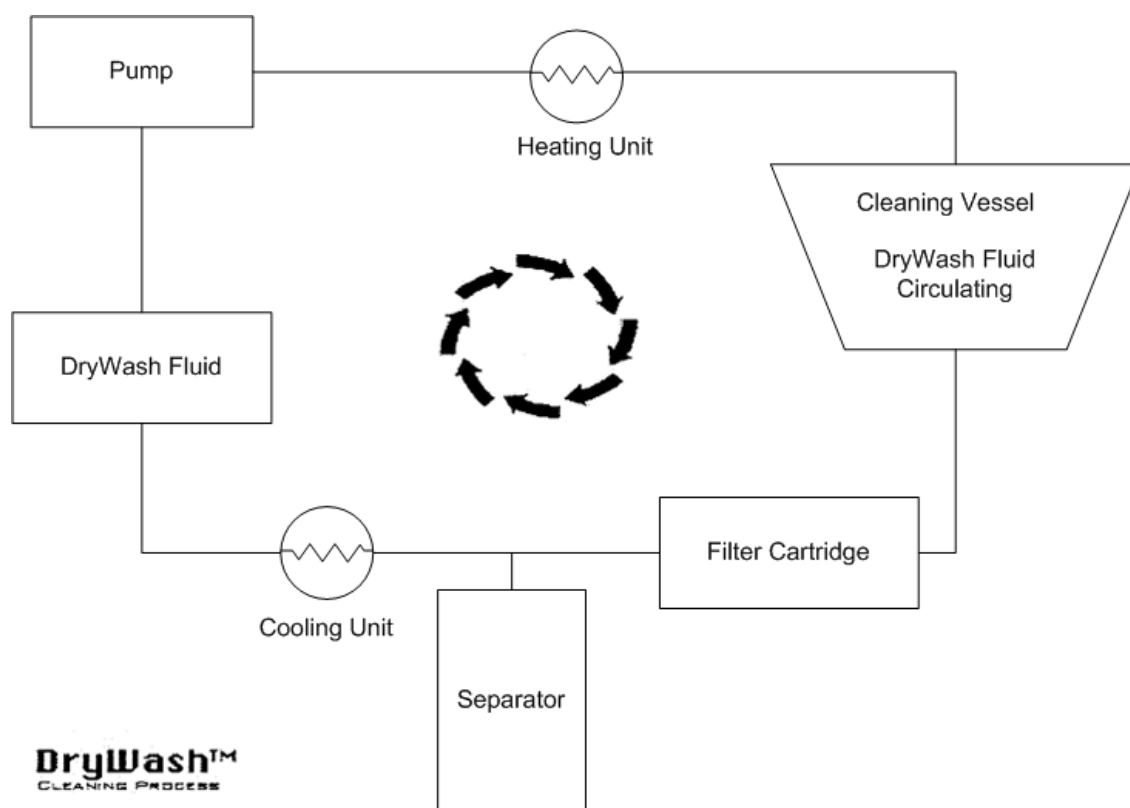


Figure 2.3: DryWash process schematic

At the end of the cleaning cycle, the liquid CO₂ is drained from the cleaning vessel and is converted into a gas in the still. The dirt carried from the garments is collected at the bottom of the still, and the clean, gasified CO₂ is then re-condensed for the next cycle [19]. A general overview of the process is given in [20].

In the following years, the DryWash license program was used for the development of the following machines:

- Genesys by Alliance Laundry Systems, USA [21]
- SailStar by SailStarUSA, USA [22]
- CoolClean Technologies, USA [23]
- Electrolux, Sweden [24]
- COMECO2, Italy.

Genesys and COMECO2 machines employ both rotating drum and jet spray while the other machines only use rotating drum.

Except for COMECO2, currently all the machines are still in operation in USA and Europe. Sail Star and Alliance decided to not continue in CO₂ dry cleaning business, leading to difficulties in obtaining spare parts and maintenance for these machines. Electrolux does not produce CO₂ dry cleaning machines at this moment. Cool Clean Technologies is only actively selling machines for a new product line called Solvair machine, which employs hydrocarbon solvent based washing and CO₂ based rinsing [25].

2.5. CO₂Nexus

The latest commercial development in CO₂ dry cleaning equipment is the launching of CO₂Nexus machines in USA [26]. One of their latest models, the Tersus series, has been designed for regular dry cleaning operations. The company also has designed and constructed machines for other, specialized textile cleaning needs such as clean-room garment. They all use the NexWash cleaning process, which is registered in [27]. The process diagram of the cleaning process is given in Figure 2.4. In the cleaning system, the mechanical agitation is provided by a rotating inner drum with baffles. The garments go through a cleaning cycle where CO₂ is circulated through a series of filters to remove particulates. After the washing and rinsing cycle are complete, the chamber is depressurized, thereby returning CO₂ to a gaseous form and leaving the garments dry. The CO₂ is then distilled to remove soluble impurities, and returned for reuse.

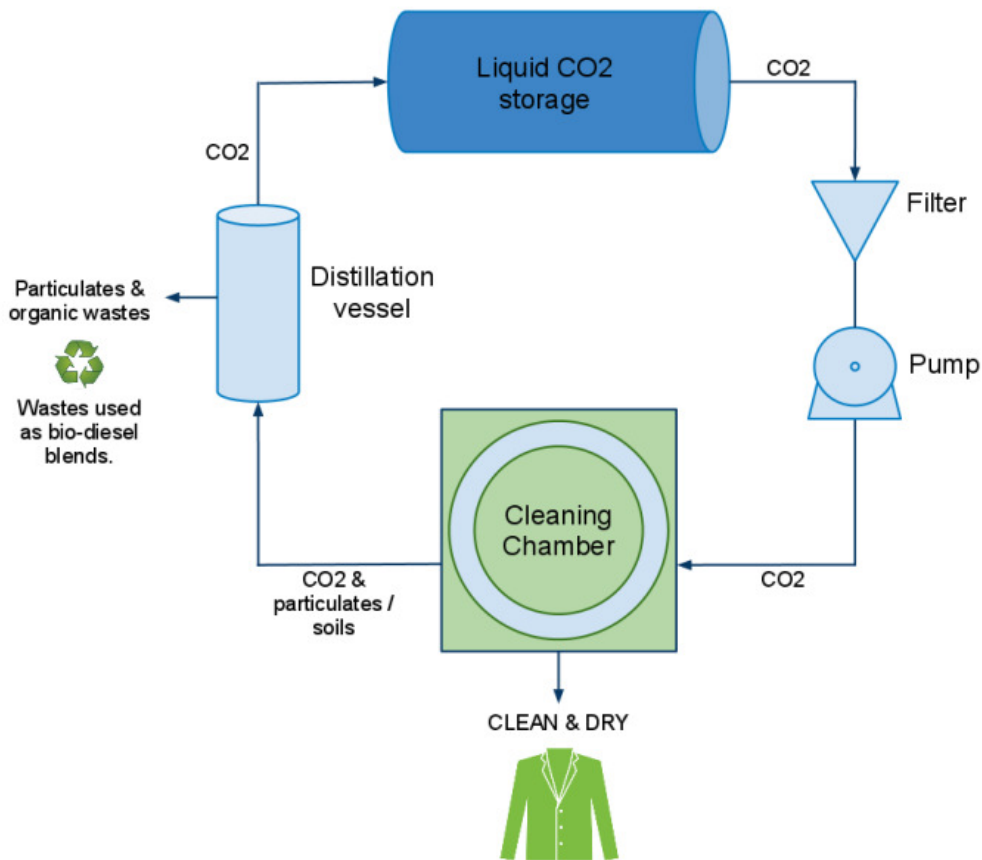


Figure 2.4: CO₂ Nexus process flow diagram

This machine always employs a new batch of clean CO₂ at the start of each washing and rinsing steps and circulates CO₂ through filters, thus eliminate the high probability of the redeposition, which supports the finding in this study that CO₂ circulation through the right filtration system could eliminate redeposition problem (Chapter 2). Furthermore, the capacity of the CO₂ reclamation unit of this machine is designed as such that the used CO₂ of each cycle is completely distilled by the time the washing time is finished. Table 2.1 shows the summary of the existing commercial brands of dry cleaning machines, except for COMECO2.

2.6. Academia

Several journal papers have been published for the CO₂ dry cleaning process. Scientific investigations were found in The Journal of Supercritical Fluids conducted by van Roosmalen et. al. [28-31]. The four Sinner's factors (chemical action,

mechanical action, washing time, and washing temperature) have been investigated in these studies by modeling the mechanical action and conducting washing experiments in a 25 L apparatus. The experimental results indicate that the removal of non-polar soils in CO₂ is comparable to that in PER, whereas the removal of particulate soil in CO₂ is lower. Sousa et. al. [32] and Rowe et. al. [33] have successfully employed high density CO₂ with the aid of alcohol co-solvents to clean old textiles and archeological artifacts, respectively.

Another aspect that has been investigated to some extent is the effect of the CO₂ dry-cleaning process on the physical and mechanical properties of fabrics. Rombaldoni et. al. [34] investigated the change in properties of six different wool and wool/cashmere fabrics. Their results show that the combined effect of CO₂, surfactant, small quantities of water and isopropyl alcohol result in loss of tension of the fabrics, swelling and changes in their structure. The swelling of the fibers leads to thicker and fuller fabrics. A significant modification of the shear hysteresis was measured, i.e. the CO₂ dry-cleaning process resulted in a loss of elasticity of the fabrics under shear. However, no particular modifications were noted for bending and tensile properties or crease pressing performance, and the changes in the properties of the fabrics were within acceptable limits for dry-cleaning applications. Despite all these studies, the mechanism of CO₂ dry cleaning is at best partially understood.

2.7. CO₂ dry cleaning in the Netherlands and Europe

In Europe, Electrolux was the main supplier of the CO₂ dry cleaning machines, although they currently do not actively sell this product line anymore. The first CO₂ dry cleaner in Europe, founded in 2004, was located in Stockholm, Sweden as a part of the Hangers franchise consortium. A couple of months later, another Hangers Cleaners was founded in Amersfoort, Netherlands. In 2005, the Hangers stores were bought by Linde Gas who collaborated with Electrolux to sell the franchise concept throughout Europe under the name Fred Butler. However, the market development did not go as planned and consequently in 2011 Linde decided to stop this project.

Table 2.1: Comparison of existing CO₂ dry cleaning machines

Machine	MiCO2	Genesys	Sail Star	Cool Clean	Electrolux	CO2Nexus
Mechanical action	Rotating drum	Rotating drum with nozzles in baffles	Rotating drum	Rotating drum	Rotating drum	Rotating drum
Load capacity (kg)	20	13	20	20	15	20
Temperature (°C)	Room T	Room T	Room T	Room T	Room T	Room T
Pressure (bar)	Equilibrium with T	Equilibrium with T	Equilibrium with T	Equilibrium with T	Equilibrium with T	Equilibrium with T
Rotational speed (rpm)	25	35	25	25	30	30
Circulation	None	Yes	None	None	None	Yes
Filtration	Only when CO ₂ is released	Yes	Only during rinsing	Only during rinsing	Only when CO ₂ is released	Yes
Rinsing	No rinsing	Available with mixture of used and clean CO ₂	Available with mixture of used and clean CO ₂	Available with mixture of used and clean CO ₂	Available with clean CO ₂	Available with clean CO ₂

In 2013, the only existing dry cleaners using CO₂ in Europe are Kymi Rens (Aalborg, Denmark) and Fred Butler (Copenhagen, Denmark).

2.8. Closing words

CO₂ dry cleaning technology has undergone significant technical development since it was invented in the 1970's. Its commercialization however, is still difficult because of several barriers, such as poor solubility of many chemical compounds in CO₂ and the nature of dense CO₂ which requires high pressure equipment which leads to relatively high initial investment costs. Nevertheless, CO₂ has a high potential to replace PER for textile dry cleaning. The development of powerful surfactant, increasing the amount of mechanical action without textile deterioration, and also the understanding of cleaning mechanism and textile movement are necessary to obtain a comparable performance with PER.

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Chapter 3

Redeposition in CO₂ Dry Cleaning

Abstract

Perchloroethylene (PER) is commonly used as cleaning solvent in the textile dry-cleaning industry but this chemical is toxic by nature. One of the potential PER replacements is carbon dioxide (CO₂), which is non-toxic, cheap, and widely available. Previous studies have indicated that the particulate soil removal with CO₂ is lower compared to that of PER. While the particulate soil removal of the CO₂ dry-cleaning was studied, it was found that redeposition of particulate soil occurs. Several experiments have been carried out to study and reduce this problem. In these experiments, textiles stained with different kinds of particulate soils were cleaned using a 25 L CO₂ dry-cleaning apparatus. It was found that the redeposition level increases along with washing time, while rinsing has little influence. Modifying the filtration system by using scavenger textile, or adding a cellulose compound to the cleaning vessel as anti redeposition agent can significantly reduce redeposition.

3.1. Introduction

Dry cleaning is a process of soil removal from substrate, in this case garment/textile, which involves a non-aqueous solvent. This process was developed because some types of textile material are damaged by water, e.g. they wrinkle, shrink, etc. The most common solvent used in conventional dry cleaning is perchloroethylene (PER). Despite its good cleaning performance, PER has several drawbacks such as a toxic effect to the human body. The known LD50s of PER are 4700 mg/kg (ipr-mouse) and 8850 mg/kg (oral-rat) [1]. Studies have shown that repeated exposure of PER by inhalation and mouth causes kidney and liver damage as well as cancer in animals, as likewise in humans [2].

These drawbacks of PER have started the investigations of several alternative solvents for textile dry cleaning, including hydrocarbon solvents, silicon based

solvents and carbon dioxide (CO₂) [3]. CO₂ has several advantages compared to the other solvents. It is non-toxic, non-flammable, non-corrosive, safe for the environment, cheap, easily recovered, and available on a large scale. Furthermore, the drying step is not necessary because CO₂ evaporates from the fabrics during the depressurization step.

Previous studies have indicated that the cleaning performance of CO₂ for non-particulate soil removal is comparable to that of PER. However, the particulate soil removal with CO₂ is lower [4, 5]. When the particulate soil removal of CO₂ dry cleaning process was studied [6], it was found that redeposition of particulate soil occurred. Redeposition is a process of soil transfer from one textile to another, and happens when the released soil is not properly stabilized in or removed from the cleaning medium. Once redeposition happens, it usually cannot be reversed which leads to greying of the fabric and unsatisfying cleaning results [7]. This problem has been mentioned in a previous study [8] and is also found by several commercial CO₂ dry cleaners.

In water based cleaning, redeposition is solved by the incorporation of anti redeposition agents in the detergent formulation, such as sodium carboxy methyl cellulose, polymeric cellulose acetate, and polyvinyl alcohol [9]. The principal action of anti redeposition agents are charge stabilization by increasing the electrostatic repulsion between soil particles and/or steric stabilization. For CO₂ dry cleaning, no commercial anti-redeposition agents are commercially available.

Several patents have suggested various methods to reduce redeposition in CO₂ dry cleaning. US Patents 5267455 [10] and 5412958 [11] suggest a rinsing step with compressed purge gas (such as nitrogen or air) after the cleaning step. It is believed that this purge gas will interpose between the fabric and removed soil and thus preventing redeposition. US Patents 5467492 [12] and 5651276 [13] mention using a high flow rate (1 gallon per minute per pound garment) of recycling of CO₂ stream through a series of filter (such as paper filters) to lower the chance of redeposition, which is also studied in this paper. US Patent 5651276 [13] also suggests to employ ionized incoming gas to eliminate static charge and US Patent 6346126 [14] suggests using acoustic energy to improve soil removal and prevent its

redeposition onto the fabric. As to the author's knowledge, to date these methods are not proven and no commercial solution is yet available.

Because of the scarcity of available information, some fundamental questions about redeposition in CO₂ dry cleaning remain to be answered, such as: Which soil is redeposited? How does cleaning time and rinsing affect redeposition? Lastly and most importantly, how to prevent redeposition? This work aims to answer these questions with conducting experiments in a pilot-scale dry-cleaning apparatus.

3.2. Materials and methods

3.2.1. Materials

Fifteen pieces of soiled test fabric of 6.5 x 7.5 cm² (Center for Testmaterials B.V., the Netherlands) were used in each washing experiment. These soiled test fabrics were spiked with a larger amount of soil than would be found in a typical commercial washing situation. Unless mentioned otherwise, they consist of either three types of textile - cotton, polyester or wool-, each stained with one type of particulate soil -clay, sebum colored with carbon black, sand, lipstick, or dust- (see Figure 3.1). These monitors were fabricated (dipped in a concentrated soil solution, except for sand soiled materials which are hand-stained) as such that each piece of the same type contains a similar soil load. Along with the monitors, cotton filling materials of 25 x 25 cm² were added into the cleaning chamber to reach the desired washing load of 400 g. These materials were also used as indicators to measure redeposition level.

Six kg of CO₂ grade 2.7 (Linde Gas Benelux B.V., the Netherlands) was used in each washing and rinsing step. Several additives were used in the experiments: 10 g Amihope LL or *N*-lauroyl-L-lysine (Ajinomoto Co. Inc., Japan) [15] as solid surfactant or ClipCOO (Kreussler, Germany) as liquid surfactant, 250 g 2-Propanol (IPA) with a stated purity >98% (Prolabo, the Netherlands) and 25 g tap water as co-solvents, as well as 10 g 200 µm sand or 5-8 mm gravel as additional particles to enhance the mechanical action (Filcom B.V., the Netherlands). Sand or gravel have been used to increase mechanical action and thereby particle removal, which leads to (more) redeposition and gives us the chance to study this phenomenon. Polyvinyl

alcohol, Carboxy methyl cellulose, and Cellulose acetate (Sigma Aldrich, the Netherlands) were used as anti redeposition agents.

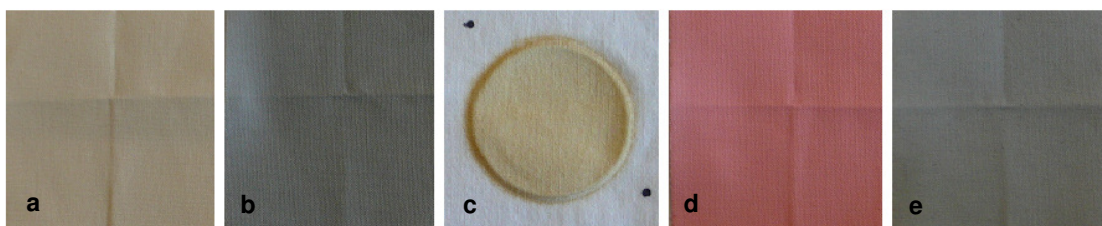


Figure 3.1: Picture of cotton monitors: clay (a), sebum colored with carbon black (b), sand (c), lipstick (d), and dust (e)

3.2.2. Apparatus

The dry-cleaning experiments were conducted in a CO₂ dry-cleaning apparatus, which is schematically presented in Figure 3.2. The pilot-scale apparatus was designed and constructed at the Laboratory for Process Equipment, Delft University of Technology, the Netherlands. The cleaning chamber (Van Steen Apparatenbouw B.V., the Netherlands) has 0.25 m inside diameter and 25 L volume, equipped with an inner drum with diameter of 0.21 m and volume of 10 L. The inner-drum, which is perforated and connected to a rotating shaft of 75 rpm, is used to provide the mechanical action (tumble) as in a regular washing machine.

3.2.3 Procedure

At the beginning of the experiment, the soiled monitors, the filling materials, and additives were placed inside the cleaning chamber. The system was then filled with CO₂ by opening the inlet valve until the desired amount of 6 kg was reached. CO₂ was circulated through the closed-loop system by a centrifugal pump. During each cycle of circulation, CO₂ passed through a heat exchanger to control the temperature which regulated the system pressure. CO₂ also passed through a filter with a pore size of 11 µm in order to prevent particles in the stream from entering the pump. After the washing step of 20 min. was complete, the used CO₂ was replaced by fresh CO₂ from the storage. The fresh CO₂ was also circulated for a short period of 10 min. to

rinse the fabric. After the rinsing step, CO₂ was then released from the system by opening the outlet valve.

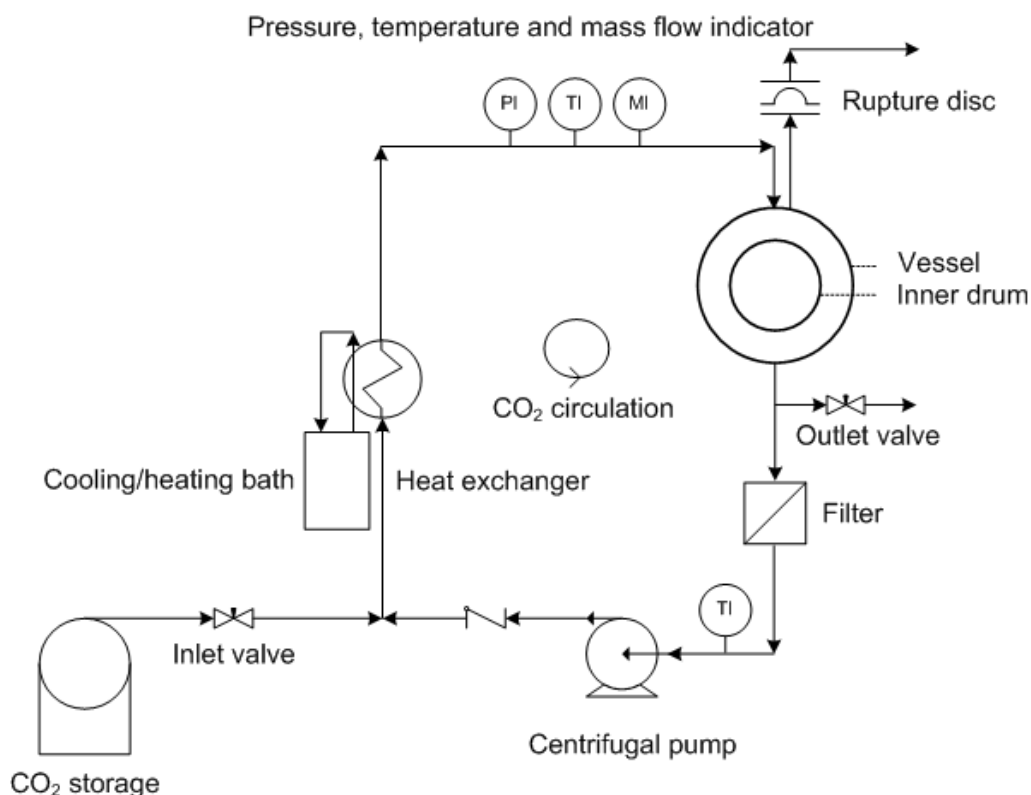


Figure 3.2: Schematic representation of the dry-cleaning apparatus

The temperature, pressure, fluid density, and circulation rate were monitored throughout the experiment by manually controlling the indicators every 3 minutes period. Unless mentioned otherwise, the standard process conditions which are given in Table 1 have been used. All additives in Table 3.1 were used at the same time in each washing experiment. The type and the amount have been optimized in a previous study [15] with regards to the cleaning performance. In Section 3.3.2, Amihope and sand were replaced with ClipCOO and gravel to avoid blockage of the new filtration system. All given data in this study are average values based on two or more replications for each experiment.

Table 3.1: Process conditions of CO₂ dry cleaning

Process Condition	Value	Unit
Rotation speed of inner drum	75	rpm
Washing load	400	g
Temperature	283	K
Pressure	45	bar
Washing time	20	min.
Rinsing time	10	min.
Amount of CO ₂	6	kg
Amount of water	25	g
Amount of IPA	250	g
Amount of Amihope LL	10	g
Amount of sand	10	g

3.2.4. Analytical method

To monitor the cleaning results, the color of the fabric was measured before and after washing with a spectrophotometer Data Color 110, using Standard Illuminant C as light source (average daylight, excluding ultraviolet light). CIE 10° Supplementary Standard Observer was chosen as the viewing angle. The color was measured using the L*a*b* color space or CIELAB system. It is visualized as a cylindrical coordinate system in which the axis of the cylinder is L* which indicates the lightness and ranging from 0% to 100% and the radii are the chromaticity coordinates a* and b*: +a* is the red direction, -a* the green direction, +b* the yellow direction, and -b* the blue direction [16]. In this color space, the color difference (ΔE) is defined by Equation 3.1:

$$\Delta E_{1-2} = \left((L_1^* - L_2^*)^2 + (a_1^* - a_2^*)^2 + (b_1^* - b_2^*)^2 \right)^{0.5} \quad \text{Eq. 3.1}$$

The particulate soil removal is represented by Cleaning Performance Index (CPI), which is defined in Equation 3.2:

$$CPI = \left[1 - \frac{\Delta E_{\text{washed-unsoiled}}}{\Delta E_{\text{soiled-unsoiled}}} \right] \cdot 100\% \quad \text{Eq. 3.2}$$

Similarly, the color difference of the cotton filling as reference was measured before and after washing to estimate the level of redeposition. These values are the average of several cotton filling pieces used in each experiment.

To achieve more insight about redeposition process, some textile and soil samples were also analyzed with Scanning Electron Microscope (SEM) - JEOL JSM 5400 and Electron Microprobe (EMP) - JEOL 8800 M JXA Superprobe. SEM was used to provide images of surface topography of the fabric samples while EMP was used to provide qualitative measurement of soil elements. In EMP measurement, solid sample is fired with an electron beam. Consequently, each element in the sample emits X-rays at a characteristic frequency. The specific X-ray wavelength or energy are selected and counted by wavelength dispersive X-ray spectroscopy which use Bragg diffraction from crystals and direct then direct them to detectors [17].

3.3. Results and discussion

3.3.1. Redeposition study

Redeposition of various soil types

Each experiment was performed with 15 pieces of monitors of the same soil on three different types of fabric (5 pieces per type of fabric). The cleaning results of these experiments (the average values with standard deviation) are shown in Figure 3.3. The negative CPI observed for the clay-wool and dust-cotton monitors clearly indicate redeposition. Redeposition is most visible for these monitors due to their low reflectance compared to the other monitors.

The ΔE difference of the cotton filling is given in Table 3.2 for each type of soil used in the experiments. This table shows that all types of particulate soils released during the washing process lead to a color difference of the cotton filling and therefore redeposition. Unfortunately, since a mass balance cannot be constructed, this number cannot be related to a quantitative amount of redeposited soil. Although the numbers for the different soil types cannot be compared, the higher the number for a certain soil type, the higher the redeposition level.

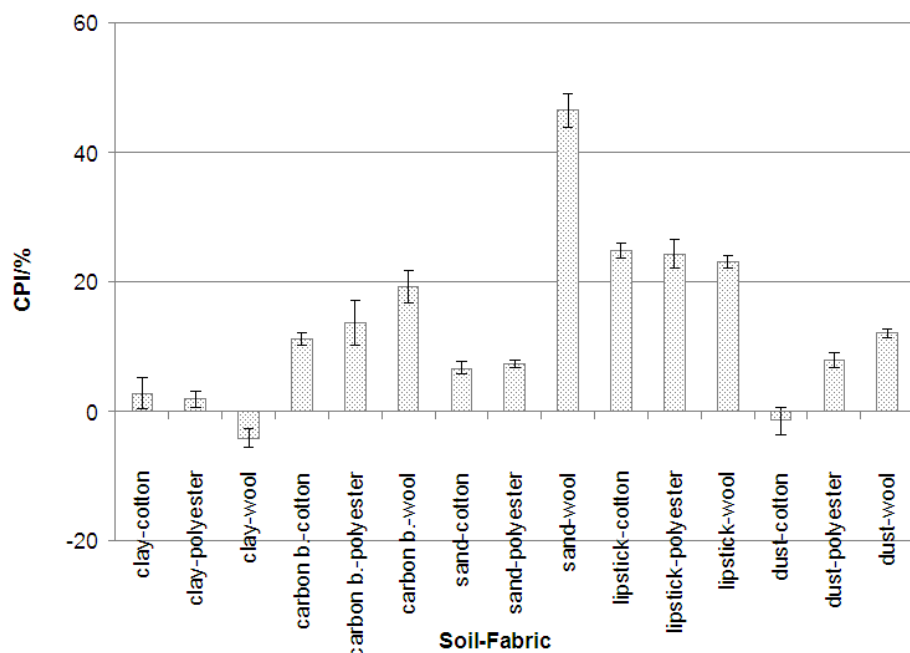


Figure 3.3: Cleaning result with different types of soil

Table 3.2: ΔE difference of cotton filling for different types of soil

Soil type	ΔE difference
Clay	2.4
Sebum colored with carbon black	5.6
Sand	1.9
Lipstick	4.2
Dust	3.8

Influence of rinsing on redeposition

The effect of a rinsing step on the redeposition level has been examined. In the first experiment, the standard rinsing procedure is used. In the second experiment, the rinsing step is eliminated while the other variables are kept constant. The cleaning results are shown in Figure 3.4. In general, the cleaning performance without rinsing is slightly lower than with rinsing which is to be expected because soil is removed from the textile during rinsing and rinsing step helps to remove the dislodged soil.

The ΔE of cotton filling with and without rinsing process is given in Table 3.3. Since all test monitors are cleaned together in one experiment, it cannot be indicated

which soils cause this redeposition. It seems that the effect of rinsing on the redeposition level is not significant. There are two possibilities which might happen: 1) Washing results increase by rinsing (as shown above) so chances for redeposition increase. However, rinsing may also remove the dislodged particles which leads to the same degree of redeposition overall. 2) The redeposition process has already occurred during the washing step and it is known that this process is hard to reverse [7].

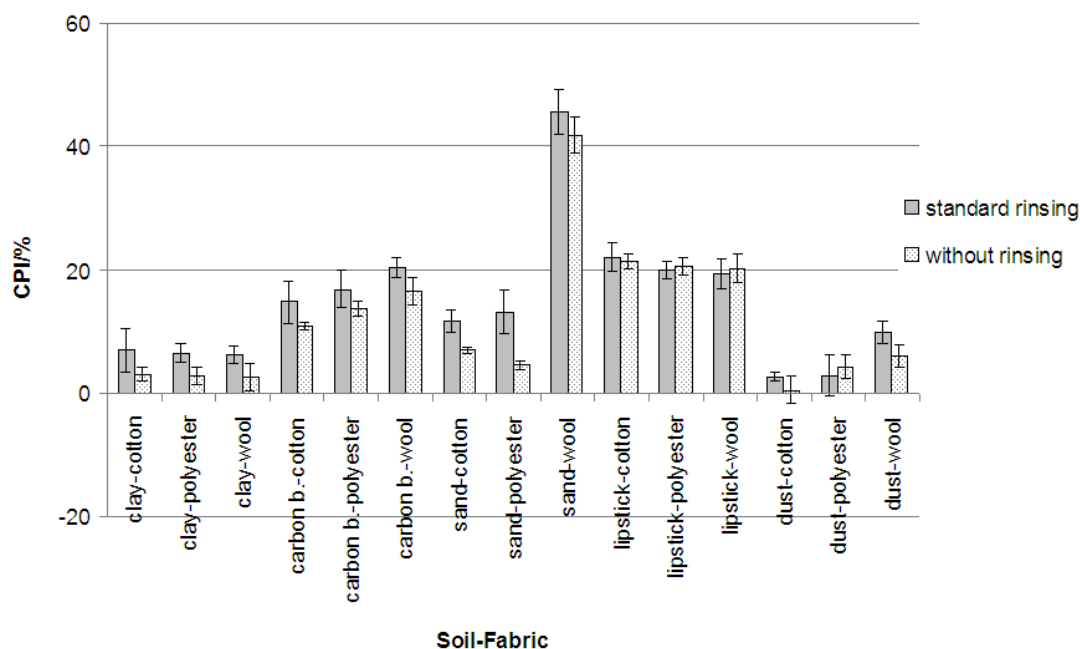


Figure 3.4: Influence of type of rinsing on cleaning result

Table 3.3: ΔE difference of cotton filling for different type of rinsing

Rinsing	ΔE difference
Standard rinsing	2.6
Without rinsing	2.7

Influence of washing time on redeposition

The cleaning performance and redeposition level as function of washing time have been studied (see Figure 3.5 and Table 3.4, respectively). It has been found that a longer washing time of 420 min has a slightly positive influence on the cleaning

performance for most cases, but a negative influence on redeposition. Since more soil is removed over a longer period, the chance of redeposition is higher.

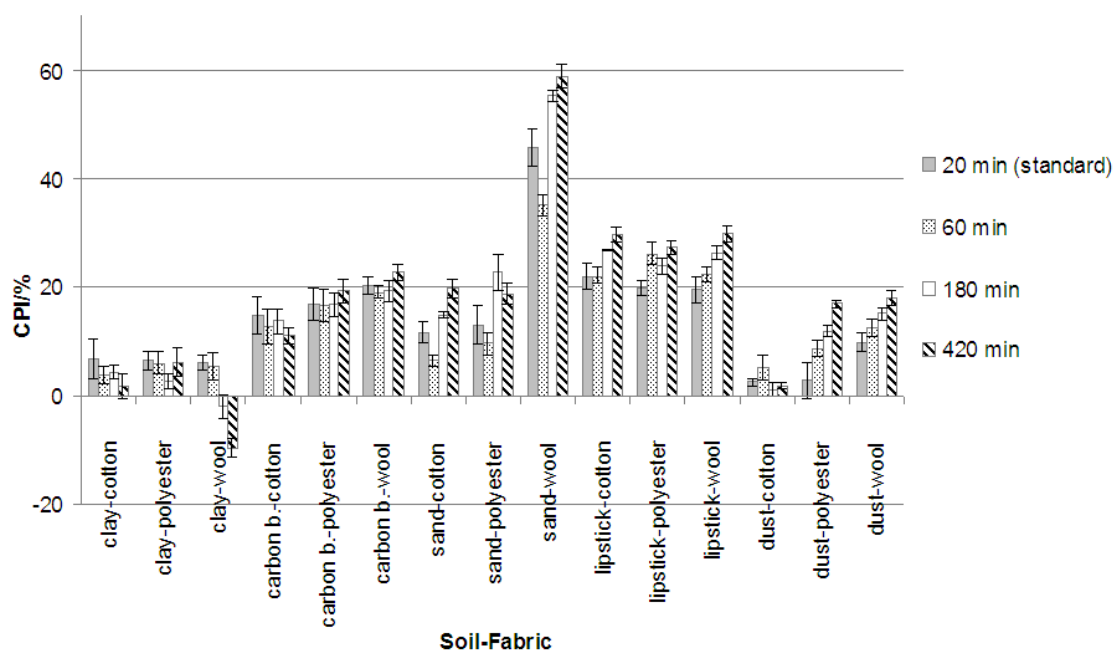


Figure 3.5: Influence of washing time on cleaning result

Table 3.4: ΔE difference of cotton filling for different washing time

Washing time (min.)	ΔE difference
20	1.9
60	3.4
180	4.2
420	11.1

The color difference distribution of the individual cotton filling pieces after the longest cleaning time of 420 min is almost equal with standard deviation 0.85, while the standard deviation for the shorter washing time is between 1.5-2, showing that the redeposition is more evenly distributed over the filling material with longer washing times compared to shorter cleaning times. A possible explanation is that the dislodged soil in liquid CO₂ has a higher chance to be redeposited evenly with longer washing time. It is not recommended to use washing time that is longer than 20 min;

although longer washing time may lead to an increase in cleaning performance for several soil/fabric combinations, it also leads to an increase in redeposition and also costs.

SEM and EMP measurements

SEM pictures show redeposition of particles for the carbon black on cotton monitor (Figure 3.6) and for the cotton filling used in the washing experiment (Figure 3.7). Besides carbon black, SEM analysis were also performed for other types of soils (clay, sand, lipstick and dust), and similar results were observed. The SEM measurements were performed 4 times on different areas of each piece of sample. These results show that redeposition occurs on all textile surfaces i.e. cotton filling and the monitors.

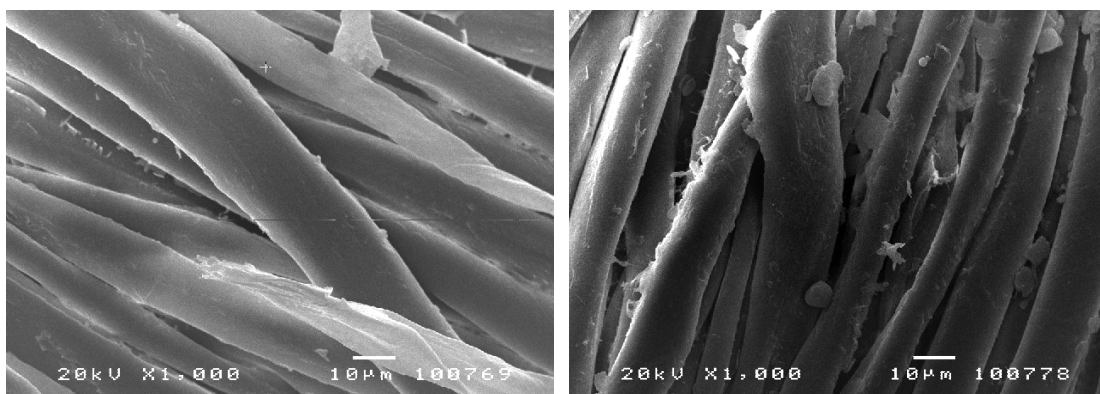


Figure 3.6: SEM of sebum colored with carbon black on cotton before (left) and after (right) washing

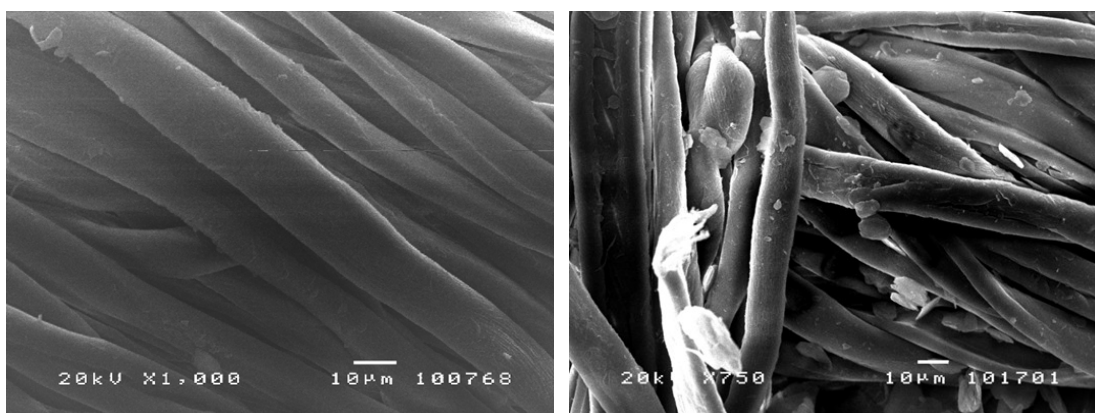


Figure 3.7: SEM of cotton fillings before (left) and after (right) washing

The result of EMP analysis on the particles present on the carbon black monitor after washing (Figure 3.6) is given in Figure 3.8. The analysis was conducted using 3 different channels (Ch1, Ch2, Ch3) and 4 different crystals (LDE1, TAP, PET, LIF) to measure 4 different wavelength range between 1-50 Angstrom. Figure 3.8 showed that beside Carbon and Oxygen (which are the main elements of the soil and the textile), elements of Cuprum and Barium are also present. Since Barium is a heavy element, it has several energy levels which produces several peaks. These elements can only originate from other particulate soils, which proves the presence of other particulate soil on the textile monitor after washing and thus the occurrence of redeposition. The size of the sand used as additives is too big to get into the textile fibers.

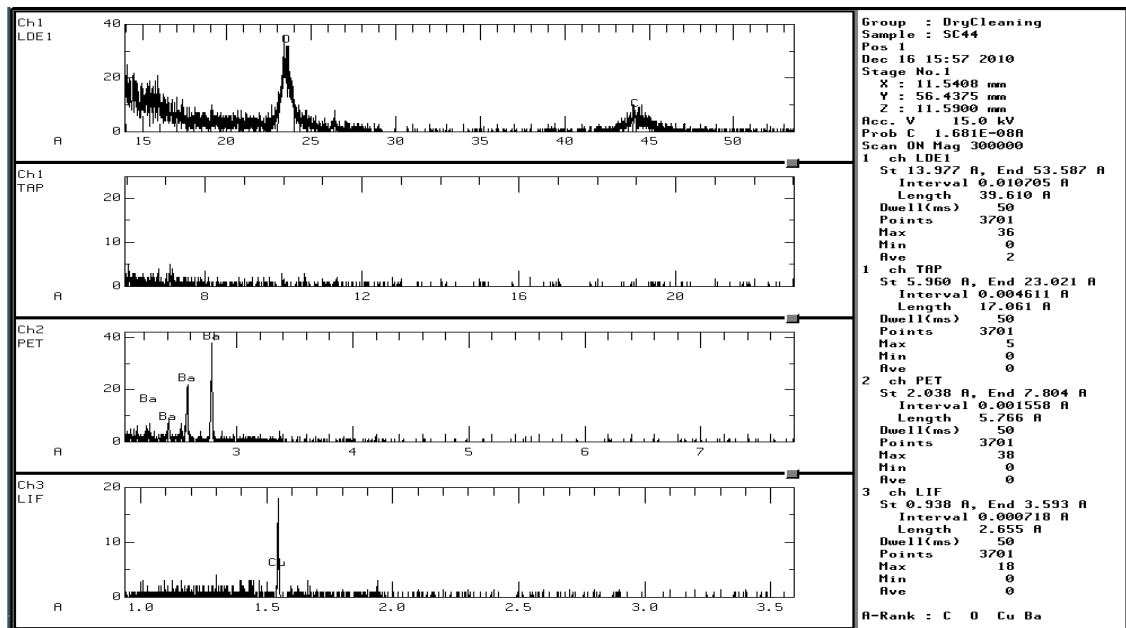


Figure 3.8: EMP graph for sebum colored with carbon black on cotton after washing

3.3.2. Reducing redeposition

Modifying the filtration system

Several approaches to solve the redeposition problem in CO₂ dry cleaning have been investigated. Firstly, the filtration system of the CO₂ dry-cleaning apparatus has been modified. The filtration system was initially built to protect the circulation pump from

damage caused by threads, dirt particles, etc. The existing filtration system consisted of:

- A filter in the cleaning vessel (Figure 3.9a) to filter the threads etc. from the CO₂ stream (Figure 3.9c)
- A main filter of 38.5 cm² 10 µm wire mesh (Figure 3.9d) with a holder in the filter house (Figure 3.9b).

It is desirable to improve the filtration system so that it can also be used to remove the released particulate soil from CO₂ stream and thus prevent redeposition. Several measures have been taken:

- A more rigid filter holder (Figure 3.9g) was installed in the filter house to keep the main filter better in place, eliminating the possibility of deformation due to pressure difference over the filter.
- The filter in the vessel was also replaced with a new one with a better fit to the cleaning vessel outlet and the surface area was increased from 9.1 cm² to 36.5 cm² (Figure 3.9f).

More than 20 experiments have been conducted to find the best balance of the main filter pore size (0.5 µm, 3 µm and/or 10 µm) and the circulation flow rate. It was found that the 10 µm filter is most suitable to achieve a required circulation flow rate of 150-250 kg/h to maintain the process temperature in our system.

With the new filtration system, no solid additive in micron size can be used because these additives rapidly block the filter. Therefore, Amihope LL and sand were replaced with ClipCOO and gravel as surfactant and mechanical action enhancer, respectively. To further reduce the redeposition level, pre-filters of textile material were added to the existing filters (Figure 3.9f and 3.9g). Experiments have been performed to determine the optimal textile type for the pre-filters. Various scavenger textile materials have been investigated. Scavenger textile is textile with a high specific surface area and has a higher affinity to the particulate soils than the currently used fabrics. When the CO₂ stream with the dislodged particulate soil flows through this filtration system, the soil may be attached to this scavenger textile instead of being redeposited on other textile surface, and thus redeposition may be reduced. The scavenger materials used in this study are cotton velveteen, cotton terry cloth, cotton flannel and poly-suede.

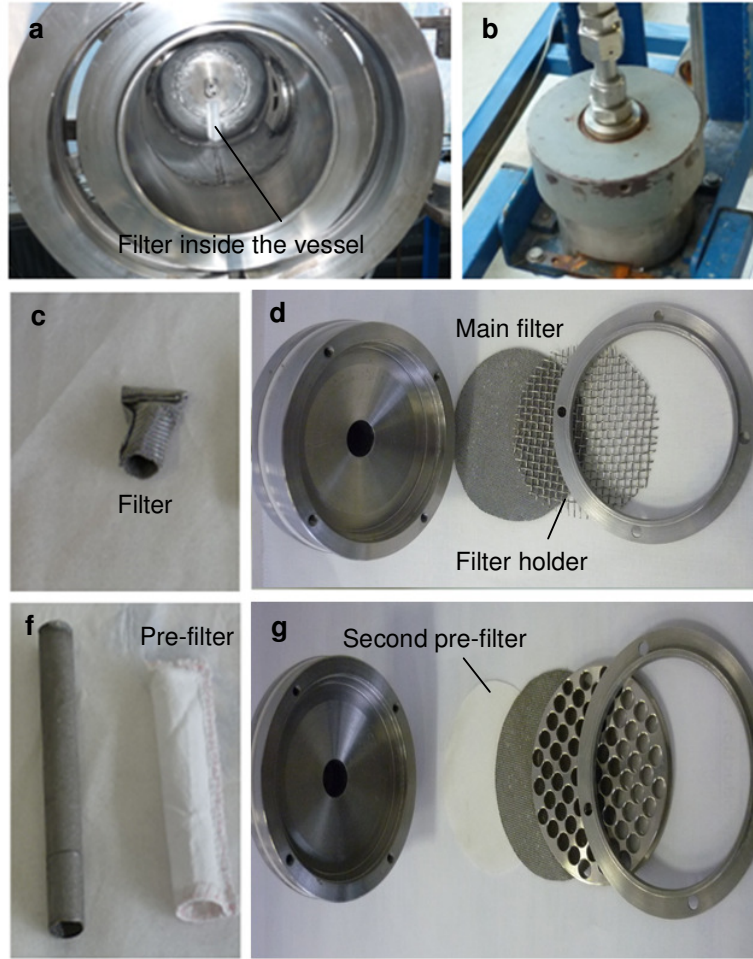


Figure 3.9: The vessel with filter (a); the filter house (b); the existing filtration system: the filter (c) and the main filter (d); the new filtration system: the filter (f) and the main filter (g)

Figure 3.10 and Table 3.5 show the cleaning performance and redeposition level, respectively, using different types of scavenger textile as pre-filter (Figure 3.9f) and using cotton as second pre-filter material (Figure 3.9g). Figure 3.11 and Table 3.6 show the washing results for using scavenger textile as second pre-filter and cotton as pre-filter material. Furthermore, as a reference, results are shown for the unmodified filter system. Since the surfactant was changed to ClipCOO, the washing performance is lower (resulting in lower redeposition and no negative washing results for the reference system).

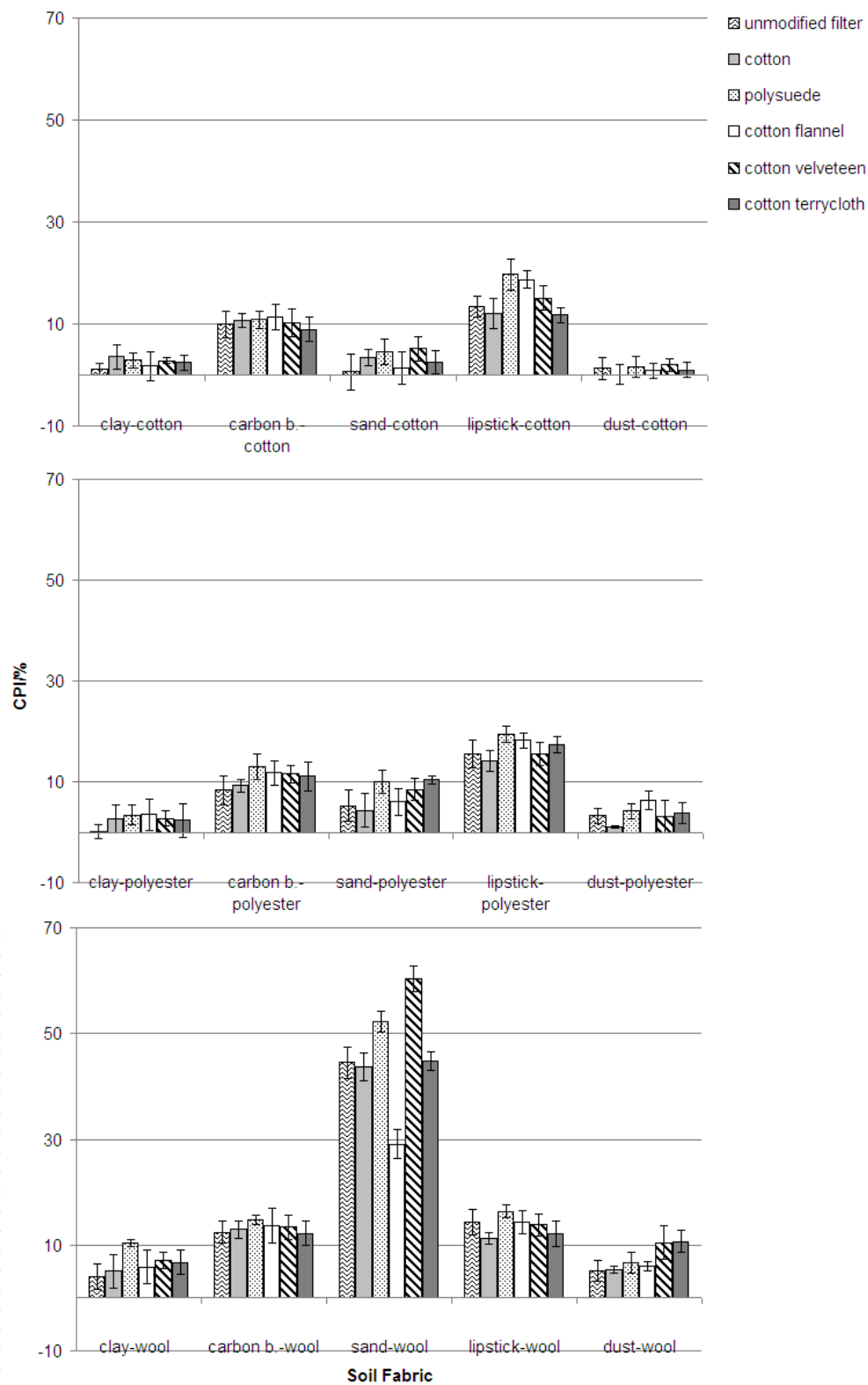


Figure 3.10: Influence of using different textile materials as pre-filter on CPI

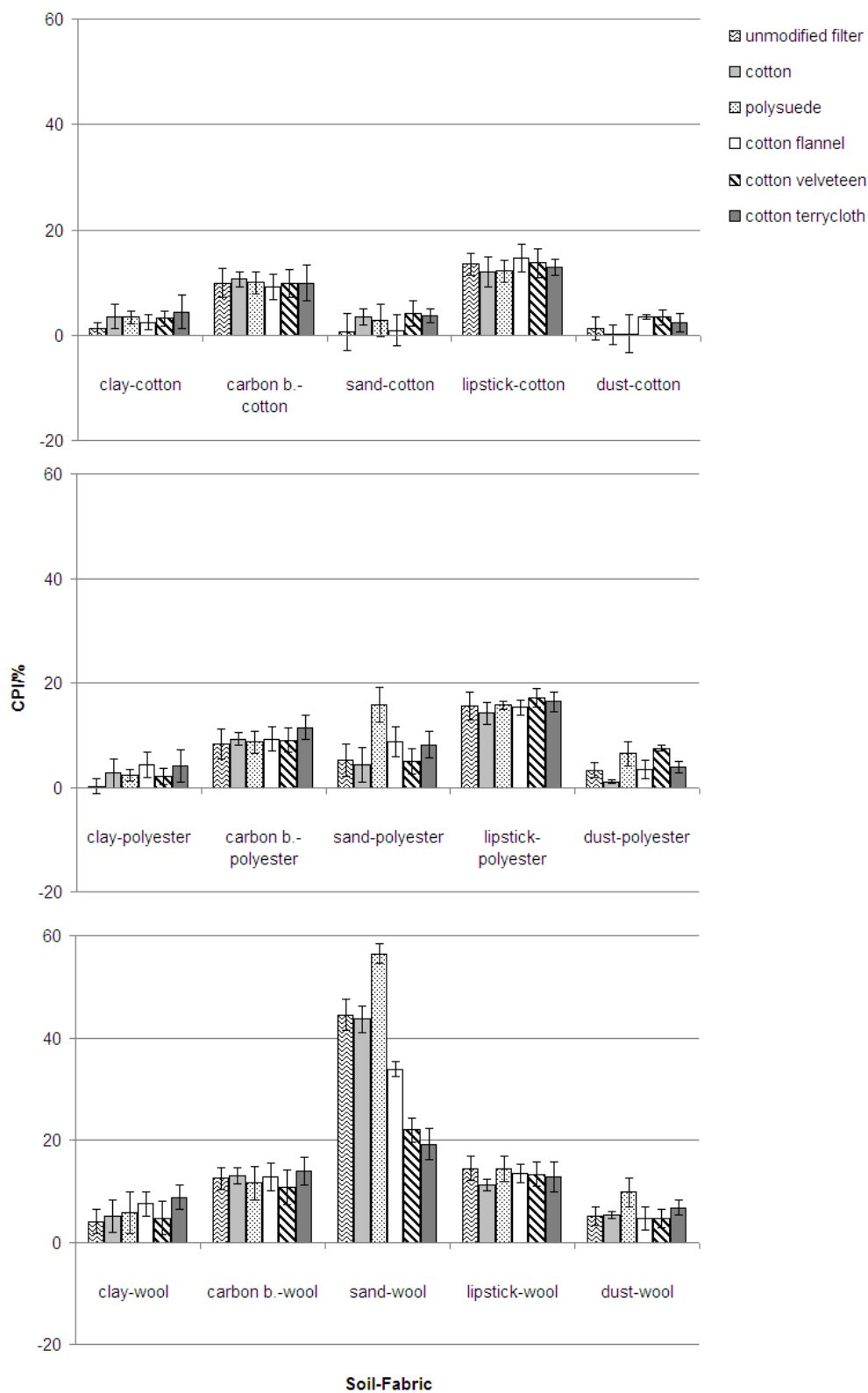


Figure 3.11: Influence of using different textile materials as second pre-filter on CPI

Table 3.5: ΔE difference of cotton filling for different types of textile materials as pre-filter

Scavenger textile	ΔE difference
Unmodified filtration system	2.9
Cotton	2.3
Polysuede	0.2
Cotton flannel	0.1
Cotton velveteen	0.3
Cotton terrycloth	0.3

Table 3.6: ΔE difference of cotton filling for different types of textile materials as 2nd pre-filter

Scavenger textile	ΔE difference
Unmodified filtration system	2.9
Cotton	2.3
Polysuede	0.4
Cotton flannel	0.4
Cotton velveteen	0.4
Cotton terrycloth	0.2

When cotton was used for the pre-filters in the new filtration system, the washing results show a similar cleaning performance compared to the unmodified filtration system, but a notable decrease in redeposition (20%). In general, using different types of scavenger textile as pre-filters does not give any significant difference on cleaning performance except on sand-wool material. The inconsistent and fluctuating CPI value of sand-wool material was also noted in previous work [18].

All scavenger textiles as pre-filters give significantly lower redeposition level compared to cotton and the unmodified filtration system up to 96%. It is observed that the redeposition is even less when scavenger textile is used as pre-filter than as second pre-filter. When scavenger textile was used as pre-filter and as second pre-filter at the same time, the washing performance and redeposition level did not show significant improvement.

Using anti redeposition agent

The most commonly used chemicals as anti redeposition agent in water based cleaning were also tested in CO₂ dry cleaning: polyvinyl alcohol, carboxy methyl cellulose, cellulose acetate. We have also considered and tried other substances as anti redeposition agents (e.g. different types of acids and zeolites), but they are either harmful or they did not significantly lower the redeposition level. The new filtration system with cotton as pre-filter materials, ClipCOO as surfactant, and gravel as mechanical action enhancer were used in the experiments. Only 1 g of each anti redeposition agent (all in solid forms) was added to the vessel because the new filtration system is easily blocked with high amount of solid. Results are shown in Figure 3.12 and Table 3.7.

In water, the agents increase the electrostatic repulsion between soil particles and fabric, as well as increase the steric stabilization. However, CO₂ has a low dielectric constant and thus charge stabilization of particulate soil is almost impossible. Furthermore, as most polymers are insoluble in CO₂ at the used process conditions, steric stabilization is not expected either [19]. Although it is unlikely that in CO₂ the agents follow the same mechanism as in water, it is observed from our experimental results that adding these agents generally helped to reduce redeposition up to 87%. Agents with cellulose reduce redeposition more than polyvinyl alcohol because cellulose may also act as adsorbent material with affinity to dislodged soil particles (see Figure 3.13).

3.4. Conclusion

From the washing experiments, the occurrence of redeposition in CO₂ textile dry cleaning was observed. Each type of particulate soil used in the experiments shows redeposition while no reduction in redeposition is observed by adding a rinsing step. It is also found that the redeposited particles are more evenly distributed and that the redeposition is more severe by using a longer washing time. Modifying the filtration system and using scavenger textiles as pre-filter materials helped to reduce redeposition significantly. Another method to reduce redeposition is by adding cellulose based chemicals in the cleaning vessel as anti redeposition agent.

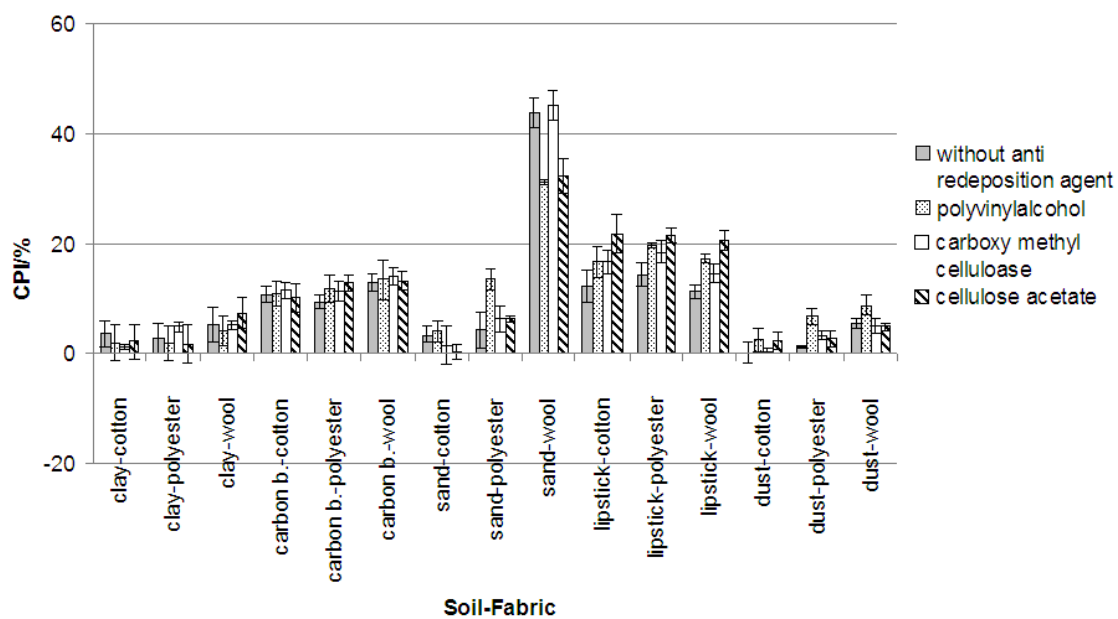


Figure 3.12: Influence of using different types of anti redeposition agents on CPI with cotton as pre-filter materials



Figure 3.13: Cellulose acetate before (left) and after (right) washing

Table 3.7: ΔE difference of cotton filling for different types of anti redeposition agents

Anti redeposition agent	ΔE difference
None	2.3
Polyvinyl alcohol	1.1
Carboxy methyl cellulose	0.4
Cellulose acetate	0.3

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Chapter 4

Performance Enhancement with Additional Particles

Abstract

CO₂ is a potential alternative for perchloroethylene (PER), a common textile dry-cleaning solvent. Previous studies have indicated that the particulate soil removal with CO₂ is lower than with PER. Thus, this study investigates the effect of adding particles on particulate soil removal in CO₂ dry cleaning. Several types of soiled fabric were cleaned using a 25 L CO₂ dry-cleaning apparatus. Sand or other particles were used in the experiments. The particle addition could improve the average Cleaning Performance Index (CPI) with 67%. The increase was especially for high for lipstick and sand soiled materials. Nevertheless, the average cleaning result with CO₂ after optimization was still lower at 65% of the results with PER. Hence, another method to further improve particulate soil removal needs to be developed.

4.1. Introduction

Fabric that is sensitive to water, like wool, is usually washed by professional dry cleaners. Dry cleaning is a process of removing soils from substrate, in this case a textile, using a non-aqueous solvent. The most common solvent in conventional dry cleaning is perchloroethylene (PER). Despite its satisfactory cleaning performance, PER has several drawbacks such as toxic effects to the human body. It also causes air and ground pollution. These drawbacks have led many studies to investigate the possibility of using other solvents, such as hydrocarbon solvents, silicon based solvents, and carbon dioxide (CO₂), in textile dry cleaning [1].

CO₂ has several advantages compared to the other alternative solvents. It is non-toxic, non-flammable, non-corrosive, safe for the environment, cheap, easily recovered and available on a large scale. As an additional advantage, a drying step is not necessary because CO₂ evaporates from the fabric when the cleaning

chamber is depressurized. Furthermore, previous studies [2, 3] have reported that the performance of CO₂ was comparable to that of PER in non-particulate soil removal. This is because CO₂ is non-polar and thus interacts well with non-polar soil e.g., fat and oil. Nevertheless, several issues remain to be addressed in order to have similar dry-cleaning results in CO₂ and PER. CO₂ removes significantly less particulate soil than PER. This is due to the low density difference between liquid and gas phase of CO₂ which leads to low level of mechanical action in CO₂ dry cleaning.

To fill in this gap, this study aims to improve the particulate soil removal in CO₂ textile dry cleaning by enhancing the amount of mechanical action applied to the fabric. A previous study showed that increasing the mechanical action by the addition of surfactant particles leads to a higher particulate soil removal [4]. In this study, the addition of particles as means to enhance mechanical action has been studied in more detail. This will be done by conducting washing experiments in a pilot-scale dry cleaning apparatus in the presence of co-solvent and surfactant, in which extra particles will be added in the cleaning chamber. The chamber will also contain textile samples soiled with several types of particulate soil and filling material. Furthermore, the process parameters, such as process temperature and washing time, will be varied to optimize the cleaning performance.

4.2. Materials and methods

4.2.1. Apparatus

The dry-cleaning experiments were conducted in a CO₂ dry-cleaning apparatus, which is schematically presented in Figure 4.1. The pilot-scale apparatus was designed and constructed at the Laboratory for Process Equipment, Delft University of Technology (the Netherlands). The cleaning chamber (Van Steen Apparatenbouw B.V., the Netherlands) has 0.25 m inside diameter and 25 L volume, equipped with an inner drum, with diameter of 0.21 m and volume of 10 L. The inner-drum, which is perforated and connected to a rotating shaft with speed of 75 rpm, is used to provide the mechanical action tumbling as in a regular washing machine.

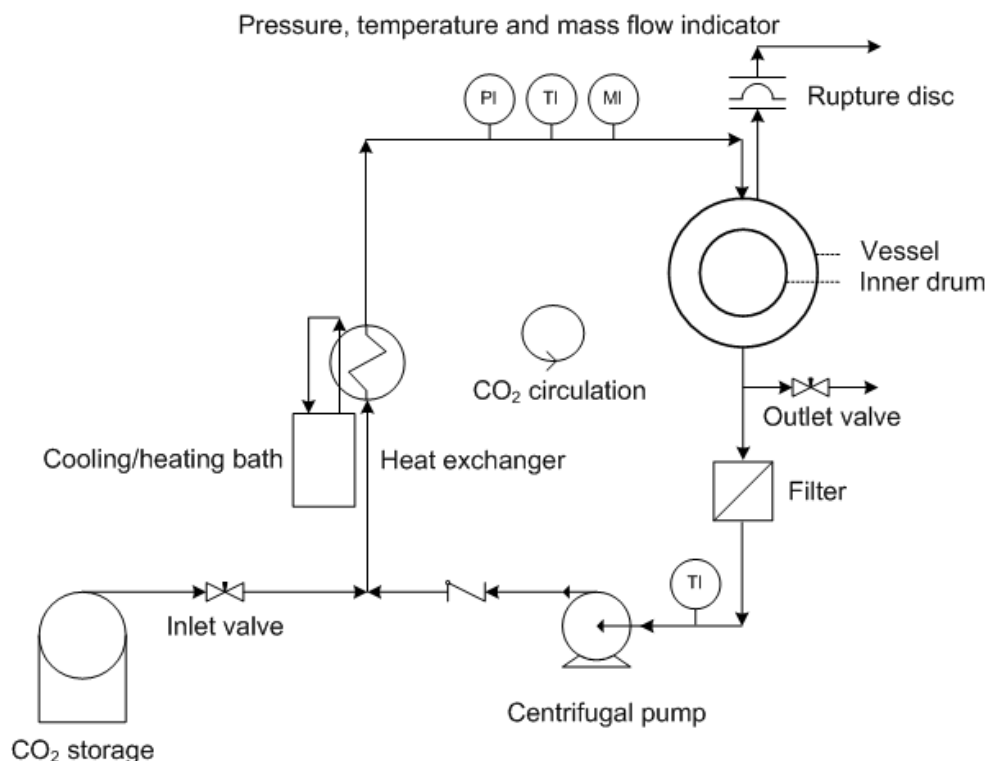


Figure 4.1: Schematic representation of dry-cleaning apparatus

4.2.2. Procedure

At the beginning of the experiment, 15 pieces of soiled monitors, the filling materials, and additives were placed inside the cleaning chamber. The system was then filled with CO₂ by opening the inlet valve until the desired amount of 6 kg was reached. CO₂ was circulated through the closed-loop system by a centrifugal pump. During each cycle of circulation, CO₂ passed through a heat exchanger to control the temperature which regulated the system pressure. CO₂ also passed through a filter with a pore size of 11 μm in order to prevent particles in the stream from entering the pump. After the washing step of 20 min. was complete, the used CO₂ was replaced by fresh CO₂ from the storage. The fresh CO₂ was also circulated for a short period of 10 min. to rinse the fabric. After the rinsing step, CO₂ was then released from the system by opening the outlet valve.

The temperature, pressure, fluid density, and circulation rate were monitored throughout the experiment. Unless mentioned otherwise, the standard process conditions that are given in Table 4.1 have been used. The influence of the additive type and amount, the CO₂ amount, the process temperature, the washing time, and the rinsing time were investigated. As a benchmark, the soiled fabrics were also cleaned in PER by a professional dry cleaner (Stomerij Buis, Delft). A standard dry-cleaning procedure and no pre-treatment were used. All given data are average values based on two or more replications for each experiment. More replications were performed when the standard deviation (σ) of the CPI is >3 because it is difficult to distinguish a trend if 95% of confidence (2σ) is used.

Table 4.1: Standard process conditions of CO₂ dry cleaning

Process Condition	Value	Unit
Rotational speed of inner drum	75	rpm
Washing load	400	g
Temperature	283	K
Pressure	50	bar
Washing time	20	min.
Rinsing time	10	min.
Amount of CO ₂	6	kg
Amount of water	25	g
Amount of IPA	250	g
Amount of Amihope LL	10	g
Amount of sand 0.2 mm	10	g

4.2.3. Materials

The materials consist of soiled monitors, filling material, CO₂, and several additives. Fifteen pieces of soiled test fabric (Center for Testmaterials B.V., the Netherlands) of 6.5 x 7.5 cm² were used in each washing experiment. They consist of three types of textile: cotton, polyester and wool, each stained with one type of particulate soil: clay, sebum colored with carbon black, sand, lipstick, and dust (see Figure 4.2). These monitors were fabricated by dipping the textile into the soil solution as such that each

piece of the same type contains a similar soil load, except for sand soiled materials which are hand-made. Note that sand on wool is not a standard test material, but has been custom-made for this study. Along with the monitors, cotton filling materials, 25x25 cm², were added into the cleaning chamber to reach the desired washing load of 400 g.

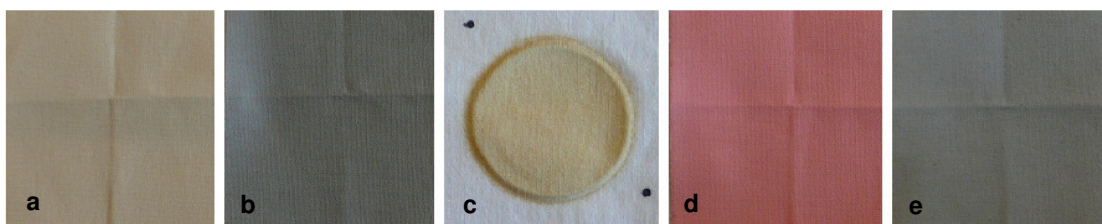


Figure 4.2: Picture of cotton monitors: clay (a), sebum colored with carbon black (b), sand (c), lipstick (d), and dust (e)

In each washing and rinsing step 6 kg of CO₂ grade 2.7 (Linde Gas Benelux B.V., the Netherlands) was used. Several types of surfactant were used in the experiments: 10 g of Amihope LL or *N*-lauroyl-L-lysine (Ajinomoto Co. Inc., Japan), Washpoint 2 (Linde Cleaning, USA), ClipCOO (Kreussler, Germany). The co-solvents were 250 g 2-Propanol (IPA) with a stated purity >98% (Prolabo, the Netherlands) and 25 g tap water. The additional particles were 10 g of 0.2, 0.5, 2, 5 mm sand (Filcom B.V., the Netherlands), or other additional particles as shown in Table 4.2. Unfortunately, further information such as density, of these particles is not available.

4.2.4. Analytical method

To monitor the cleaning results, the color of the fabric was measured before and after washing with a spectrophotometer Data Color 110, using Standard Illuminant C as light source: average daylight, excluding ultraviolet light. CIE 10° Supplementary Standard Observer was chosen as the viewing angle. The color was measured using the L*a*b* color space, where L* indicates the lightness, and a* and b* are the chromaticity coordinates: +a* is the red direction, -a* the green direction, +b* the yellow direction, and -b* the blue direction [5]. In this color space, the color difference (ΔE) is defined by Equation 4.1:

$$\Delta E_{1-2} = \left((L_1^* - L_2^*)^2 + (a_1^* - a_2^*)^2 + (b_1^* - b_2^*)^2 \right)^{0.5} \quad \text{Eq. 4.1}$$

The particulate soil removal is represented by Cleaning Performance Index (CPI), which is defined in Equation 4.2:

$$CPI = \left[1 - \frac{\Delta E_{\text{washed-unsoiled}}}{\Delta E_{\text{soiled-unsoiled}}} \right] \cdot 100\% \quad \text{Eq. 4.2}$$

Table 4.2: Additional particles and their suppliers

Particle	Supplier
Glass beads M 5011-99-5	Sigmund Lindner, Germany
SBA LewatitMonoplus M500	Caldic, Belgium
SAC LewatitMonoplus S100	Caldic, Belgium
(NH ₄) ₂ SO ₄	DSM, the Netherlands
Na ₂ SO ₄	Sigma Aldrich, Germany
Zinc oxide P0134	Lamers, the Netherlands
Ni oxide CF1018	Engelhard, USA
Tin oxide Nyacol SN15SD	PQ, USA
Al oxide/Co oxide/Mo oxide 465	Crosfield, England
Titanium dioxide CRS 31WT2	Rhone-Poulenc, France
Al oxide RV1570	Degussa, Germany
Mordenite T4559	SudChemie, USA
Na-ZSM-5 2122272	Akzo Nobel, the Netherlands
ZSM-5 Eka EZ472	Akzo Nobel, the Netherlands
Molecular sieve 5A	Uetikon, Germany
Silica sphere S 980 G 2.3 X3241	Shell, the Netherlands
SiC SIKA IV F16	Notox, the Netherlands
Al extrudates 1.6 M2154	Condea, Germany
Zeolite β extrudate T 4546	SudChemie, USA
Zeolite γ extrudate T4558	SudChemie, USA
CrO ₂ 11 T532	Harshaw, USA
α-Al ₂ O ₃ SA3235	Norton, USA

4.3. Results and discussion

4.3.1. Influence of additives

Influence of the type of additive on cleaning performance

The influence of additive types on cleaning performance has been investigated by performing the following washing experiments: CO₂ without any additives, with one additive -water, IPA, Amihope LL or sand- each time, and with all additives. The results are presented in Figure 4.3. Sand on wool, the non-standard test material, showed a large standard deviation and this material is thus excluded from the drawing of conclusion.

Figure 4.3 shows that only the cleaning results of lipstick and sand show positive influence of additives while the results of clay, carbon black, and dust do not show any significant influence. While big soil particles, e.g., sand, are more likely to be trapped between the fibers and yarns, the adherence of small soil particles, e.g. clay and dust, on the fabric is primary caused by Van der Waals forces, which makes the detachment of these small particles more difficult [6, 7].

From the washing results it can be concluded that the addition of co-solvents water and IPA tends to slightly increase the washing performance, as also found in the previous study [8, 9]. It was also found that negative cleaning results were obtained when IPA was used, mainly noticed on clay soiled materials and dust on cotton due to small ΔE of the fabric. Since the negative results are due to the soils which are released during the washing process (redeposition), it means that IPA triggers the soil release and is quite an important additive for the CO₂ dry cleaning result. These negative results were not observed in previous studies [4] because the particulate soil load was much lower.

In general, the presence of sand and Amihope LL -a surfactant that is present during the process as solid particles- tend to increase the cleaning results as presented in Figure 4.3. These results were consistent with those of a previous study [10]. Their presence might enhance the mechanical action by collision with the soil particles, releasing them out of the textile surface [11]. When all additives are used together, it considerably improves the cleaning performance for all types of material.

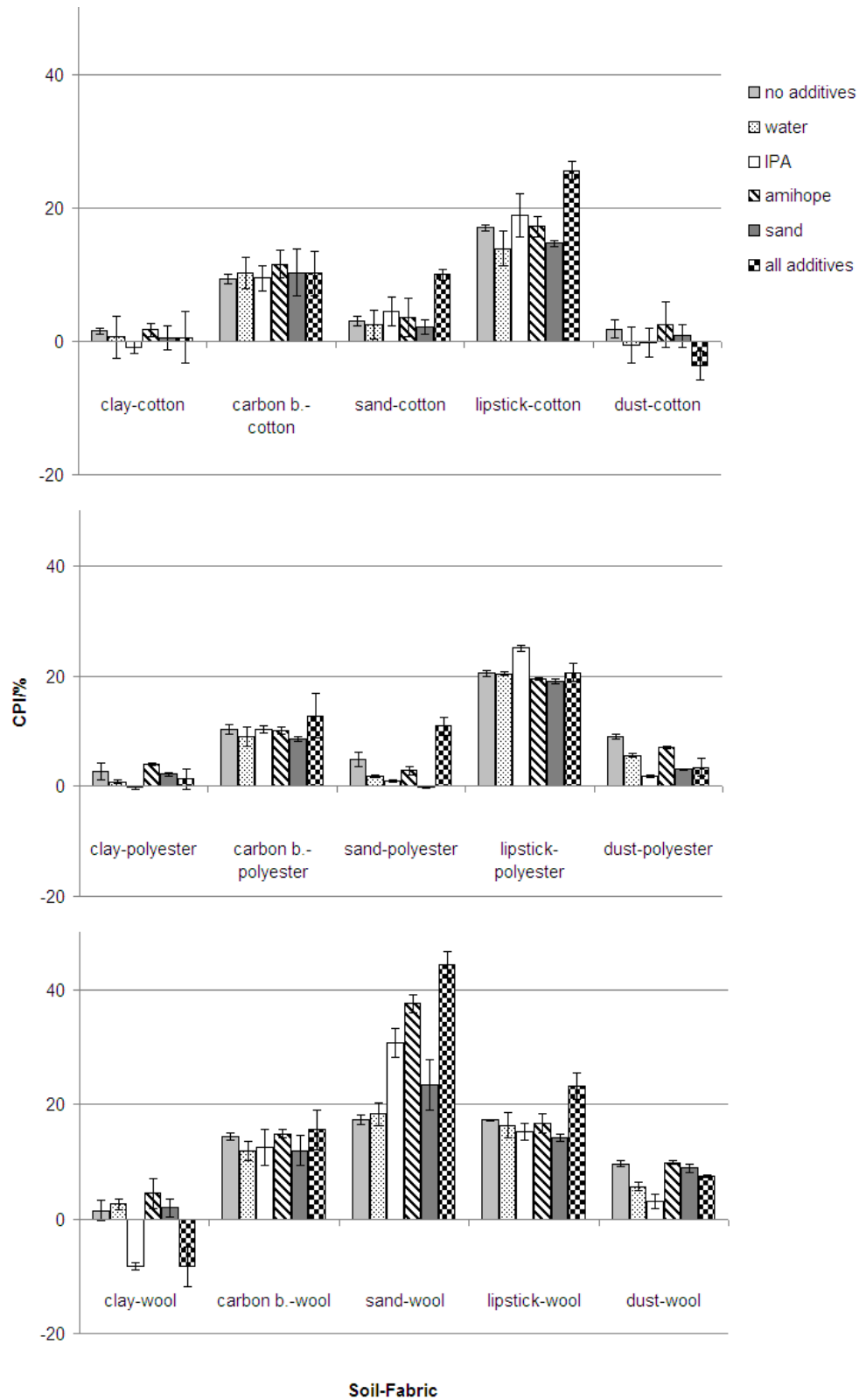


Figure 4.3: Influence of additive type on CPI for different types of soiled material

The presence of these additives gives the highest soil removal due to the enhancement of mechanical action or change of surface roughness. All additives were used for the rest of the experiments.

Influence of type of surfactant on cleaning performance

Using all additives in Table 4.1, surfactants for CO₂ dry cleaning were compared. Figure 4.4 shows that the washing performance of Amihope is inclined to be higher than ClipCOO and Washpoint. ClipCOO is the most commonly used surfactant in commercial CO₂ dry cleaners. In the previous study, the solubility test showed that Amihope is not soluble in CO₂ at the prevailing process conditions [4], and the possible cleaning mechanism has been explained. Based on these positive results, Amihope was used for the rest of the experiments.

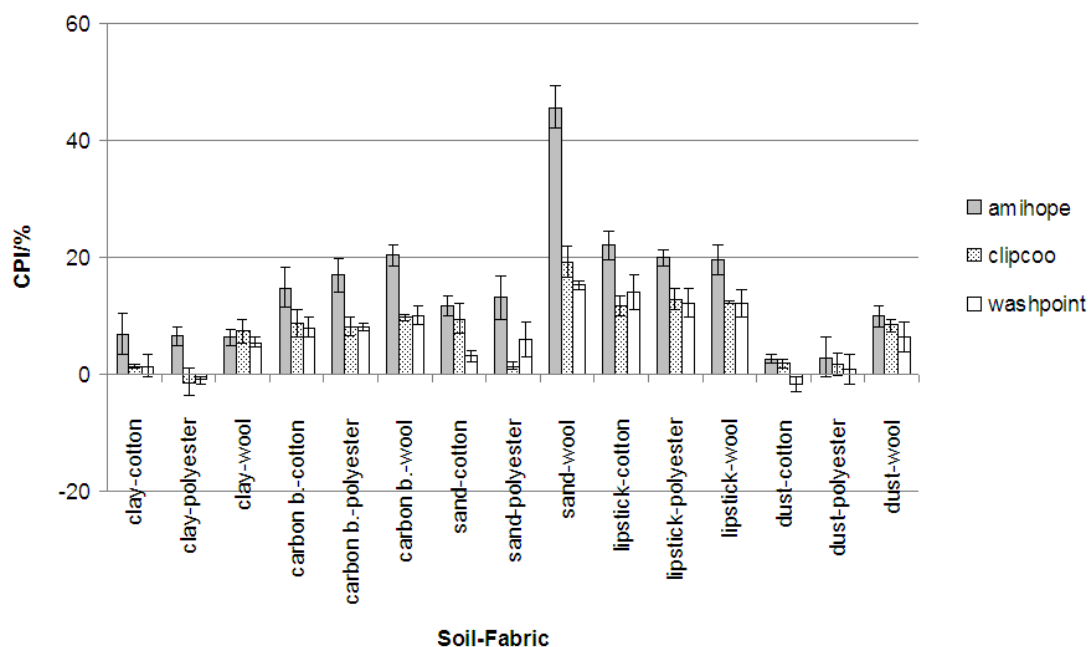


Figure 4.4: Influence of surfactant on CPI

Influence of particle diameter on cleaning performance

In these experiments, different sizes of sand particles were tested. Figure 4.5 shows the results using all additives, with the same amount of weight of sand particles in different diameters: 0.2 mm, 0.5 mm, 2 mm and 5 mm. In general, the results show no significant influence of sand diameter on cleaning performance. If each sand particle acted as a getter or carrier that attracts the soil particle on its surface, then the increase of particle size would decline the cleaning performance due to less surface area.

Furthermore, if this mechanism occurred, an experiment with same specific surface area (surface area/mass) of different sand diameter should have produced similar washing performance. However, the results shown in Figure 4.6 do not support this hypothesis. Some exceptions were observed on soiled wool material, where small diameter leads to better cleaning performance. Based on these results, 0.2 mm sand was used in the subsequent experiments.

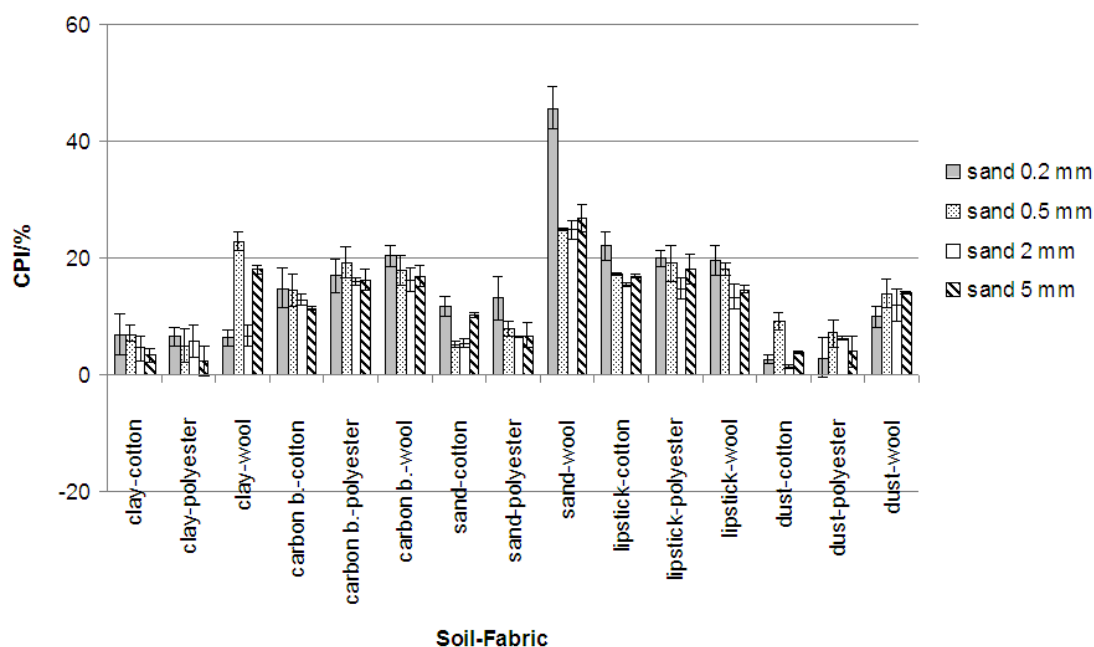


Figure 4.5: Influence of sand diameter on CPI

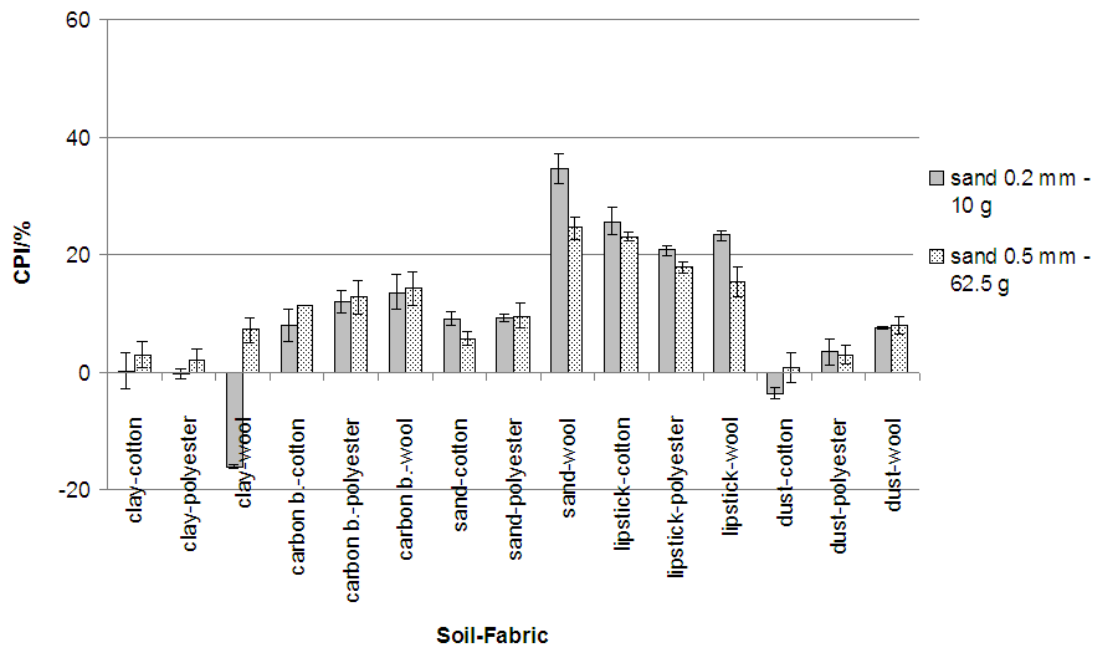
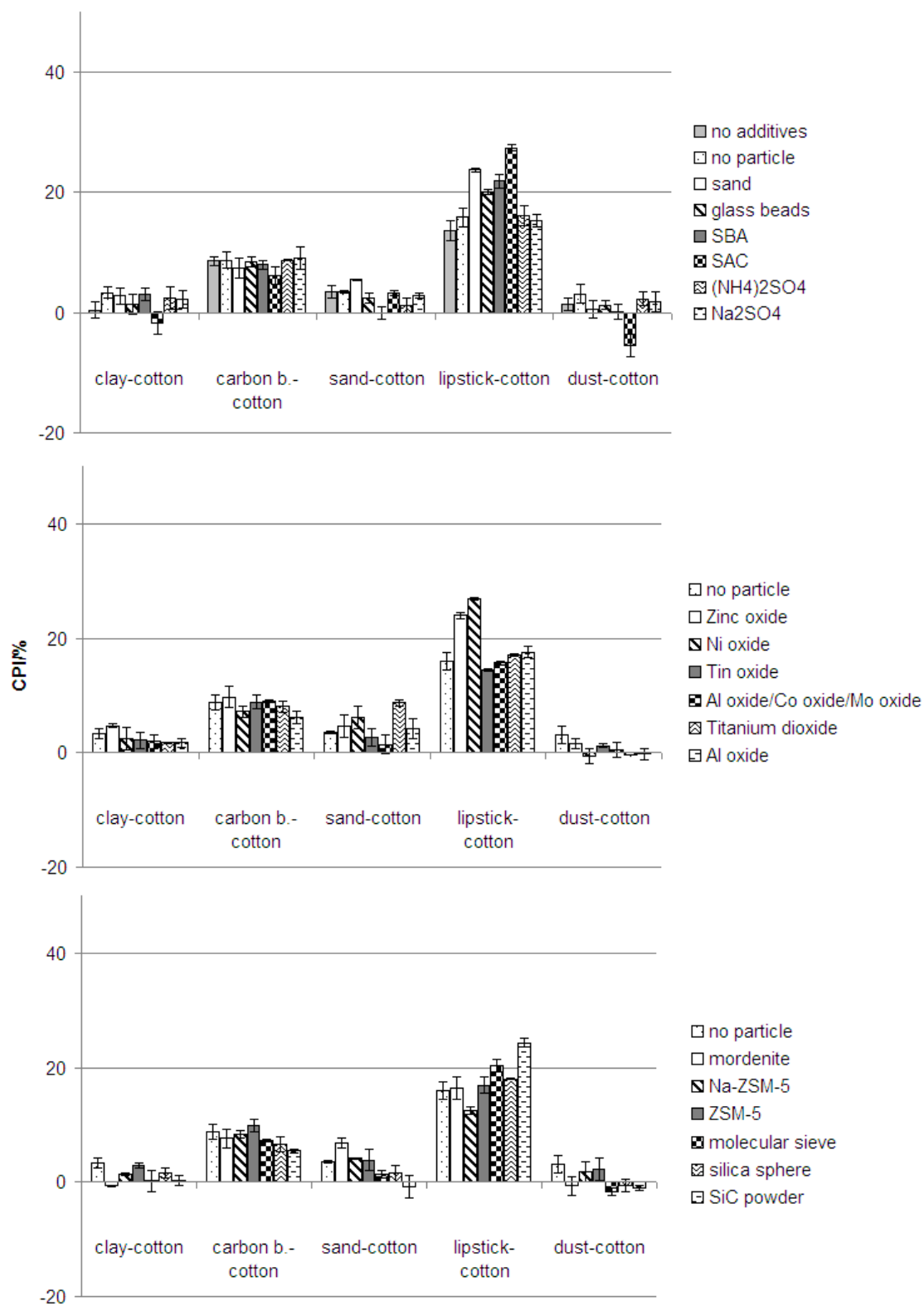


Figure 4.6: Influence of same specific surface area, different sand diameter on CPI

Influence of the type of additional particles on cleaning performance

Using operating conditions listed in Table 4.1, various types of additional particle in Table 4.2 were tested using all additives. The results are shown in Figure 4.7. These particles, ranged from salt, oxide, catalyst, etc., had been carefully chosen to be non-toxic, non-corrosive and non-harmful. Some of these particles, i.e. sand, glass beads, silica sphere, are not expected to react with the soil, textile, or CO₂. The opposite is true for the rest of the particles. To reduce the redeposition, the soil load was reduced to 5 pieces of soiled cotton material. Cotton soiled monitors were chosen because in general they show a lower washing performance compared to polyester and wool, so the effect of redeposition would be less pronounced. Only lipstick showed a tendency of an increase in soil removal around 10% by adding sand, SAC resin, zinc oxide, nickel oxide, SiC powder, and CrO₂ 11. For economic reasons, it was decided to continue using sand as additional particle for the rest of the experiments.



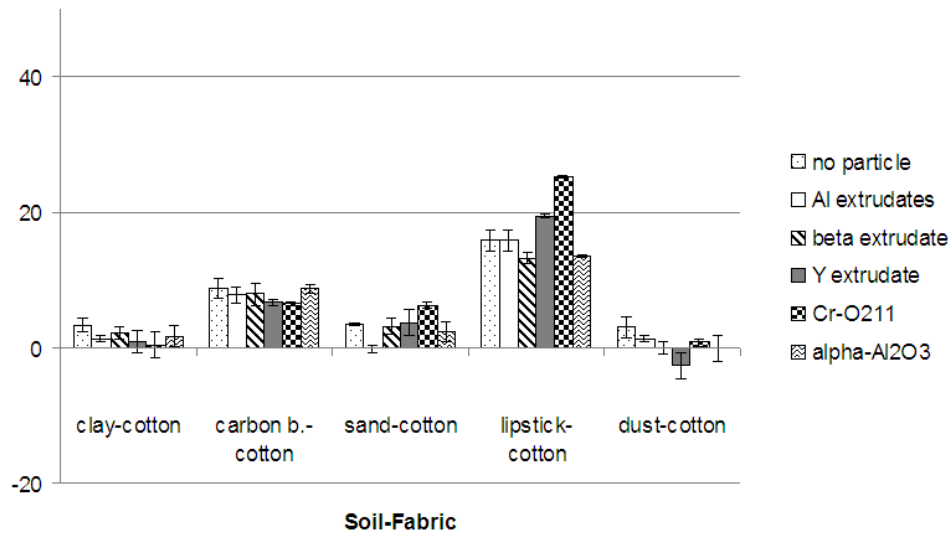


Figure 4.7: Influence of type of additional particles on CPI

Influence of particle amount on cleaning performance

The graph in Figure 4.8 shows the influence of the particle amount when all additives are applied together. Unless mentioned otherwise, the amount of each additive used in the experiment is given in Table 4.1: 25 g water, 250 g IPA, 10 g Amihope and 10 g sand. The amounts of water and IPA were not varied since they had been investigated in a previous study [4]. From Figure 4.8, it can be concluded that in some cases, increasing the amount of Amihope LL and sand shows a trend of better washing results because the amount of mechanical action is also increasing. The increase on the washing performance might be because of collision of sand or Amihope particles with the soil particles which helps the release of soil from textile surface.

4.3.2. Influence of the amount of CO₂ on cleaning performance

When the amount of CO₂ is increased from 6 kg (see Table 4.1) to 10 kg while other process parameters remain the same, in some cases the soil removal tends to increase as well. The comparison is shown in Figure 4.9. It is suspected that when a higher amount of CO₂ is used, the concentration gradient of soil is higher which triggers higher soil transfer.

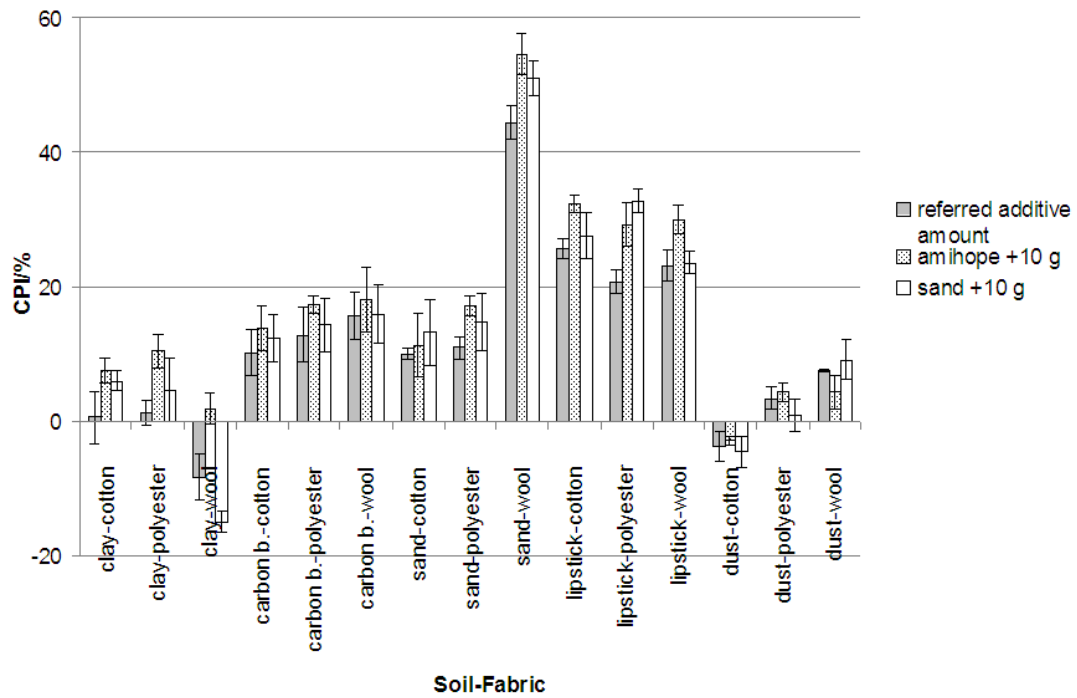


Figure 4.8: Influence of particle amount on CPI

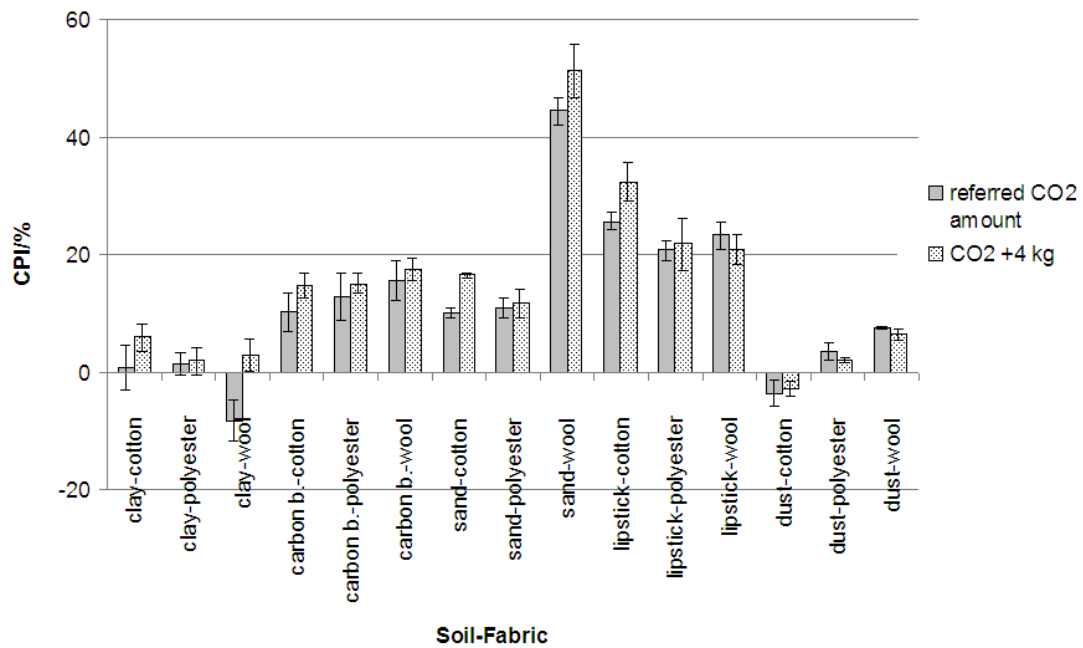


Figure 4.9: Influence of CO₂ amount on CPI

This is especially observed for the sebum colored with carbon black monitors and the lipstick monitors. Although the particulate soils, i.e. carbon black and color pigment, are not soluble in CO₂, the sebum and fat which binds these particles together are soluble in CO₂ (dissolution mechanism) [12].

4.3.3. Influence of process time and temperature on cleaning performance

From Figure 4.10 it can be seen that increasing washing and rinsing time from 20 and 10 to 40 and 20 minutes, respectively, does not significantly affect the washing results except slightly higher CPI for sand soiled materials. While increasing process temperature from 7°C to 25°C gave lower CPI especially for sand soiled material because the density difference between gaseous and liquid CO₂ at high temperature is lower, and thus the mechanical action produced was also lower (see Figure 4.11). The result is in line with the finding in a previous study [4], that removal of big particulate soil such as sand is more sensitive to the amount of mechanical action compared to small particulate soil.

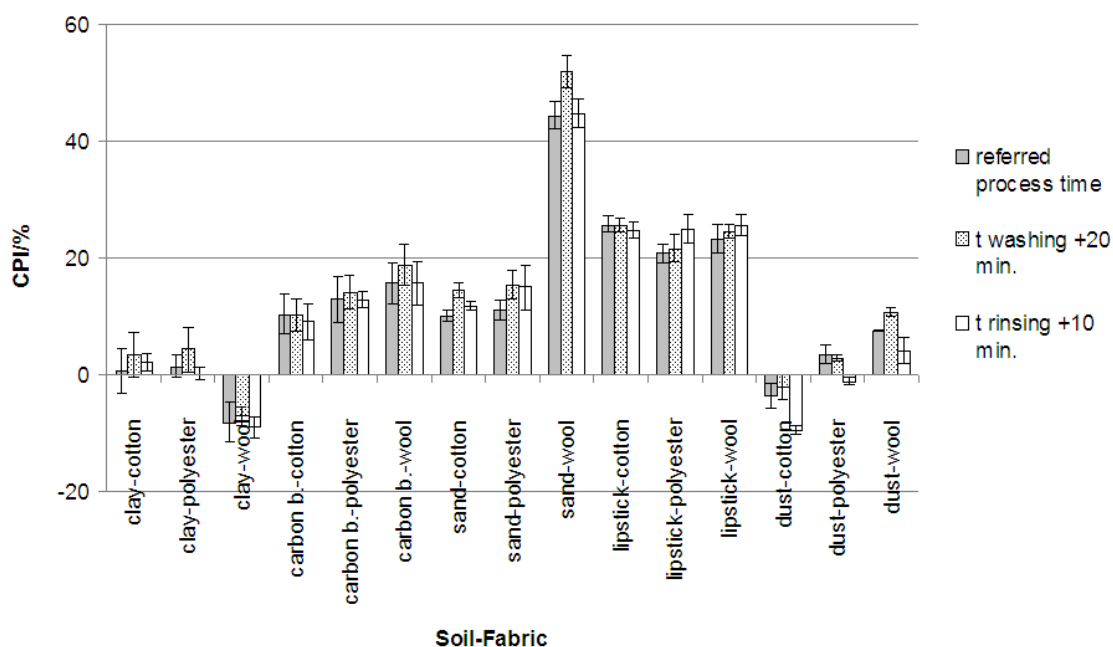


Figure 4.10: Influence of washing and rinsing time on CPI

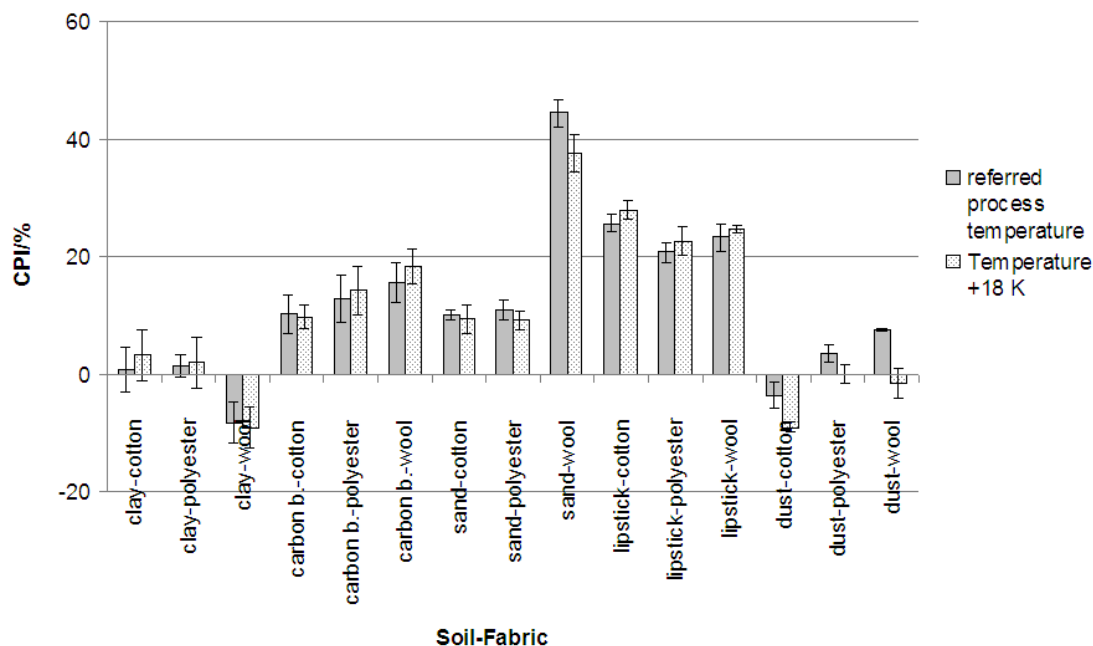


Figure 4.11: Influence of process temperature on CPI

4.3.4. Optimization of CO₂ dry cleaning and comparison with PER

The process conditions which gave the highest soil removal were combined in the experiment: 10 kg CO₂, 20 g sand, 20 g Amihope LL, 283 K (see Figure 4.12). As can be seen from the graph, the washing results with the optimized conditions are likely to be higher than the referred conditions in Table 4.1. The addition of particle and other additives could increase the absolute value of the average CPI from 9% to 15%, so with 67%. The cleaning performance of PER for the same materials are also given in this graph. It can be observed that the best washing results with CO₂ dry cleaning are on average still 65% lower than those with PER (relative difference). However, in reality it is hard to compare these results because of the difference in various parameters (such as soil load, amount of solvent compared to wash load, etc.) of both processes.

Graphs in Figures 3-8 show negative results due to redeposition: severe on clay soiled wool, light on other clay and dust soiled monitors. None of the negative results are observed in cleaning with PER. The rest of the results, although not negative, are also likely to be influenced by redeposition.

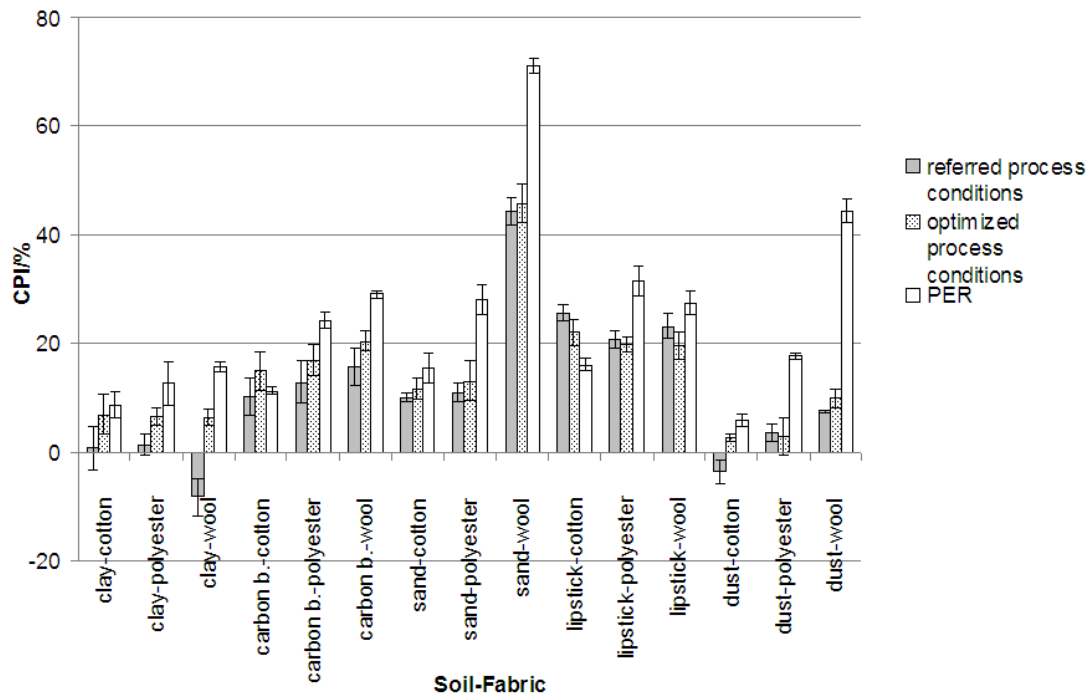


Figure 4.12: CPI of CO₂ and PER dry cleaning

4.4. Conclusion

In this study, the presence of additional particles for enhancing the cleaning performance has been investigated. The type, the size, and the amount of particles were varied. In addition, the amount of CO₂, the process time and the temperature were optimized to achieve a higher washing performance. From the experimental results, it is concluded that particle addition could increase the absolute value of the average CPI from 9% to 15%, with 67%. The increase was especially high for lipstick and sand soiled materials. It might be due to collision of these particles with the soil, which dislodged them from the textile surface. No influence of particle diameter or type of particles has been observed. Compared to other particles, sand is so far the most suitable extra particle from economical point of view. However, using loose sand particles in commercial scale dry cleaning might not be practical due to the difficulty of cleaning the vessel after the washing process and might eventually cause mechanical attrition in the dry cleaning system. Using Amihope LL as surfactant also

tends to give a higher CPI than commercial surfactants (ClipCOO and Washpoint). The optimal conditions for CO₂ dry cleaning in our apparatus are: 10 kg CO₂, 20 g sand, 20 g Amihope LL, 283 K. However, the cleaning performance using these optimized conditions in CO₂ dry cleaning is still lower (65%) than that of PER. Hence, another method to further improve particulate soil removal needs to be developed.

Acknowledgments

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Chapter 5

Acoustic Cavitation and Other Mechanisms to Induce Mechanical Action

Abstract

High pressure carbon dioxide (CO₂) is a potential solvent for textile dry cleaning. However, the particulate soil (e.g. clay, sand) removal in CO₂ is generally insufficient. Since cavitation has been proven to be beneficial in other CO₂ cleaning applications, this study aims to investigate the possibility of improving the performance of CO₂ textile dry cleaning by using ultrasound or other mechanisms to induce the mechanical action such as bubble spray and jet spray. In the experiments, several types of textiles soiled with a mixture of motor oil and soot were cleaned using 1 L and 90 L CO₂ dry cleaning apparatus. Using either ultrasound, stirring, liquid spray or bubble spray does not give a significant improvement on particulate soil removal from textile. It was also found that the additional use of ClipCOO detergent does not give a significant improvement on particulate soil removal either. The cleaning performance of CO₂ is 50% lower than that of PER and thus another method to increase the particulate soil removal in CO₂ textile dry cleaning still needs to be developed.

5.1. Introduction

Dry-cleaning is a process of soil removal from substrate, in this case garment/textile, which involves a non-aqueous solvent. This process was developed because some types of textile material are sensitive to water (wrinkle, shrink, etc.). perchloroethylene (PER) is commonly used as cleaning solvent in the textile dry cleaning industry. Unfortunately, this chemical is toxic, classified as probable carcinogenic, and harmful for the environment [1]. These drawbacks of PER have prompted the minimizing of PER exposure to below safety levels. However, the most elegant solution is to use alternative solvents for textile dry-cleaning. Carbon dioxide

has several combined advantages compared to other solvents such as Stoddard, Pure Dry, Green Earth or Rynex [2]. It is non-toxic, non-flammable, non-corrosive, safe for the environment, cheap, easily recovered, and available on a large scale. Furthermore, a drying step is not necessary because CO₂ evaporates from the fabric during the depressurization step.

Previous works [3, 4] have indicated that the performance of CO₂ was comparable and in several cases even better than PER for non-particulate soil removal (e.g. fat, proteins). On the other hand, the removal of particulate soil (e.g. sand, clay) using CO₂ was significantly lower compared to that of PER. Particle removal can be increased by mechanical action enhancement, which is the focus of this study. One of the available methods to improve the mechanical action in a cleaning process is by using ultrasound to generate cavitation.

Cavitation is the formation and immediate implosion of bubbles which generates fluid jets and shock waves that can be used for cleaning. Cavitation can be induced by an impeller or ultrasound. The rotation of impeller blades causes the formation of low pressure regions in the cleaning medium. When the vapour pressure is reached, the fluid vaporizes and small gas bubbles are created. The collapse of these bubbles then creates jets and shock waves [5]. Ultrasound is a longitudinal pressure wave with a frequency above 16 kHz. The frequencies of 20-120 kHz are often used for cleaning [6]. When ultrasonic sound waves travel through the cleaning medium, the negative acoustic pressure generates cavitation bubbles while the positive acoustic pressure causes these bubble to collapse [7].

The type of cavitation in textile cleaning is transient cavitation in which the formed bubbles are not stable. The pressure within the bubble cannot sustain the size of the bubble, leading to implosion of the bubbles. In the bulk liquid, the collapsing bubbles remain spherical while near the solid boundary, the asymmetrical implosion of bubbles generating liquid jets and shock waves which cause the cleaning effects [8].

Although little information is available on cavitation in CO₂ textile cleaning, it has been proven to be beneficial in other CO₂ cleaning applications such as cleaning of microelectronic components [9], spare parts [10], medical parts [11] and historical art pieces [12]. Furthermore, studies have reported successful application of

ultrasonic systems for water-based textile cleaning [13-15]. A Japanese washing manufacturer has a water based washing machine that uses ultrasound waves [16]. However, other studies have reported unsatisfactory results due to the erosion effect and the formation of air bubble layers [17, 18].

In this study, the possibility to improve the cleaning performance of CO₂ textile dry cleaning by using acoustic cavitation and other available mechanisms has been investigated. Washing experiments were performed in 1 L and 90 L pilot-scale CO₂ dry cleaning apparatus equipped with different mechanisms to induce mechanical action. In addition, the influence of the commercial surfactant ClipCOO was also examined. Besides the cleanability, special attention is given to so-called redeposition which has been observed in a previous study [19]. Redeposition is a process of soil transfer from one position to another or from one piece of textile to another, in situations where the released soil is not properly stabilized in or removed from the cleaning medium.

5.2. Materials and methods

5.2.1. Materials

Soiled test fabric (4 x 4 cm²) was used in the washing experiments. A mixture of motor oil with soot - on four different types of textile (cotton, polyester, polyester/cotton 65/35 (polycotton), and wool) was used. These monitors were purchased from WFK (Germany) and fabricated using a spraying method in such a manner that each piece contains a similar soil load. The average value and the standard deviation of reflection coefficient (R) of all soiled samples before washing that were used in the experiments is given in Table 5.1.

Table 5.1: Average and standard deviation of R of unwashed samples

Fabric	Average R_{sample}	Standard Deviation R_{sample}
Cotton	38968,24	39,84
Polyester	42933,16	36,86
Polycotton	39600,88	40,72
Wool	40627,89	27,47

CO₂ grade 3.7 was purchased from Linde Gas Benelux B.V. (the Netherlands) for the 1 L apparatus, and technical grade CO₂ (99.9%) from Air Liquide for the 90 L apparatus. In some of the experiments, Clip-COO (Kreussler, Germany) was added to the cleaning vessel as a detergent in CO₂ dry cleaning. The used amount was 1 mL in 1 L set-up and 10 mL in 90 L set-up. Clip-COO is used in this study because it is the detergent which is utilized by existing CO₂ dry cleaners and thus it is expected to improve the cleaning performance.

5.2.2. Apparatus and procedure of 1 L apparatus

A dry-cleaning apparatus containing a high pressure cell was used for cleaning soiled monitors in CO₂ (see Figure 5.1). The cell is equipped with a hollow wall which does not reach the top of the cell, and connected to a cooling/heating water bath so that it serves as a cooling/heating jacket. The cell has a diameter of 8 cm, length of 25 cm and 1 L working volume. The apparatus was developed by Unilever (Vlaardingen, The Netherlands). The washing time was fixed to 1 hour. The temperature (12°C) and the pressure (47 bar) of the system were regulated with a cooling/heating bath. Mechanical action was provided by 1) regulating the process temperature (*bubbling*) or by 2) a rotating stirrer with paddles blade at velocity of 60 rpm or with 3) an ultrasound transducer at the bottom of the cell (power output of amplifier 180 W; optimum frequency of 24.5 kHz was obtained by plotting the measured output power on different frequencies and then opting the frequency that gave the minimum power i.e. most of the energy was adsorbed by the system and the strongest cavitation was observed).

In each experiment 0.72 L of liquid CO₂ was used. Before each experiment, the cell was cleaned with ethanol and rinsed with de-ionized water and then flushed with CO₂. In all cleaning experiments, 2 samples of each textile material were cleaned together: one unstained sample to monitor the redeposition level [19], and one stained sample. The cleaning experiments were repeated three times for each fabric. The presented data are the average values with the error bars. After cleaning, both fabric samples were characterized with respect to their cleanability and soiling degree due to soil re-deposition during the cleaning process.

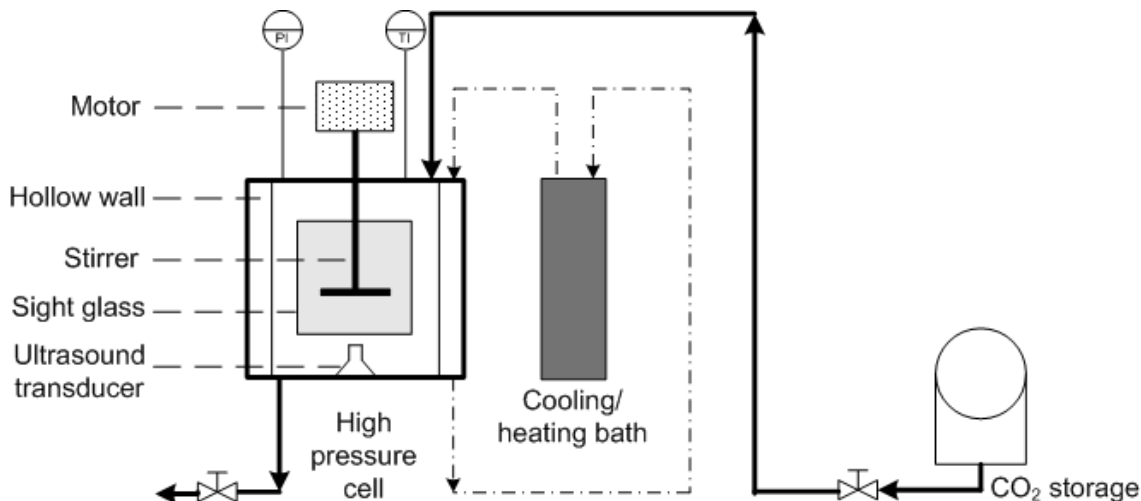


Figure 5.1: The schematic diagram of 1 L apparatus

5.2.3. Apparatus and procedure of 90 L apparatus

A prototype of a liquid CO₂ machine (elCO₂) from Amsonic Precision Cleaning AG/SA was used for textile cleaning. The apparatus has been used with liquid CO₂ at a temperature of 15-20°C and a pressure of 51–57 bar. The 90 L cleaning chamber (autoclave) contains a washing basket. The mechanical action upon the textile material was provided by three different mechanisms: 1) gaseous CO₂ flow through several holes that were located at the bottom of the autoclave i.e. bubble spray, or 2) an integrated ultrasonic transducer or 3) liquid spray of CO₂ flow from several holes located at the top of the autoclave with a maximum flow rate of 240 L/min (Figure 5.2). The apparatus was equipped with a CO₂ compressor and a series of filters between 25 µm and 5 µm to remove particles from the CO₂ flow. The drawing of this apparatus which is located at Fraunhofer IPK, Germany, and a detailed procedure has been described in a previous study [11].

At the beginning of the washing process, 400 g of textile material was placed in the cleaning basket. The autoclave was first pressurized with gaseous CO₂ and then filled with liquid CO₂ from the storage unit. During the washing process, one of the three mechanical actions was applied. At the end of the washing process, the liquid CO₂ was drained from the autoclave into the storage tank by the compressor

and subsequently the pressure in the autoclave is reduced again to atmospheric conditions.

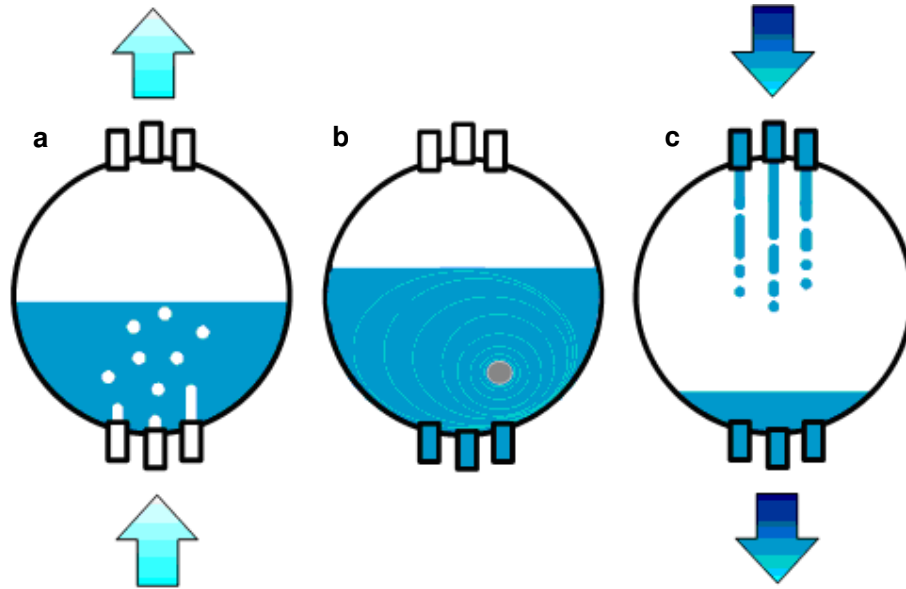


Figure 5.2: Schematic illustration of the mechanical actions in 90 L apparatus: a) bubble spray; b) ultrasound; c) liquid spray

5.2.4. Analytical method

The soiling degree was evaluated by measuring the colour difference of the textile samples using a scanner. A detailed procedure has been described in a previous study [20]. From the measured reflection coefficient (R), the soiling additional density (SAD) can be calculated using Equation 5.1.

$$SAD = \log \frac{R_{reference}}{R_{sample}} \quad \text{Eq. 5.1}$$

Where $R_{reference}$ is the reflection coefficient of a reference (without soiling) and R_{sample} is the reflection coefficient of a soiled or washed sample. The percentage cleanability (Γ) is defined in Equation 5.2.

$$\Gamma = \frac{SAD_{before washing} - SAD_{after washing}}{SAD_{before washing}} \cdot 100\% \quad \text{Eq. 5.2}$$

Using Equation 5.3, the redeposition level (RL) can be calculated by measuring the reflection of the reference before and after washing.

$$RL = \frac{SAD_{before washing} - SAD_{washed reference}}{SAD_{before washing}} \cdot 100\% \quad \text{Eq. 5.3}$$

5.2.5. PER dry cleaning

The soiled fabrics were also cleaned in PER by a professional dry cleaner (Buis Stomerij, Delft, the Netherlands), using a standard dry-cleaning procedure with rotating drum and no pre-treatment, and used as a benchmark.

5.3. Results and discussion

5.3.1. Optical observation of the bubbling process

In a preliminary study, the 1 L high pressure cell was used to optically observe the occurrence of bubbling. Since no extra energy source was used, these bubble formations were expected to be driven by thermodynamics. After filling the cell with CO₂, the temperature of the cooling medium (water) was lowered to reach the desired process temperature of 12°C. The behaviour of CO₂ inside the cell as a function of time is shown in Figure 5.3. It was observed that bubbling starts upon decrease of temperature, and after a while the bubble size gets larger, and in time the bubble size decreases while bubble amount increases.

After the final temperature had reach steady state, the bubbling effect was still observed for hours. Since the content of the cell was not mixed, the equilibrium state was reached slowly. During this period, the bubbling effect was constantly observed although the amount of bubbles were decreasing in time. It took 36 h before the bubble disappeared completely. The temperature sensor was located on the top of the vessel (gas phase). The L-V phase diagram of CO₂ during one of the observations of the bubbling process is presented in Figure 5.4.

It is hypothesized that as temperature is being lowered (Figure 5.4), the change in temperature demands different equilibrium vapour pressures with time. Since the thermodynamic driving force dictates to stay in equilibrium, the system automatically tries to bring down its pressure to keep it equal to the continuously decreasing equilibrium vapour pressure, which corresponds to the continually

decreasing liquid temperature. To bring down the pressure, some gas is automatically condensed (both at the walls and the interface). However, during condensation, latent heat of condensation is liberated, thus providing energy in the system.

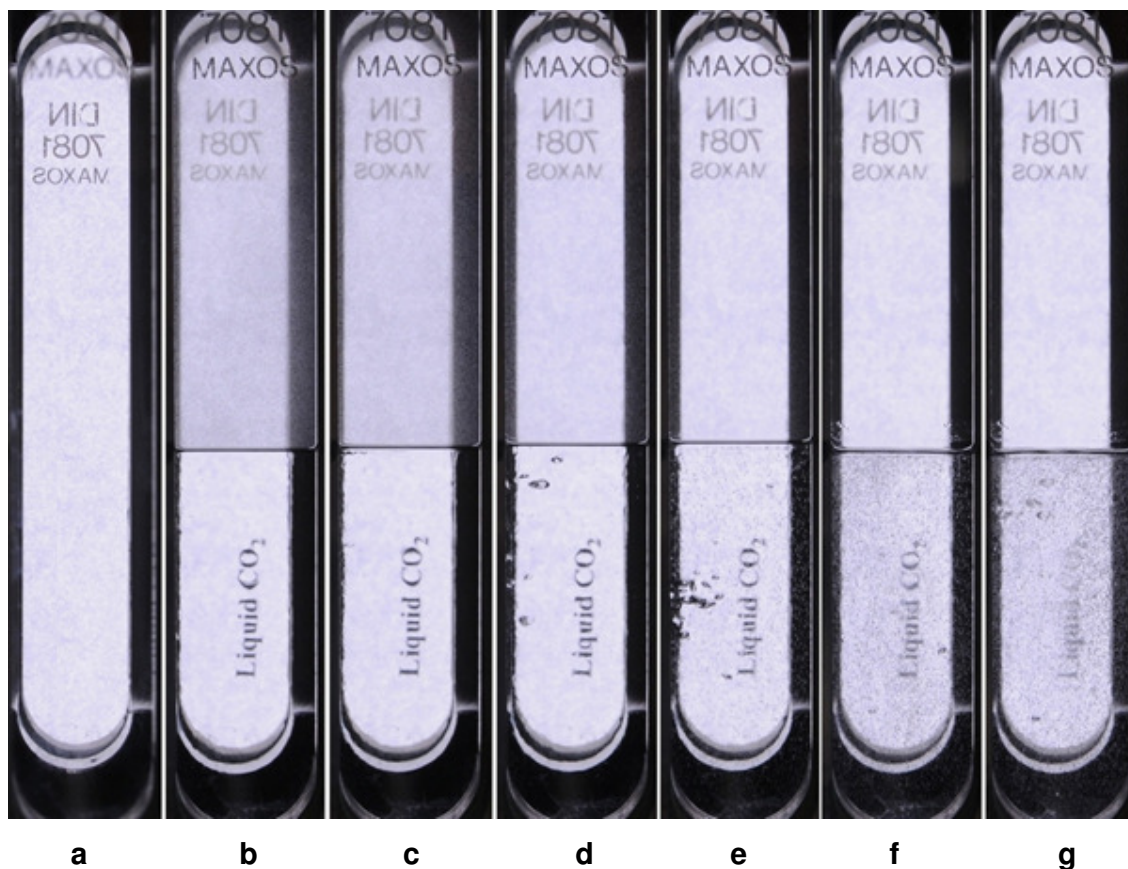


Figure 5.3: Different states of CO₂ in a high pressure cell: a) the cell before filling; b) the cell is filled with CO₂; c) bubbling starts at the interface upon decrease of temperature; d) and e) bubble size gets larger with time; f) and g) bubble size decreases while bubble amount increases

In addition, the design of the cell is as such that the cooling jacket does not reach the top of the cell (see Figure 5.1). Since the top of the cell is at ambient temperature, there is also some sensible heat transfer from the top of the cell to the inner content of the cell which is at a lower temperature (surrounded by cooling jacket). The sum of these two energy inputs into CO₂, in turn results in the evaporation of some CO₂. This evaporation is seen as bubbling. This

condensation/evaporation goes back and forth since the content of the cell is not stirred. Therefore, the pressure-temperature diagram fluctuates around the thermodynamic vapour pressure curve, but ultimately, the trend follows the slope of the vapour pressure curve. Thus, it confirms that the driving force for the observed phenomenon is to keep the system at the equilibrium conditions.

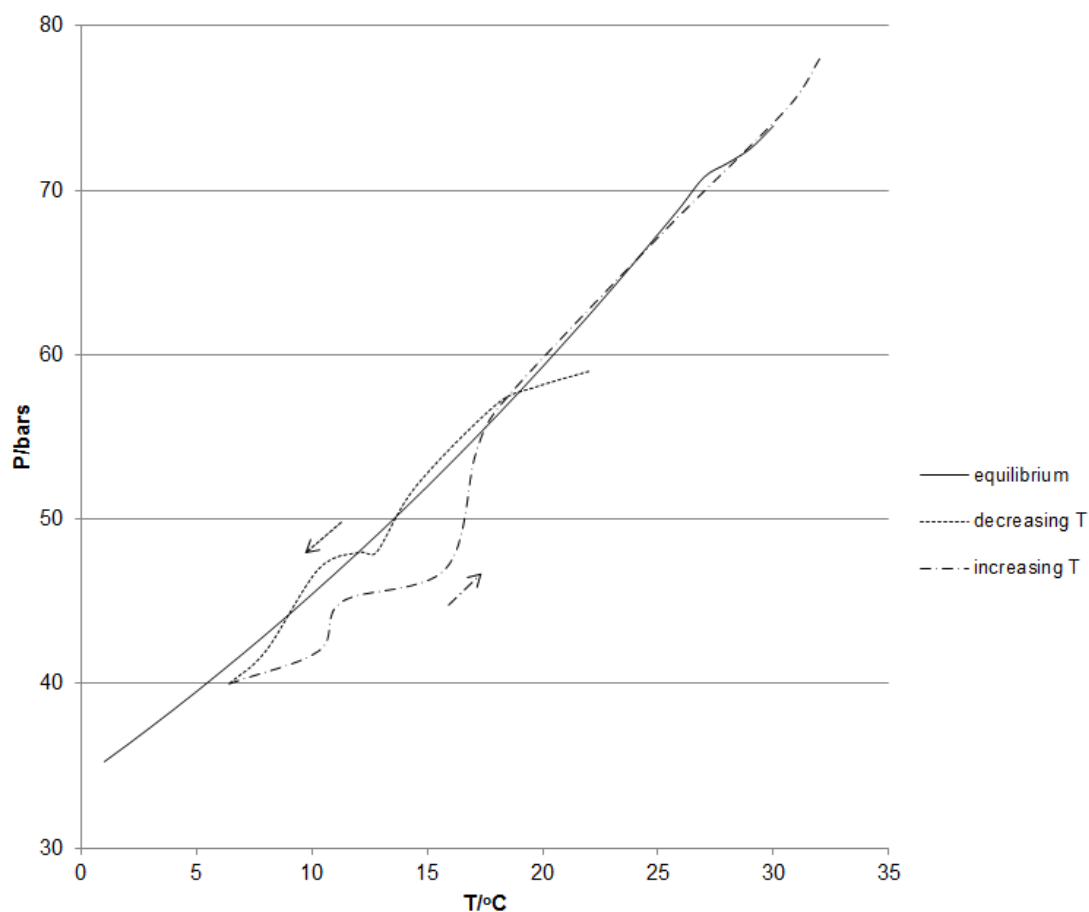


Figure 5.4: CO₂ L-V phase diagram during the observation of bubbling process at decreasing temperature from 23°C (room T) to 12°C, and then from 12°C to 7°C, followed by increasing temperature from 7°C to 12°C, and then 12°C to 33°C

Similar behaviour was also observed when the temperature of the water was raised (Figure 5.4) but less bubble formation was observed. The reason behind this observation is however still unclear.

5.3.2. Influence of different types of mechanical action

The influence of different types of mechanical actions on cleaning performance and redeposition level in the 1 L apparatus are presented in Figure 5.5 and Figure 5.6, respectively. Unfortunately, a process condition with a complete absence of mechanical action (cavitation) cannot be reached in liquid CO₂ due to the way the apparatus was constructed, and thus cannot be used as a reference. Therefore, bubbling data with decreasing temperature have been used as a reference for the absence of the external mechanical action in the 1 L apparatus.

For most substrates, ultrasound does not significantly increase soil removal compared to bubbling, although according to the calculation in Appendix 5.1, the ultrasonic transducer used in the 1 L apparatus is powerful enough to induce cavitation. The limited increase in cleaning performance may be due to the relatively large distance between the textile and the transducer or because the surface of the textile is not parallel to the surface of the transducer.

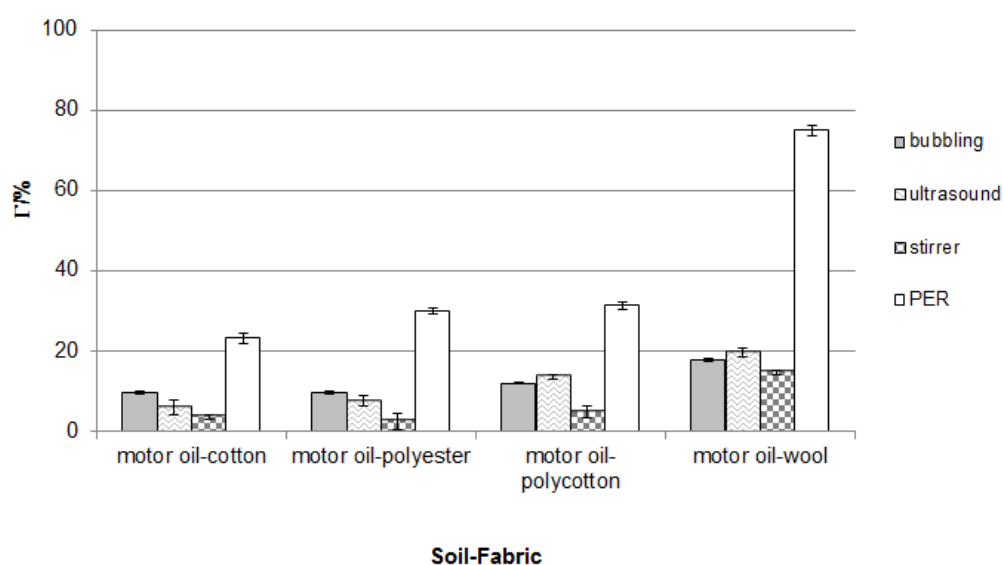


Figure 5.5: Influence of different types of mechanical action on cleanability with 1 L apparatus

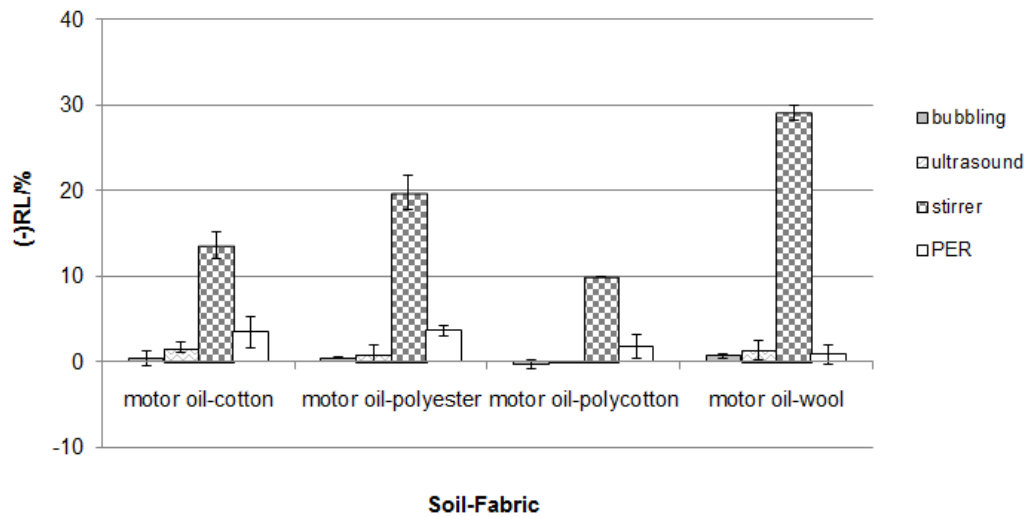


Figure 5.6: Influence of different types of mechanical action on redeposition level with 1 L apparatus

Stirring induced high turbulence and thus high redeposition level because the apparatus is not equipped with circulation or filter to remove the dislodged soil. However, the high redeposition level shows that many particles have been dislodged from the textile. In bubbling and ultrasound, the particulate soil has a greater probability (compared to stirring) of settling on the bottom of the cell due to gravitational force. Because of the way the equipment is built and the high redeposition levels, it cannot be concluded which is the best way to remove particles from the textile from the 1 L apparatus.

Additional experiments have been conducted in a pilot plant from Amsonic Precision Cleaning AG/SA. The influence of different mechanical actions on the cleaning performance in the 90 L apparatus is presented in Figure 5.7, with no mechanical action (none) as reference. It appears that among the available types of mechanical action (bubble spray, ultrasound and liquid spray), liquid spray for most cases shows the highest cleaning performance. However, the overall influence of all three sources of mechanical action on the cleaning results is not significant. The soil redeposition level was low (<1%) due to the continuous soil removal by a filtration system. Please note that the results of 1 L and 90 L apparatus cannot be directly compared because these apparatus were designed differently.

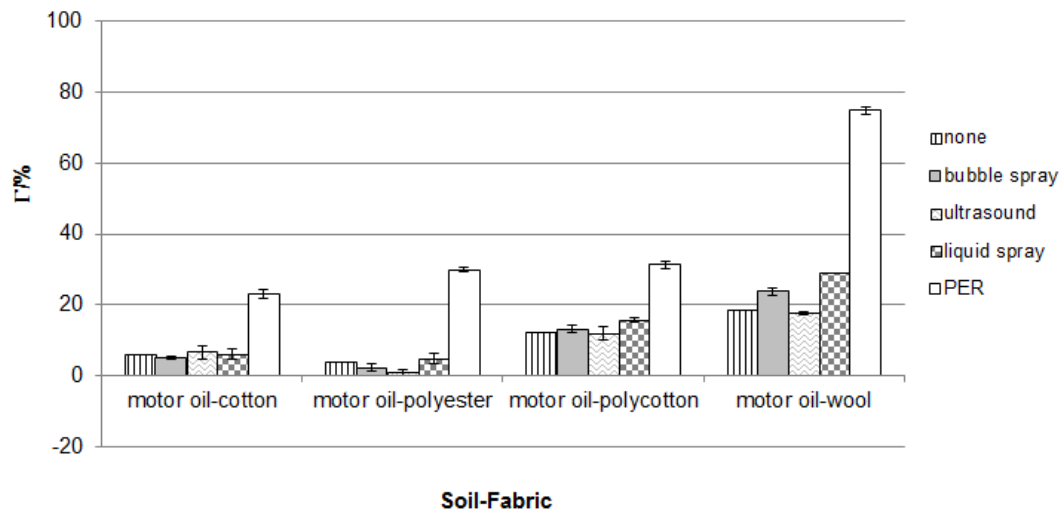


Figure 5.7: Influence of different mechanical actions on cleanability with 90 L apparatus

Figures 5.5-5.7 also give the comparison of cleaning performance and redeposition level of CO₂ dry cleaning with those of PER, performed by a professional dry cleaner as a benchmark. In all cases, the cleaning performances of CO₂ dry cleaning are 50% lower than those of PER.

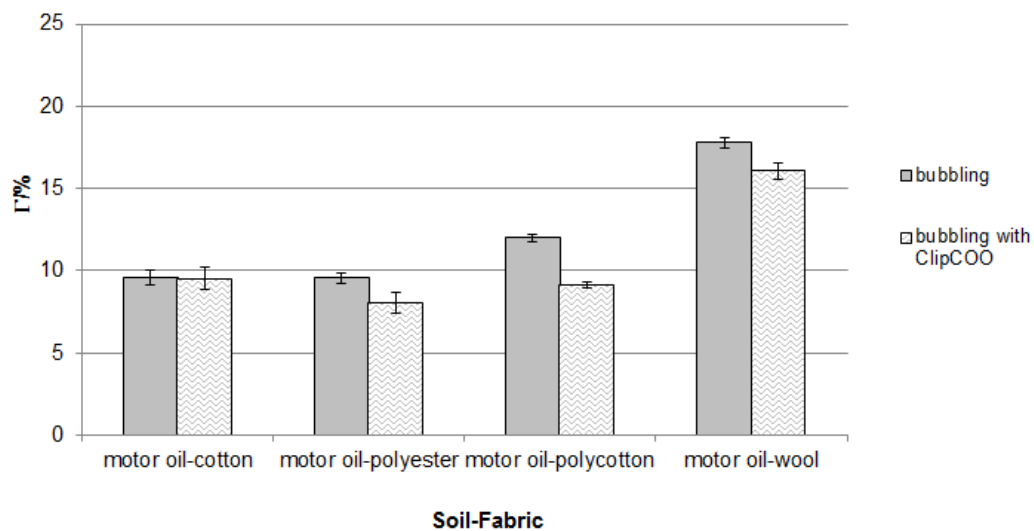


Figure 5.8: Influence of ClipCOO detergent on cleanability with 1 L apparatus

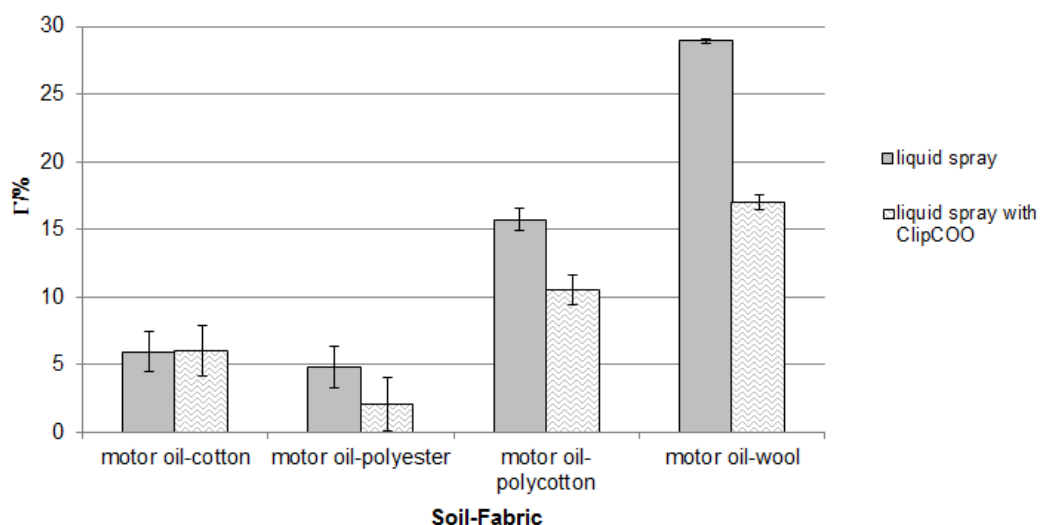


Figure 5.9: Influence of ClipCOO detergent on cleanability with 90 L apparatus

5.3.3. Influence of using ClipCOO detergent

The influence of using ClipCOO (a mixture of non-ionic surfactants commonly used by professional CO₂ dry cleaners) as detergent in combination with various ways to increase mechanical action on cleaning performance is illustrated in Figure 5.8 and Figure 5.9. The comparison was performed for bubbling in 1 L apparatus and liquid spray in 90 L apparatus. It is observed that in both cases using ClipCOO does not improve the cleaning performance which in this case, particulate soil removal.

5.4. Conclusion

Using either ultrasound, stirring, liquid spray or bubble spray does not give a significant improvement on soil removal within the tested operating range. The additional use of ClipCOO detergent also does not give a significant improvement on particulate soil removal. The cleaning performance of CO₂ is still 50% lower than that of PER and thus another method to increase the soil removal in CO₂ textile dry cleaning needs to be developed or currently tested methods should be adapted.

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Appendix 5.1

The purpose of this appendix is to determine if the ultrasonic transducer used in the 1 L apparatus is powerful enough to induce cavitation. First, the Blake threshold pressure i.e. the minimum acoustic pressure to initiate the growth of a cavitation bubble in CO₂ dry cleaning system is calculated based on [21] using the CO₂ data from NIST table. The Blake threshold pressure is defined in Equation 5.4:

$$P_B = P_0 - P_V + \frac{4}{3} \times \sigma \times \sqrt{\frac{2}{3} \times \frac{\sigma}{\left(P_0 + 2 \times \frac{\sigma}{R_0} - P_V\right) \times R_0^3}} \quad \text{Eq. 5.4}$$

With	P_B	=	Blake threshold pressure	Pa
	P_0	=	Ambient pressure	Pa
	P_V	=	Vapor pressure	Pa
	σ	=	Surface tension	N/m
	R_0	=	Equilibrium bubble radius	m

The high vapour pressure in CO₂ reduces the Blake threshold and thus enables cavitation to occur in liquid CO₂. At the dry cleaning conditions of 12°C and 47 bar ($P_0 = 4.7 \cdot 10^6$ Pa), the vapour pressure (P_V) is $4.7 \cdot 10^6$ Pa. The surface tension is $2.3 \cdot 10^{-3}$ N/m and to create a bubble with a radius of 10^{-5} m (average bubble size [21]), the calculated Blake threshold pressure is 177 Pa.

Secondly, the required sound intensities to create cavities for a certain acoustic pressure can be calculated with Equation 5.5:

$$I = \frac{P_A^2}{2\rho v} \quad \text{Eq. 5.5}$$

With	P_A	=	Acoustic pressure	Pa
	ρ	=	Medium density	kg/m ³
	v	=	Sound velocity	m/s
	I	=	Intensity of sound	w/m ²

The velocity of sound (v) in CO₂ is 415 m/s, and having the density (ρ) of liquid CO₂ to be 841 kg/m³, the corresponding intensity for the Blake threshold pressure of 177 Pa is $4.5 \cdot 10^{-6}$ W/cm².

The power given by the amplifier is 180 W with the surface area of the transducer of 1 cm^2 , leading to the available sound intensity of 180 W/cm^2 . Since the available intensity is higher than the threshold intensity, it can be concluded that the transducer is powerful enough to overcome the threshold pressure and thus theoretically cavitation can occur.

Chapter 6

Mechanical Action in CO₂ Dry Cleaning

Abstract

High-pressure carbon dioxide (CO₂) is a potential alternative for perchloroethylene (PER), a common but harmful textile dry cleaning solvent. Previous studies have indicated that the particulate soil removal with CO₂ is lower compared to that with PER, because of the low amount of mechanical action in CO₂. It is the objective of this study to achieve more insight in the influence of various types of mechanical action on the cleaning results in CO₂ dry cleaning. In the experiments, various mechanisms of mechanical action, such as rotating drum, CO₂ spray, and ultrasound were investigated. Several types of textiles stained with different kinds of particulate soils were cleaned using 25 L and 90 L CO₂ dry cleaning apparatus. The washing results show that liquid CO₂ spray may be a suitable additional mechanism to provide textile movement. The average CPI of CO₂ over all soils using the best combination of commercial machine and process was still 25% lower than the results with PER and 18% lower than the results with water, but 11% higher than K4 solvent while the average redeposition level was significantly lower, showing that CO₂ has a good prospect as an alternative solvent to replace PER. An endoscopic camera has been installed in the 25 L apparatus to get an insight in the textile movement inside the rotating drum. The results show that no plug formation occurs and the textile movement in CO₂ is sluggish, which means that the mechanical movement of textile in CO₂ dry cleaning does not follow the simplified tumbling-movement model which was developed in a previous study, and the mechanical action is much less than predicted.

6.1. Introduction

Dry cleaning is a process of soil removal from substrate, in this case garment/textile, which involves a non-aqueous solvent. This process was developed because some types of textile material are damaged by water, e.g. they wrinkle, shrink, etc. The most common solvent used in conventional dry cleaning is perchloroethylene (PER). Despite its good cleaning performance, PER has several drawbacks such as various toxic effects to the human body. Approach to mitigate these effects is either to avoid exposure or to develop alternative solvents or technologies.

Several alternative solvents for textile dry cleaning include hydrocarbon solvents, silicon based solvents and carbon dioxide (CO₂) [1]. CO₂ has several advantages compared to the other solvents. It is non-toxic, non-flammable, non-corrosive, safe for the environment, cheap, easily recovered, and available on a large scale. Furthermore, the drying step is not necessary because CO₂ evaporates from the fabrics during the depressurization step. However, previous studies [2,3] have indicated that CO₂ removes significantly less particulate soil than PER.

Generally there are two steps in particulate soil removal from textile: the soil loosening step where the binding forces between the soil and the textile are broken, followed by the soil transfer step where the dislodged soil is transported from textile to solvent [4]. In both steps, mechanical action is necessary to create textile deformation by bending, twisting or stretching the yarns, so that liquid flow of solvent can penetrate deeper into the yarns and aid the soil removal steps [5]. In regular washing machines, this liquid flow is provided by a rotating drum. In a CO₂ dry-cleaning machine with a rotating drum, the low density difference between the liquid and the gas phase of CO₂ leads to a low level of mechanical action in CO₂ dry cleaning compared to water and PER. There is also a lack of understanding of the textile movement inside a rotating drum.

This study aims to achieve more insight in the influence of various types of mechanical action on the cleaning results in CO₂ dry cleaning and the textile movement inside a rotating drum. This is done by conducting washing experiments in pilot-scale dry cleaning apparatus and introducing various mechanical actions, such as rotating drum, CO₂ spray and ultrasound in the presence of additives.

Experiments were also performed in existing industrial scale dry cleaning machines with rotating inner drum and/or jet spray. Furthermore, the performance of CO₂ dry cleaning is compared with other commercial solvents. Besides the cleaning performance, the redeposition level is also monitored. Redeposition is a process of soil transfer from one textile to another, and happens when the released soil is not properly stabilized in or removed from the cleaning medium. More explanation about this phenomenon can be found in [6]. Finally, an endoscopic camera has been installed in the 25 L apparatus to get an insight in the textile movement inside the rotating drum.

6.2. Materials and methods

6.2.1. 25 L Delft apparatus

The dry-cleaning experiments were conducted in a CO₂ dry-cleaning apparatus at TU Delft, the Netherlands, which is schematically presented in Figure 6.1. The pilot-scale apparatus was designed and constructed at the Laboratory for Process Equipment, TU Delft. The cleaning chamber (Van Steen Apparatenbouw B.V., the Netherlands) has a 0.25 m inside diameter and 25 L volume, is equipped with an inner drum with a diameter of 0.21 m and has a volume of 10 L. The inner-drum, which is perforated and connected to a rotating shaft which is set to rotate at 75 rpm, is used to provide the mechanical action (tumble) as in a regular washing machine. The detailed procedure of the washing experiment has been described in a previous publication [7].

Fifteen different pieces of soiled test fabric of 6.5 x 7.5 cm² (Center for Testmaterials B.V., the Netherlands) were used in each washing experiment. They consist of three types of textile -cotton, polyester or wool-, each stained with one type of particulate soil -either clay, sebum colored with carbon black, sand, lipstick, or dust-. These monitors were fabricated as such that each piece of the same type contains a similar soil load. Along with the monitors, cotton filling materials of 25 x 25 cm² were added into the cleaning chamber to reach the desired washing load of 400 g. Six kg of CO₂ grade 2.7 (Linde Gas Benelux B.V., the Netherlands) was used in each washing and rinsing step. Several additives were used in the experiments: 10 g

Amihope LL (Ajinomoto Co. Inc., Japan) as surfactant, 250 g 2-Propanol (IPA) with a stated purity >98% (Prolabo, the Netherlands) and 25 g tap water as co-solvents, as well as 10 g 200 μm sand as additional particles to enhance the mechanical action (Filcom B.V., the Netherlands). All given data are average values based on two or more replications for each experiment. To monitor the cleaning results, the color of the fabric was measured before and after washing with a spectrophotometer Data Color 110. The detailed procedure has been described in a previous study [8].

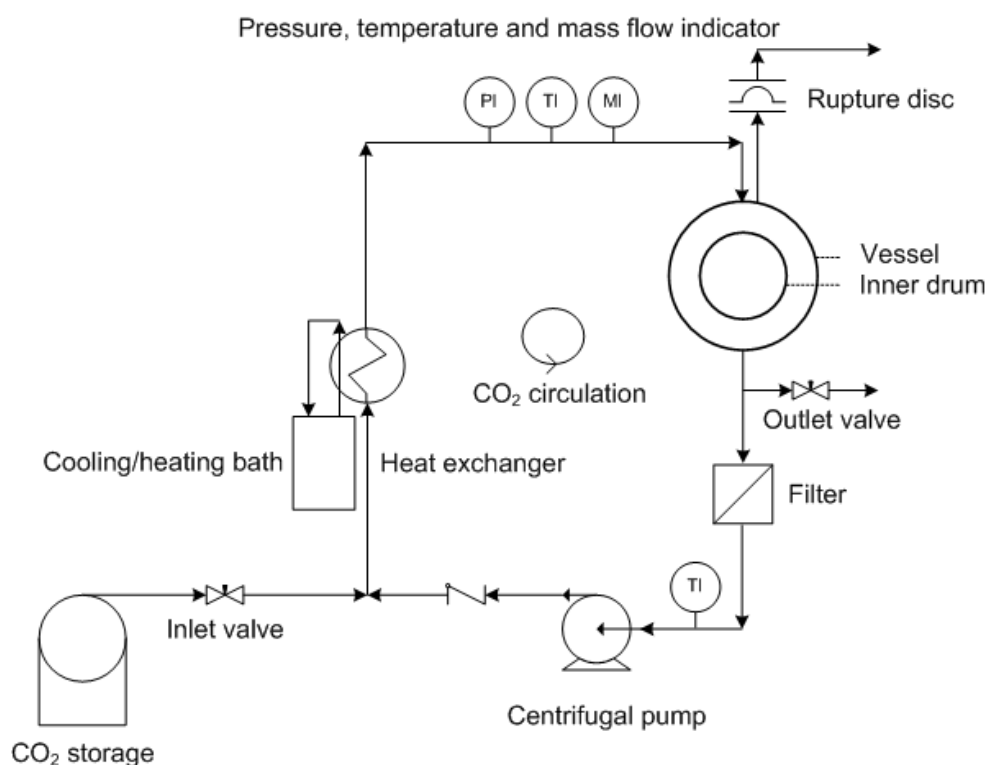


Figure 6.1: Schematic representation of 25 L Delft dry-cleaning apparatus

6.2.2. 90 L Amsonic apparatus

A prototype of a commercial liquid CO_2 -plant (el CO_2) from Amsonic Precision Cleaning AG/SA was used for textile cleaning. The apparatus was operated with liquid CO_2 at a temperature of 15-20°C and a pressure of 51-57 bar. The 90 L cleaning chamber (autoclave) contained a washing basket. The mechanical action upon the textile material was provided by three different mechanisms: 1) gaseous CO_2 flow through several holes that were located above and below the autoclave or

2) an integrated ultrasonic transducer or 3) liquid CO₂ flow (Figure 6.2). The apparatus was equipped with a CO₂ compressor, and a series of filters between 25 µm and 1 µm to remove particles from CO₂ flow. The drawing of this apparatus which is located at IPK Fraunhofer, Germany, and a detailed procedure have been described in a previous study [9]. The textile material and analytical methods used in the washing experiments were similar as in 25 L Delft apparatus. The CO₂ level was set to 2/3 of the height of the autoclave and 10 ml of ClipCOO (Kreussler, Germany) was used as surfactant.

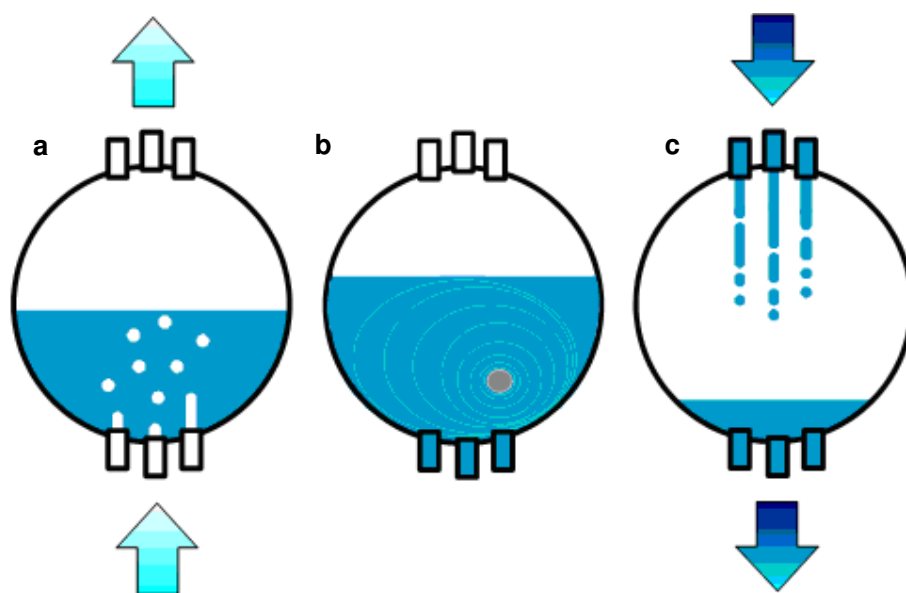


Figure 6.2: Schematic illustration of the mechanical actions in 90 L Amsonic apparatus: a) bubble spray; b) ultrasound; c) liquid spray

6.2.3. Commercial CO₂ dry cleaning machines

Currently, there are around 20 commercial CO₂ dry cleaning machines in the US (mostly on West Coast) and 10 in Europe (Denmark, Sweden) in operation [10]. Washing experiments were performed in five different commercial dry cleaning machines with their own process conditions: Machine A, B, C, D and E. Unfortunately however, the permission to publish the process conditions and the washing results of these experiments has not been obtained.

The textile material and analytical method were similar as in the 25 L Delft apparatus. In each washing process, 15 pieces of soiled monitors attached to white pieces of textile (as reference) were used. In these machines, the monitors are treated as in regular laundry processes but without any pre- or post- spotting treatment. Clean and neutral coloured loads such as comforter were added to reach the recommended washing load of each machine. In each machine, the amount of CO₂ is about 1/3 of the vessel height. The differences of these processes thus lie in the available mechanical action (rotating drum or rotating drum+jet spray, rotational speed of drum), the CO₂ circulation rate, temperature/pressure, washing time, additives, rinsing step, surfactant concentration, and the filtration system.

6.2.4. Dry cleaning with other solvents

The same soiled monitors as used in 25 L Delft apparatus were also treated by professional dry cleaners in different solvents using their standard dry-cleaning procedure with their standard commercial detergents and no pre- or post- spotting treatment. Experiments with PER were performed by Buis Stomerij, the Netherlands, while experiments with Dibutoxy methane (K4) and wet cleaning (water) were performed by Kymi Rens, Denmark.

6.3. Results and Discussion

6.3.1. Mechanical actions in CO₂ dry cleaning

In this study, various mechanical actions have been investigated in 2 different apparatus. These mechanical actions are:

- Rotating drum (25 L Delft apparatus)
- Additional particles (25 L Delft apparatus)
- Ultrasound (90 L Amsonic apparatus)
- Bubble spray (90 L Amsonic apparatus)
- Liquid spray (90 L Amsonic apparatus)

A rotating drum as in the 25 L Delft apparatus is most commonly used in commercial dry cleaning machines to provide the mechanical action. The results are

presented in Table 6.1. Data for rotating drum+additives and rotating drum+additives+particles have been taken from a previous study [11]. To enhance readability, only the average of CPI is given in Table 1. Please refer to Figure 6.5 for the complete data.

From the experiments conducted in the 25 L apparatus, it was found that in most cases, using only CO₂ in a rotating drum increases the soil removal compared to when no additional mechanical or chemical action is used (only CO₂ in non-rotating drum). Using additives (solid surfactant particles and co-solvents) in most cases further increases the washing performance and using additional particles like sand in the rotating drum, gives for some cases a further increase of CPI. It seems that the redeposition level increases along with the cleaning performance which is consistent with the findings in the previous study [6]. Generally, the redeposition level obtained in the 25 L Delft apparatus are acceptable (<2). The filtration system in the apparatus has been modified as such that continuous CO₂ stream is circulated through 2 filter units of 10 µm to remove the dislodged soil.

Table 6.1: CPI and redeposition level for 25 L Delft apparatus

Process Condition	Average CPI (%)	Redeposition level
No rotating drum	7.12	0.21
Rotating drum	9.33	0.39
Rotating drum + additives	13.99	0.85
Rotating drum + additives + particles	14.57	1.27

Experiments to test different kinds of mechanical action were also conducted in a 90 L Amsonic apparatus at IPK Fraunhofer. This apparatus is equipped with three different actions: ultrasound, bubble spray, and liquid spray. The results are shown in Table 6.2 while the complete CPI data are shown in Figure 6.6. It appears that among these actions, liquid spray for most cases shows the highest cleaning performance. However, the overall influence of all three sources of mechanical action on the cleaning results is small. In general, this apparatus also does not show much redeposition because it is equipped with filtration units of 25 and 5 µm to remove the dislodged soil, and the CO₂ stream is continuously circulated through the filters.

Table 6.2: CPI and redeposition level for 90 L Amsonic apparatus

Process Condition	Average CPI (%)	Redeposition level
None	8.14	0.63
Ultrasound	8.47	0.59
Bubble spray	8.87	0.60
Liquid spray	9.52	0.32

6.3.2. Comparison of commercial CO₂ machines and processes

Five different CO₂ dry cleaning machines and processes have been compared: A, B, C, D and E. Average CPI and redeposition level have been used to monitor the cleaning results for different machines. In most cases Machine and process A gives the highest CPI. The most notable differences between Machine A and the other machines are the presence of the jet spray and the highest circulation rate. Based on the experiments on the 25 L apparatus in the previous section, we expect that the liquid CO₂ spray is partially responsible for the better cleaning performance. Since it cannot be excluded that this effect is caused by other differences between the machines, further experiments needs to be performed to explain the better cleaning performance of Machine A. The redeposition levels for most of the machines and processes are acceptable. Nevertheless, machines which have circulation through a filter during the washing process (A and B) have a lower redeposition level than the others because the dislodged soil is continuously removed from the CO₂ stream.

6.3.3. Comparison of cleaning solvents

CPI and redeposition level are also given for different types of textile cleaning solvent in Table 6.3, while the complete data are presented in Figure 6.7. Table 6.3 shows that the average CPI using CO₂ performed by machine A (which gave the best washing performance among other CO₂ machines) was still 25% lower than the results with PER and 11% lower than the results with water. However, when compared with K4 which has a similar KB value (a measure of the strength or degreasing ability of solvent), the average CPI of CO₂ is 11% higher and the

red deposition level was significantly lower than in K4. These results show a good prospect of CO₂ as an alternative solvent to replace PER.

Table 6.3: CPI and redeposition level for different cleaning solvent

Cleaning solvent	Average CPI (%)	Redeposition level
CO ₂	17.92	1.30
K4	16.01	5.22
Water	21.64	0.88
PER	23.87	0.90

The comparison with PER is in agreement with the results published by TKT (Dutch technical knowledge centre for the textile care industry and the laundry industry) [12]. In contrast, they found that the performances of K4 and water were higher than with CO₂. Since TKT did not publish the used materials and methods for their experiments, it is difficult to trace the source of this discrepancy.

6.3.4. Textile movement in a rotating drum

An endoscopic camera has been installed in the 25 L apparatus at TU Delft to observe the textile movement inside a rotating drum (see Figure 6.3). It was reported that the use of a high pressure compatible camera inside a high pressure reactor cell was utilized in the 1990s at Los Alamos National Laboratory (King, J., personal communication, 2014). The following process parameters were varied and the effect on the textile movement was studied:

- Degree of textile filling
- Amount of CO₂
- Process temperature and pressure

Under supercritical conditions, no visual image is available. It might be because the light source is not transmitted through the supercritical phase.

- Pump circulation rate

An example of picture shots taken during the observation is given in Figure 6.4. Using the video camera, it has been observed that the textile movement in CO₂

is sluggish (i.e. it does not rotate as fast as the speed of the drum), which means the mechanical action is much less than the one that was predicted.

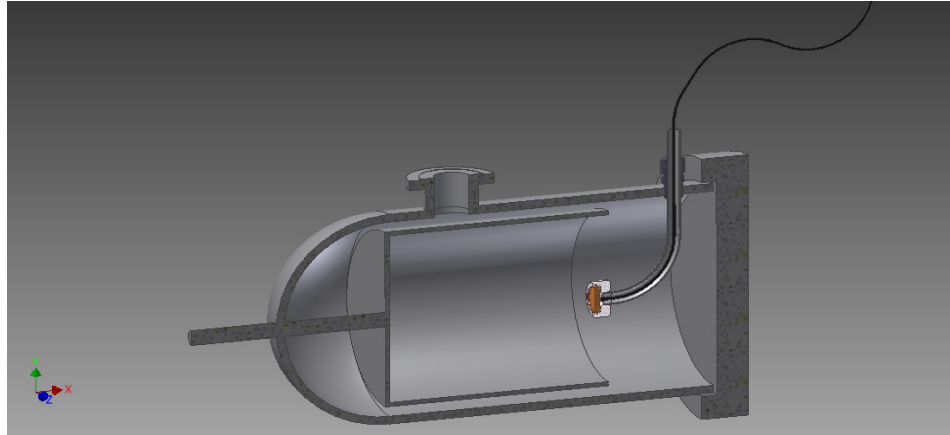


Figure 6.3: Endoscopic camera installation inside 25 L Delft apparatus with rotating drum

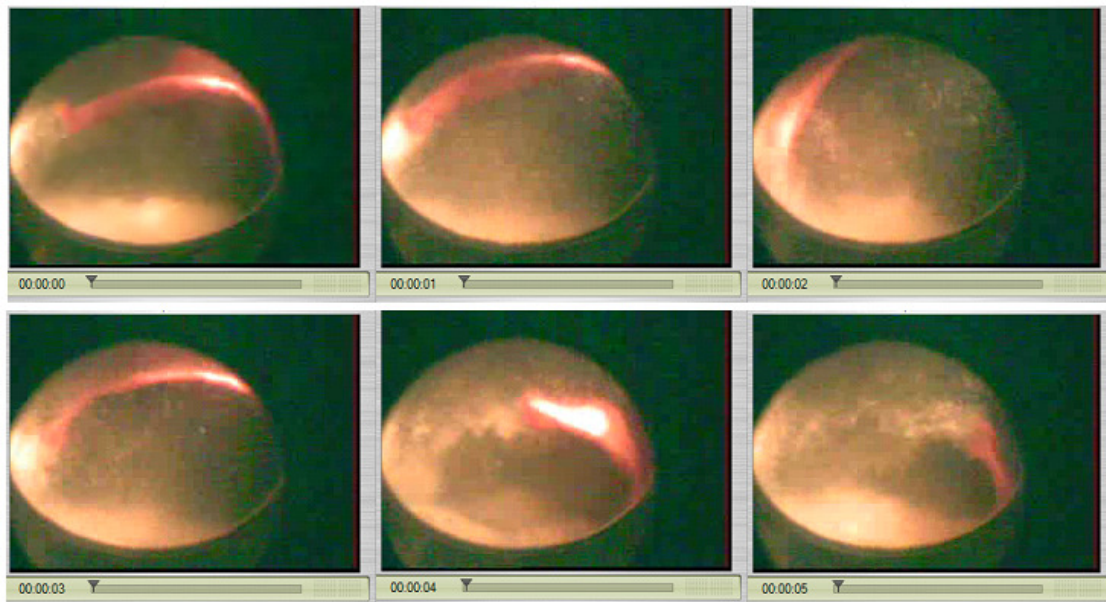


Figure 6.4: Textile movement inside a rotating drum for 1 piece of textile, rotation speed: 75 rpm, rotation direction: clockwise-counter clockwise, amount of CO₂: 6 kg, T: 10°C, no pump circulation, no baffle

It was also observed that no plug formation occurs. This means that the simplified mechanical movement of textile in CO₂ dry cleaning does not follow the simplified tumbling-movement model which was developed in a previous study [8]. This model was based on water-based washing-machine by Van den Brekel [13], where the textile was assumed to be a cylinder plug with diameter and length of 5 cm. The shape of textile in CO₂ (which is not ideal to make the tumbling movement) might contribute to the low amount of mechanical action in the washing process.

When the higher filling degree (8 pieces of textile) was used, the textile moved slightly slower, which implies a lesser amount of mechanical action. The model implied that 10-11 o'clock for counterclockwise rotation and 1-2 o'clock for clockwise rotation are desirable as the drop-off point of the textile. On several cases, when using a high degree of filling, it was observed that the textile was stuck in a certain position and did not rotate along with the drum until the rotation direction was changed, or that the textile rotated along with the drum without the falling action or fell before reaching the desired point. Without the impact from falling and hitting-the-wall movements, the mechanical action in CO₂ dry cleaning is reduced significantly, resulting in low cleaning performance.

The amount of CO₂ affects the liquid CO₂ level inside the rotating drum and thus determines whether the fallen textile will hit the wall (desirable) or hit the liquid. When the amount of CO₂ was increased to 10 kg, the liquid CO₂ level reached the middle of the rotating drum (while 6 kg of CO₂ only reached the bottom of the drum). It was observed that the movement of textile was more sluggish in 10 kg than in 6 kg of CO₂ which indicates that the mechanical action in 10 kg of CO₂ is lower than in 6 kg.

The process temperature affects the density difference between liquid and gaseous CO₂. It is expected that the lower density difference between liquid and gaseous CO₂ at higher temperature results in a higher drag force and lower net gravitational force for the falling textile, and thus in a lower terminal velocity and lower mechanical action [8]. However, when a higher temperature (25°C) was used instead of 10°C, no significant difference in the speed of textile movement was observed, even though the liquid CO₂ level was less than at 10°C.

The pump circulation could act as a liquid CO₂ spray that stimulates the textile movement. By using the video camera, it has been observed that the textile movement can be significantly enhanced by CO₂ circulation with a pump, liquid CO₂ flow that was circulated by the pump at 150-250 kg/h created a turbulent flow of liquid CO₂ inside the cleaning vessel, which increased the textile movement and thus increased the amount of mechanical action in the washing process. The observation supports the results from the previous section that a liquid CO₂ flow (i.e. liquid spray) stimulates textile movement. These results will be used to modify the model of textile movement in CO₂ inside a rotating drum which was developed in a previous study.

6.4. Conclusion

The washing results in the 25 L machine show that the rotating drum with additives and additional particles gives the highest cleaning performance. However, the use of additional particles is not practical for industrial-scale dry-cleaning. Liquid CO₂ spray may be a suitable additional mechanism to provide textile movement, as suggested by the results with commercial machines and experiments with the endoscopic camera. The average CPI of CO₂ was still 25% lower than the results with PER, 11% lower than the results with water, but 11% higher than K4 which has a similar KB value, and the redeposition level was significantly lower than in K4. The observations with the endoscopic camera show that no plug formation occurs and the textile movement in CO₂ is sluggish, which means that the mechanical movement of textile in CO₂ dry cleaning does not follow the tumbling-movement model which was developed in a previous study and the mechanical action is much less than the one that was predicted.

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Appendix 6.1

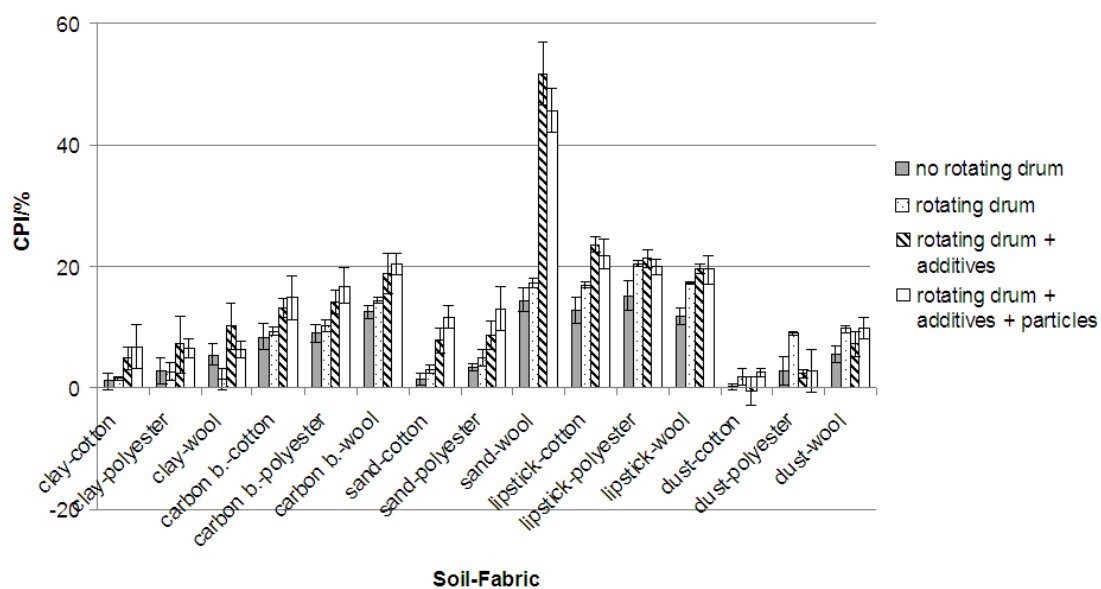


Figure 6.5: Cleaning Performance Index in 25 L Delft apparatus

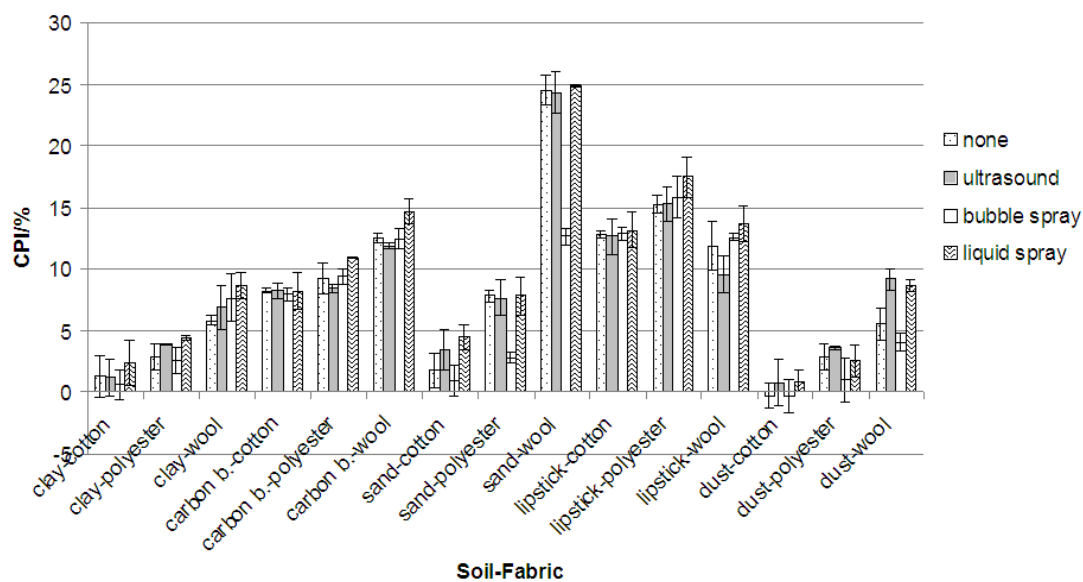


Figure 6.6: Cleaning Performance Index in 90 L Amsonic apparatus

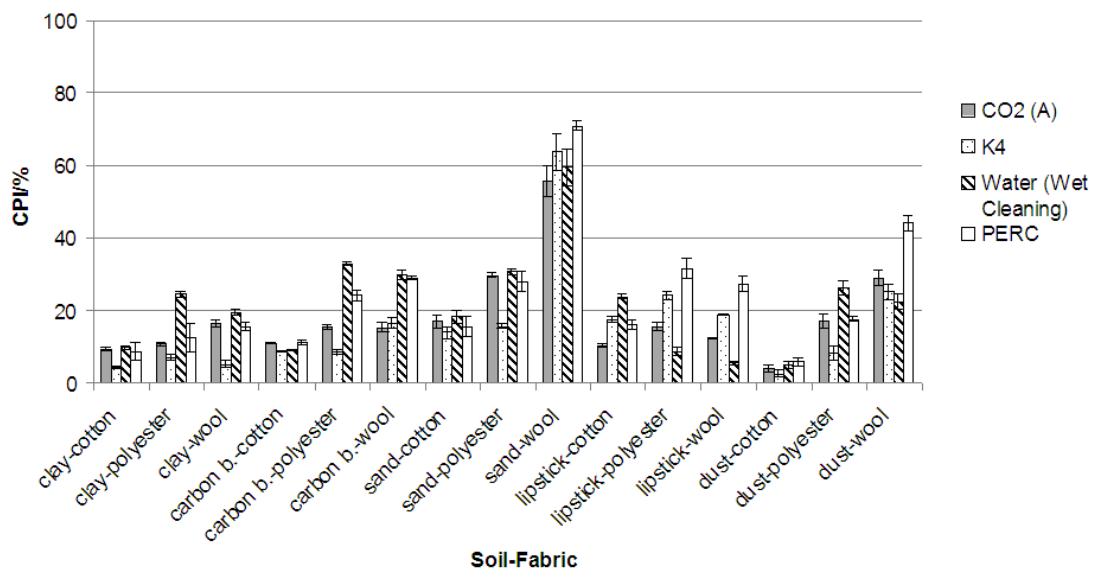


Figure 6.7: Cleaning Performance Index for different cleaning solvents

Chapter 7

Mechanical Forces in Observation Cell

Abstract

High-pressure carbon dioxide (CO_2) is a potential alternative for perchloroethylene (PER), a common but harmful textile dry cleaning solvent. Previous studies have indicated that the particulate soil removal with CO_2 is lower compared to that with PER, because of the low amount of mechanical action in CO_2 . It was the objective of this study to achieve more insight in the soil particle removal in CO_2 dry cleaning through investigation of directly applied well defined forces on the textile, and use these results to perform a quantitative analysis of the mechanical forces in the observation cell and a CO_2 dry cleaning machine. The removal of different kinds of particulate soils from cotton textile monitors was studied using an observation-cell apparatus equipped with a mechanical actuator. Experimental results show that for certain particulate soils (e.g. lipstick), a more rigorous textile movement leads to higher particle removal. For other particulate soils (e.g. clay) the maximum amount of particles that can be removed by mechanical action alone has been reached with a very small amount of mechanical action. The quantitative analysis of mechanical forces in observation cell for clay particles show that the amount of force that is exerted by the actuator is higher than theoretically required to remove all clay particles from the textile surface and also higher than the available force in a commercial dry cleaning machine. However, without the help of chemical action from a suitable detergent, higher mechanical action does not lead to a higher soil removal for clay particles because of the high interaction forces between the clay and the textile in the CO_2 medium.

7.1. Introduction

Dry cleaning is a process of soil removal from substrate, in this case garment/textile, which involves a non-aqueous solvent. The most commonly used solvent in dry cleaning is perchloroethylene (PER). Despite its good cleaning performance, PER has several drawbacks such as various toxic effects to the human body when the safe concentration exposure level is exceeded. Several alternative solvents for textile dry cleaning include hydrocarbon solvents, silicon based solvents and carbon dioxide (CO₂) [1]. CO₂ has several advantages compared to the other solvents. It is non-toxic, non-flammable, non-corrosive, safe for the environment, cheap, easily recovered, and available on a large scale. Furthermore, a drying step is not necessary because CO₂ evaporates from the fabrics during the depressurization step. However, previous studies [2,3] have indicated that CO₂ removes significantly less particulate soil than PER.

Generally there are two steps in particulate soil removal from textile: the soil loosening step where the binding forces between the soil and the textile are broken, followed by the soil transfer step where the dislodged soil is transported from textile to solvent [4]. In both steps, mechanical action is necessary to create textile deformation by bending, twisting or stretching the yarns, so that liquid flow of solvent and additives can penetrate deeper into the yarns and aid the soil removal steps or physically move the yarns from the particle or vice versa [5]. In regular dry-cleaning machines, mechanical action is provided by a rotating drum with addition of detergent. The presence of a detergent is essential since a surfactant is used to lower the binding forces between the soil particle and the textile and an anti redeposition agent is used to stabilize the released soils and prevent redeposition of these soils.

In a CO₂ dry-cleaning machine with a rotating drum, the low density difference between the liquid and the gas phase of CO₂ leads to a low level of mechanical force (compared to water and PER) and the low viscosity of 10⁻⁴ Pa.s leads to a low momentum transfer and up to date, the available detergents increase particulate soil removal but not to a level comparable to the one in PER.

This study aims to achieve more insight in the soil particle removal in CO₂ dry cleaning through investigation of directly applied well defined forces on the textile. Cotton monitors stained with different kinds of particulate soils were used in the experiments using an observation cell apparatus equipped with a mechanical actuator. This actuator is used to impose various mechanical forces at the in-situ process conditions. Furthermore, the theoretical amount of forces required for particulate soil removal and the amount of forces provided by the actuator in the observation cell and a commercial dry cleaning machine were calculated, and an overall quantitative analysis was performed.

7.2. Materials and methods

The experiments were conducted in a CO₂ observation cell apparatus at TU Delft, the Netherlands, which is schematically presented in Figure 7.1. The apparatus was designed and constructed at the Laboratory for Process Equipment, TU Delft, together with FeyeCon Carbon Dioxide Technologies. The cell chamber has a 0.42 L volume (6 cm width x 7 cm length x 10 cm height), equipped with textile holders (length of 4.5 cm each) at the top and the bottom of the cell. The bottom holder is fixed while the top holder is moveable and attached to a programmable actuator. The textile is fixed to the holders with screwed clamps. The actuator is a Festo Swivel/linear drive units DSL-B with a shaft diameter of 20 mm. This actuator is used to provide mechanical action (rotating, vertical or combination of both) directly on the textile and operated by pressured air of ~7 bar with a linear stroke of 10 mm, and rotation of 180°. The seal that connects the moving shaft to the cell is especially designed and produced by Saint Gobain, Belgium.

The experiments were conducted at a temperature and pressure of 10°C and 45 bar. In some cases, CO₂ is circulated at 150 L/h through a series of filters and a cooling bath by a circulation pump. In each of the experiments, a piece of soiled cotton monitor of 4.5 x 7.5 cm² (Center for Testmaterials B.V., the Netherlands) was used. The fabric was stained with one type of particulate soil, either clay, sebum colored with carbon black, sand, lipstick, or dust. These monitors were fabricated with a special machine such that each piece of the same type contains a similar soil

load, except for the sand soiled monitor which is circular ($d = 4$ cm) and hand made by the same supplier but each piece still contains similar soil load. The monitor is sewn together with a piece of unsoiled cotton fabric as a reference to monitor the redeposition level, since it was found to be a problem in CO₂ dry cleaning in a previous study [6]. CO₂ grade 2.7 (Linde Gas Benelux B.V., the Netherlands) was used in each washing (20 min) and rinsing step (10 min). All given data are average values based on at least two replications for each experiment. To monitor the results, the color of the monitors and the reference was measured before and after the experiment with a spectrophotometer Data Color 110. The detailed monitoring procedure has been described in a previous study [7].

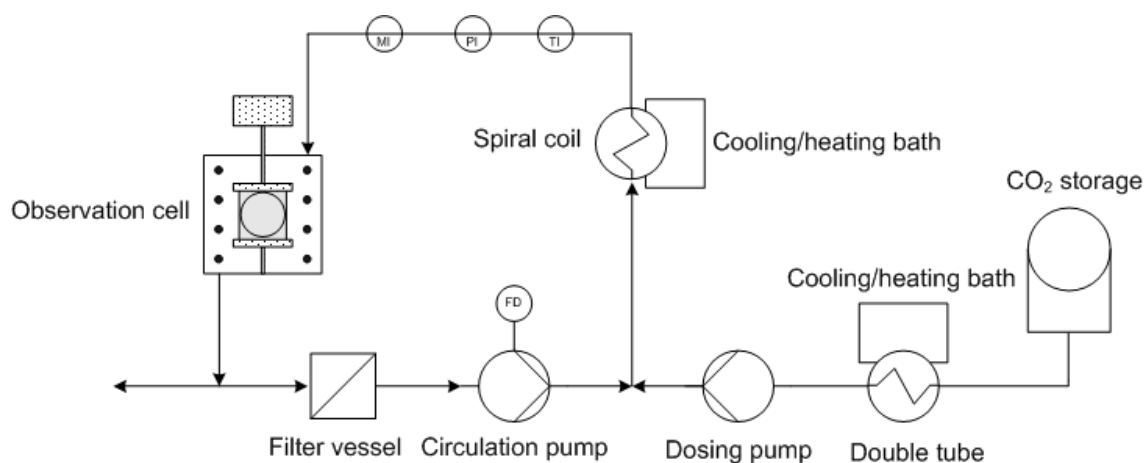


Figure 7.1: Schematic representation of observation cell apparatus

7.3. Results and discussion

7.3.1. Experiments with observation cell

The mechanical actuator in the observation cell apparatus can be programmed to perform 3 different movements: rotating movement with 180° angle, linear vertical movement and combination of rotating and vertical movement. The speed is set to the maximum level (43 strokes/min). The amount of particles removed is determined by measuring the cleaning performance index (CPI). Figure 7.2 shows the results of the experiments with different types of movements in the observation cell with no action without circulation used as a reference. A CO₂ circulation flow (including

filters) might be beneficial for cleaning as explained above and in Chapter 6 and in [8]. Thus, the influence of CO₂ flow (including filters) compared to only mechanical action from the actuator is also investigated in this study.

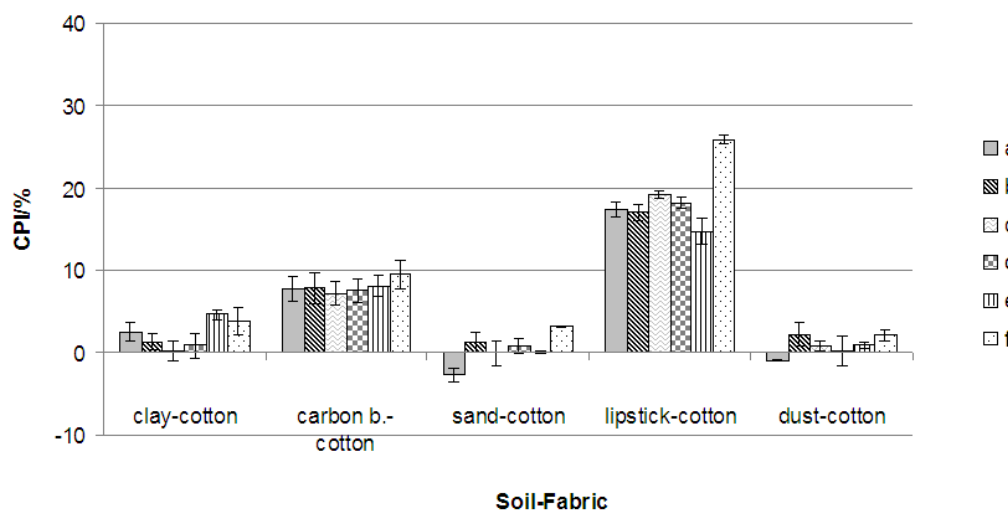


Figure 7.2: Cleaning Performance Index for various types of actuator movement with and without circulation: a) no action without circulation; b) no action with circulation; c) rotating action with circulation; d) vertical action with circulation; e) rotating+vertical action without circulation; f) rotating+vertical action with circulation

When no action without circulation is exerted, the CPI has a negative value for two soil types and it was found that the ΔE difference of the unsoiled cotton as the reference is also higher for these monitors. They both show the occurrence of redeposition which happened in these experiments without circulation and thus CO₂ did not pass through a filter. Redeposition is a process of soil transfer from one textile to another, and happens when the released soil is not properly stabilized in or removed from the cleaning medium. Once redeposition happens, it usually cannot be reversed which leads to greying of the fabric and unsatisfying cleaning results. This phenomenon has been elaborately explained in Chapter 3.

In general, the combination of rotating and vertical movement with circulation gives the highest CPI, compared to the other movements. However, because of the presence of redeposition, it is hard to translate the measured CPI into particle removal. Next, no action with circulation, rotating+vertical action without circulation,

and rotating+vertical action with circulation can be compared with the reference. The CPI difference for most cases is not significant, even though the forces in no action with circulation and especially in the case of the reference are much lower. It might be that the maximum amount of particulate soil that can be removed by mechanical action alone from some of these monitors (e.g. clay) has been reached (e.g. by only the mechanical action that is present during the cell filling). Without the aid of detergent it is hard to achieve a higher soil removal (see also calculation in Section 7.3.2). For lipstick, the combination of CO₂ circulation with filters and mechanical action from the actuator provides the highest CPI.

When the CO₂ circulation rate in the observation cell was increased from 150 L/h to 225 L/h, instead of having a CPI increase, the opposite was true. The dust on cotton monitor even shows a negative CPI value, which means the occurrence of redeposition. This is probably because the filter does not work as effectively when a higher circulation rate is used. Therefore, no conclusion can be drawn with regards to the influence of a higher circulation rate on particle removal.

For the rotating+vertical movement with circulation, another experiment was performed at equal conditions but with a lower actuator speed (33 strokes/min). It was found that in general the difference in particle removal at both speeds is not significant i.e. the CPI and the redeposition level are almost equal. This might be because at the speed of 33 strokes/min the limit of the amount of particles that can be removed by mechanical action alone has been reached.

Experiments with longer and shorter washing time (30 and 10 min, respectively) were also performed for rotating+vertical movement with circulation. The results of these tests confirm the conclusion drawn in Chapter 3 and Chapter 4 that using a short washing time (10 minutes in this case) may lead to an insufficient soil removal while using a long washing time (30 minutes in this case) could lead to a redeposition problem since there is a longer lag time available for the dislodged soil to redeposit on other textile surface. For the rest of the experiments with observation cell, a time of 20 minutes has been used.

The influence of additives (ClipCOO as liquid detergent and IPA as co-solvent) on soil removal was also investigated in the observation cell as shown in Figure 7.3. For these experiments it was found that the additives do not increase the CPI and

induce the occurrence of redeposition (~40% higher) even though CO₂ circulation was used in these experiments. Because of higher redeposition, it is difficult to compare the particle removal of both cases.

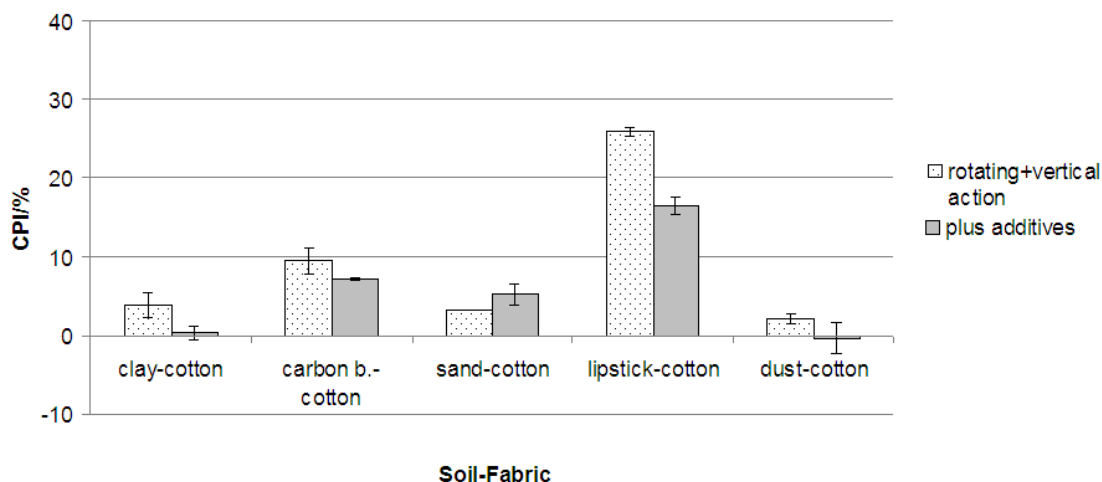


Figure 7.3: Cleaning Performance Index with and without additives

7.3.2. Quantification of mechanical force in observation cell

For particulate soil removal in a dry cleaning process without the use of surfactants, the given mechanical action should overcome the forces which bind the particulate soil to the textile. In this section, the interaction forces between particulate soil and textile are discussed using the model to determine the theoretical amount of force required for particulate soil removal which was developed by our colleagues in Wageningen and published in [9]. In addition, the mechanical forces provided by the actuator in the observation cell have been calculated and an overall quantitative analysis of mechanical forces in the observation cell and a commercial machine with a rotating drum has been made.

Interaction forces between particulate soil and textile

The particulate soil interaction with the textile fiber (adhesion forces) in the CO₂ medium at dry cleaning operating conditions (10°C, 45 bars) is mainly defined by

dispersive and electrostatic interactions [9]. The other interactions (such as chemical interactions) are not considered in this case for simplicity reason.

The dispersive interaction is calculated through the Van der Waals interaction energy between soil and fabric interacting through solvent using the sphere-plate model [10-12]. The van der Waals interaction energy as a function of the distance between particle/textile for PER, water and CO₂ solvents is shown in Figure 7.4. Figure 7.4 shows that in PER there is almost no Van der Waals attraction between the particle and the textile, while in CO₂ this attraction is strong. This might contribute to the low particulate soil removal in CO₂ dry cleaning.

The electrostatic interaction between particles and textile in the CO₂ medium can be calculated by using DLVO model [13]. The electrostatic stabilization in CO₂ is low because the contributing factors such as surface charge density and the zeta potential are low. This means that the electrostatic interaction in CO₂ can be neglected [9].

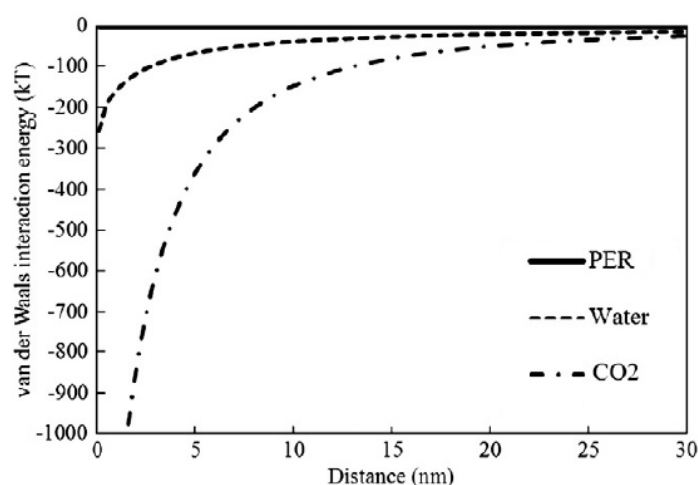


Figure 7.4: Van der Waals interaction energy between a model soil particle (silica radius 3 μm) and model fabric (cellulose) in PER, water and CO₂ [9]

Forces for particulate soil removal

The magnitude of Van der Waals/adhesion force (F_{adh}) between soil particle and fabric in CO₂ medium can be estimated with:

$$F_{adh} = \frac{A_{132}R}{6d^2} \quad \text{Eq. 7.1}$$

Where A_{132} is the Hamaker constant [14] of soil (component 1) and textile (component 2), interacting through solvent (component 3). R is the radius of soil particle and d is the distance between the soil and textile. Based on SEM measurements of clay (one of the soil types used in the experiments), we take $R = 5 \mu\text{m}$ and $d = 1 \mu\text{m}$ [9].

The Hamaker constant can be calculated with:

$$A_{132} = \left(\sqrt{A_{11}} - \sqrt{A_{33}} \right) - \left(\sqrt{A_{22}} - \sqrt{A_{33}} \right) \quad \text{Eq. 7.2}$$

The individual Hamaker constants interacting through vacuum (A_{ii}) can be calculated from the Lifshitz approximation [14]. Using Equation 2 and the Lifshitz approximation, the value of A_{132} has been calculated as $\sim 14.k_B.T$ in which k_B is the Boltzmann constant and T is the process temperature [9]. Using the numbers above, this leads to $F_{adh} = 4.56.10^{-14} \text{ N}$.

During the cleaning process, a certain amount of mechanical action is required to dislodge the particulate soil from the textile fiber. A model has been developed for a model particle and model textile [9]. It is assumed that the particles are held on the textile by above mentioned Van der Waals/adhesion force and friction force. To remove the particle, the mechanical action provided to the system should be equal or higher than the sum of these two forces. The force balance is shown in Figure 7.5.

Friction force can be calculated by:

$$F_{fric} = \mu N \quad \text{Eq. 7.3}$$

In which μ is friction coefficient and N is normal force. If μ is taken as 1 [9], and N equals F_{adh} , the sum of Van der Waals and friction forces is assumed to be twice the adhesion force. Thus a minimum force of $9.11.10^{-14} \text{ N}$ is required to remove one soil particle of $5 \mu\text{m}$ radius from the textile surface in CO_2 medium at the operating conditions.

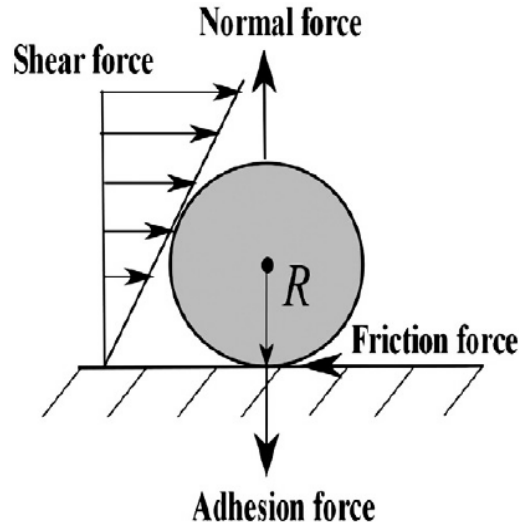


Figure 7.5: Force balance of a model particle that is attached on a model textile by Van der Waals and frictional forces, experiencing shear force [9]

Mechanical forces in the observation cell

This section tries to quantify the forces given to the textile by combined vertical and rotating movement actions from the actuator as well as the circulation. See Figure 7.6 for a simplified diagram of the system.

The vertical action of the actuator gives the linear force (F_{lin}) while the rotating movement gives the torque (F_{rot}). The amount of the forces provided by the actuator on the textile (F_{act}) can be estimated by measuring the air pressure supplied to the actuator to calculate the forces exerted by the actuator, then subtract it by the force required to overcome the friction in the seal (F_{fric}).

$$F_{act} = F_{lin} + F_{rot} - F_{fric} \quad \text{Eq. 7.4}$$

In the data supplied by Festo, it is shown that at the used pressured air of 6-7 bars, the theoretical force advancing is 159 N and the theoretical force retracting is 120.5 N, leading to F_{lin} of 279.5 N. The theoretical torque is 2.5 Nm. The value of F_{rot} is a function of the lever arm of the system, in this case the length of the holder (l). A distance of 0.5 l will be taken at which F_{rot} maximum = 111.1 N. The supplied F_{fric} data from Saint Gobain is 67.9 N at 125 bar (the maximum pressure of the seal). Since in this case the friction force is directly proportional to the working pressure, we

estimate that F_{fric} at the operating pressure of 45 bar is 24.4 N. This leads to F_{act} of 322.7 N.

When the circulation pump is used, the liquid CO_2 stream gives sheer force (F_{sh}). For a spherical particle, the relation between the F_{sh} and the wall shear stress (τ) is given by [15]:

$$F_{\text{sh}} = 32\tau R^2 \quad \text{Eq. 7.5}$$

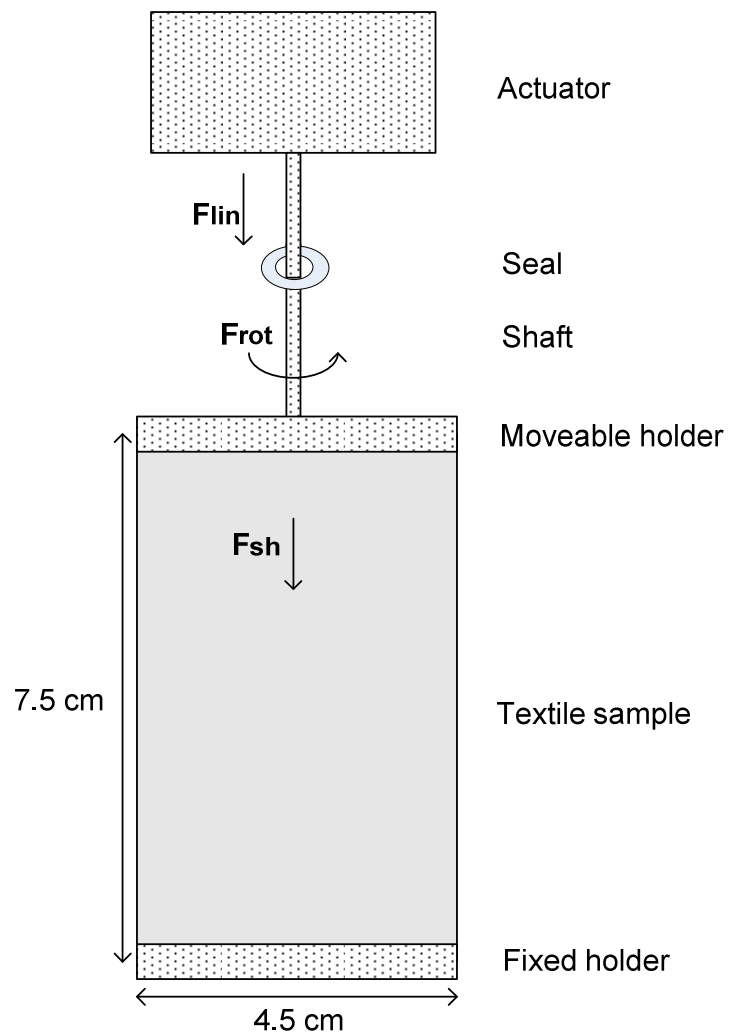


Figure 7.6: Force diagram in observation cell

τ is related to the wall shear rate ($\dot{\gamma}$) by the viscosity of the fluid (η) as:

$$\tau = \eta \dot{\gamma} \quad \text{Eq. 7.6}$$

And the flow velocity (v) around the particle with radius R can be written as:

$$v = \dot{\gamma} R \quad \text{Eq. 7.7}$$

Since the volumetric flow rate (Q_v) and surface area (A) of the inlet tubing -3/8" OD with inner diameter of 4.93 mm- are known, we can calculate v from:

$$v = \frac{Q_v}{A} \quad \text{Eq. 7.8}$$

After exiting the tube, the area is enlarged (become equals to the surface area of the cell) and thus the velocity decreases. However, for this calculation we use the maximum value of v , when the fluid just exits the tube which leads to an overestimation of F_{sh} .

From Eq. 5-8, F_{sh} can be calculated with:

$$F_{sh} = \frac{32\eta Q_v R}{A} \quad \text{Eq. 7.9}$$

At the operating conditions, the viscosity of CO_2 is 10^{-4} Pa.s, leading to $F_{sh} = 3.5 \cdot 10^{-8}$ N.

Analysis of mechanical forces in observation cell

It has been calculated that the minimum force of $9.11 \cdot 10^{-14}$ N is required to remove one soil particle of 5 μm radius from textile surface in CO_2 medium at the operating conditions. The textile monitors were made by Center for Testmaterials B.V. as such that it can be assumed that the soiling degree is uniform on all over the textile surface. Manual calculation of the amount of clay particles from SEM results shows that there are ~25 clay particles in 130 μm x 100 μm area of textile monitor. Thus for a piece of textile monitor with the size of 4.5 cm x 7.5 cm, it is estimated that there are $1.3 \cdot 10^7$ clay particles. This leads to required minimum force of $1.2 \cdot 10^{-6}$ N to remove all clay particles from the surface.

Meanwhile it has also been calculated that the mechanical action given to the textile by the actuator (rotating and vertical movement) is 322.7 N, with assumption that all the mechanical forces from actuator can be transferred to the particles.

However, even though this force is much higher than the calculated force necessary to remove all particles, the CPI for these forces is much lower than 100%.

The shear force from the circulation flow is $3.5 \cdot 10^{-8}$ N as calculated in previous section. Although the forces of the shear flow are much lower than the actuator forces, the particle removal of both for clay are comparable (see Figure 7.2). It might be that the maximum amount of clay particles that can be removed by mechanical action alone has been reached with a very small amount of mechanical action and that without the aid of detergent it is hard to achieve a higher soil removal.

Analysis of mechanical forces in commercial dry cleaning machine

Calculation of the mechanical forces in a commercial machine with a rotating drum (whose specifications are available in Chapter 8) is performed. A previous study [7] has described that the mechanical forces in a rotating drum (F_{rd}) can be calculated with:

$$F_{rd} = F_{g,net} + F_d \quad \text{Eq. 7.10}$$

$F_{g,net}$ is net gravitational force and can be calculated with:

$$F_{g,net} = \left(m_{plug} - \frac{1}{4} \pi D_{plug}^2 l_{plug} \rho_{gCO_2} \right) g \quad \text{Eq. 7.11}$$

With m_{plug} the mass of textile plug including the amount of fluid absorbed. It is assumed that the amount of liquid CO_2 absorbed by textile is the same as the amount of water absorbed by textile.

$$m_{plug} = \left(0.1 \rho_{textile} + 0.3 \rho_{lCO_2} + 0.6 \rho_{gCO_2} \right) \cdot \left(\frac{1}{4} \pi D_{plug}^2 l_{plug} \right) \quad \text{Eq. 7.12}$$

D_{plug} is the diameter of textile plug (0.05 m), l_{plug} is the length of textile plug (0.3 m). $\rho_{textile}$ is the density of textile (1300 kg/m³), ρ_{gCO_2} is the density of gaseous CO_2 (135 kg/m³), and ρ_{lCO_2} is the density of liquid CO_2 (861 kg/m³) at the operating conditions of 45 bars and 283 K. g is gravitational acceleration (9.8 m/s²). The drag force, F_d , can be calculated with:

$$F_d = -\frac{1}{2} c_d \rho_{gCO_2} l_{plug} D_{plug} v \quad \text{Eq. 7.13}$$

With c_d is the drag coefficient. Since the textile plug is modeled as a cylinder c_d is taken as 1. v is the velocity of textile plug. Assuming that the largest pressure drop difference is created by the impact movement, v can be calculated with:

$$v = \left(9\omega^2 R^2 - \frac{8\omega^6 R^4}{g^2} \right)^{0.5} \quad \text{Eq. 7.14}$$

With ω is the angular velocity of the drum (30 rpm or 3.14 rad/s) and R is the radius of the drum (0.75 m). This leads to F_{rd} of 3 N. It is suspected that the actual number is even smaller because from investigations with an endoscopic camera in Chapter 6, it was observed that the plug formation did not occur and that the impact of textile hitting the wall was barely existing.

The mechanical action in a rotating drum is smaller than the available forces exerted by the actuator in the observation cell (322.7 N), but higher than the shear force induced by the circulation flow in the observation cell ($3.5 \cdot 10^{-8}$ N). However, the clay removal is in the same range (5-6%). This supports our conclusion that the maximum amount of clay particles that can be removed by mechanical action alone has been reached with a very small amount of mechanical action and that without the aid of detergent it is hard to achieve a higher soil removal.

Analysis of mechanical forces in other cleaning solvents

Lastly, we compare CO_2 with other cleaning solvents with regards to their properties that play a role in mechanical action. Our colleagues in Wageningen have calculated the Reynolds number (Re), which is the ratio between inertial and viscous force [16], for different dry cleaning solvents as shown in Figure 7.7.

It is assumed that the mechanical force given to the particles come from shear force only (the gravitational, lift and torque are negligible):

$$Re = \frac{Dv\rho}{\eta} \quad \text{Eq. 7.15}$$

With D is the ratio between the cross-sectional area of the flow and the wetted parameter, v is velocity, ρ is the density and η is the viscosity of the fluid.

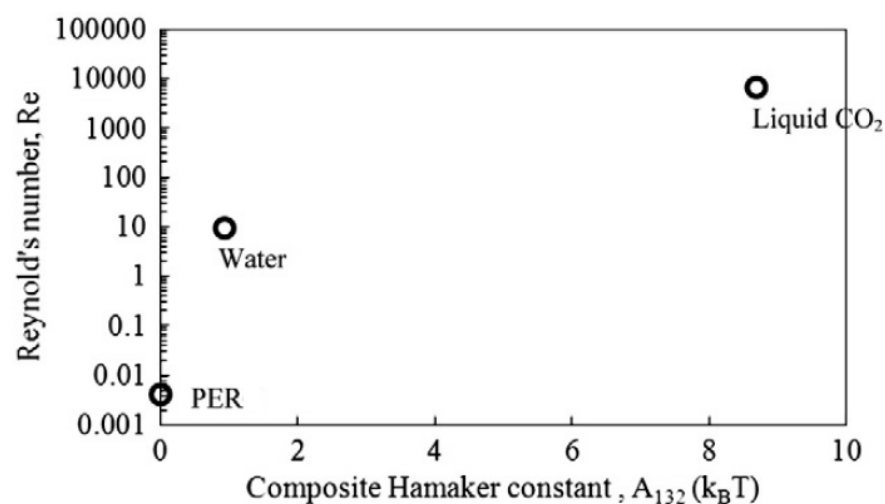


Figure 7.7: Re number versus Hamaker constant for particle removal from textile in PER, water and CO₂ medium [9]

Figure 7.7 shows that CO₂ requires high Re number to remove particle from textile (in magnitude of 10^4) compared to water (10^1) and PER (10^{-2}). From mechanical action point of view, dry cleaning in CO₂ medium possess some challenges because of the high Van der Waals interaction between textile soil particles and textile, the low density difference between gas and liquid CO₂, and the low momentum transfer due to the low viscosity of CO₂. Even though in the observation cell the last two hurdles have been removed by applying a high magnitude of mechanical action from the actuator directly onto the textile, it seems that the particulate soil removal cannot be increased further by mechanical action only as shown in the results in Section 7.3.1. The high interaction forces between the soil and textile in CO₂ medium need to be overcome by the aid of chemical action.

7.4. Conclusion

Experimental results show that for certain particulate soils (e.g. lipstick), a more rigorous textile movement leads to higher particle removal. However, for other particulate soils (e.g. clay), the maximum amount of particles that can be removed by mechanical action alone has been reached with a very small amount of mechanical action (e.g. mechanical action by filling of the cell) and that without the aid of

detergent it is hard to achieve a higher soil removal. The quantitative analysis of mechanical forces on clay particles in the observation cell shows that the amount of force that is exerted by the actuator is higher than theoretically required to remove all the clay particles from the textile surface and is also higher than the forces in a commercial dry cleaning machine. However, without the help of chemical action from a suitable detergent, it was hard to overcome the high interaction forces between the soil and the textile in CO₂ medium, and thus a high amount of mechanical action alone does not lead to a higher clay removal.

7.5. Recommendation

It is desirable to get a better understanding of the behavior of textile and different types of soils when different forces are applied in CO₂. Experiments using a high speed camera are thus recommended. To measure the amount of forces from the actuator that are transferred to the textile, it is recommended to install a force measurement device such as foil strain gauge. Other than the mechanical action, the development of a novel surfactant for CO₂ dry cleaning is important because the existing ones are not able to overcome the high adhesive forces between the soil and the textile in the CO₂ medium. There are also other factors and these need to be considered in future studies to get a better understanding of the mechanical action in CO₂ dry cleaning, such as the shape of the soil particle, the surface structure of the textile, the hydrophilicity/hydrophobicity of soil and the textile, the presence of water (which might form capillary bridges between the soil and the textile [9]), the age of the soil, the storage temperature of the monitor, etc.

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Chapter 8

Towards An Ideal CO₂ Dry Cleaning Machine and Process

8.1. Introduction

This chapter describes an optimized equipment and process for CO₂ textile dry cleaning. It is a combination of best practices, new insights obtained from the results of this study, and the best available technologies. The given description is based on a standard existing commercial machine: the Electrolux Wascator S35. This approach is adopted due to limited time and technical resources. The Wascator machine has been manufactured in Sweden and is still in operation at several dry cleaning sites in Europe. It is chosen because all required information is available from the manufacturer and users.

8.2. Specification of Electrolux machine

The flow diagram and a picture of the Electrolux Wascator machine are given in Figure 8.1 and Figure 8.2, respectively. The information about the machine is obtained from [1] and personal communication with the users and the manufacturer.

A summary of the process conditions is given in Table 8.1. A typical washing process follows the following sequence:

- Pre-treatment
Garments are divided based on the color (dark and light), the weight (heavy and light) and the texture (regular or fragile). Acetate materials are not to be washed in CO₂. Inspect the garment for stains, clean with pre-spotters (steam and other stain removal products: dry or wet side, depending on the stain) if necessary.
- Evacuation and pressurization
The garments are placed in the cleaning chamber, 100 g of ClipCOO as detergent is added into the drum, the door close is closed and a vacuum pump

starts to evacuate the air in the drum to ~ 0.1 atm. The cleaning chamber is pressurized by gaseous CO_2 from the top of the storage vessel. When equilibrium has occurred between cleaning chamber and storage vessel, liquid CO_2 flows from the storage vessel to the cleaning chamber. The filling is complete when the chamber is filled to 1/3 of machine height (~ 120 kg).

- Washing step

The washing step of 15 minutes is performed with mechanical action from a rotating drum at temperatures between 5 and 20°C . The drum has a reverse action (back and forth) to avoid the wound-up of the garments.

- Rinsing step

When the washing step is finished, CO_2 is drained into the distilling unit. The rinsing step (second bath) starts with a filling of clean CO_2 from the storage vessel to the cleaning vessel. The rinsing step lasts for 5 minutes.

- De-pressurization

After the rinsing step, liquid CO_2 is drained into the distilling unit and subsequently the compressor evacuates the cleaning chamber. When the pressure in the cleaning chamber has reached ~ 1.5 atm, the remaining CO_2 (2 kg) is purged into the atmosphere. The door is opened and the garments are ready to be collected.

- Distillation

Parallel to the rinsing step, the distillation of used liquid CO_2 in the washing step is carried out. The top product of distillation is liquefied in the cooling unit and transferred to the storage tank while the bottom product is collected in a waste drum as residue. The heat produced by the compressor is used to heat up the cleaning vessel and the distillation unit. After the rinsing step, the unit continues with distilling liquid CO_2 from the rinsing step. After this step, the machine is ready for the next cleaning cycle.

- Post-treatment

The washed garments are sent to the finishing section to be pressed and packed.

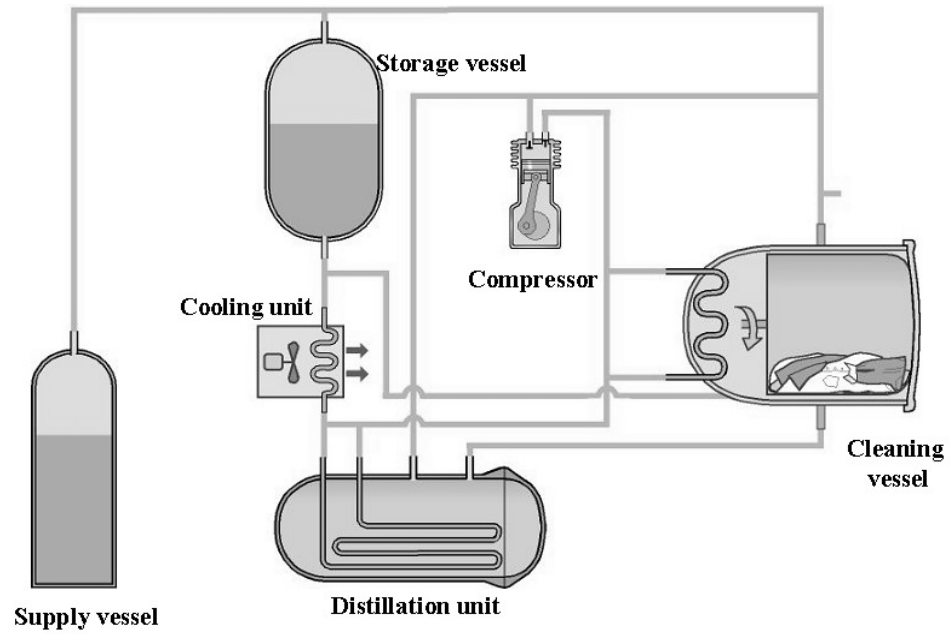


Figure 8.1: Flow sheet of Electrolux Wascator machine [1]



Figure 8.2: Picture of Electrolux Wascator machine

Table 8.1: Process parameters of Electrolux Wascator machine

Parameters	Value
Mechanical agitation	Rotating drum with 3 baffles
Rotational speed (rpm)	30
Load capacity (kg)	17
Temperature (°C)	5-20
Pressure (bar)	Equilibrium with T
Circulation rate (L/min)	None
Number of baths	2 (washing and rinsing)
Cleaning time (min)	15
Rinsing time (min)	5
Total cycle time (min)	30
Filtration	None
Additives	100 g ClipCOO
Electric consumption (kWh)	2.2
CO ₂ consumption (kg)	2
Width x depth x height (m ³)	1.75 x 1.65 x 2.33
Weight (kg)	3600
Vessel diameter (m)	0.75
Vessel length (m)	1.7
Inner drum diameter (m)	0.7
Inner drum length (m)	0.55

Several additional details for this machine include:

- The material of the vessel is carbon steel.
- There is no circulation of CO₂ during the washing and rinsing process.
- There is no filtration unit for CO₂. The process includes a complete distillation of the used CO₂ before it is transferred to the storage tank.
- The only filter in the system is a 25 µm paper filter protecting the gas compressor from dust and particles, located just before the gas compressor.

- For maintenance, the filter and the wall of the cleaning vessel should be cleaned every week, the waste drum for the distillation tank residue must be removed every week.

8.3. Modification of Electrolux Wascator machine and process

Based on the results of this study (Chapter 3-7), modification of several parts of the Electrolux Wascator machine is proposed to improve the cleaning performance of the CO₂ dry cleaning process, especially the particulate soil removal.

8.3.1. Mechanical agitation

The mechanical agitation in the Electrolux Wascator is provided by a perforated rotating drum inside a cleaning chamber as described in Section 8.2. The new design keeps the rotating drum with baffles. However, it is proposed to add multiple flow openings in the form of nozzles because Chapter 6 shows that using additional CO₂ flow or spray might help to increase the mechanical action. The multiple openings created by using several nozzles might induce more movement of textile. Placing the nozzles in the machine leads to slightly higher investment costs. The filling and draining steps take longer and lead to higher operating costs but a quality trade-off is obtained i.e. the cleaning performance (especially for particulate soil removal) is expected to improve up to 20% (Chapter 6).

Figure 8.3a and 8.3b show different proposed configurations of nozzles in CO₂ dry cleaning. They were taken from [2] and [3], respectively. The configuration in Figure 8.3a places the nozzles in a straight line at one side of the vessel wall. Liquid CO₂ enters the cleaning vessel through the inlet pipe (22a) and is distributed through a manifold (52) which in this case is a pipe with several nozzles as the outlets through which the liquid is distributed and then flows into the rotating basket. A circulation pump is required to supply a continuous flow of liquid CO₂. The advantage of using this configuration is that it is easy and relatively economical to construct. The disadvantage is that only a partial section of the clothes (i.e. the part that is close to the nozzle) gets the effect from the spray flow and the clothes may be damaged by the manifold that is inside the vessel. In the configuration shown in Figure 8.3b, CO₂

flows from the inlet (27) into two pipes that act as manifolds (17). The manifolds are located between the vessel and the rotating basket, and have several openings which contain the spray nozzles (15). As in Figure 8.3a, a circulation pump is necessary to continuously produce CO₂ flow. This configuration requires higher costs to be built than Figure 8.3a and the spray is continuously interrupted by the rotating vessel.

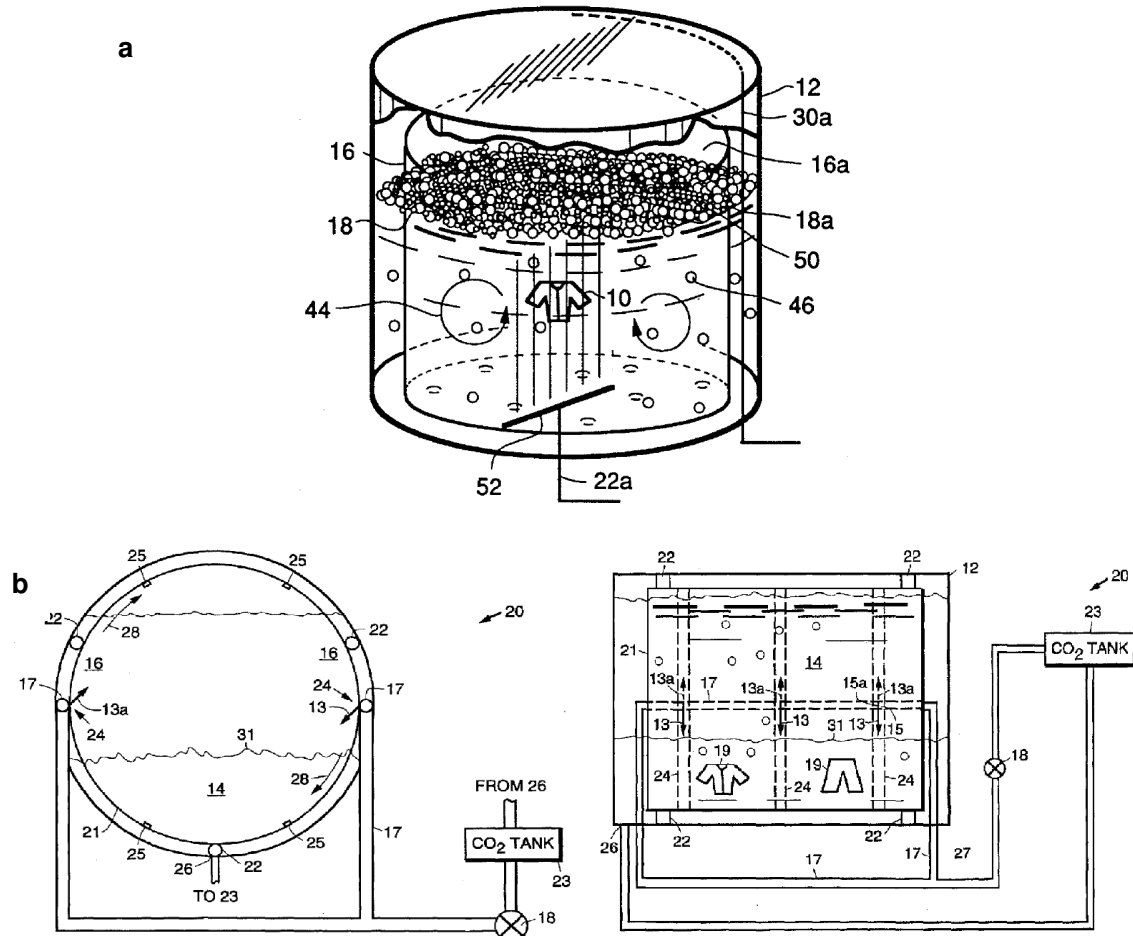


Figure 8.3: Different configuration of nozzles in CO₂ dry cleaning machine

For the optimized equipment, it is proposed to use the configuration in Figure 8.5 with 16 nozzles lined up on 2 manifolds. Also in this configuration, the spray is continuously interrupted by the rotating vessel. The preferred maximum total CO₂ circulation flow is ~1000 L/min [2] or 64 L/min through each nozzle using the selected pump at its maximum speed to get an optimum coverage and impact. In Chapter 9 the technical specification (the required pump head including the estimated pressure

drop of the system) and the economic feasibility (the price) of the selected pump will be evaluated further. Thus, for these reasons, there might be a possibility that the actual flow through these nozzles is less than expected. The nozzles are chosen upon input of Spraying Systems Co. [4]. They are Washjet solid stream nozzles with 0 spray angle and 4.1 mm orifice diameter (Serial number SAB1/4MEG-0040).

For some particulate soils, it may also be an option to add laundry balls to the cleaning vessel to create more mechanical action due to collision between these balls and the fabric. Our previous investigation in Chapter 7 shows that adding more mechanical action by an agitator (mechanical actuator) helped to improve the cleaning performance for certain soil types (e.g. lipstick). However, for a commercial process, it is not practical to use such an agitator inside the cleaning chamber. If instead of the agitator laundry balls are used, it is expected that they might also help to increase textile movement inside the rotating drum. Several laundry balls made from light metal or Teflon (depends on the soil load) might help to further enhance the mechanical action in the vessel.

8.3.2. CO₂ circulation

The Electrolux Wascator machine does not have any CO₂ circulation during the washing and rinsing process. From our studies, it was found that a CO₂ circulation with a pump is essential for:

- Creating CO₂ flow to increase the washing performance (see Section 8.3.1).
- Regulating the temperature of the process during the washing and rinsing step by passing it through the temperature regulating unit (see Section 8.3.3).
- Circulating CO₂ through a series of filters during the washing and rinsing process to remove the released soil (see Section 8.3.4).

It is important to use the optimum circulation speed. Flow rates that are required range from 100 L/min for a small load up to 1000 L/min for large loads, according to the experimental data in [2]. When the washing load is small, the amount of required mechanical action is also lower and thus a lower flow rate is sufficient.

8.3.3. Temperature regulating unit

The Wascator machine has a cooling system between the distillation and the storage tank, but the process temperature during the cleaning is only changed by using the compressed (and heated) CO₂ to warm up the content of the cleaning vessel (see Figure 8.1), which was reported insufficient by several users. Thus, it is desirable to be able to regulate the process temperature by circulating CO₂ through a cooling/heating bath during the cleaning process.

8.3.4. Filtration system

There is no filtration system in the Electrolux Wascator, only 100% distillation of the used CO₂. However, the results of redeposition study in Chapter 3 show that using an appropriate filtration unit could significantly reduce the occurrence of redeposition. Therefore, it is proposed to circulate CO₂ through a series of filters to remove the released soil during the cleaning steps. According to the results in Chapter 3 and communication with experts, a filtration system for CO₂ dry cleaning might consist of at least 4 different types of filter in series:

- The first filter made of wire mesh of 100 µm to remove the buttons, beads and threads
- The second filter made of fine wire mesh of 10 µm to remove lint and fibers
- The third filter made of scavenger textile (Chapter 3) to remove particulate soils
- The fourth filter made of granular carbon to remove dye.

In this way, the resistance and pressure drop of the filters can be reduced and the soil and other compounds are removed from the CO₂ stream to prevent redeposition (Chapter 3).

8.3.5. Additives formulation

The current process uses ClipCOO detergent around 100 g/cycle. The new process might keep this formulation since according to the results in Chapter 4, ClipCOO gives better cleaning results than Washpoint and is therefore the best available commercial option. However, an amount of water of around 10-15% of the detergent

weight may be added as co-solvent (Chapter 4). Our colleagues from Wageningen University have shown that loose water droplets can form capillary bridges between particulate soil and textile and are thus enhancing the adhesion force. Therefore, it is important to add surfactant (in their case, Igepal) along with the water to keep the extra water inside the reverse micelle [5]. Addition of extra alcohol is not necessary since this has been incorporated in the ClipCOO formulation. The used detergent, extra surfactant and water end up with the soluble soil as residue in the distillation unit. The relatively high price of a recovery unit for the detergent and the relatively low price of the detergent seem to make recovery of the additives economically unfeasible. Unfortunately, a commercial detergent that is able to overcome e.g. the strong interaction between the particulate soil and the textile in the CO₂ medium is not yet available.

8.3.6. Constant parameters

The other process parameters (washing and rinsing time, process temperature and the number of baths) are kept the way they are since the results obtained from this study show that these process conditions so far give the highest cleaning performance. We do not encourage changing the material of the apparatus from carbon steel to stainless steel since the current Electrolux Wascator machine with carbon steel has been running for 14 years and is expected to last another 6 years without any problems (Porsmose, M - Kymi Rens, personal communication, 2012). Changing the material to more expensive stainless steel does not seem to have an added value.

The principle of CO₂ recycling in the optimized machine is also similar to that in the Wascator machine. After the washing or rinsing cycle is complete, the liquid CO₂ is drained from the cleaning vessel into the distillation unit. In the distillation unit, liquid CO₂ is heated to above the boiling point of CO₂ so that it evaporates. The top product (CO₂ gas) of the distillation unit is cooled down by a cooling unit to become liquid and sent to the storage vessel. The bottom product of the distillation unit, which is a mixture of surfactant and soil is collected as residue. In the Netherlands, this residue is regularly collected by a special company to be treated as chemical waste.

Furthermore, the heat integration with the CO₂ flows from and to the compressor in the Wascator machine is also maintained.

8.3.7. Flow diagram and rotating drum design of the optimized machine

The simplified flow diagram and the rotating drum design of the modified apparatus are given in Figure 8.4 and Figure 8.5, respectively.

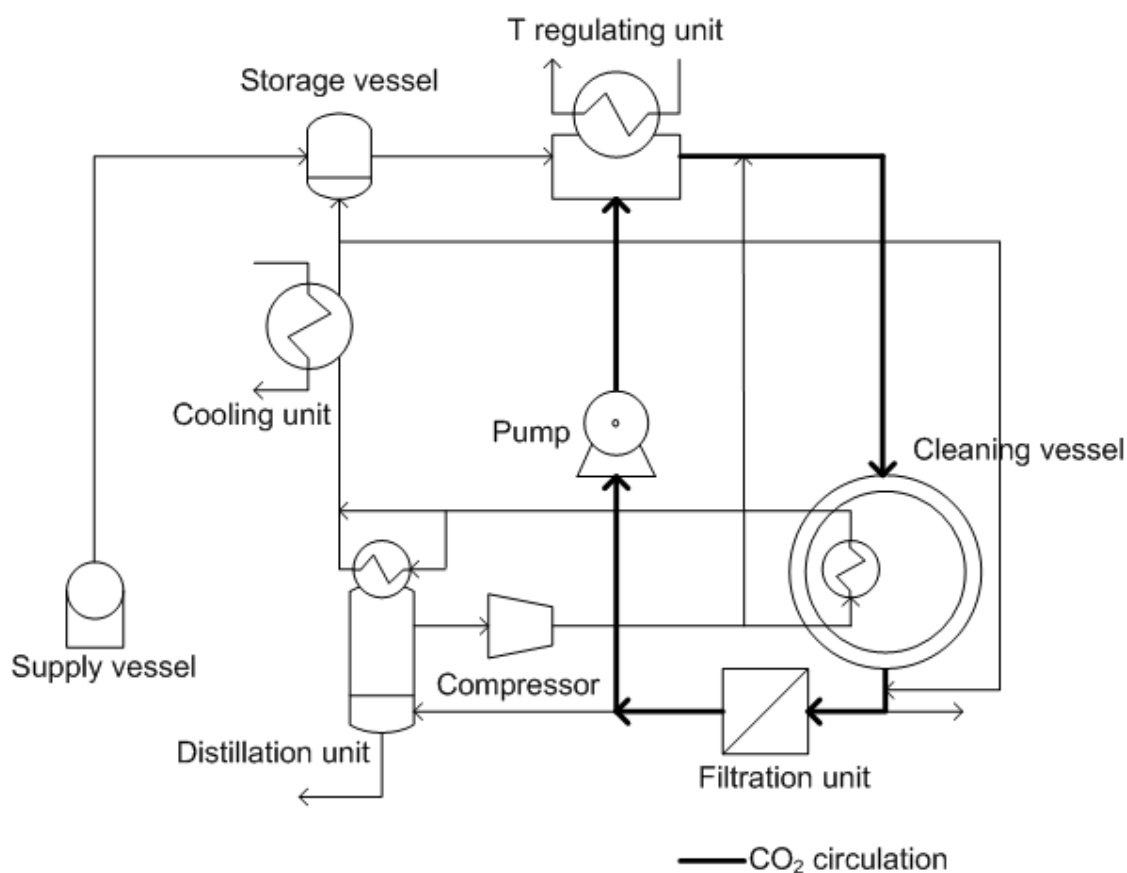


Figure 8.4: Flow diagram of the optimized CO₂ dry cleaning machine

8.4. Closing words

Besides of having a good cleaning performance, a dry cleaning machine should ideally be an affordable investment and have low operating costs as well as produce a low amount of chemical waste. The performance and investment costs of CO₂ dry cleaning are not yet comparable with the conventional or the other alternative

solvents. However, we believe that CO₂ is the only real green solvent for textile dry cleaning and our studies have shown that it has a high potential to replace PER in the future. Especially when the regulation of using PER is tightened, and the design of the whole process, the equipment and the surfactant are further developed. The future (increasing) energy price might also have some influence since the utility consumption of CO₂ dry cleaning is lower than PER (Chapter 9). As shown in this study, it is essential to have a suitable surfactant which can overcome the strong Van der Waals interactions between particulate soils and textile in the CO₂ medium because mechanical action alone is not sufficient to improve the cleaning performance.

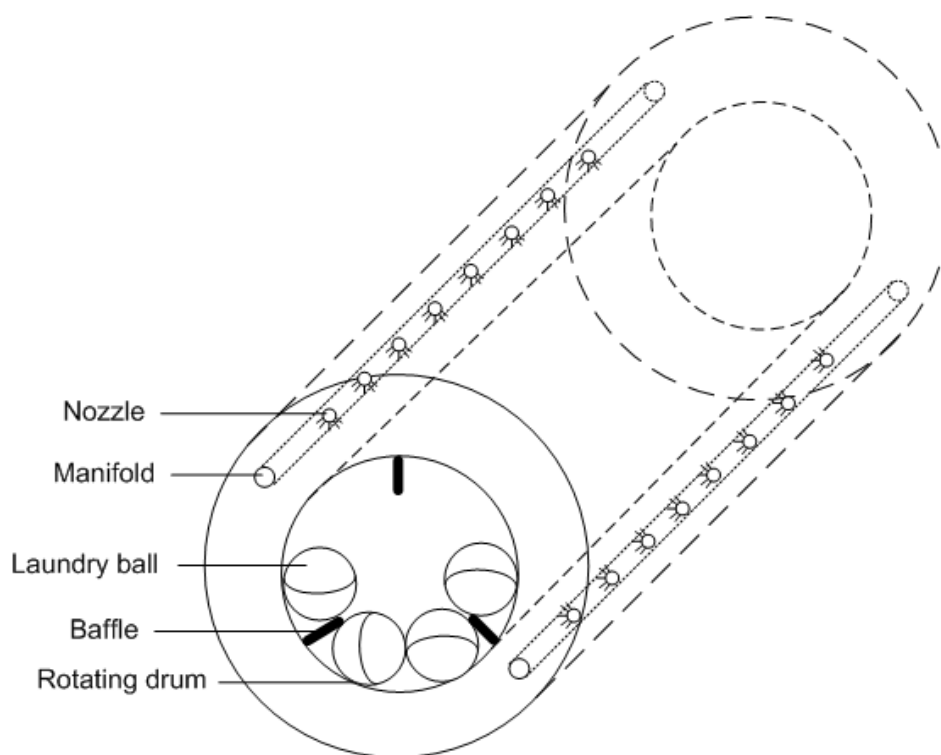


Figure 8.5: Cleaning vessel of the optimized CO₂ dry cleaning machine

References

- [1] H. Van Kuijk, (Krom Stomerijen B.V.), Demonstration textile CO₂ treatment introduction validation effort – DETECTIVE, 2005, Netherlands, Available from

http://ec.europa.eu/environment/life/project/Projects/files/laymanReport/LIFE00_ENV_NL_000797_LAYMAN.pdf

- [2] C.W. Townsend, et. al., Liquid carbon dioxide dry cleaning system having a hydraulically powered basket, US Patent 5669251, Issued 23 September 1997.
- [3] Purer, et. al., Dry-cleaning of garments using gas-jet agitation, US Patent 5651276, Issued 21 July 1997.
- [4] <http://www.spray.com/>
- [5] S. Baneerje, S. Sutanto, J.M. Kleijn, M.J.E. van Roosmalen, G.J. Witkamp, M.A.C. Stuart, Colloidal interactions in liquid CO₂ - a dry-cleaning perspective, Advance Colloid Interface Science 175 (2012) 11-24.

Chapter 9

Economic Evaluation

9.1. Introduction

In this chapter, the costs for the new CO₂ dry cleaning machine and process as described in Chapter 8 are compared to the costs for the dry cleaning process using PER.

9.2. Summary of modifications

To be able to read this chapter separately, a summary of the main proposed modifications of the existing Electrolux Wascator S35 machine from Section 8.3 is given below. The process flow diagram and the vessel design of the machine are given in Figure 9.1 and 9.2, respectively.

- **Mechanical agitation**
Besides the rotating drum with baffles which is already in the Wascator machine, we propose to add 16 nozzles with 4.1 mm orifice diameter, placed on two manifolds between the vessel and the drum to increase the mechanical action (Figure 9.2). In addition, we also propose to add several laundry balls made from light metal or Teflon to help the removal of certain types of soil. The price of the nozzles, the manifolds and the laundry balls is estimated at € 500.
- **CO₂ circulation**
The Wascator machine does not have any CO₂ circulation. However, our studies show that CO₂ circulation with a pump is essential to create CO₂ flow to increase the washing performance during the washing and rinsing process. In the circulation loop, CO₂ passes through a series of filters and through a temperature regulating unit (Figure 9.1). The preferred CO₂ circulation flow is ~1000 L/min at the pump's maximum speed. Discussion with a pump manufacturer leads to a centrifugal pump which allows circulation at the required pressure without

significant change in process pressure. The pump has sufficient head to overcome the pressure drop in the circulation loop but the maximum available flow rate is 200 L/min which is lower than the desired value. The pump is estimated to cost € 20,000.

- Temperature regulating unit

The process temperature of the Wascator machine during the cleaning step can only be changed by using the heat integration with the outlet flow from the compressor. This was reported not sufficient to reach the desirable value by several users. Thus we propose to use a temperature regulating unit (cooling/heating bath) which is placed in the circulation loop. Discussion with the manufacturer leads to a cooling/heating bath with an estimated price of € 7000.

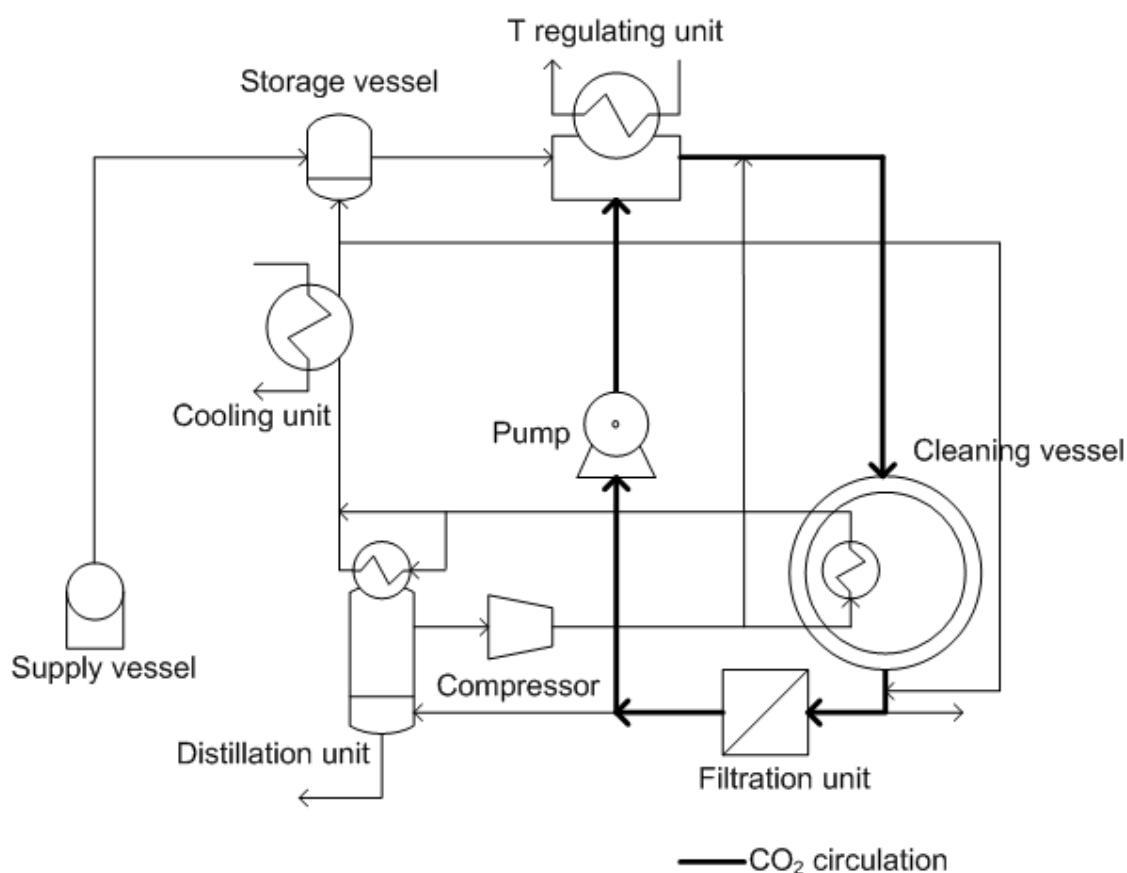


Figure 9.1: Flow diagram of the optimized CO₂ dry cleaning machine

- Filtration unit

Electrolux Wascator is also lacking of filtration of CO₂. In the modified machine, we propose a filtration unit to reduce the occurrence of redeposition (Figure 9.1).

The filtration unit consists of:

- The first filter, made of wire mesh of 100 µm to remove the buttons, beads and threads
- The second filter, made of fine wire mesh of 10 µm to remove lint and fibers
- The third filter, made of scavenger textile to remove particulate soils
- The fourth filter, made of granular carbon to remove dye.

The price of this filtration system is estimated at € 1000.

- Additives formulation

Beside of using 100 g of ClipCOO surfactant/cycle as in the existing CO₂ dry cleaning process, the new additives formulation also adds 10-15% water of surfactant weight to get a better cleaning performance. However, we assume that these extra costs are negligible.

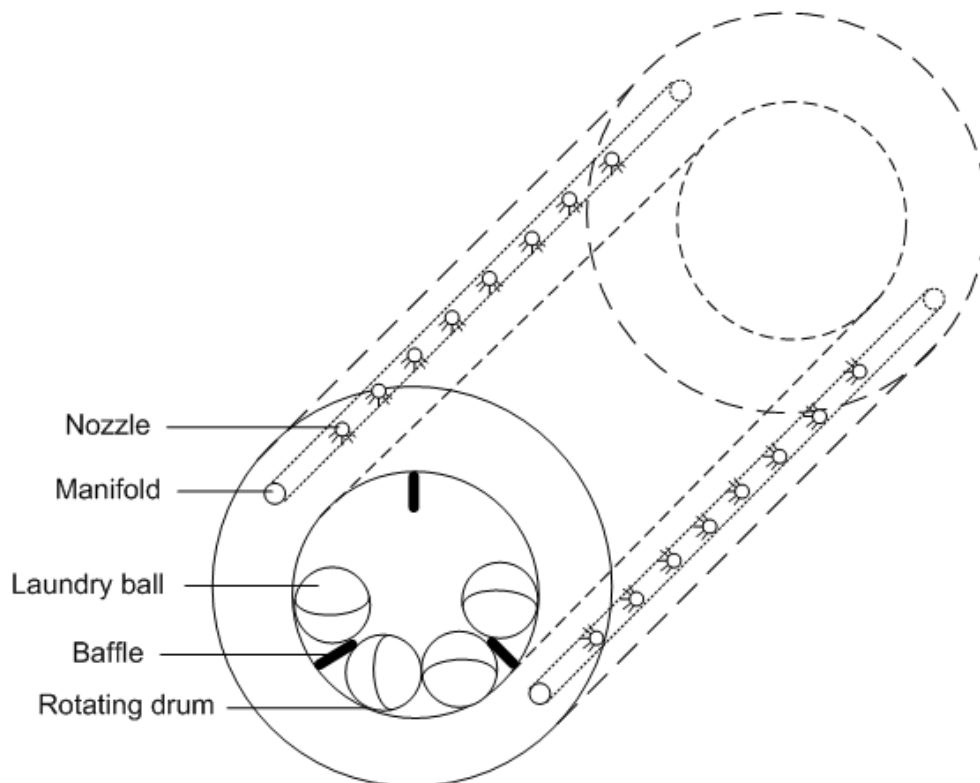


Figure 9.2: Cleaning vessel of the optimized CO₂ dry cleaning machine

9.3. Basis of calculations

The price of the modified CO₂ machine as given in Table 9.1 is based on the basic price from Electrolux Wascator S35 machine which is obtained from Kymi Rens (a CO₂ dry cleaner in Denmark), increased with the price of modified parts of the equipment. We keep the material to carbon steel since so far no rust issues were encountered with the existing Electrolux machines. The price of a PER machine with similar capacity as the CO₂ machine (16 kg) is obtained from the supplier (Bowe, premium line M16).

Table 9.1: Costs of a modified CO₂ dry cleaning machine

Cleaning unit	Price (Euro)
Electrolux Wascator S35	120,000
Modification	
Nozzles, manifolds and laundry balls	500
Circulation pump	20,000
Temperature regulating unit	7000
Filtration unit	1000
Total investment costs	148,500

Table 9.2: Data for PER and CO₂ dry cleaning process

Parameters	Unit	PER	CO₂
Capacity	kg	16	17
Cycle time	min	48	30
Cycles per day		7	12
Working days per annum		250	250
Investment costs	Euro	55,000	148,500

The data used as the basis of the cost comparison between PER and CO₂ processes are summarized in Table 9.2. Some fixed costs are not considered,

because they are equal for both processes. The cost evaluation is based on the use of a 2 bath process: washing and rinsing. It is assumed that both machines are used to the full capacity.

9.4. Economic evaluation

The costs of the dry-cleaning process with CO₂ are compared with those of PER. The costs are calculated per kg of cleaned fabric, based on the method used by Van der Donck and Verbeek [1]. The results of the economic evaluation are shown in Table 9.3. Depreciation is calculated using straight line method, with assumption that the value of the machine is nil at the end of the used period which is assumed 10 years. The utility data are obtained from mass and enthalpy balances [2] with taking into account the proposed modifications. The operating labour data are obtained from dry cleaning companies. The price of CO₂ make-up already includes the rental costs of the storage vessel. The amount of surfactants used in this evaluation is based on the actual usage in the commercial dry cleaning process.

From Table 9.3, it can be concluded that the overall costs of CO₂ textile cleaning are 3% lower than of PER dry cleaning (3.39 versus 3.49 €/kg garments, respectively), although it requires higher capital costs at the beginning (€ 148,500 versus 55,000). The labour costs of CO₂ textile cleaning are comparable to PER dry cleaning. The costs of utilities with CO₂ are lower because no drying step is required. In addition, no specific solvent disposal is required with CO₂. The material handling prior to and after the cleaning process (sorting, spotting and finishing) is the largest cost item.

9.5. Conclusions

The operating costs for dry-cleaning using CO₂ are comparable to the costs of using PER. Labour costs are the largest cost item.

Table 9.3: Economic evaluation of PER and CO₂ dry cleaning

Parameters	Unit	PER	Costs (Euro/kg)	CO ₂	Costs (Euro/kg)
Cleaning and drying					
Labour			0.18		0.17
Labour price	Euro/h	35		35	
Required labour	h/cycle	0.1		0.1	
Depreciation			0.20		0.29
Time	years	10		10	
Investment costs	Euro	55000		148500	
Maintenance			0.04		0.06
Rate of investment		2%		2%	
Investment costs	Euro	55000		148500	
Power			0.18		0.15
Power price	Euro/kWh	0.2		0.2	
Required power	kWh/cycle	14.9		13.0	
Steam			0.07		0
Steam price	Euro/kg	0.1		0.1	
Required steam	kg/cycle	11.3		0	
Water			0.09		0
Water price	Euro/m ³	2.0		2.0	
Required water	m ³ /cycle	0.7		0	
Detergent			0.03		0.03
Detergent price	Euro/kg	5.5		5.5	

Required detergent	kg/cycle	0.1		0.1	
Solvent make-up			0.09		0.12
Solvent price	Euro/kg	5		1	
Required make-up	kg/cycle	0.3		2	
Disposal			0.03		0
Disposal costs (Euro/kg)	Euro/kg	2		0.5	
Disposal of waste (kg/cycle)	kg/cycle	0.2		0.1	
Total cleaning and drying			0.91		0.82
Pre and post treatment					
Labour - Sorting and Spotting			0.58		0.58
Labour price	Euro/h	35		35	
Required labour	kg/h	60		60	
	h/day	1.9		3.4	
Labour - Finishing			1.40		1.40
Labour price	Euro/h	35		35	
Required labour	kg/h	25		25	
	h/day	4.5		8.2	
Depreciation			0.06		0.06
Time	years	10		10	
Investment costs	Euro	18000		18000	
Maintenance			0.01		0.01

Rate of investment		2%		2%	
Investment costs	Euro	18000		18000	
Power			0.11		0.11
Power price	Euro/kWh	0.19		0.19	
Required power	kWh/h	12		12	
Steam			0.40		0.4
Steam price	Euro/kg	0.1		0.1	
Required steam	kg/h	80		80	
Total pre and post treatment			2.57		2.57
Total costs			3.49		3.39

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- [1] J.C.J. van der Donck, M.A. Verbeek, Inzetbaarheid van alternatieve reinigingsmethoden, TNO Rapport 007.60067/60068, TNO RTT, Delft, 2001.
- [2] H. Van Kuijk, (Krom Stomerijen B.V.), Demonstration textile CO₂ treatment introduction validation effort – DETECTIVE, 2005, Netherlands, Available from http://ec.europa.eu/environment/life/project/Projects/files/laymanReport/LIFE00_ENV_NL_000797_LAYMAN.pdf

Appendix A

Pictures of Apparatus

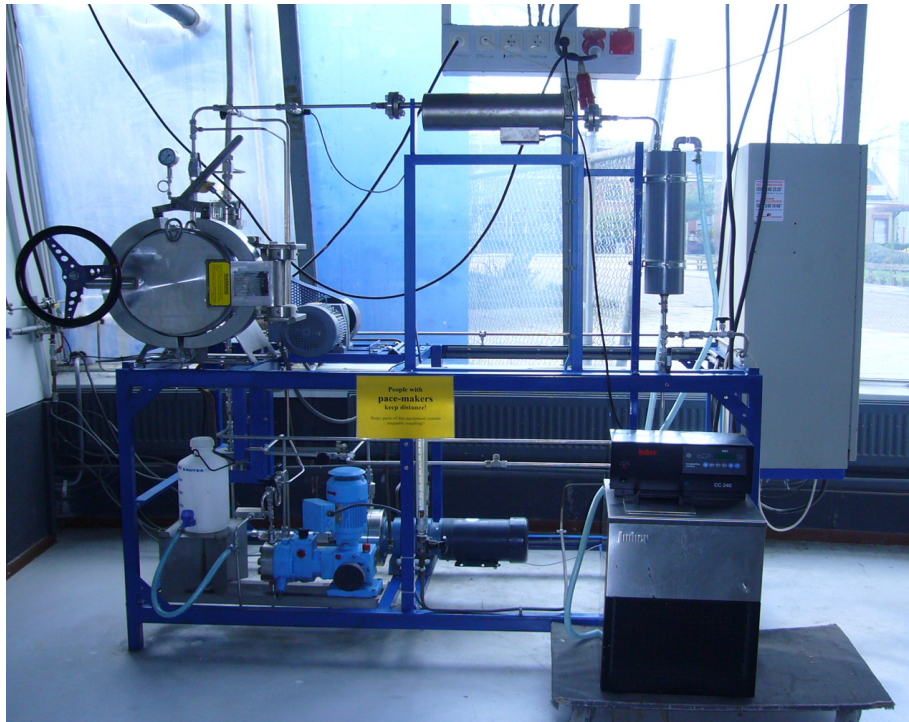


Figure A.1: Picture of 25 L CO₂ dry cleaning apparatus at TU Delft



Figure A.2: Picture of 1 L CO₂ dry cleaning apparatus at Twente University

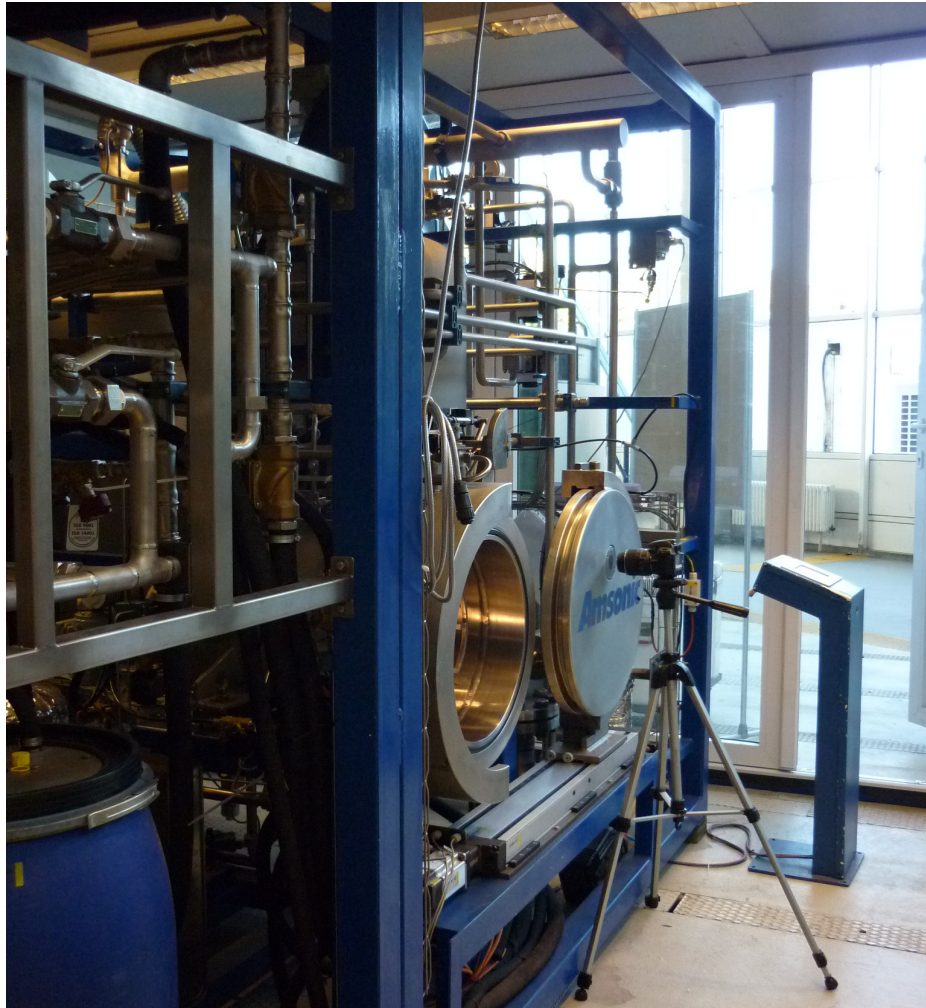


Figure A.3: Picture of 90 L CO₂ dry cleaning apparatus at IPK Fraunhofer



Figure A.4: Picture of observation cell apparatus at TU Delft

List of Publications

- Redeposition in CO₂ Textile Dry Cleaning, S. Sutanto, M.J.E van Roosmalen, G.J. Witkamp, the Journal of Supercritical Fluids 81 (2013) 183-192.
- Mechanical Action in CO₂ Dry Cleaning, S. Sutanto, M.J.E van Roosmalen, G.J. Witkamp, accepted by the Journal of Supercritical Fluids.
- CO₂ Dry Cleaning: Acoustic Cavitation and Other Mechanisms to Induce Mechanical Action, S. Sutanto, V. Dutschk, J. Mankiewicz, M.J.E van Roosmalen, M.M.C.G. Warmoeskerken, G.J. Witkamp, accepted by the Journal of Supercritical Fluids.
- CO₂ Textile Dry Cleaning: Performance Enhancement with Additional Particles, S. Sutanto, M.J.E van Roosmalen, G.J. Witkamp, submitted to Textile Research Journal.
- Colloidal Interactions in Liquid CO₂ – A dry-cleaning Perspective, S. Banerjee, S. Sutanto, J. M. Kleijn, M. J. E. van Roosmalen, G.J. Witkamp, M. A. Cohen Stuart, Advances in Colloid and Interface Science 175 (2012) 11-24.
- A Surfactant Formulation for Particle Release in Liquid CO₂ Dry-Cleaning, S. Banerjee, S. Sutanto, J. M. Kleijn, M. A. Cohen Stuart, Colloids and Surfaces A: Physicochemical and Engineering Aspects 415 (2012) 1-9.
- Cleanability of Textile Materials in Liquid CO₂, V. Dutschk, S. Sutanto, A. Calvimontes, Tenside Surfactants Detergents 50 (2013) 21-25.
- Textile Cleaning in Liquid and Supercritical CO₂, V. Dutschk, S. Sutanto, A. Calvimontes, in preparation.

Curriculum Vitae

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Delft, February 2014
Stevia