Compressed Carbon Dioxide – An Innovative Washing Fluid

Dennis Rebien[1], Johannes Mankiewicz[2], Martin Bilz[2], Sabine Kareth[1*], Marcus Petermann[1]
(1) Institute for Thermo and Fluid Dynamics, Ruhr-University Bochum, IB 6/126,
Universitaetsstr. 150, 44801 Bochum, Germany
(2) Fraunhofer IPK, Berlin, Germany
kareth@vtp.rub.de, Fax: +49 234 32 14277

INTRODUCTION

Production of mechanical precision parts or electronic parts often requires diverse production steps. Either intermediates or the final products need to be cleaned from processing fluids or mechanical pollutions. Conventional cleaning processes are either based on isoparaffins or water based requiring the use of surfactants. Subsequently the wet parts need to be dried in a cost-intensive drying step. The used aqueous cleaning fluids need to be deposited as waste. In some cleaning processes still hazardous Chlorofluorocarbons (CFCs) are applied as degreasing solvents.

The use of compressed gases like carbon dioxide as degreasing solvents might provide an environmental friendly and cheap alternative. CO_2 can be applied in the supercritical as well as liquid state for extraction purposes. Extraction of hops is a well known example.

Cleaning can be achieved by dissolving the contamination in carbon dioxide but the carbon dioxide will dissolve as well in the impurity thus facilitating and supporting the cleaning process by reducing the viscosity of the contaminating oil, reducing the interfacial tension of the contaminant as well as decreasing the density of the contamination. Dry parts can be taken from the cleaning chamber after cleaning, thus avoiding an additional drying step. An additional benefit might be that carbon dioxide shows antibacterial capacity, this can be advantageous for the cleaning of medical parts.

Application of carbon dioxide as cleaning solvent has already been investigated for different cleaning purposes as for example the cleaning of textiles [1-5] and flash cleaning of turbine blades. [6-10]

Based on the results of thermo and fluid dynamic studies first cleaning experiments, in lab and pilot scale, were performed with highly porous sinter metal filters (average pore size: 8 µm). Loaded with an alkane-based cutting fluid the parts are proving the cleaning power of compresses carbon dioxide at room temperature and pressures between 50 and 60 bar. Subsequently the suitability for more complex parts provided by industry partners made of metals like Cu, CuZn, aluminum and steel (1.0037, 1.4301), thermo-sensitive polymers like PE and PP as well as PTFE and Silicone were investigated.

MATERIALS AND METHODS

“Real” cutting fluids used in industry were supplied by project partners. [11,12].

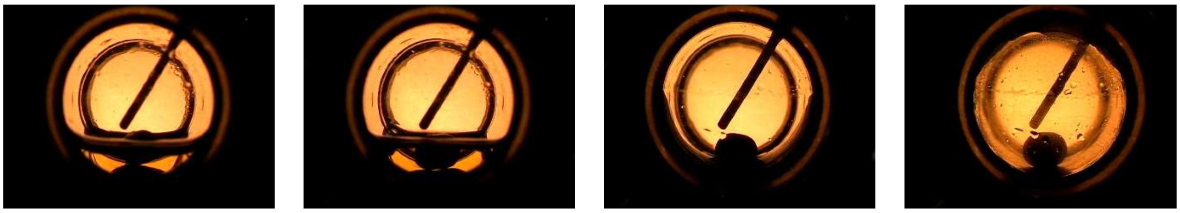
In this work a cutting fluid based on mineral oil with mainly paraffinic compounds and some not identified additives was used. Carbon dioxide was supplied by Yara, Germany, with a purity of 99.9 % v/v.

Qualitative phase behaviour was studied in view cell of 25 ml volume designed for a maximum temperature of 100 °C and a maximum pressure of 250 bar. An autoclave plant designed by Natex, Austria, was used for quantitative phase behaviour experiments ($V = 1$ l, $T_{max} = 150$ °C, $p_{max} = 350$ bar). Solubility measurements were executed following a static-analytical standard procedure. Cleaning experiments were performed at lab scale in a variable volume view cell supplied by NWA, Germany, equipped with an ultrasound sonotrode ($V_{max} = 330$ ml, $T_{max} = 200$ °C, $p_{max} = 700$ bar) and at pilot scale in a precision cleaning plant provided by Amsonic, Switzerland.

RESULTS

Aim of research was to investigate if carbon dioxide is a suitable alternative for the cleaning of precision parts from residual processing aides like cooling lubricants and adhering particles.

Thermodynamic studies on the phase equilibrium of the system cutting fluid - carbon dioxide were conducted. Figure 1 shows the phase behaviour of the cutting fluid at 25 °C.



ambient pressure p = 51 bar p = 99 bar p = 198 bar

Figure 1: Qualitative phase behaviour of the system cutting fluid carbon dioxide at 25 °C

The first picture shows the cutting fluid at atmospheric conditions. With rising pressure the level of the lower, oil rich phase is decreasing until almost no second phase is visible. Most of the cutting fluid is soluble in carbon dioxide and only a small separate phase is left. Due to the fact that the system is a multinary mixture it is possible that the mineral oil compound(s) of the cutting fluid are completely soluble in carbon dioxide while the minor compounds, for example the additives, stay in a separate phase. For higher pressure a phase inversion is found where the density of the liquid carbon dioxide phase is higher than the density of the cutting fluid rich phase.

Solubility measurements of the system cutting fluid – carbon dioxide are shown in figure 2.

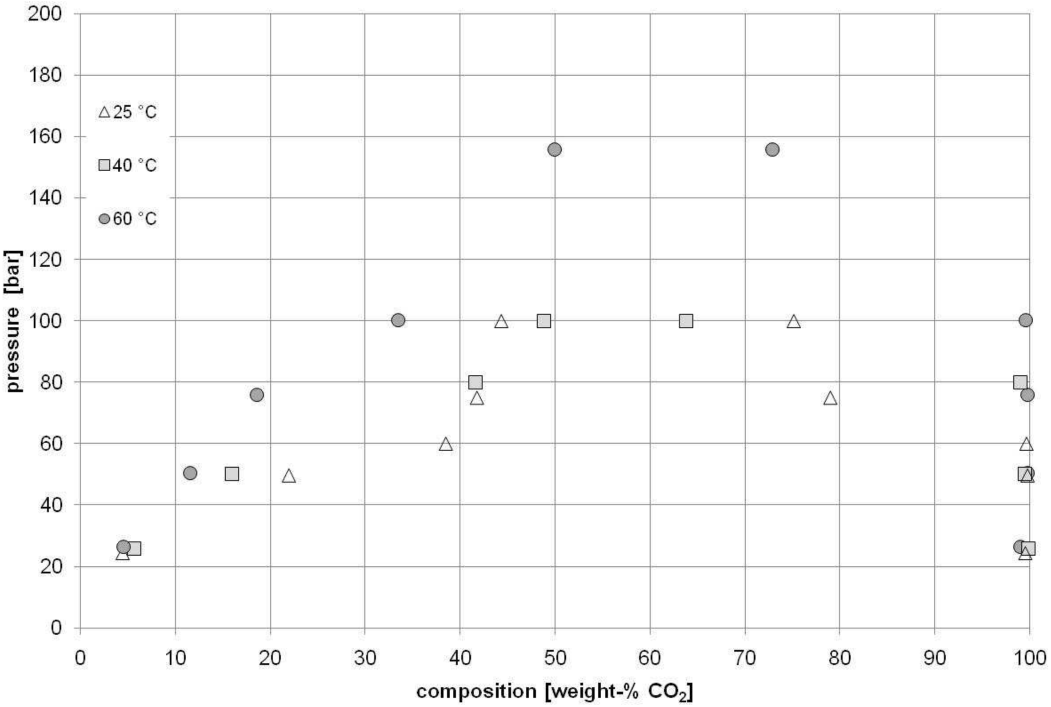


Figure 2: Phase equilibrium of the system cutting fluid - carbon dioxide

The mutual solubility of the cutting fluid and carbon dioxide was measured at temperatures from 25 – 60 °C at pressures up to 200 bar. With rising pressure the solubility of carbon dioxide in the cutting fluid and of cutting fluid in carbon dioxide is increasing. For all temperatures the cutting fluid and CO_2 are not completely miscible in the investigated pressure range. At 25 °C the solubility of the cutting fluid in carbon dioxide increases significantly as carbon dioxide liquefies. For 40 and 60 °C the solubility increases at pressures higher than 80 respectively 100 bar. At lower pressures almost no cutting fluid is soluble in carbon dioxide. In contrary the cutting fluid dissolves already at low pressures high quantities of carbon dioxide.

One possible drawback for parts-cleaning with compressed carbon dioxide is the fact that carbon dioxide will form carbonic acid under pressure especially if water is present. This could lead to corrosion of the metal parts during cleaning. To examine the corrosion potential six different metal samples from copper, brass, aluminium, construction steel S235JR (St37), zinc coated steel and stainless steel (VA) were put to the view cell at room temperature and saturation pressure for carbon dioxide for 72 h. The ethanol cleaned samples have been placed inside the view cell separated by PTFE spacers during the experiments avoiding direct contact of the samples (Figure 3). No corrosion was observed for all metals except for the construction steel for specimens scratched before the experiments to simulate the metal processing.

Figure 3: Specimen for the corrosion tests

The cleaning of particle soil is a challenge for all cleaning processes. In aqueous system application of ultrasound shows great effects on the removal of particles from surfaces. A possible transfer of this technique to cleaning with carbon dioxide was investigated using different types of sonotrodes supplied by NWA, Germany, and Weber Ultrasonics, Germany. The variable volume view cell could be equipped with both sonotrodes. Figure 4 shows a sonotrode acting at room temperature at saturated vapour pressure of carbon dioxide. The phase boundary is highly agitated.

Figure 4: Ultrasound sonotrode acting in two phasic pure carbon dioxide at ambient temperature [13]

In water ultrasound can cause cavitation of droplets strong enough not only to remove the particles but also to harm the metal part’s surface. The use of ultrasound in carbon dioxide facilitates the removal of particles but the effect is not strong enough to harm the surface of the cleaned parts.

Ultrasound will also help with the cleaning of blind holes and undercuts. Here big amounts of residual oils can be found after processing not easy accessible for washing fluids. At elevated pressure carbon dioxide will dissolve in the cutting lubricant (fig. 2) changing its properties like viscosity and surface tension. Application of ultrasound will lead to degassing of carbon dioxide from the lubricant helping to drive the oil out of the blind holes. This effect can also be achieved by flash cleaning (fig. 5). Here a pressure drop will initiate the removal of the oil form the tapped hole.

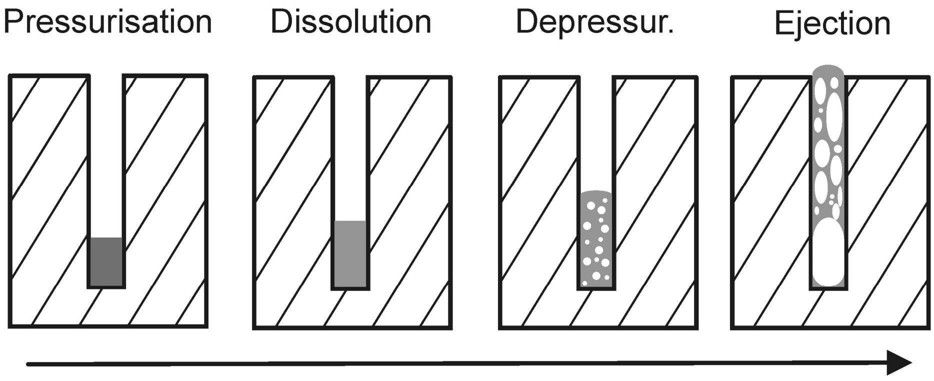


Figure 5: Stages of flash cleaning [13]

From labscale to pilot scale

Scale up experiments were performed in a precision cleaning plant provided by Amsonic, Switzerland. The plant is operating at saturation vapour pressure. The cleaning vessel has a Volume of 90 l and is operated with liquid carbon dioxide. For particle removal different cleaning procedures using ultrasound or additional injection of liquid carbon dioxide can be applied. The parts to be cleaned can be mounted in a rotating basket. The rotation supports the cleaning process by moving the parts repeatedly through the phase boundary.

Figure 6 shows a pilot plant from Amsonic, Switzerland, used in this work.

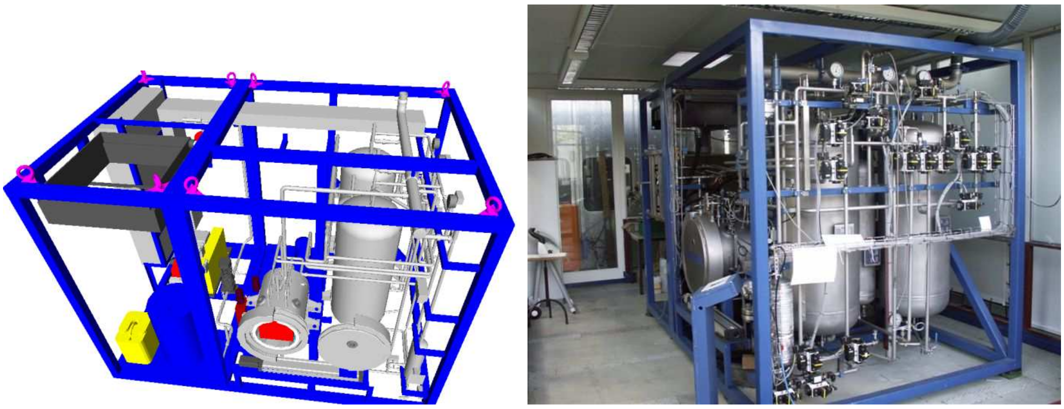


Figure 6: Pilot plant for precision cleaning [13, 14]

The plant is equipped with two storage tanks for carbon dioxide. One tank is holding the used and impure carbon dioxide while the second tank is the supply and storage for pure and clean carbon dioxide. The cleaning of carbon dioxide is achieved by evaporating the soiled carbon dioxide from the first storage tank at saturation vapour pressure to the second storage tank holding the pure carbon dioxide supply that will be used in the process. Impurities will be drained from the first tank in regular intervals. Carbon dioxide is pressurised and cycled by a plunger pump supplied by Speck, Germany. Several programs for the operation of the plant allow the flooding of the cleaning vessel from the lower or upper section as well as the additional injection of liquid carbon dioxide through nozzles in the upper section.

Figure 7: Sinter metal specimen

Sinter metal specimen artificially soiled with the cutting fluid, have been cleaned to investigate the applicability of the operation conditions found by labscale experiments in a view cell. For the cutting oil investigated a cleaning efficiency of 99.3 % was found for pilot plant experiments.

CONCLUSIONS AND OUTLOOK

The applicability of carbon dioxide as cleaning fluid for an industrial cleaning process of metal parts has been proved based on thermo dynamic investigations on the system cutting fluid carbon dioxide at elevated pressure. The cleaning performance and efficiency of an industrial pilot plant was enhanced.

Besides the sinter metal specimen industrial parts provided by project partners were successfully cleaned. Especially the cleaning of blind holes and undercuts is problematic for cleaning processes. The application of liquid carbon dioxide as washing fluid is advantageous for this task as flash cleaning induced by a pressure drop or by ultrasound facilitates the cleaning of parts with difficult geometries.

Corrosion caused by carbonic acid was investigated for different metal samples like brass, aluminium and different sorts of steel. Only a sample of construction steel (st 37) showed corrosion after exposure to carbon dioxide, all other samples were not affected.

Particulate soils are a challenge in parts cleaning. Mechanical assistance of the washing process can be provided by ultrasound, movement through the phase boundary or additional injection of liquid carbon dioxide, thus enhancement of the cleaning performance can be achieved.

First experiments on the reduction of germs on the items showed excellent results. This is an advantage for the cleaning of medical parts. Further experiments on the cleaning of medical parts are in progress e.g. the cleaning of an implantable left ventricular assist device (fig. 8).

Figure 8: Superior pump - heart function support system (courtesy of Berlin Heart)

Decontamination of cultural heritage items is task for museums all over Europe. First experiments on the cleaning of artifacts supplied by the University of Applied Science Potsdam and the Staatliche Museen Berlin are promising (fig. 9). The tests show good results for the reduction of DDT, lindane, PCP, arsenic and quicksilver.

Figure 9: Feather headdress for decontamination [13]

ACKNOWLEDGEMENT

The authors want to thank BMWi VDI/VDE Innonet-Projekt Kodiwasch for financial support.

REFERENCES

[1] http://www.fredbutler.com/

[2] VAN ROOSMALEN, M.J.E., VAN DIGGELEN, M., WOERLEE, G. F., WITKAMP, G. J., Dry-cleaning with high-pressure carbon dioxide-the influence of mechanical action on washing-results, *The Journal of Supercritical Fluids*, 27(1), **2003**, p. 97-108**.**

[3] VAN ROOSMALEN, M.J.E., WOERLEE, G.F., WITKAMP, G.J., Surfactants for particulate soil removal in dry-cleaning with high-pressure carbon dioxide, *The Journal of Supercritical Fluids*, 30, **2004**, p. 97-109.

[4] VAN ROOSMALEN, M.J.E., WOERLEE, G.F., WITKAMP, G.J., Dry-cleaning with high-pressure carbon dioxide – the influence of process conditions and various co-solvents (alcohols) on cleaning results, *The Journal of Supercritical Fluids*, 27, **2003**, p. 337-344**.**

[5] *Supercritical Fluid Cleaning – Fundamentals, Technology and Applications* (Eds. J. McHardy, S.P. Sawan), Noyes Publications, Westwood **1998.**

[6] Patent DE 10218519C1 (26-06-2003). DaimlerChrysler AG. Pr.: 10218519 25-04-2002. Verfahren zur Reinigung von Gegenständen mittels eines komprimierten Reinigungsmediums, **2003.**

[7] Patent DE 102006061444A1 (26-06-2008). MTU Aero Engines GmbH. Pr.: 102006061444 23-12-2006. Verfahren und Vorrichtung zur Aufbringung eines Schutzmediums auf eine Turbinenschaufel sowie Verfahren zur Einbringung von Kühlbohrungen in eine Turbinenschaufel, **2006**.

[8] PIETSCH, A., UNGER, M., Flashreinigung von Turbinenschaufeln mit überkritischem CO_2, Vortrag auf der ProcessNet Fachausschusssitzung Hochdruckverfahrenstechnik, http://www.mtu.de/de/technologies/engineering_news/production/Unger_Flashreinigung_von_Turbinenschaufeln_de.pdf, Fulda, **2010.**

[9] PURTELL, R., ROTHMAN, L., Precision parts cleaning using supercritical fluids, *J. Vac. Sci. Technol. A*, 11(4), **1993**, p. 1696-1701**.**

[10] DAHMEN, N., PIOTTER, V., HIERL, F., ROELSE, M., Überkritische Fluide zur Behandlung und Herstellung komplexer Werkstoffe und Oberflächenstrukturen, Wissenschaftliche Berichte FZKA6585, Forschungszentrum Karlsruhe, Karlsruhe, **2001.**

[11] KRIEG, M.C., BILZ, M., MANKIEWICZ, J., Trends in der industriellen Teilereinigung – Welches Potenzial hat Kohlendioxid?, *Chemie Ingenieur Technik*, 81(11), **2009**, p. 1845–1851**.**

[12] Entwicklung einer dezentralen Anlagentechnik zur wirtschaftlichen Reinigung mit flüssigem und überkritischem Kohlendioxid, IN-6532, 16IN0590, Innonetprojekt Kodiwasch, BMWi, http://www.vdivde-it.de/innonet/projekte/in_pp205_kodiwasch.pdf/, **2007.**

[13] KILZER, A., KARETH, S., WEIDNER, E., Recent Developments of Cleaning and Separation Processes with Near and Supercritical Fluids, *Chemie Ingenieur Technik,* 83(9), **2011**, p. 1405-1418.

[14] Amsonic Precision Cleaning A.G., http://www.amsonic.ch/