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## Current advances in sustainable Metalworking Fluids research

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**Abstract:** Metalworking Fluids (MWFs) have a history of harming the environment and the health of workers, resulting in pressures to re-design them in accordance with sustainable manufacturing principles. In this paper, we review research being performed at the University of Michigan to minimise the life cycle environmental and health impacts of MWFs while simultaneously improving manufacturing performance. We highlight research contributions in the following areas:

- formulation design
- biological sensors
- advanced recycling
- the use of supercritical fluids.

We conclude that it is possible to design more sustainable metalworking fluid systems either by extending dramatically the in-use lifetime of water-based MWFs or better yet by switching to gas-based Minimum Quantity Lubrication (MQL) systems.

**Keywords:** Metalworking Fluids; MWFs; Life Cycle Assessment; LCA; Minimum Quantity Lubrication; MQL; vegetable-based lubricants; supercritical carbon dioxide; biological sensors.

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Andres F. Clarens is an Assistant Professor of Civil and Environmental Engineering at the University of Virginia. He received his PhD from the University of Michigan in 2008 where he explored the use of  $\text{scCO}_2$  as a metalworking fluid. Prior to graduate school, Andres served for two years in the US Peace Corps. He has a BS Degree in Chemical Engineering from the University of Virginia and an MSE Degree in Environmental Engineering from the University of Michigan. He is currently continuing his research in sustainable manufacturing with a focus on energy and carbon sequestration applications.

Fu Zhao is an Assistant Professor of Mechanical Engineering at Purdue University. He received his PhD in Mechanical Engineering in 2005 from the University of Michigan where he investigated the design and recycling of metalworking fluids. He received his MS (1996) and his BS (1993), both in thermal engineering, from Tsinghua University, China. His current research interests focus on design for the environment, environmentally conscious manufacturing, industrial ecology, life cycle assessment and alternative energy.

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## 1 Introduction

*Sustainable manufacturing adds value to materials, components, or products while maintaining the availability of natural resources and environmental quality for future generations.* In this paper we describe contributions to sustainable metalworking fluid systems that form an integral part of a sustainable manufacturing strategy.

Although MWFs are coolants and lubricants that have been synonymous with metals manufacturing for centuries, the first instinct we have in sustainable manufacturing is to eliminate the metalworking fluid since it is not embodied in final products. Indeed dry machining has proven successful in numerous operations. However for today's challenging machining processes, such as milling titanium for lighter aircraft or boring compacted graphite iron for next generation vehicles powered by bio-fuel, MWFs are required. This is because the absence of cooling and lubrication provided by MWFs results in accelerated tool wear, residual stresses, dimensional errors, and poor surface finish. In such cases MWFs increase tool life, improve part quality, and allow faster manufacturing. From a life cycle perspective, MWF use can also reduce environmental impacts of tools by reducing the rate of consumption. Replacing machining tools, especially when highly alloyed and coated, at times can result in sizable environmental emissions that exceed the emissions associated with extending the tool life using a MWF.

Over the past century, MWFs have usually been formulated as either straight-oils or as a combination of water, oil, surfactants, and additives. Worldwide, manufacturers currently consume over 2 billion litres of water-based and straight-oil MWFs each year creating a significant demand for non-renewable feedstock (Glenn and van Antwerpen, 2004). In use, MWFs are highly susceptible to contamination by microorganisms, leading to potential health risks for workers from infection, inhalation of bio-aerosols, or dermal contact with biocides utilised to control the biological growth. This biological growth, along with physicochemical changes of the MWF and the buildup of metal particles and oils, also deteriorates manufacturing performance and ultimately necessitates disposal. This disposal is challenging and costly, which is serving to drive change in the industry. The large volumes of aqueous waste carry toxic metals from manufacturing (e.g., cobalt and lead) into the environment, along with a host of chemicals such as corrosion inhibitors, defoaming agents, surfactants, chlorinated fatty acids and chelating agents that pose environmental risks. MWF treatment and release to the environment can also lead to significant oxygen depletion and nutrient loading in surface waters further posing environmental risks.

Given the state-of-the-art, MWF systems are excellent candidates for sustainable manufacturing research since simultaneous improvements in economic, environmental, and health dimensions are possible and critically necessary. Recent activity towards implementing sustainable MWF systems has focused on Environmentally Adapted Lubricants (EALs). EALs have been defined in the European Union as lubricants that have high biodegradability and low toxicity with performance equal to or better than conventional alternatives (Theodori et al., 2004). Several classes of EALs have been developed, including vegetable oil based (oleochemical) ingredients which are being substituted into traditional water-based and straight-oil formulations as renewable and biodegradable alternatives to conventional fluids (Norrby, 2003; Clarens et al., 2004). Approximately 5% of all lubricants in the EU are now being sold as EAL oil-in-water emulsions, primarily as vegetable-based formulations, and their market share is growing (Theodori et al., 2004).

Minimum Quantity Lubrication (MQL) techniques represent another growing class of EALs. MQL typically involves sprays of compressed air and a small amount of oil to provide the function of a MWF without the large volumes of aqueous waste (Adler et al., 2006). However, air is an inefficient coolant and today's oil-in-air MQL systems are only suitable for mild machining operations that do not require significant

heat removal. Therefore research is currently focused on developing new approaches that extend the reach of MQL to more intense machining processes.

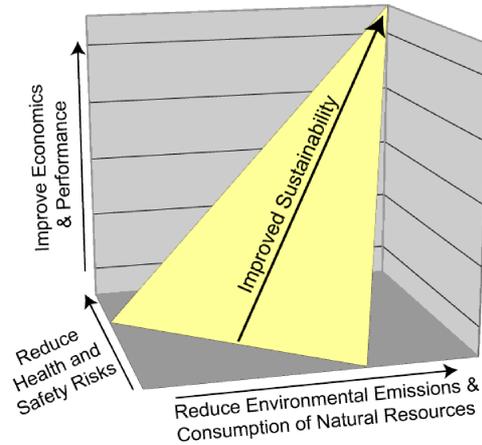
The importance of reducing the impacts of MWFs has become central to improving the sustainability of metals manufacturing. In this paper we summarise 15 years of research by members of the Environmental And Sustainable Technologies (EAST) Laboratory at the University of Michigan to develop new knowledge and technology in support of sustainable metalworking fluid systems. In Section 2, we discuss the landscape of design options available to increase the sustainability of metalworking fluid systems. We consider both water-based and gas-based MWF systems. In Section 3 we describe our research that has shown how to extend the life of water-based MWFs that currently dominate industry. Specifically we describe research advances in the following areas:

- microbial detection
- membrane filtration
- emulsion stability
- formulation design and life cycle assessment with bio-based feedstocks.

In Section 4, we describe research that has extended the reach of MQL to new machining applications. Specifically we discuss a new class of MWF that we have developed based on rapidly expanding sprays of dissolved oil carried in supercritical carbon dioxide and show how this new type of MWF can increase machining performance relative to traditional MQL and water-based MWFs. We then compare the life cycle environmental and health characteristics of supercritical carbon dioxide MWFs, oil-in-air MWFs, and water-based MWF microemulsions. We conclude that current efforts to switch from petroleum to bio-based feedstocks within water-based systems are less beneficial to the goals of sustainability than either extending the life of a water-based MWF or switching to gas-based MWFs. Therefore we expect that the future of sustainable MWFs research will entail the use of renewable lubricants in the context of new delivery systems that reduce consumption rates and health risks simultaneously while increasing manufacturing process performance and profitability.

## **2 Design approaches for sustainable metalworking fluid systems**

Figure 1 identifies design targets for a sustainable MWF system. These targets apply either for water-based or gas-based MWF systems and can be achieved by changing the MWF consumption rate and/or the chemistry of the MWF. A major difference between water-based systems and gas-based systems is that water-based systems are recirculated while MQL sprays are used only once. Therefore the concept of consumption takes on different meanings in these systems. In a gas-based system, the consumption rate is determined by the flowrate of the spray. In a water-based system, the consumption rate is determined by the volume of MWF and the interval between system disposals (which is usually measured in weeks or months). Therefore design approaches to reducing MWF consumption rate and minimising life cycle emissions are different for water- vs. gas-based systems.

**Figure 1** Target objectives for sustainable MWF systems

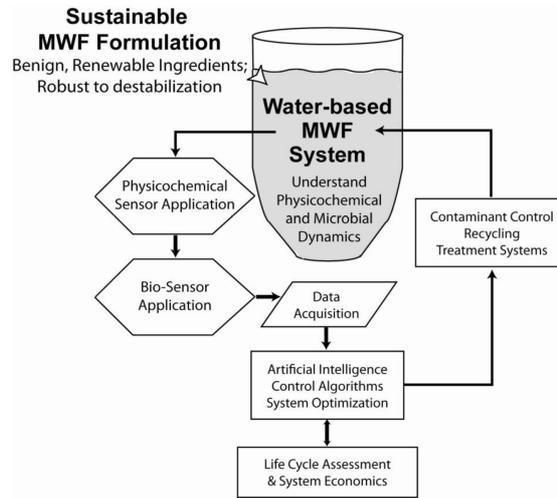
### 2.1 Water-based MWFs

Improving the sustainability of water-based MWFs is a complicated endeavour. A typical water-based MWF will contain water, oil, surfactants and approximately ten other specialty chemicals. In centralised systems these MWFs require maintenance technologies such as depth filtration, centrifugation, and biocide application to delay their inevitable deterioration over time. It is this deterioration that leads to microbial growth and health risks, in-process fluid failure, and eventual disposal, all factors that negatively impact the sustainability of MWF systems.

The deterioration of the MWF arises from many sources: the fundamental incompatibility of oil and water, the susceptibility of emulsions to microbial growth, the evaporation of water, the capability of hardwater ions to destabilise emulsions, and the foaming of surfactants when mechanically agitated. Therefore increasing the lifetime of a water-based MWF is determined by its resistance to microbial growth as well as its resistance to fluctuations in the concentrations of active MWF components that may be consumed in-process (or evaporate in the case of water). Furthermore the MWF must also be robust to destabilisation caused by contaminants such as leak oils, ion accumulation and the buildup of metal particles from the cut parts. As these factors also facilitate microbial proliferation, the protection of human health and safety is a synergistic benefit resulting from contaminant control and stability of water-based MWF systems. From this discussion it becomes clear that improving the sustainability of a water-based MWF requires a two pronged design approach:

- to select an environmentally benign MWF chemical formulation
- to deploy an appropriate control system for this formulation that maximises the MWF lifetime on the shop floor.

A selection of research topics related to designing MWF control systems based on this approach is illustrated in Figure 2.

**Figure 2** Approaches to improving the sustainability of water-based MWF systems

The system input to Figure 2 is a MWF designed for maximum stability and minimum life cycle environmental impact and health risks. For water-based MWFs that are emulsions of oil droplets stabilised in water using surfactants, the MWF formulation and chemistry must be selected so that the oil-in-water emulsion does not destabilise under field conditions. This is a matter of selecting the appropriate surfactants for the oil under consideration (e.g., petroleum oil, soybean oil, etc.) as well as applying the surfactants in the correct concentrations. EASTlab research that has yielded guidelines for achieving these tasks is discussed in Section 3.1.

One approach to designing more sustainable MWFs is to use bio-based oils and chemicals. Due to their inherently higher biodegradability, bio-based formulations have the potential to reduce the waste treatment costs required to meet the new MWF effluent limitation guidelines and standards published by the US EPA in the Metal Products and Machinery Rule (US EPA, 2003). Also, bio-based formulations could reduce the occupational health risks associated with petroleum oil based MWFs due to their lower reported toxicity (Raynor et al., 2005) while providing a renewable feedstock alternative that has been shown to perform better in manufacturing operations such as thread cutting (Clarens et al., 2004). The principal technical limitation of vegetable oil lubricants, their low oxidative stability, has been addressed by genetic alternation, chemical modification and use of various additives (Rose and Rivera, 1998). The principal economic limitation of vegetable based lubricants, their high cost relative to petroleum oils, is diminishing as petroleum prices increase (Ash and Dohman, 2005). Section 3.2 describes research results from a life cycle comparison of representative bio-based and petroleum-based MWFs.

Once the formulation is selected, the MWF is then maintained using a control system comprised of a coordinated system of contaminant detection and removal technologies. This control system involves detection of physical, chemical, and biological contamination levels in regular and short enough time intervals to enable an appropriate engineering response that eliminates their negative impacts on the MWF. This use of sensors to acquire process information is also critical to minimising the environmental impact of the contaminant control technology itself. Since all control technologies have

their own environmental footprint, including in some cases consumable media that must be disposed (e.g., filter media in depth filtration), it is desired to use any contaminant control technology only at its minimum required rate understood from sensor readings.

Sensing of microbial species and total biomass levels present in water-based MWF systems is particularly important. In the absence of biologically inhibiting chemicals water-based MWFs are essentially nutrients for bacterial and fungal growth. This growth leads to metabolic destruction of active ingredients and degrades MWF performance. While ordinary microbes pose minimal infection risk for workers, some hazardous species such as *Mycobacteria sp.* and *Legionella sp.* have caused worker illness. Thus water-based formulations require bio-inhibiting ingredients to keep microbial populations at bay. While generally effective, there is a desire in the industry to minimise biocide application volumes since excessive concentrations carry their own health risks such as acute dermatitis. Heat pasteurisation and ultraviolet irradiation have been proposed as alternatives to biocide use, but their use is not widespread for economic reasons. Alternatively, membrane filtration has proven capable of dramatically extending the life of MWFs in pilot-studies while also controlling microbial growth (Wentz et al., 2007). Section 3.3 describes the use of membrane filtration to improve upon currently available biological and physical contaminant control strategies.

As shown in Skerlos and Zhao (2003), the size, cost, and application rate of membrane filtration systems designed for biological control depends on the biological growth rate in the system. This means that microbial sensors are important not only for detecting harmful bacteria but also for optimising the operation of the system. Currently available microbial detection strategies, however, are only order-of-magnitude accurate and require up to 48 hours to yield information. This response time is too long for dynamic online control of MWF systems, or to prevent a microbial outbreak from running its course. Section 3.4 describes a microbial detection approach suitable for application to MWF systems that can in real-time quantify microbial contamination and identify specific bacterial species.

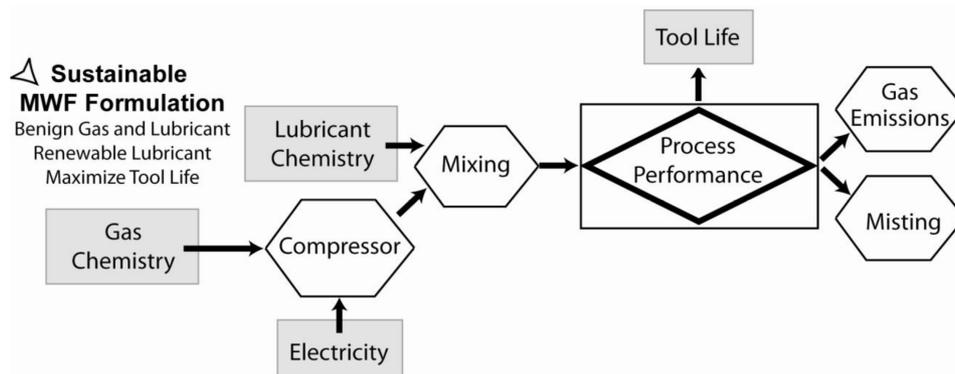
## 2.2 *Gas-based MWFs*

In the USA, a growing number of manufacturers are making the transition to oil-in-air MQL to reduce costs while also removing environmental and health risks. Much of the cost savings comes from the elimination of plant infrastructure required for water-based fluids such as grates, drains, storage tanks, chillers, pumps and pipes. The lubricant volumes managed in MQL at any given time are also much lower and although there are challenges related to cooling, the technology is being deployed successfully in the field for common machining operations. Sections 4.1 and 4.2 describe the characteristics and performance of a new MQL system based on rapidly expanding sprays of oil dissolved in supercritical carbon dioxide. The goal of this technology is to extend MQL applications beyond common machining operations to more severe machining operations for which today's MQL systems are ineffective.

Conceptualising sustainability improvements in a gas-based MWF system is a much simpler task than in the case of a water-based system. Environmental issues to be considered are the life cycle emissions associated with the gas and lubricant and the volumes utilised. Unlike recirculating water-based systems, gas-based systems do not reuse the lubricant or gas. Instead, the goal is to deliver the gas-phase fluids at the rate they are consumed in the process. Excess application can lead to mist; however it has

been well-documented that through tool delivery of MQL reduces mist considerably, even below detection limits (Furness et al., 2006). The environmental profile of MQL systems is also highly influenced by the energy consumption of the gas compressor and pressure characteristics of the delivery system. Research issues related to reducing the environmental impact of MQL systems are illustrated in Figure 3. Section 4.3 summarises the research results from a life cycle assessment that was conducted to compare MQL with water-based metalworking fluid systems.

**Figure 3** Considerations for improving the sustainability of gas-based MQL systems



MQL technologies are relatively new and therefore face technical and economic barriers to implementation. They require new delivery systems dissimilar to those used for aqueous systems. Pilot-scale implementation has shown that MQL systems are less expensive to operate but require significant upfront investments in both infrastructure and expertise. Unless environmental and health costs are considered, many companies have deemed these costs too high to warrant switching from current systems. On the other hand, at least one automaker in the USA is making significant investments in MQL due to cost savings and higher performance, as well as for environmental and worker health reasons. Several other large OEM and supplier companies are currently following suit.

### 3 Research advances to increase the lifetime of water-based MWFs

Approximately 40% of the North American market for MWFs is comprised of semi-synthetic MWF formulations (Byers, 1994). These MWFs are comprised of water, a base oil, surfactants, and specialty additives. In general, semi-synthetic MWFs are sold as concentrates with 10–30% petroleum oil and are diluted 10–20 times with water before use as MWFs. The diluted fluids are stable, translucent and often called 'microemulsions', with emulsified oil droplet sizes less than 100 nm. The selection of surfactants to disperse the oil and other hydrophobic additives in water is critical for producing a stable microemulsion. In this section we primarily consider semi-synthetic MWFs, although many of the concepts generally apply to all water-based MWFs.

### *3.1 Research in the design of robust MWF microemulsions*

In Zhao et al. (2006a) we outlined guidelines for producing stable bio-based MWF microemulsions with minimum necessary concentrations of surfactants. First it was shown that a combination of two surfactants, one nonionic and one water soluble co-surfactant (either nonionic or anionic) is preferred over a single surfactant. While formulations with a single surfactant are feasible, they require very high surfactant concentrations leading to health risks and foaming. Second it was shown that the nonionic surfactant should have a carbon tail length greater or equal to the nominal carbon chain length of the fatty acids in the oil and a head group that is not excessively small or large. Third it was shown that the difference in tail lengths between the surfactant and the co-surfactant should be less than six carbon units to maximise the feasible range of oil to surfactant ratios yielding stable emulsions. By applying these guidelines, it is possible to consider the range of possible surfactants and develop a feasible set of candidates from which a more sustainable MWF microemulsion can be formulated.

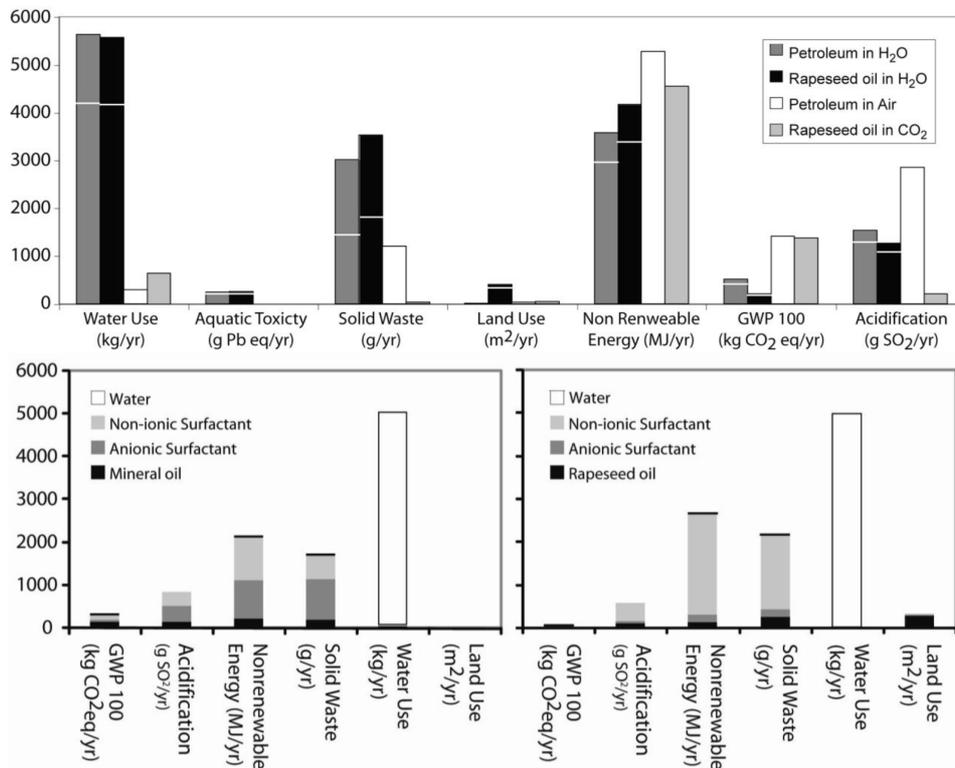
Once the surfactant chemistries are selected, their concentrations must be determined. We have shown that the optimal surfactant concentration can be derived from studying the flow of microemulsions through membranes, since the flow is directly influenced by emulsion destabilisation. In Zhao et al. (2006b) we developed a mathematical equation describing the flowrate of microemulsions through microfiltration membranes as a function of surfactant concentrations. Taking the derivative of this equation and setting it to zero provides the exact concentrations of surfactants that maximise the microemulsion flowrate through microfiltration membranes. It turns out that this surfactant concentration also provides maximum stability for the microemulsion. Therefore there is a synergistic benefit of designing the MWF formulation for maximum recyclability, as this also leads to a MWF with its maximum resistance to emulsion destabilisation regardless of whether membrane filtration recycling is conducted. At the same time, this optimisation of surfactant concentrations does not impact MWF performance since the concentrations of oil and water are not changed.

### *3.2 Research into the life cycle emissions of bio- and petroleum MWFs*

Given the sentiment by many in industry that a switch to bio-based oil feedstocks for water-based MWF systems is a strong move towards environmental sustainability, a thorough life cycle comparison is warranted to provide quantitative support for this position. We recently completed an inventory for a semi-synthetic MWF system containing oil, two surfactants, and water. Two oils were considered (petroleum oil and rapeseed oil) and four surfactants were considered (two petroleum-derived surfactants and two bio-derived surfactants). Considering the surfactants was important since we found that the surfactants play a dominant role in the overall environmental emissions of water-oil-surfactant systems. This also suggested that perhaps the approximately ten other ingredients found in typical water-based MWFs (which were not included in the study) could significantly increase life cycle environmental emissions even though they are found at concentrations 5–10 times less than surfactants by weight. It is worth noting here that these surfactants and other specialty chemicals (besides oil) are usually not found in MQL MWFs.

Table 1 details the compositions of the petroleum and rapeseed oil MWFs considered in the life cycle assessment. The functional unit was one year of machining time assuming that the functionality of the two MWFs was identical and that the formulations were equally stable during recirculation. Figure 4 compares the material production impacts broken down by component. The results suggest that surfactants dominate the emissions for four of the eight impact categories: GWP, acidification, energy, and solid waste. The rapeseed oil-in-water formulation has slightly lower GWP and acidification potential but requires more energy and land/pesticide use, while creating more solid waste. The need for surfactants in both water-based systems means that although modest tradeoffs exist between petroleum- and bio-based fluids, neither system has a significantly lower impact than the other. We therefore argue in Section 4 that a move away from water-based emulsion systems to gas-based MQL systems would be a much stronger move towards sustainability than a mere switch in feedstock from petroleum to bio within a water-based MWF. On the other hand, at the current time MQL alternatives to water-based MWFs do not exist for many advanced manufacturing applications. This calls for research into new MQL technologies capable of performing well in severe manufacturing conditions.

**Figure 4** Comparative LCA of rapeseed vs. petroleum microemulsions (top). Rapeseed and petroleum microemulsion impact categories broken down by ingredient (bottom). Units are presented under the x-axis for each plot. White lines for aquatic systems represent approximate reductions possible if implementing microfiltration recycling



**Table 1** Compositions of water-based petroleum and rapeseed oil MWFs and representative gas-based MQL systems. The top row lists appropriate classifications of the systems. RESS is an acronym for Rapidly Expanding Supercritical Solutions

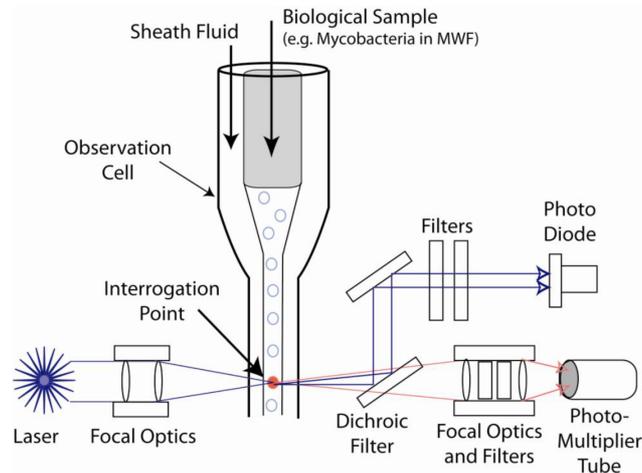
	<i>Conventional</i>	<i>EAL</i>	<i>EAL, MQL</i>	<i>EAL, MQL, RESS</i>
Components	Petroleum oil in water	Rapeseed oil in water	Petroleum oil in air	Rapeseed oil in scCO <sub>2</sub>
Oil	0.75	0.75	1	2
Anionic surfactant				
Sodium petroleum sulphonate	0.3			
Alcohol sulphate		0.25		
Nonionic surfactant				
Diisopropanol amine	0.4			
Ethoxylated glycerol ester		1.25		
Water	98.55	97.75		
Compressed air			99	
CO <sub>2</sub>				98

### 3.3 Research in biological sensors

The susceptibility of water-based MWFs to biological contamination and the potential for this to lead to health risks associated with bio-aerosols and infection requires new technology to quantify microbial growth at frequent intervals. A fast response is especially important since microbial outbreaks can occur faster than dip-slides can detect harmful microbial species.

In the future, we believe that applications of flow cytometry will offer the opportunity to conduct real-time analysis of microbial species and total biomass load. Flow cytometry is widely used in clinical diagnosis and molecular biology research. As shown in Figure 5, flow cytometry works by fluorescence detection. A specific fluorescent dye that binds specifically only to the microorganisms of interest (including the possibility of detecting all microorganisms present) is mixed with the MWF sample and introduced to the flow cytometer. The hydrodynamic focusing design of the system encourages bacterial and fungal cells to line up individually so they can be interrogated by a laser as suggested by Figure 5. An optical filter then separates fluorescent emissions from laser scatter allowing an accurate count of the specific microbial population of interest.

In Skerlos et al. (2003) we demonstrated the use of a specific labelling method and flow cytometry to detect harmful *Mycobacteria sp.* in MWFs. In Tung et al. (2003) we also presented a technology approach with potential to reduce the size and cost of flow cytometry by an order of magnitude, enabling future applications of the technology on the shop floor. Based on this research, fully functional flow cytometers are soon expected to be available on the market for about \$30,000, which is over four times less than just a few years ago (Accuri Instruments, 2007).

**Figure 5** Flow cytometer principle of operation for detecting bacteria and fungus

### 3.4 Research in membrane filtration recycling

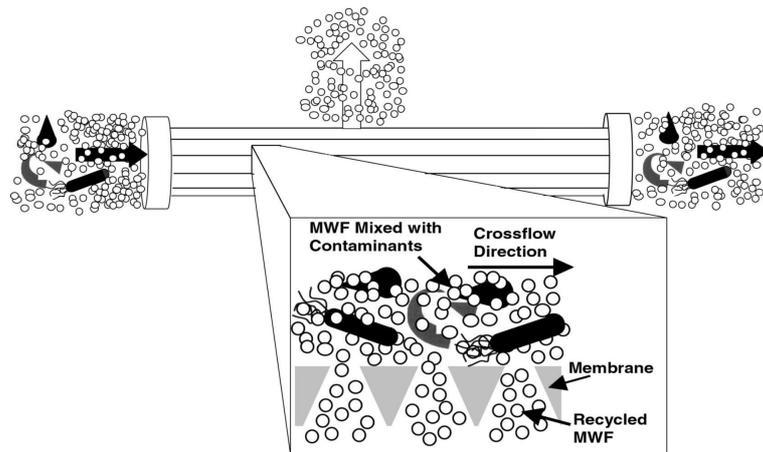
Some form of contaminant control and chemical addition is almost always performed in recirculating MWF systems, driven by costs of MWF acquisition and disposal. In an ideal MWF system, such control systems would achieve a perfect separation of contaminants and return the MWF to its 'as new' state. However, contaminant removal on its own cannot address issues such as accumulation of hardness ions, evaporation, pH reduction due to microbial growth, and loss of surfactants. Therefore, even under ideal separation, direct chemical maintenance and biological control is required to extend the life of the MWF.

Microfiltration is a membrane-based separation technology that can not only remove microorganisms, but can also remove contaminant particles and free oil from MWF to produce a high quality recycle. A major difference between conventional filtration and membrane filtration is that conventional filters operate by capturing particles within a filter matrix, and the filters cannot be regenerated after use. As shown in Figure 6, membrane filtration is typically performed with filtration tangential to the channels of bulk fluid flow. This crossflow mode of operation discourages the accumulation of particles within the filter matrix, and the separation takes place at the surface. Membranes can be cleaned and re-used for long periods of time, and essentially indefinitely for ceramic membranes. Therefore, rather than filter clogging with contaminants, the principal limitation to high filtration rates in microfiltration and ultrafiltration is the physical-chemical interaction of MWF ingredients with the membrane surface (Skerlos et al., 2000).

Membrane filtration processes, while challenging, have proven to be able to restore the MWF to 'good as new' condition and to reduce life cycle environmental impacts as shown in Figure 4. For instance, research has demonstrated the technical feasibility of using ceramic microfiltration membranes to supplement or replace biocides and other treatment technologies as a means to control MWF contamination and create a recycled MWF indistinguishable from new MWFs (Rajagopalan et al., 2004). However the primary limitation to wider application of membrane filtration technology is its sensitivity to MWF formulation design, particularly to the selection of oils and

surfactants and their concentrations. While it is possible to design semi-synthetic MWFs to greatly increase their flowrates through microfiltration membranes (as discussed in Section 3.1), no commercially available MWFs have yet used this approach, even though it leads to more stable microemulsions regardless of whether they are recycled using membrane filtration. This makes membrane filtration, as an approach to improve the sustainability of MWF systems, less economical than it should be and consequently the technology has yet to see widespread application.

**Figure 6** Principle of cross-flow membrane filtration for advanced MWF recycling



#### 4 Research advances in gas-based MQL systems

The environmental, health, performance, and economic benefits of switching from water-based systems to gas-based MQL systems have been observed in industry and are starting to be documented in the literature. The cost savings mostly arise by eliminating major infrastructure components in the plant, which represent a significant fraction of water-based MWF system costs. This is important since life cycle MWF costs can represent 10–17% of metals manufacturing costs (Furness et al., 2006). Delivery of minimum quantities of lubricants using a spray of air (also called near dry machining or MQL) reduces purchase and operational costs while dramatically reducing energy consumption at the MWF system level. MQL systems are even claimed to increase safety and operator morale, largely from the elimination of mist and other oily waste associated with flood delivery of water-based MWFs (Furness et al., 2006). To date however, MQL has only been adopted on a limited basis because most process engineers are not familiar with how to design and implement MQL systems. Technical questions also remain about how to achieve sufficient cooling using MQL in challenging machining operations involving advanced materials.

In this section we introduce a new type of MQL MWF based on rapidly expanding sprays of supercritical carbon dioxide ( $\text{scCO}_2$ ). Carbon dioxide above its critical temperature and pressure ( $T_c = 31.1^\circ\text{C}$  and  $P_c = 72.8 \text{ atm}$ ) effectively dissolves many lubricating oils and forms chilled microparticles of lubricant as it expands out of a nozzle. Therefore sprays of oil carried from  $\text{scCO}_2$  can extend the reach of MQL technology into

more challenging machining domains not achievable today with air-based MQL due to the need for more cooling, chip evacuation, and higher pressure. The scCO<sub>2</sub> approach is mechanically much simpler than oil-in-air MQL systems since the solubility of the lubricant in scCO<sub>2</sub> eliminates elaborate mixing strategies required to aerosolise the oil in air. Process characteristics of scCO<sub>2</sub> MWFs are described in Section 4.1 and results of manufacturing process testing are presented in Section 4.2.

A full life cycle analysis of air and CO<sub>2</sub> MQL systems is summarised in Section 4.3 and compared with water-based systems. The results reveal that the environmental benefits of these MQL systems correlate well with the financial savings that are now being observed in industry. It is seen that the environmental impacts of gas-based MWF systems are significantly lower than water-based systems in many impact areas primarily because the systems usually contain only two components: gas and lubricant. By eliminating additives required in water-based systems, including surfactants, MQL processes eliminate much of the environmental footprint and health risks associated with water-based MWFs.

#### 4.1 scCO<sub>2</sub> process characteristics

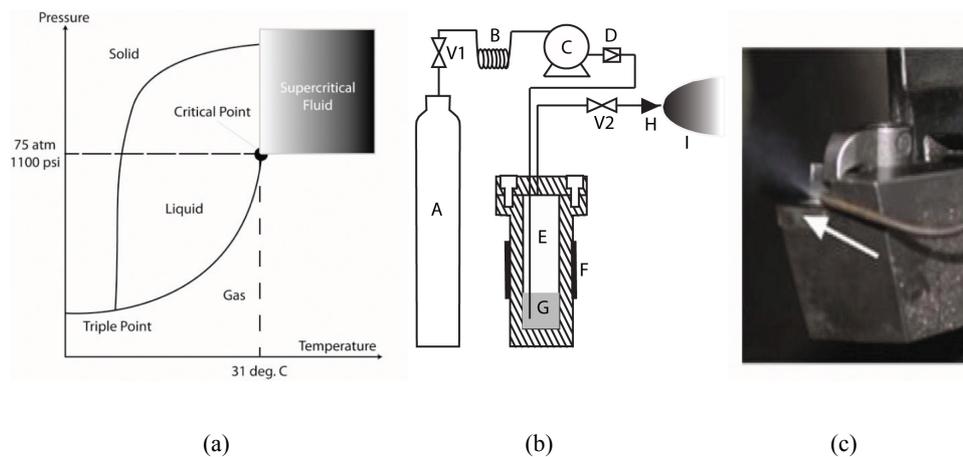
The rapid expansion of supercritical solutions for coating and spraying applications has been well-documented. These rapidly expanding solutions of scCO<sub>2</sub> can reach temperatures below -80°C with a uniform coating of the solubilised material forming on the spray target (Diefenbacher and Turk, 2002). scCO<sub>2</sub> is a tunable substitute for organic and aqueous solvents and can dissolve many common MWF lubricants at pressures and temperatures above the critical point of CO<sub>2</sub> (73 atm, 31°C) (Reverchon and Sesti Osseo, 1994). Figure 7(a) illustrates the supercritical region for CO<sub>2</sub> as a function of temperature and pressure. Under supercritical conditions, CO<sub>2</sub> has compressibility and viscosity of a gas phase while having high density and solvency of a liquid phase. This makes scCO<sub>2</sub> a convenient MWF carrier because it will dissolve lubricants under pressure and carry them to the process without the need for mixing. As the scCO<sub>2</sub> expands, temperatures drop and provide superior cooling to today's oil-in-air MQL systems. Figure 7(c) provides a photograph of an expanding scCO<sub>2</sub> spray.

Creating a scCO<sub>2</sub> MWF is a straightforward process that starts by compressing CO<sub>2</sub> above 73 atm (1100 psi) at just over room temperature, and bubbling the gas through a pool of process lubricant (e.g., bio-based oil or petroleum oil) as shown in Figure 7(b). The process lubricant may not be needed in certain applications. Flexible high pressure tubing can be used to deliver the supercritical fluid from the pressure vessel to the cutting zone. A valve actuates the release of the scCO<sub>2</sub>-based MWF to the machining process. Since the pressure of the scCO<sub>2</sub> drops as the fluid flows through the nozzle, the spray cools to cryogenic temperatures forming dry ice while cold liquid oil particles form as they precipitate out of the scCO<sub>2</sub> solution. These high-speed sprays allow good penetration of the cold oil into the cutting process. The sprays also clear chips effectively, leaving the work area free of debris and oily waste.

Achieving a supercritical state for the CO<sub>2</sub> MWF is important for several reasons. Lower system pressures lead to a lesser pressure drop across the nozzle and the formation of warmer sprays than when spraying the higher pressure scCO<sub>2</sub>. Further, in the gas phase, CO<sub>2</sub> does not solubilise lubricants as it does in the supercritical state. This is important because sprays of supercritical processes are distinct from traditional aerosol processes such as MQL since the particles form through a precipitation process rather

than by shear forces exerted by the surrounding air. The result is a more uniform and even coating of lubricant on the machining surface. Lower pressure sprays also have lesser ability to remove chips from the machining process, which is important in through tool applications.

**Figure 7** (a) CO<sub>2</sub> phase diagram indicating supercritical fluid conditions; (b) schematic of scCO<sub>2</sub> MWF delivery system A. cylinder of food-grade CO<sub>2</sub>, B. cooling unit, C. pump, D. one-way valve, E. high pressure vessel, F. heating element, G. soybean oil, H. nozzle, I. spray of scCO<sub>2</sub>-based MWF, V1 and V2 are valves and (c) photograph of rapidly expanding scCO<sub>2</sub> spray over a turning insert



In the supercritical state, the solubility of oil in CO<sub>2</sub> is finely tunable via the system temperature, pressure, and nozzle geometry. For instance, increasing pressure from 73 atm to 350 atm (1100–5000 psi) further increases oil solubility, while the sprays are frozen, leading to a larger number of colder droplets penetrating the process. This means, unlike water-based systems, that cooling potential and lubricating potential are not mutually exclusive in scCO<sub>2</sub> systems. In microemulsions, higher oil concentrations lead to less cooling and more lubricity while higher water concentrations lead to more cooling and less lubricity. In contrast, increasing pressure beyond the minimal conditions for the supercritical state increases both cooling and lubricity simultaneously.

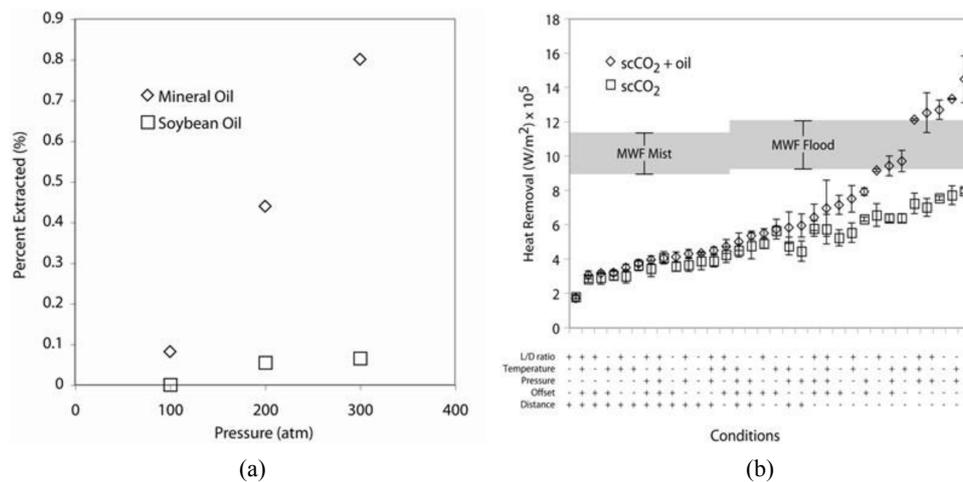
One example of a scCO<sub>2</sub> MWF delivery system is provided in Figure 7. In this system food-grade CO<sub>2</sub> is compressed from 48 atm (700 psi) to supercritical pressures above 73 atm (1100 psi) using a compressor. The CO<sub>2</sub> is bubbled into a 1 litre high-pressure vessel containing lubricating oil (e.g., soybean oil). The outlet from the vessel removes supercritical fluid phase CO<sub>2</sub> and oil and delivers it through a nozzle aimed at the working zone. The system can be mounted on a small cart with the exception of the CO<sub>2</sub> tank, and the whole system can be easily retrofitted to existing machine tools.

#### 4.1.1 Oil solubility

We have examined several characteristics of scCO<sub>2</sub> MWFs such as solubility of MWF lubricants in scCO<sub>2</sub> and the heat removal capacity of scCO<sub>2</sub> sprays. For instance, we have shown that different amounts of soybean oil can be carried to the manufacturing process

simply by adjusting the pressure as shown in Figure 8(a). Some oils are also more soluble than others. In fact petroleum oils are much more soluble in  $\text{scCO}_2$  than soybean oil as shown in Figure 8(a). However, this may not lead to higher performance and to the extent that higher oil consumption rates are unnecessary, using petroleum vs. bio-based oil can lead to the wasting of oil. Moreover, in our experience lower concentrations of vegetable-based oil are more effective than higher concentrations of oil in  $\text{scCO}_2$  systems. A related point is that we have observed shop floor tests with petroleum oil-in-air MQL that required oil flow rates of up to 1 mL/min to achieve the desired performance, while the solubility limit of soybean oil in  $\text{scCO}_2$  places an upper limit of oil flow rate to approximately 0.1 mL/min (at 100 atm) for the arrangement shown in Figure 7. Given that we have found equal or better performance for soybean oil in  $\text{scCO}_2$  relative to petroleum oil-in-air MQL, these lower flow rates indicate the potential to significantly reduce oil consumption by using  $\text{scCO}_2$  MWFs.

**Figure 8** (a) Comparison of oil ‘extractability’ (a measure of oil concentration in the supercritical fluid phase) as a function of pressure and (b) heat flux of  $\text{scCO}_2$  delivery of soybean oil under all combinations at two levels each of (+/-): nozzle length to diameter ratio (1000/400), vessel temperature in  $^\circ\text{C}$  (45/32), vessel pressure in atm (175/100), on-axis distance to target in cm (3/1), and off-axis orthogonal distance to target in cm (2/0)



#### 4.1.2 Cooling potential

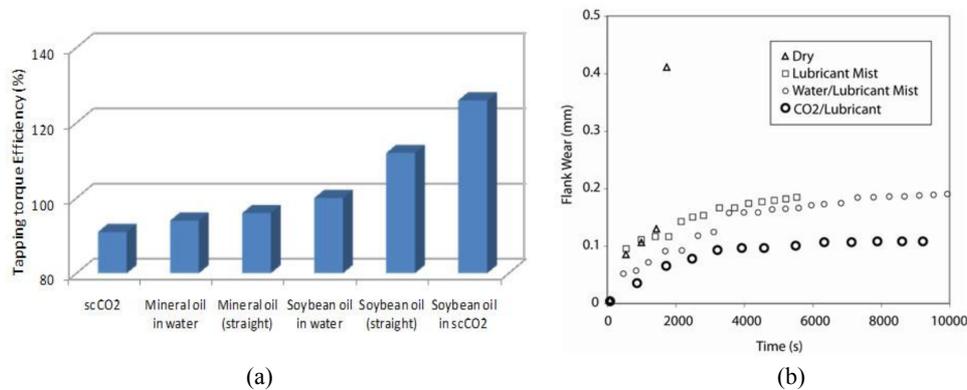
The cooling potential of an  $\text{scCO}_2$  system is a function of (in order of importance): distance of the nozzle to the target, the  $\text{scCO}_2$  pressure, the off-axis position of the nozzle relative to the target, the length to diameter ratio of the nozzle, and the temperature of the  $\text{scCO}_2$  inside the pressure vessel. The relationship of these factors to heat removal capacity is shown in Figure 8(b).

The data indicate that operating conditions for  $\text{scCO}_2$ -based MWF can be selected to produce higher cooling potential by increasing the pressure. This has the synergistic effect of dissolving more oil as shown in Figure 8(a), leading to a simultaneous increase of oil flow rate and cooling potential. Specifically, as pressure is increased from 100 atm to 175 atm (~1500–2600 psi) there is a significant rise in heat removal capability that increases dramatically in the presence of oil. Figure 8(b) shows the cooling potential of

the scCO<sub>2</sub> alone vs. scCO<sub>2</sub> carrying oil. Carrying oil, the spray achieves a heat flux almost 100% higher than that of the scCO<sub>2</sub> spray without lubricant. The synergistic nature of the scCO<sub>2</sub>/lubricant spray is likely attributed to a capacitance effect provided by the oil that stores the cold generated during the expansion of CO<sub>2</sub>. Under higher pressure there is more oil, and colder oil, that is being delivered to the manufacturing process at higher velocity.

It should be noted that the scCO<sub>2</sub> cooling potential may not be greater than MWF floods depending on operating conditions. This is despite the much colder temperature of the spray and is due to the lower molecular density of the rapidly expanding scCO<sub>2</sub> spray relative to water. In a flood of liquid, many more water particles are available to remove heat than CO<sub>2</sub> dry ice particles. However, this can be at least partially offset by the cooling provided by oil droplets that form in the rapidly expanding scCO<sub>2</sub> sprays. Another issue to consider is access of the spray to the cutting zone. Because of their lower molecular density, gases can be delivered to the cutting zone at much higher pressures than liquids without disrupting the cutting process and therefore can gain access to interstitial spaces to remove heat at locations that may be inaccessible to aqueous MWF sprays. On balance, this is why scCO<sub>2</sub> MWFs can exhibit better cooling characteristics than aqueous MWFs under certain conditions as shown for instance in the tool wear data of Figure 9.

**Figure 9** (a) Tapping torque efficiency of scCO<sub>2</sub> alone and carrying soybean oil. Straight soybean oil was the best tapping torque efficiency previously observed by the authors in trials with about 200 different types of MWF over five years and (b) reduction in flank wear rate when cutting CGI under single point turning conditions: speed = 225 m/min, feed = 0.034 cm/rev, depth of cut = 0.0025 cm



While the spray temperature is cryogenic, rapidly expanding scCO<sub>2</sub> sprays do not significantly change the bulk temperature of the tool or workpiece since the dry ice particles and oil droplets are dispersed. This is different from achieving cryogenic temperatures using liquid nitrogen, which is denser and completely floods the tool and workpiece. Cryogenic liquid nitrogen has been used successfully in some machining operations that produce significant amounts of heat and require little lubrication. However liquid nitrogen application can lead to dramatic temperature gradients that can compromise tools or affect part tolerances in certain operations. In addition, nitrogen has a large environmental footprint compared to other gases because it is typically produced via the energy-intensive fractional distillation of air.

#### 4.2 *scCO<sub>2</sub> performance testing*

To evaluate the performance of scCO<sub>2</sub> MQL relative to oil-in-air MQL and water-based semi-synthetic MWFs, several common machining tests have been performed including tapping (to measure lubrication potential) and single point turning (to measure cooling potential and tool wear). In previous research we provided experimental guidelines that permit the tapping torque test to be used as a high resolution method to evaluate the boundary (Zimmerman et al., 2003) and extreme pressure (Zhao et al., 2007) lubrication performance of MWFs. In Figure 9(a), we compare the tapping torque efficiency of conventional microemulsions and straight oils with soybean oil delivered in scCO<sub>2</sub>. 100% corresponds to the average tapping torque observed for a specific market-available soluble oil that was utilised as a reference fluid (Clarens et al., 2006). Higher efficiency corresponds to increased lubricity.

The data reveal that soybean oil is a better lubricant than petroleum oil in the tapping process, either in straight oil or emulsified form, as previously observed in Clarens et al. (2004). Figure 9(a) also indicates a synergistic performance advantage when combining scCO<sub>2</sub> with soybean oil in MWF applications. It is observed that the soybean oil/scCO<sub>2</sub> system performs on average approximately 10% better than straight soybean oil, 20% better than the soybean oil microemulsion, and 30% better than scCO<sub>2</sub> without oil (Clarens et al., 2006).

Although the tapping torque test is effective at measuring the lubricity of a MWF, it is not a test that reflects the cooling potential of a MWF, which is important in processes such as turning and milling. To evaluate the performance of scCO<sub>2</sub> as a machining coolant, single point turning tests were performed when cutting Compacted Graphite Iron (CGI) and titanium. These pilot-scale tests featured accelerated wear under conditions known by industrial partners to be strongly correlated with performance of actual machining conditions they observe on the shop floor. The CGI workpieces were turned using Polycarbonate Diamond (PCD) tipped inserts and the titanium (6Al4V) workpieces were turned using carbide CNGP432FS Grade K313 inserts by Kennametal (Latrobe, PA).

The single point turning tool wear tests shown in Figure 9(b) illustrate that scCO<sub>2</sub>-based MWF can provide a significant tool life improvement relative to air/lubricant mists. After 3 h of CGI turning, the observed amount of PCD tool wear during turning using scCO<sub>2</sub> MWF was approximately one half that observed when turning using the oil-in-water mist system. The wear scar was about half of the best available oil-in-air mist alternative that had been previously identified. Similar results were observed for 6Al4V titanium turning, with tool life increases ranging from 300–1000% relative to oil-in-air MQL sprays.

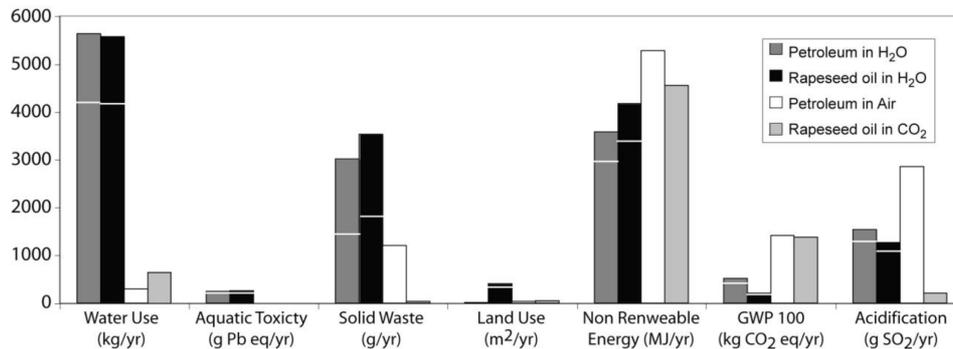
#### 4.3 *Comparative LCA of gas-based and water-based MWF systems*

In the move toward sustainable manufacturing, informed MWF selection is not possible without systematically considering life cycle impacts of alternative system approaches. To that end, we created a Life Cycle Assessment (LCA) model of MWF emissions that included the material production phase, use phase, and disposal phase for four MWFs: a semi-synthetic microemulsion of petroleum oil-in-water, a semi-synthetic microemulsion of rapeseed oil-in-water, a petroleum oil-in-air MQL spray, and a rapeseed oil-in-scCO<sub>2</sub> MQL spray. The model was designed to capture variations in

MWF delivery recognising that MWF usage varies significantly by operation and by operator preference. The functional unit for the study was the amount of MWF required to run one stand-alone machine tool for one year; additional impacts from centralised MWF systems were not considered. Also the impacts of tool production were not included.

Figure 10 presents overall life cycle emissions for the four MWFs with system boundaries, functional unit, and assumptions described in Clarens et al. (2007). It is seen that tradeoffs exist across the impact factors although there is one clear trend: namely that the environmental impacts of the gas-based lubricant systems are lower than the water-based lubrication systems in five out of the seven categories. Although the gas-based systems are somewhat higher in the global warming potential category, we see that the total greenhouse gas emissions from all MWF systems are relatively small: less than about 1500 kg CO<sub>2</sub> eq/yr, or roughly 1/3 of the CO<sub>2</sub> emitted from the tailpipe of a typical US automobile in a year (Keoleian et al., 1997). We also note that several GWP impacting factors were not included in the water-based MWF system that may be found in centralised systems such as aeration and recirculation pumps, depth filtration and other maintenance equipment, and the formulation of MWFs with specialty additives that must be replenished regularly.

**Figure 10** Comparative LCA results for representative water-based and gas-based MWFs (units listed under x-axis). White lines for aquatic systems represent approximate reductions possible if implementing microfiltration recycling

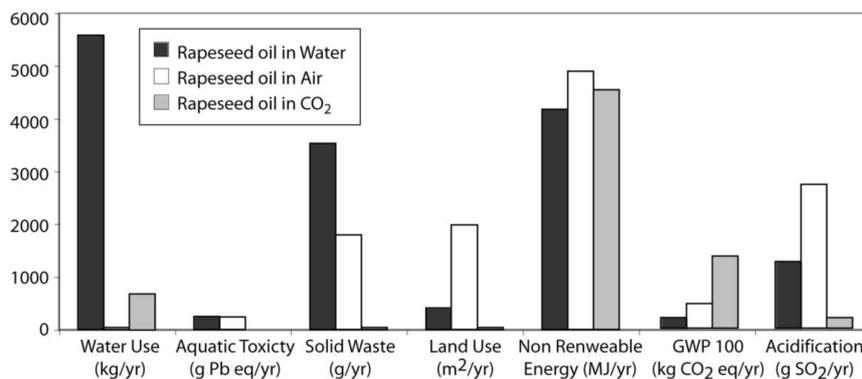


With respect to GWP, it may be surprising that the scCO<sub>2</sub> GWP value is actually slightly lower than the petroleum oil-in-air MQL system. This is because in the petroleum oil-in-air MQL system, the GWP value is largely driven by the much higher (petroleum) oil consumption rate. In the rapeseed oil-in-scCO<sub>2</sub> system, the GWP value is largely driven by the CO<sub>2</sub> utilisation rate. It should be noted that how exactly to handle the use of byproduct CO<sub>2</sub> in industrial processes is still a matter of discussion in the LCA community (Overcash et al., 2007). Figure 10 uses a price allocation for CO<sub>2</sub> created during the ammonia synthesis process (the most GWP intensive method commonly used to generate CO<sub>2</sub>). In reality, CO<sub>2</sub> is a byproduct of numerous industrial processes, and the use of CO<sub>2</sub> in low quantities as a MWF would be unlikely to result in the generation of CO<sub>2</sub> that would not have been produced anyway. So one can assert that while scCO<sub>2</sub> MWFs *utilise* CO<sub>2</sub> they do not exactly *drive the creation* of this CO<sub>2</sub>. The CO<sub>2</sub> utilised by scCO<sub>2</sub> MWFs is largely the economically driven re-use of an industrial by-product.

Another methodological question that needs to be asked for all the MWF systems is whether it is appropriate to assume equivalent functional units. For instance, the use of scCO<sub>2</sub> MWF has been shown to increase tool life by more than 100% compared with MQL alternatives for the turning of compacted graphite iron (e.g., see Figure 9 with flank wear limit set to 0.15 mm). This reduces the life cycle GWP of the tooling system which itself is significant, especially for alloyed and coated tools.

To create an ‘apples-to-apples’ comparison, we modelled the life cycle emissions of rapeseed oil-in-air (which are not commonly used) vs. rapeseed oil-in-scCO<sub>2</sub> MWFs. Figure 11 illustrates trade-offs between these systems. scCO<sub>2</sub>-based MQL is better with respect to aquatic toxicity, solid waste, land use, non-renewable energy, and acidification since this system uses low amounts of oil. Air-based MQL using rapeseed oil is better with respect to GWP, by a magnitude that is largely driven by allocation assumptions about the use of CO<sub>2</sub> as a MWF. Water use is also higher in the scCO<sub>2</sub> system than the air-based system but this use is quite small compared to water-based MWF systems.

**Figure 11** Comparative LCA results for rapeseed oil MQL systems based on air and scCO<sub>2</sub> (units listed under x-axis)



Based on this discussion we strongly recommend using gas-based MQL systems instead of water-based MWF systems to make progress towards the goals of sustainable manufacturing. The gas-based systems should employ renewable lubricants and be applied whenever they can achieve performance and cost advantages relative to water-based MWFs. We believe that this condition can usually be met. While conventional oil-in-air MQL is difficult to apply in severe machining applications such as the turning of titanium or CGI (Figure 9), scCO<sub>2</sub> has been successfully applied to achieve tool wear rates significantly less than water-based MWFs. Given the early state of development for gas-based MWFs, such results are encouraging to suggest a bright future for this new technology which virtually eliminates the most significant health and water pollution risks associated with today’s metalworking fluid systems.

## 5 Conclusions

We conclude that MWF systems can be designed in better harmony with the goals of sustainable manufacturing. This paper has shown that these goals can be partially addressed in water-based MWFs by extending the fluid lifetime in-process using

new approaches to MWF formulation, property sensing, and recycling as described in Section 3. Where possible, we recommend a switch from water-based to gas-based MQL systems as discussed in Section 4. Gas-based systems reduce costs, health risks, and most environmental emissions dramatically, while not creating major concerns about climate change. Gas-based MWFs do not require sophisticated control systems for abating fluid deterioration. Their only significant drawback to date has been their lack of cooling. We believe that advancements in gas-based MQL systems, such as the development of  $\text{scCO}_2$  MWFs, have the potential to extend MQL to severe manufacturing applications for which today only water-based MWFs can be utilised.

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