CARBON DIOXIDE BASED METALWORKING FLUIDS

by

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For my family

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Chapter 1

Introduction

Public concern about the environment is more prevalent than it has been since the birth of the environmental movement in the 1960s (Pope 2005). Driven largely by widespread fear over the dangers of global warming, the eminence of water shortages, and the scarcity of easily accessible petroleum reserves, the recent surge in public interest reflects a clear departure from attitudes observed in the previous three decades. Where the focus previously had been on reducing emissions or remediation of waste sites, the interest now is on creating environmentally sustainable systems that will prevent impacts from current and future generations (Softing et al. 1999). This work explored the potential for such a system. The proposed technology would use carbon dioxide, a waste from other industrial processes, as an environmentally benign and technically superior way to deliver lubricants in metals manufacturing operations. The water-based coolants used today present numerous occupational and environmental health impacts that inhibit the long-term sustainability of manufacturing processes. Most of these impacts are effectively eliminated if lubricants can be delivered in minimum quantities through sprays of carbon dioxide. This work explored the following technical questions associated with these novel metalworking fluids: Do they perform as well as conventional coolants? If so, why? And are the overall life cycle impacts of CO_2-based fluids lower than water-based? The results will pave the way for a possible reinvention of metalworking fluids that, if implemented, could lead to significant reductions in the environmental impacts associated with manufacturing processes.

1.1 Background

The original US environmental movement was driven by the clear impacts associated with wanton emissions into local and regional environments. Workers got sick on the job and toxic waste went untreated into local ecosystems. With widespread commitment and federal money, treatment plants multiplied, contaminated land cleared, and discharge laws were passed to protect air, water, and land emissions. The results were dramatic and environmental quality improved vastly in the US over the subsequent 30 years. But as this improvement evolved so did popular and governmental complacence. Nearly all Americans claimed to support environmental conservation, but few were making life style changes to contribute to that conservation. In addition, as the problems grew from the regional to the global scale, governments have become less capable of mandating change.

Today's environmental problems present novel challenges because they cross economic, national, and generational boundaries. Issues related to wealth and consumption are ever growing. As the populations of developing countries becomes more affluent, so too does their taste for automobiles and electricity. With markets becoming increasingly globalized, the environmental burdens are being shifted far away, often out of the countries with more sophisticated regulatory structure. Scarcity in natural resources like petroleum and water has already spurred international disputes. Global warming and other complex environmental problems will take decades to be understood and felt fully. Political institutions face hurdles implementing expensive programs to combat these dangers particularly given that the impacts will not be felt in full for 50 to 100 years.

In response to these complex challenges, applied and social scientists have argued that human processes must become more environmentally sustainable. By mimicking ecological cycles, human processes could equitably provide for the needs of current generations without compromising the needs of future generations. In nature, the waste of one process becomes the food for another. Complex chemical reactions take place elegantly in water, not in harsh industrial solvents. If humans learned to prevent waste rather than to treat it, many of the unintended consequences of our activities would be eliminated.

As the designers of transportation, manufacturing, communication, and built infrastructure, engineers play a pivotal role in the move toward more sustainable man-made systems. Engineers have increasingly come to recognize that markets and governments significantly affect their decision-making. Cognizant of the dynamic interplay between regulatory, financial, and technical interests, engineers have developed broad guidelines to aid in decision-making toward more sustainable systems. The 12 principles of green engineering are an example (Table 1.1)

The idea of green engineering is a marked contrast to the status quo. Where conventional engineering problem solving would increase energy production to meet growing demand, green engineering looks for efficiency measures to do more with less. Where traditional toxic release inventories would motivate remediation technologies for the most polluting processes, green engineering looks for ways to make the waste of one process the feedstock of the next.

Table 1.1. The 12 principles of green engineering. Adapted from (Anastas and Zimmerman 2003)

Principle	Explanation
1. Inherent Rather Than Circumstantial	All materials and energy inputs and outputs are as inherently nonhazardous as possible.
2. Prevention Instead of Treatment	It is better to prevent waste than to treat or clean up waste after it is formed.
3. Design for Separation	Separation and purification operations should minimize energy and materials use.
4. Maximize Efficiency	Products and processes should maximize mass, energy, space, and time efficiency.
5. Output-Pulled Versus Input-Pushed	Products and processes should be "output pulled" through energy and materials.
6. Conserve Complexity	Embedded entropy must be saved through recycle, reuse, or beneficial disposition.
7. Durability Rather Than Immortality	Targeted durability, not immortality, should be a design goal.
8. Meet Need, Minimize Excess	Design for unnecessary capacity or capability solutions should be considered a design flaw.
9. Minimize Material Diversity	Material diversity in multicomponent products should be minimized to promote disassembly.
10. Integrate Material and Energy Flows	Design of products, processes, and systems must include integration and interconnectivity.
11. Design for Commercial "Afterlife"	Products, processes, and systems should be designed for a commercial "afterlife."
12. Renewable Rather Than Depleting	Material and energy inputs should be renewable rather than depleting.

In the move to engineer more sustainable systems, the first challenge is to identify the areas in which the most significant changes could be affected. A focus on industrial processes seems prudent, given the large fraction of total energy consumed by manufacturing and the large contribution to toxic releases attributed to certain industries. Metals manufacturing in particular is a significant consumer of electricity and producer of toxic waste, much of this associated with the fact that metals manufacturing is wet. Industry consumes close to 1/3 of the energy produced in the US (Figure 1.1A). Of the toxic emissions cataloged by the US federal government, most comes from two industries, notably electricity and metals (Figure 1.1B). Energy consumption and toxic release by US sector and industry respectively are shown in Figure 1.1.

Most manufacturing processes that cut or form metal parts, e.g., automotive and aerospace, use metalworking fluids (MWFs) to cool and lubricate the cutting zone. Metal-on-metal contact results in shortened tool life or low product quality if MWFs are not used. The widespread use of these fluids in manufacturing has led to concern over the occupational and environmental health impacts they can produce. In an effort to reduce the impacts, some researchers and manufacturers have investigated the recycling of metalworking fluids to maintain their quality and reduce disposal frequencies. Other work has been conducted on the use of vegetable-based components to formulate fluids that are benign and renewable (Zimmerman 2003).

A significant amount of interest has been placed recently on the development of

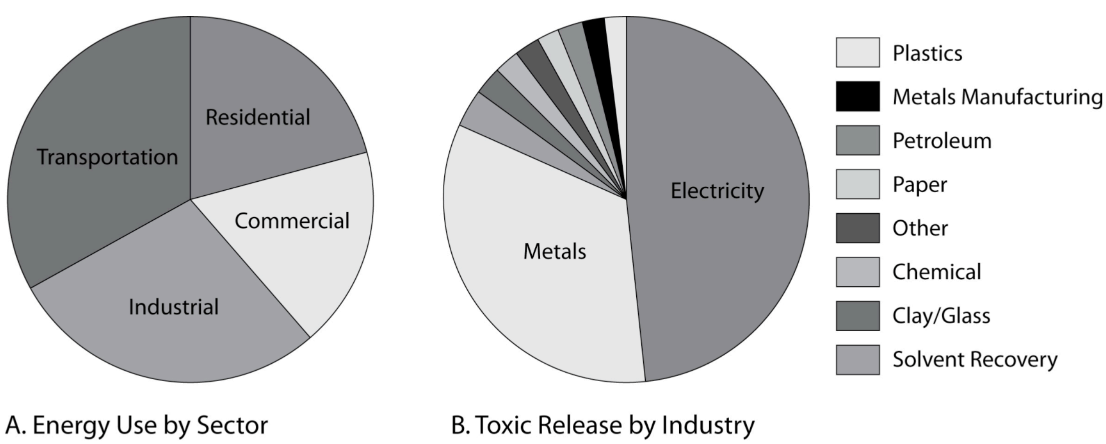


Figure 1.1. Energy use by sector and toxic release by industry for the United States in 2006 (EIA 2007; TRI 2007)

dry or near-dry machining operations. In minimum quantity lubrication (MQL) operations, a small amount of MWF is delivered in a spray of air and no fluid is recycled, eliminating much of the infrastructure typically associated with conventional water-based MWFs (Figure 1.2). Though some processes work well using this new technology, it requires expertise to operate properly because air cannot cool as well as water. Nevertheless, the potential savings in pumping and infrastructure maintenance costs have manufacturers actively pursuing MQL opportunities. Certainly, the potential savings are large. Over 2 billion gallons of MWF are consumed in the US each year (Byers 2006). General Motors alone manufactures 37,000 engines and 33,000 transmissions every day (Dasch 2007). The scale of the problem is significant, and despite recent efforts to advance the sustainability of metals manufacturing, the manner in which MWF are used is much the same today as it was 40 years ago (Childers 1994).

1.2 Problem Statement

A walk through a typical large metals manufacturing facility confirms that MWF are ubiquitous. Pumped from large tanks in the basement through centralized pumping units, fluids are sent to machine tools where they are sprayed onto cutting operations before they drip back through the floor to holding tanks (Figure 1.2). Microfiltration units are often installed, as well as skimmers, course filters, and centrifuge units to remove contaminants (Skerlos and Zhao 2003). Additives must be mixed into the holding tank to control bacterial growth (Gordon 2004). Mist collectors must be used to keep aerosols in the workplace at low levels, as inhalation is the primary health risk associated with working around MWFs (Simpson et al. 2003). When the fluid has degraded due to microbial accumulation or hard water ion buildup compromising the emulsion stability, the fluid is disposed of at a wastewater treatment plant (Skerlos et al. 1998). Here, the metals-laden water is typically discharged into the municipality and the solids disposed of as hazardous waste.

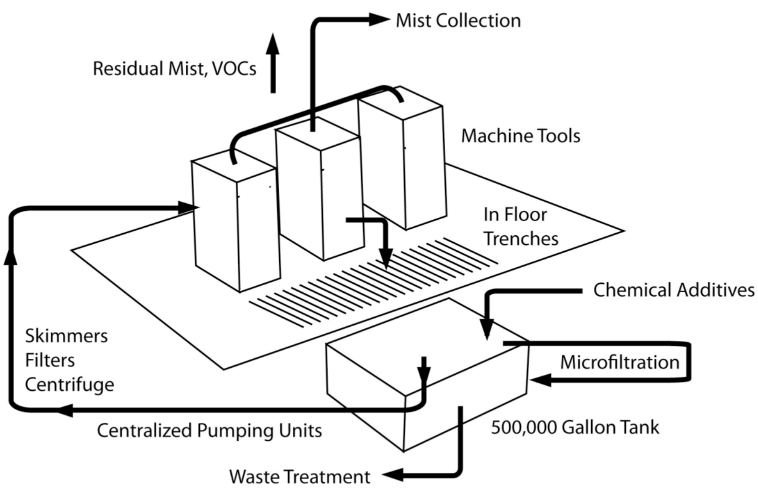


Figure 1.2: Schematic of metalworking plant illustrating the flow of MWFs.

The oil and water mixtures that comprise most MWFs are a serious environmental and occupational health problem. Microorganisms thrive in the fluids, aerosols from the fluids cause decreased air quality in the workplace, and water picks up metals and carries other organic constituents, making them a hazardous waste problem when they reach the end of their useable life. MWFs also require a significant input of energy to maintain and circulate through a large manufacturing facility. Many of the additives that are included in traditional MWFs, such as anti-corrosion agents, biocides, and defoamers, are toxic and pose a waste treatment problem (Sheng and Oberwalleney 1997).

In addition to the health impacts of fluids, the oil and water mixtures are inadequate lubricants in some state-of-the-art machining operations. High performance alloys and light metals are often extremely difficult and expensive to machine. The limiting factor in many of these machining operations is the MWF quality (Kishawy et al. 2005). In these cases, more effective cooling and better lubricant delivery than that afforded by conventional MWFs is necessary. Micromachining, such as that performed in many biomedical applications, is a growing area that requires new methods of lubrication. In these applications, fluids with reduced surface tension are needed to ensure the integrity of the product.

Because of the numerous technical and health limitations associated with MWFs, they are an expensive part of typical machining operations. Figure 1.3 shows the cost associated with manufacturing a typical metal part (left) and demonstrates that MWF costs are higher than tool, energy, or maintenance costs. After the cost of the machine tool

MWF are the second largest cost associated with metals manufacturing. The cost of the MWF does not come primarily from the purchase of the fluid as demonstrated in Figure 1.3A.

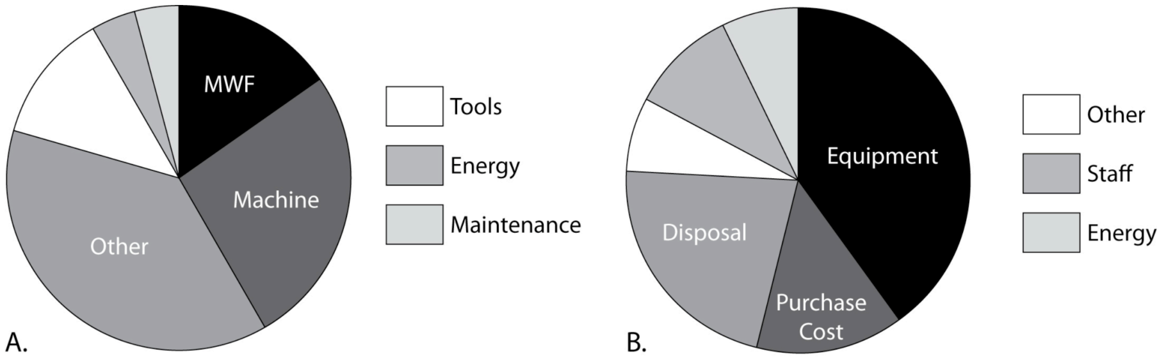


Figure 1.3: Typical costs associated with manufacturing metal (A) and with metalworking fluids (B) (Dasch 2007)

Rather, the infrastructure to move the fluids around the facility and maintain them and the cost to dispose of the MWF, outweigh the original purchase cost of the fluid (Figure 1.3B). This analysis suggests that 1) financially speaking, MWF are a significant cost that should be given as much, if not more, attention than tooling costs and that 2) the cost comes primarily from the extensive infrastructure and disposal of water-based fluids.

Despite the significant footprint that MWF have on a manufacturing setting, they are necessary to control the high temperatures and pressures created between metal tools and work pieces. Typically composed of oil and water, the oil serves to lubricate and the water cools. Surfactants are also included to ensure that the two will mix. They are often applied in large excess to both guarantee that sufficient amounts reach the cutting zone and to aid in the removal of metal chips that may form during the machining process (Su et al. 2006).

1.3 Technology Concept

A primary goal of this research is to develop the knowledge necessary to deliver minimal quantities of vegetable-based lubricants in a supercritical CO_2 carrier for metalworking applications. Minimal quantity delivery of lubricants in sprays of CO_2 can conserve resources and reduce life cycle emissions, while eliminating water removes health risks and spoilage concerns associated with traditional MWFs. Vegetable oils are desirable for use in MWF applications because they are better lubricants than mineral oils (Clarens et al. 2004a). They also come from renewable feedstocks and are less toxic during use and at the end-of-life. Supercritical carbon dioxide ($scCO_2$) is being used increasingly in industry as an alternative to traditional organic, halogenated, or aqueous solvents (DeSimone 2002). The supercritical temperature and pressure of CO_2 (T_c = 31.1 ^oC and P_c = 72.8 bar) is easily achieved in industrial environments (Clifford 1999). Under these conditions CO_2 is a good solvent for many materials, with some vegetable-based oils being highly soluble (Mukhopadhyay 2000).

Recent research efforts have looked at the use of CO_2 in spray coating applications (Debenedetti et al. 1993). Rapidly expanding solutions in CO_2 cool significantly as pressure drops and produce a uniform coating of the solubilized material on the spray surface. These characteristics make CO_2 an ideal delivery mechanism for MWFs. The uniform coating of oil that results ensures lubrication arrives at the cutting surface and the dry ice that forms during the expansion provides better cooling relative to water. Furthermore, the pressure release of CO_2 also provides a chip evacuation function previously achieved using water.

CO_2 is the primary greenhouse gas responsible for global warming, though all of the CO_2 used commercially as a feedstock today is created as a byproduct of other industrial operations (Overcash et al. 2007). As a result, the delivery of MWF using CO_2 can rely on waste CO_2 rather than creating demand for new material. Because oils are soluble in CO_2, no surfactants or the additives typically associated with water based MWFs are needed including antifoaming agents, biocides, and corrosion inhibitors.

The potential reductions in environmental impact along with the solubility and spray cooling properties of CO_2 make it an attractive candidate for MWF delivery functions. Currently lacking, however, is a fundamental understanding of the spray cooling and lubricant characteristics of CO_2-based sprays. The potential savings in machining energy and tool wear that could result from a switch to CO_2-based MWFs also have yet to be determined. Further, a comprehensive life cycle evaluation of the environmental impacts associated with a switch away from water has not yet been prepared.

1.4 Research Objectives, Scope and Overview of Thesis

The overall objective of this research is to determine the technical feasibility of switching from water-based to CO_2-based MWFs. No work has yet been published exploring the use of CO_2 in metalworking operations. The solubilizing characteristics of CO_2 have not been investigated in the context of several key metalworking lubricants. Nor have the cooling potential of CO_2 sprays been studied. In order to achieve the goals of this research, both of these fundamental properties of CO_2 are investigated within the context of machining performance.

The overarching objective of this work is to determine whether CO_2-based MWFs are a viable alternative to conventional water-based fluids and to provide guidelines for CO_2-based MWF component selection and operating conditions based on machining metrics and within a holistic life cycle design framework. Four major research objectives are comprised in this body of work:

- To develop a testbed to deliver CO_2-based MWFs for benchmarking the performance of these fluids compared to conventional MWF formulations.
- To understand the cooling potential of these CO_2 sprays within the context of tool life improvement.
- To evaluate the lubricant delivery characteristics of CO_2 by studying the solubility and delivery of several MWF classes.
- To model the life cycle impacts of several key MWF technologies to understand the overall impacts associated with a switch from water to CO_2.

Two machining operations, tapping and turning, have been used to evaluate CO_2-based MWFs. A tapping torque test is used to measure the machining energy reductions possible using different MWFs. Lathe turning tests have been applied to evaluate the tool life improvements that are possible from using sprays of CO_2. A specially designed temperature probe has also been constructed to measure and optimize the cooling potential of CO_2 under different conditions.

1.4.1 *Overview of Dissertation*

Chapter 2 provides a literature review that begins with an introduction to MWFs, their function and formulation. The benefits and environmental impacts of MWF are discussed in general followed by an overview of the alternatives currently in development including MQL and cryogenic cutting using liquid nitrogen. Chapter 2 focuses on CO_2 and its promise as a lubricant delivery medium. An overview of the chemical characteristics that make it a viable solvent is presented along with a discussion of the spray applications of CO_2 for particle formation and the chemical thermodynamics needed to describe and model lubricant solubility in CO_2.

Chapter 3 discusses the experimental methods developed to achieve the research goals of this work. These methods draw on the experimental setups of other research groups with significant modifications made to achieve the specific data needs of this work. Methods developed and discussed include the delivery of CO_2-based MWFs, spray cooling potential, tool life in orthogonal cutting, and solubility measurements in high-pressure carbon dioxide.

Chapter 4 discusses the preliminary proof of concept results that demonstrate the technical feasibility of CO_2-based MWFs. The performance of these fluids is compared to several benchmark fluids in terms of machining energy in the tapping torque test. Surface analysis of the chips is used to confirm experimental results and understand the mechanisms by which CO_2-delivery of MWF functions.

In Chapter 5, sprays of CO_2 and lubricant are tested for cooling potential using a specially designed heat flux probe. Five system-operating conditions are varied to maximize heat removal potential. The optimized sprays are used to compare the tool life differences between water or air based coolants and CO_2. A model of the heat flux is used to predict the cutting temperature reductions provided by the CO_2 to assess whether this may be responsible for reductions in flank wear rates found using CO_2 compared to water and air based coolants.

A life cycle assessment of four common MWF systems is presented in Chapter 6. These systems include several environmentally adapted lubricants including minimum quantity sprays of lubricants in air and vegetable based formulations in water. A sensitivity analysis is presented to describe the effect of system operating parameters on overall life cycle impacts.

The conclusions and future work chapter summarizes the important findings of this dissertation and discusses on-going and future research needed to optimize MWF formulation and delivery in $scCO_2$. An flow chart of the dissertation is presented in Figure 1.4.

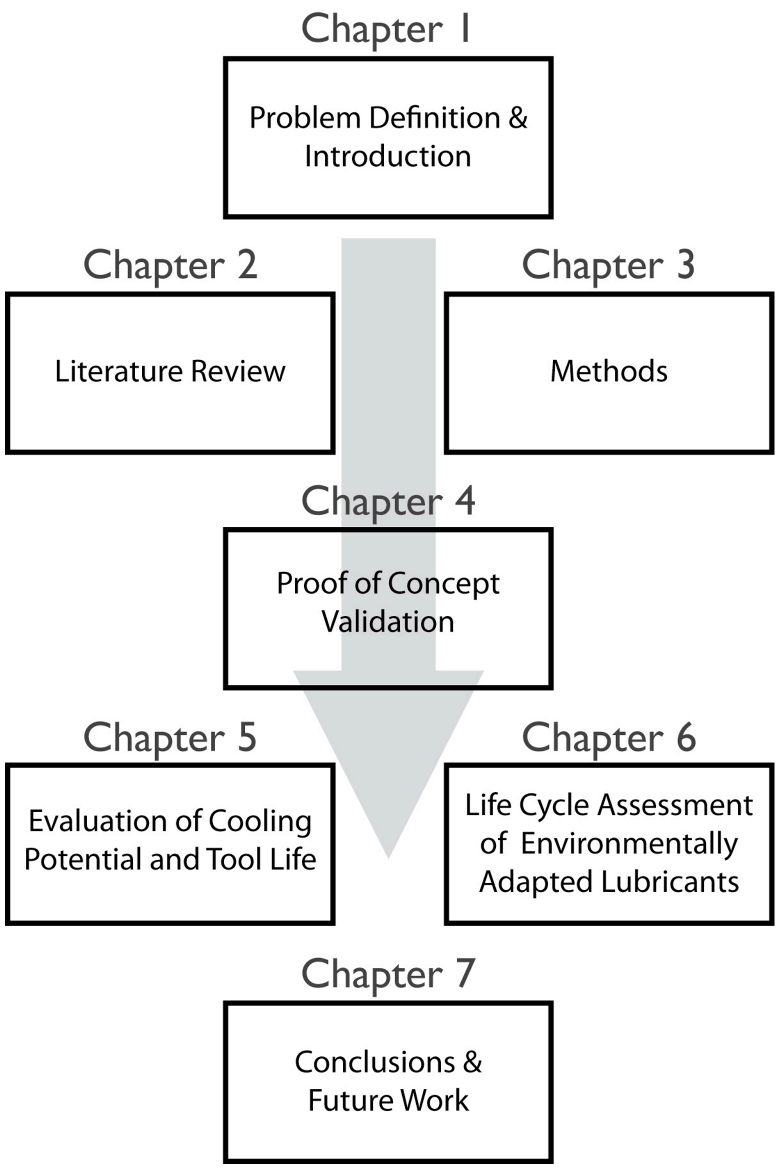


Figure 1.4: Dissertation Overview

Chapter 2

Background and Literature Review

Metalworking fluids (MWFs) have been used for centuries and their form has changed very little, though significant efforts have been made to improve their performance over the past several decades. These attempts at improvement have coincided with a better understanding of the adverse health impacts that MWFs can have on people and the environment, which has in turn driven the development of environmentally adapted alternatives. This chapter begins with an overview of MWF formulation by describing the role of MWF components. This discussion focuses on the multiple roles that MWFs play in the manufacturing setting and the alternative technologies that have evolved to meet the lubrication and cooling challenges.

The state of the art in the use of supercritical carbon dioxide as a solvent is presented. An introduction to the solubility characteristics of CO_2 and the modeling of phase behavior is also provided. This is followed by a discussion of the spray of supercritical solutions and other applications that have successfully implemented this technology as an alternative to aerosol-based sprays for coating and particle formation processes. The measurement of spray cooling potential as reported in the literature is then discussed.

A discussion on the life cycle impacts of MWF and CO_2-based technologies and efforts to model them is presented. The chapter concludes with a brief summary of the published literature that highlights the knowledge gaps and provides a justification for the current research.

2.1 Metalworking Fluid Formulation and Function

Metalworking fluids are used to lubricate, dissipate heat, and clean the cutting zone in metal machining operations. Several types of MWFs commonly encountered in metals manufacturing achieve these goals to different degrees. Straight oils, soluble oils, synthetics, and semi-synthetics are all used and can be considered to differ mainly in the amount of oil they contain with straight oils (100% oil) > soluble oils > synthetics > semi-synthetics (<1% oil). Straight oils tend to provide the most lubrication and semi-synthetics tend to provide the best cooling capacity. Because oil and water do not naturally mix, all MWFs other than straight oils contain surfactants to facilitate the formation of emulsions of oils and water.

Lubricating oils function at the interface between the workpiece and tool with the type of lubrication generally divided into four fluid film regimes: hydrodynamic, elasto-hydrodynamic, mixed, and boundary. The type of regime is correlated to the thickness of the lubricating layer that forms between the metal surface and machining tool (Bhushan 2002). Hydrodynamic lubrication is characterized by a thick film of fluid (>0.25mm). Boundary lubrication is characterized by thin monomolecular films where the contact between metal surface and tool may only be a monomolecular film (1-3 nm). Elastohydrodynamic and mixed lubrication are in between. Figure 2.1 depicts a schematic of bulk (defined as hydrodynamic, elstohydrodynamic, and mixed) and boundary layer regime. Boundary layer is the predominant MWF lubrication mechanism in high-load and low-speed machining processes (Bhushan 2002). The lubrication regime is largely controlled by the local temperature and pressure, which can vary greatly by machining operation geometry, speed, and tool condition.

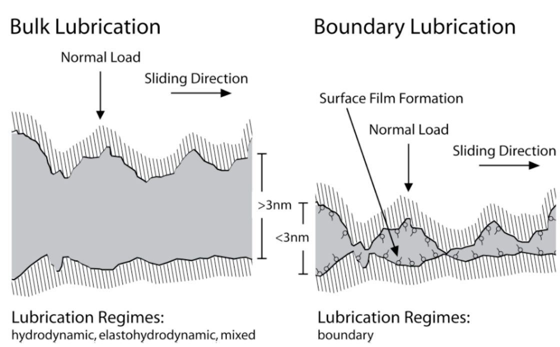


Figure 2.1: Schematic of bulk and boundary lubrication.

Several types of bulk lubricants are used in industry today. Highly refined mineral oil is most often used because it is inexpensive and MWF formulators have experience combining the oil with surfactants or additives. Several vegetable and synthetic-based alternatives have been used increasingly for specialty applications. Vegetable oils tend to be more effective lubricants and are less toxic to workers but they are expensive. Synthetic oils can be tailor made to exhibit desirable properties such as water-solubility or cooling-capacity. Each of these bulk lubricants can be used in all MWF formulation types, though some are favored in particular applications.

Extreme Pressure (EP) additives are included in MWF formulations to provide boundary lubrication. They work by reacting with the metal surface and forming a low-shear-strength, solid-film boundary layer between the work piece and the machine tool. The solid-film is not continuous but acts as a separating or parting agent where the tool meets the work piece and prevents metal-to-metal contact. Such films can form through physisorption, chemisorption, or chemical reaction. Unlike other lubricants the bulk properties of EP additives, such as viscosity, are unimportant (Bhushan 2002). More important are their melting point, shear strength, and rates of formation. All MWF classes: straight oils, soluble oils, synthetics, and semi-synthetics can be blended with EP additives if the machining operation is severe enough.

Semi-synthetics are oil-in-water emulsions that represent the largest market share of total MWF sales due to their low costs and desirable cooling performance (Byers 2006). These fluids are typically sold as concentrates and diluted 95% in water prior to use. As the water evaporates during use, make up water is added. The use of water in the mixture necessitates corrosion inhibitors particularly when machining ferrous metals. Smaller facilities tend to use tool-scale MWF application systems while large manufacturing facilities rely on centralized systems. In both cases pumping the MWF in and out of a reservoir can cause foaming (Serov et al. 1976). To prevent foaming within the distribution system, antifoaming agents are commonly included. MWFs are generally applied by spraying them out of a nozzle at 2.5-3.5 bar directly onto the work piece (Moon 2004). Fluids are generally recirculated until they degrade and affect machining performance or become an occupational health problem.

MWF emulsions degrade as a result of several factors: bacterial growth, hard water ion accumulation, and introduction of tramp oil (Skerlos et al. 2001a). Most MWF storage tanks are open to the atmosphere and provide an excellent carbon source for aerobic microbacterial growth. When pathogenic bacteria degrade the oil and the surfactant they can cause illness to workers who come in contact with the fluids. Biocides used to control microbial growth may be toxic to workers as well. Hard water ion accumulation in the MWF can neutralize charged surfactant species and destabilize the emulsion (Zimmerman et al. 2004). Chelating agents, such as EDTA (ethylene diamine tetra acetic acid), are commonly added to the MWF mixture to bind hard water ions and extend the life of the MWF. Hydraulic oils from machine tools and other sources of impurities in the manufacturing environment can also destabilize the MWF emulsion mixture. Secondary emulsifiers are typically added, sometimes in great excess, to dissolve and preempt the accumulation of waste oil. A summary of common constituents included in MWFs is given in Table 2.1.

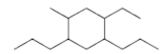
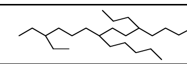
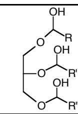
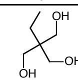
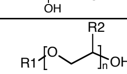
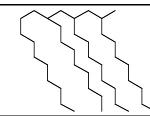
Table 2.1. Common MWF Components

Impact Factor	Class	Example
Petroleum-based oil	Bulk Lubricant	Highly refined mineral oil
Bio-based oil	Bulk Lubricant	Soybean oil
Synthetic lubricant	Bulk Lubricant	Polyalkylene glycol
Extreme Pressure Additives	Boundary Lubricant	Dimethyl disulfide
Fatty Acids	Boundary Lubricant	Steric acid
Anionic Surfactant	Emulsifier	Sodium petroleum sulfonate
Nonionic Surfactant	Emulsifier	Primary alcohol ethoxylate
Corrosion Inhibitor	Additive	Monoethanol amine borate
Biocide	Additive	Triazine
Coupler	Additive	Propylene glycol
Chelating Agent	Additive	EDTA

2.1.1 MWF Bulk Lubricants

Bulk lubricants for MWF formulations can be divided into three general classes: petroleum based, bio-based, or synthetic (Table 2.2). The market for MWF lubricants is dominated by highly refined petroleum products because of their low cost and high oxidative stability. Bio-based oils tend to be better lubricants than petroleum oils but they have traditionally been more expensive and more susceptible to oxidation and attack by microorganisms. Synthetic oils have a range of desirable properties from high stability to water solubility, but tend to be the most expensive of the three classes and tend to be used in specialty applications or as secondary lubrication additives in formulations (Rudnick 2006).

Table 2.2. The three broad classes of MWF bulk lubricants.

Class	Type	Chemical Composition
Petroleum-based	Naphthenic mineral oil	
	Paraffinic mineral oil	
Vegetable-based	Soybean oil	
	Canola oil	
	Sunflower oil	
	Trimethylol propane (TMP) trioleate ester	
Synthetic	Polyalkylene glycol (PAG)	
	Poly(α-olefin) (PAO)	

Petroleum oils – Petroleum-based oils are generally divided into paraffinic, naphthetic, or mixtures of the two. These lubricants have large molecular composition distributions but are generally classified by whether or they are straight chain hydrocarbons or they contain benzyl groups. Paraffinic oils are preferable as they are more stable to oxidation and smoke less during cutting but napthenic oils tend to solubilize in formulations better. (Childers 1994).

Vegetable oils – The most commonly used vegetable oils in MWF applications are soybean and canola oils (Byers 2006). These oils are triglycerides with identical chemical structures but different distributions of constituent fatty acids. The aromatic and trace compounds that give oils their distinctive flavors do not affect lubricity. Instead, numerous studies have shown that the composition of fatty acids determines the lubrication performance with longer fatty acid chains being desirable (Rudnick 2006).

Trimethylolpropane Esters – TMP Esters are actually a class of synthetic lubricants made of vegetable-based components. Fatty acids are reacted with a trimethylolpropane to make a molecularly monodisperse alternative to the fatty acid distributions found in vegetable oils. Trimethylopropane trioleate is the TMP lubricant commonly used in MWF applications. The advantage of TMP Esters is that the molecular distribution can be carefully controlled to define lubricity and stability properties (Zeman 1996).

Polyalkylene glycols (PAG)– are a large and diverse class of synthetic lubricants made by polymerizing alkylene oxides. Generally ethylene and propylene oxide are used and the ratio of these monomers determines the water solubility of the polymer. These copolymers can either be mixed or polymerized as blocks. Block co-polymers are better surfactants but they are characterized by excessive foaming in MWF applications (Rudnick 2006). The molecular weight of the PAG can be varied considerably to dial in the viscosity of the bulk polymer.

Polyalpha olefins (PAO) – are commonly referred to as 'synthetic hydrocarbons' because they represent a large family of polymers with molecular compositions similar to some of the napthenic or paraffinic mineral oils (Rudnick 2006). PAOs have much narrower molecular weight distribution than petroleum-based products. They are made by polymerizing alpha olefins, e.g. hexane, to produce linear or branched hydrocarbons but can also be made with olefins containing hydrocarbon ring structure. The polymerization process can be modified to control the degree of branching or the molecular weight and thereby influence the viscosity or these lubricants.

2.1.2 Theories of MWF activity

The predominant theory of MWF function is that MWFs act by penetrating the contact area between a tool and a chip to dissipate heat and lubricate (Smith et al. 1988). The tool-chip interface (Figure 2.2) is typically the highest temperature region of the cutting operation and by penetrating that interface, MWF effectively dissipate heat at the source (Williams and Tabor 1977). The presence of lubricant on the flank face also eases the chip formation process and allows the chip to more easily exit the cutting zone. Effective MWFs separate the tool from the chip by spreading across the interface between the two.

Tool wear is one of the most significant areas of concern for manufacturers for several reasons: 1) tools are expensive 2) worn tools have the potential to produce parts that are out of specification or have poor surface finish and 3) tool replacement leads to down time in production lines. Tool wear and subsequent failure has been studied extensively and occur as nose wear, tool face wear, flank wear, and crater wear. Of these, flank wear and crater wear are two of the most significant.

Crater wear takes place as chips dig out the tool material on the surface of the rake face (Figure 2.2) resulting in catastrophic failure when the tool tip breaks off. Flank wear occurs as the tool rubs against the newly exposed surface on the workpiece. Flank wear (measured at the wear land, V_B) can significantly affect the specifications of a cut part and to avoid this, tools are often replaced prematurely. MWF reduce flank wear by reducing the temperature at the cutting surface, making the tool less reactive against workpiece.

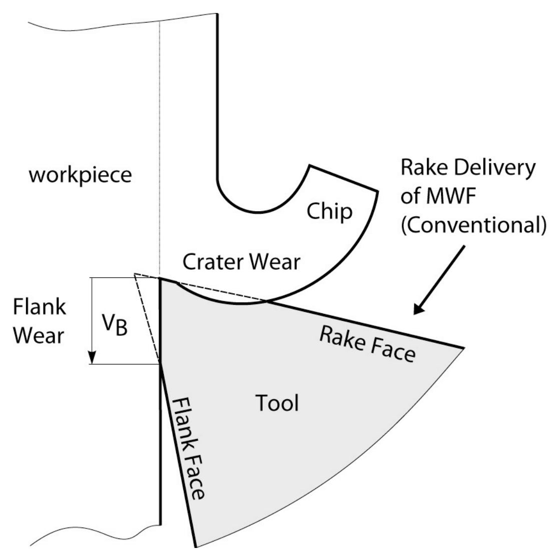


Figure 2.2: Schematic of 2-D orthogonal cutting.

2.1.3 Wear in Metalworking

Under common metalworking conditions, tools wear via several mechanisms, including adhesive, abrasive, and diffusive wear (Shaw 2005). Under typical cutting conditions the latter two dominate (Hastings and Oxley 1976). In both types of wear it is assumed that the harder tool is cutting the softer workpiece. In abrasive wear, small pieces of the tool break off forming chips that slide or roll along the cutting surface under pressure. In diffusive wear, high temperatures result in solid-state diffusion along the boundary between the tool and workpiece. The predominant mechanisms depend on materials and machining parameters. Abrasive wear generally dominates at lower speeds and diffusive wear dominates at higher speeds. These two mechanisms have been described mechanistically in the following wear rate form (Mathew 1989):

$$\frac{dW}{dt} = G(V, f) + De^{-E/R\theta_T} \qquad (2.1)$$

where $\frac{dW}{dt}$ is the wear rate over time, G is the abrasion rate and it is a function of cutting speed (V) and feed (f), and D is a constant associated with the tool and work material, E is the process activation energy, R is the gas constant and Θ_T is the process temperature.

Abrasive wear is most effectively controlled with sufficient lubrication to separate the sliding surfaces and minimize the exposure of surface asperities to the opposite side. Diffusive wear is most effectively controlled by limiting the temperature of the cutting process. For tungsten-carbide-cobalt (WC-Co) tools, a large class of commonly used tools, the cutoff between abrasive and diffusive wear has been shown to occur at approximately 700 ^oC. Above this high temperature, the Co is able to move through the dislocations in the WC matrix and Equation 2.1 simplifies to:

$$\frac{dW}{dt} = De^{-E/R\theta_T} \qquad (2.2)$$

where D and E are diffusive rate constants that change depending on the tool, workpieces, and machining conditions. Under controlled conditions where D and E can be assumed to be constant, the wear rate is an exponential function of the inverse of tool temperature (Θ_T).

Tool temperature can be either measured directly or calculated using a series of semi-empirical equations. Experimental measurement is challenging because the temperatures and the temperature gradients are large and the cutting zone is often inaccessible for temperature measurement. Semi-empirical relationships have been developed that allow for cutting temperature estimation using machining parameters. When mechanical energy is put into a metalworking process most ends up as heat. Heat is released as metal is deformed to produce a chip in the shear zone of the cutting process and heat is released by the friction between the chip and workpiece. The mean tool face temperature can be approximated using the following equation:

$$\overline{\Theta}_T \sim u\left[\frac{Vt}{k\rho C}\right]^{1/2} \qquad (2.3)$$

where Θ_T is the mean tool face temperature, u is the specific cutting energy, V is the cutting speed, t is the undeformed chip thickness, k is the thermal conductivity of the tool, and ρ is the density of the tool and C is the specific heat of the tool. Using expanded versions of the equation and cutting geometry it is possible to use the above equation to determine the fraction of energy entering the chip and the amount entering the tool. The most effective cutting processes transfer most of the energy to the chip rather than the tool.

Empirical relationships for tool life originally focused on cutting speed as a surrogate measure for cutting temperature because temperature at the cutting zone had not been accurately understood or predicted using models. The Taylor Equation is the most well known tool life relationship which effectively predicts tool life as a function of cutting speed (Figure 2.3) (Taylor 1907). On the left of Figure 2.3 are characteristic wear curves for a tool showing the effect of speed. When plotted against time, each curve demonstrates a steep break in period early on, followed by a steady wear land (V_B) growth period in which the tool wears in a controlled fashion. Eventually the tool will fail, usually denoted on these plots by a steep increase in the wear land. In the wear growth region, it is possible to select a wear limit and find the time it would take to achieve that limit as a function of several different cutting speeds. On the right side of Figure 2.3 is a plot of the log of tool life vs. the log of cutting speed with the form of the Taylor tool equation inserted. Here V is the cutting speed, T is the time to achieve a certain amount of tool wear, n is constant for tool material and C is a constant that combines the influence of other machining factors (feed rate, depth of cut, fluid, tool geometry and material, etc.). In practical terms C represents the speed that one would need to operate the process to achieve the wear limit for a set time.

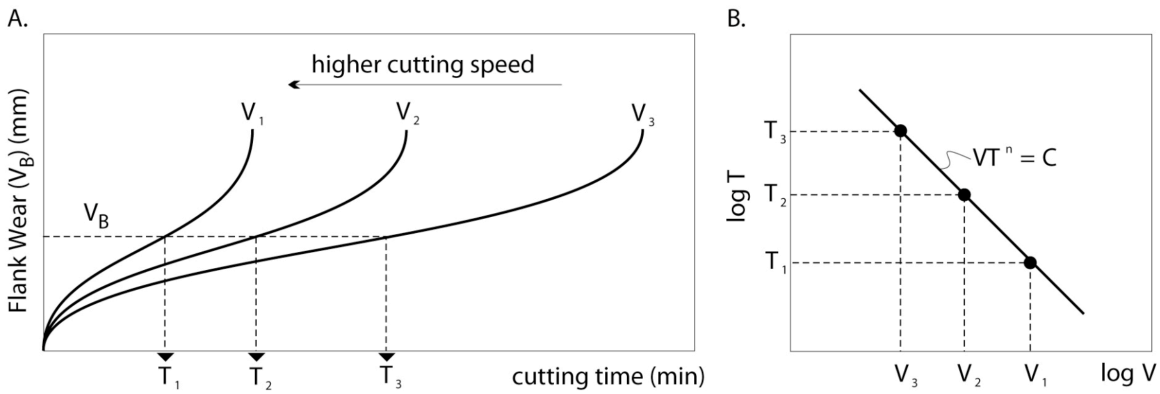


Figure 2.3. Taylor tool life relationship. A tool wears faster as cutting speed increases (A). A log plot of the speed and the time it takes to reach a certain level of wear is linear according to the equation proposed by Taylor (B).

The Taylor model is widely used and has been extended to include other machining parameters such as feed rate and depth of cut. Its empirical form makes it easily applicable to many cutting systems but identifying useful constants that correlate conditions or properties between systems can be challenging. It can be used to compare the impacts of MWFs on tool wear if all the variables are kept constant except C and MWF type. But since the constants are application specific, data comparisons between different systems is not generally expected to provide casual relationships. In addition, the Taylor relationship does not offer useful mechanistic explanations for why metalworking fluids are or are not functioning.

In recent years, more detailed mechanistic models of tool wear have been developed. Using the relationship in Equation 2.1 plus a model for adhesive wear, Li et al. have developed a predictive model of the turning process that evaluates flank wear under different cooling scenarios (Li and Liang 2007). Inputs to the model include cutting force, insert temperature, and a number of physical parameters including the heat capacity of the cooling spray, the coefficient of friction between tool and workpiece, and the position of the spray nozzle.

A combination of the Taylor equation with a temperature-based analysis of tool wear can typically provide a good understanding of the mechanisms by which tools are wearing. In this work, such an approach is used to compare and understand the potential of CO_2 sprays compared to sprays of water.

2.1.4 Technical Constraints

Harsh machining operations can often exceed the performance specifications of aqueous MWFs (Holmes 1971). High strength alloys can produce temperatures and pressures during cutting that quickly wear down the chemical components of an aqueous fluid. Soft metals like aluminum can be difficult to machine because of the galling and welding that can occur between the work piece and the tool (Itoigawa et al. 2006). Titanium is especially difficult because it conducts heat poorly resulting in an accumulation of heat around the cutting zone (Jawaid et al. 1999). Cast iron is relatively easy to cut because the graphite on the surface acts as a solid lubricant. The relative difficulty in cutting steels tends to vary depending on the hardness and the type or machining operation. Drilling is especially challenging (Figure 2.4) due to the difficulty in delivering cooling and lubrication to the cutting zone while simultaneously evacuating chips through the drill flutes. Milling is typically easier because it is an intermittent cutting process allowing tools to cool while not engaged, and since the cutting zone is continuously exposed, coolant delivery is less problematic. Tapping and similarly slower operations do not require significant heat removal but do require lubrication to ensure proper function.

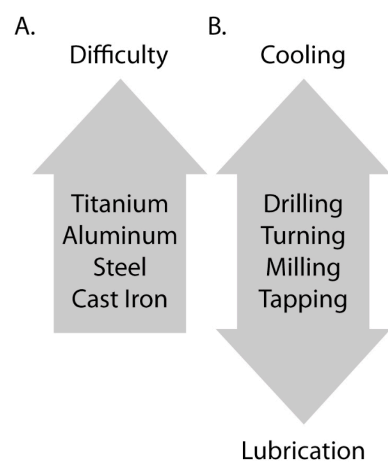


Figure 2.4: Relative difficulty of machining materials (A) and the primary function of metalworking fluids for several representative cutting operations (B).

A number of tool materials have been developed to handle the variety of machining conditions described above. In general, tool hardness at high temperatures is the most desirable feature of metal cutting tools but this is inversely proportional to the toughness of the tools (Byers 2006). Polycrystalline diamond and cubic boron nitride tools are the hardest tools available but they tend to shatter if used improperly and they are prohibitively expensive for most processes. For general applications, titanium or tungsten carbides, have found widespread applicability and by modifying the alloying agents (mostly cobalt) carbide grades can be modified for the specific machining operation. The softest tools commonly encountered in manufacturing are made of high-speed steel which is prepared through specific heat treating processes. High-speed steel tools are often produced in a coated form for most applications today. A wide variety of coatings exist on the market with TiC, TiN, and Al_2O_3 being three of the most common. Coatings extend the life of softer tools considerably but a principal drawback is that wear behaves non-linearly and can be difficult to predict.

For all tool materials, hardness is proportional to temperature such that proper temperature reduction is necessary to control tool life. The machining lubrication and cooling requirements indicate that substantial improvements in tool life and process operating conditions are possible through improved cooling. The cooling potential of CO_2 sprays has not been benchmarked against conventional water-based coolants and the implications for tool life have not been explored.

2.1.5 Health and Environmental Risks

A number of recent studies conducted by the occupational health community have highlighted the dangers associated with MWF exposure (Abrams et al. 2000; Crippa et al. 2001; Gordon 2004). These studies show that workers exposed to MWFs are at increased risk for larynx, rectum, pancreas, skin, scrotum, stomach, and bladder cancers (Calvert et al. 1998). Other studies have investigated the respiratory effects of breathing MWF mists in the workplace (Gauthier 2003), while still others have looked into the dermatitis and other irritations associated with worker contact with MWFs (Kanerva et al. 2000). Across the board, the data show that short- and long-term exposure to MWFs in the workplace causes detrimental health affects in workers.

In response to this risk the National Institute for Occupational Safety and Health (NIOSH) Standard Advisory Committee recommended the allowable mist level in manufacturing facilities that use MWF be reduced from 5.0, the widely held standard down to 0.5 mg/m^3 (OSHA 1998). The United Auto Workers have negotiated the same standard as part of their contracts. Recent efforts have been made to designate MWF mist as a suspected human carcinogen (Dasch 2007). For this to happen clarification is needed to determine whether bacteria or chemical constituents in the MWF cause the health impacts.

The fugitive emissions of MWF from industrial facilities are also problematic because of the persistent organic pollutants that are often added to MWFs as EP additives. Compounds such as short-chained chlorinated paraffins, a common type of EP additive, are believed to travel great distances and bioaccumulate in the food chain once released from a manufacturing facility (Muir et al. 2000).

At the end of use, MWF must be disposed of creating a number of environmental burdens. Treatment of MWF oily waste and release to the environment can lead to oxygen depletion and nutrient loading of water resources (Cheng et al. 2005). In 2003, the US EPA enacted technology-based effluent limitation guidelines for MWFs in the Metal Products and Machinery Rule (EPA 2003). This rule regulates the disposal of MWFs supplementary to the Clean Water Act and the Pollution Prevention Act.

2.1.6 Alternatives to Conventional Fluids

To meet the increasingly stringent MWF use regulations, disposal limits and potential occupational health hazards, recent interest has focused on either eliminating the MWF, using smaller quantities of it, or substituting environmentally adapted lubricants (EAL) for conventional MWFs. EALs have been defined in the European Union as those that have high biodegradability and low toxicity with performance equal to or better than conventional alternatives (D.Theodori et al. 2004). Each of these technologies is discussed briefly here:

Bio-Based Formulations: Vegetable oil based MWF components are being substituted into traditional formulations as renewable and biodegradable alternatives to conventional fluids (Zimmerman et al. 2003a). Recent work has focused on the formulation of vegetable based emulsions for MWF applications that are as stable as petroleum-based alternatives (Zimmerman et al. 2004). Bio-based MWFs offer a renewable alternative with increased potential for biodegradation at end of life (EOL) and improved machining performance.

Dry Machining: An obvious way to reduce the impacts and cost of metals manufacturing is to eliminate the MWF all together. In most cases this will result in shortened tool life or reduced product quality but in other cases may result in comparable performance if modifications are made to existing processes. For example, tool geometry can be modified to have wider flutes and higher helix angles on drills to make chip evacuation easier and reduce the need for lubricants to serve that purpose. The machining process can also be adjusted to reduce tool wear by slowing the cutting speed or reducing the feed rate. Tool coating technology has advanced considerably in recent years with TiN, TiCN, diamond-like carbon, providing resilient surfaces that mitigate the wear common in uncoated high speed steel or carbide tools and reduce the need for MWFs.

Minimum Quantity Lubrication: Minimum quantity lubrication (MQL) techniques use compressed air or water and a small amount of oil to provide the function of a MWF without the large volumes of aqueous waste (Silva et al. 2005). In the US, many manufacturers are making a transition to MQL to reduce health and fluid costs. Conventional water-based fluids require significant infrastructure to deliver and store fluids through a system of grates, drains, storage tanks, and pipes. The lubricant volumes used in MQL are much lower, and although such fluids have limited cooling ability, the technology is being deployed successfully in the field for certain machining application.

Cryogenic Cutting: Cryogenic cutting has been investigated using liquid nitrogen to cool the work zone and is effective in processes that do not require lubrication. Cutting using liquid nitrogen (N_2(l)) is being used primarily in niche applications to machine materials that generate significant amounts of heat (Hong 2006; Paul et al. 2001). When lubrication is required the process is not viable. N_2(l) is also expensive and difficult to handle in industrial settings. Liquid nitrogen also requires large amounts of energy to produce at cryogenic temperatures and likely increases the environmental burden relative to conventional systems.

Delivery of MWF in CO_2: In 2007, De Chiffre published work looking into the tool wear benefits associated with parting/grooving stainless steel with sprays of cryogenic CO_2 as the MWF (De Chiffre et al. 2007). This work reported minor tool wear improvements using CO_2 when compared to water based alternatives. The CO_2, however, was used in much the same way as air in MQL sprays. A nozzle system was used to mix a spray of CO_2 with lubricant and deliver it to the workplace. This effectively captured some of the cooling benefits of CO_2 but neglected the use of CO_2 to solubilze and deliver lubricating oils. Several companies have attempted to commercialize technology similar to that reported by DeChiffre.

2.1.7 Barriers for Change in MWF Use

Although compelling performance advantages exist for moving away from water based MWFs, worker safety and economic considerations also influence the impetus for change in MWF systems. One of the most significant barriers involves the infrastructure costs. A switch away from water-based systems could require large capital investments that are prohibitive for many manufacturers. Production losses are also possible as machinists learn to work with alternative MWFs. This learning curve is especially problematic given that the US manufacturing sector has a large number of veteran machinists who are well trained in the use of conventional fluids. The health impacts of MWF alternatives are also difficult to predict. Metal dust can be harmful to workers and the environment if not adequately suppressed or vented and may increase with alternative gas-based MWFs. It remains to be demonstrated whether breathing these metal fines will be worse for workers than chronic exposure to aerosol mists? Worker safety may also be compromised if incidence of fires increases as a result of the excessive temperatures present in dry cutting operations.

Preliminary trends in the industry seem to suggest that a move away from wet lubricants toward MQL machining could overcome some of the obstacles (Filipovic 2006). The decentralized distribution units are less energy intensive than centralized water-based MWF systems and require fewer auxiliary systems like filtration, drainage. But the air-based systems being widely deployed could face problems with metal dust and insufficient cooling. For this and a number of other reasons, CO_2-based MWF systems have a high potential to overcome the barriers for change in MWF use. CO_2-cools better than air and has the potential to reduce airborne metals dust by coating the cutting zone with dry ice and lubricant.

2.2 Properties of Nearcritical and Supercritical Fluids

All pure chemical compounds may exist in several phases. Solid, liquid, and gas are the states most commonly encountered. Temperature and pressure generally determine which state a chemical will be in. Figure 2.5 depicts a generic phase diagram illustrating molecular packing in the different phases. At low temperatures compounds can be found in the solid state. Molecules are packed closely together. Water, for instance exists as ice until the temperature gets above $0^{o}C$. As the temperature rises the solid melts and becomes liquid. Here the molecules are no longer aligned in a solid matrix but intermolecular interactions still exist that keep the molecules in the liquid state. If further heated, liquid water will vaporize and become a gas. In the gas phase molecules are disperse enough that interactions are relatively weak. The boundary between the liquid and gas phase is called the vapor-liquid equilibrium. At a certain critical temperature (T_c) and pressure (P_c) the vapor-liquid line ends and the distinction between a gas and a liquid disappears with a single continuous fluid phase forming. This phase is known as the supercritical fluid (SCF) phase.

The bulk fluid properties of a SCF, not surprisingly, resemble something between the properties of a liquid and a gas. A SCF generally has solubilizing properties like a liquid and high diffusivity, low viscosity, and low surface tension like a gas. The properties of the fluid in the supercritical region can be 'tuned' by changing the temperature and the pressure. Particularly at temperatures near the critical point, the bulk properties of the substance change significantly with small changes in system conditions.

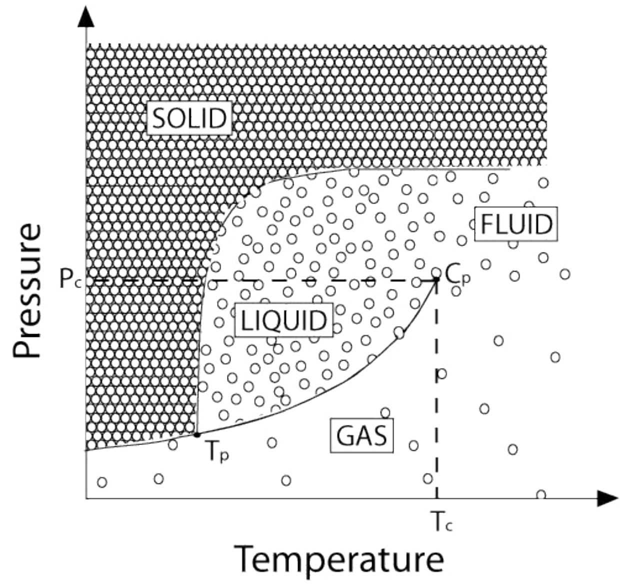


Figure 2.5: Pressure-temperature diagram for a pure component illustrating molecular packing.

In theory, all compounds could have a SCF phase but many may either degrade before they reach it or the critical point is too high for reasonable use in industrial applications. Some of the most common compounds that have been studied for SCF applications are carbon dioxide, ethane, propylene, nitrous oxide, ammonia, and water. Of these, CO_2 has received the most attention because of its relatively low P_c and T_c. CO_2 also has many other attractive characteristics that make it an appealing industrial solvent including that it is inexpensive, odorless, tasteless, nontoxic, and environmentally benign with the exception of its global warming potential.

2.2.1 Solvency

A SCF's tendency to solubilize another compound results from its fluid-like properties. Solubility of solute molecules is directly proportional to a fluid's density, which is dependent on the temperature and pressure of the system. One of the most attractive features of $scCO_2$ is that solutes can be dissolved and precipitated out of solution simply by changing the operating conditions. Figure 2.6 illustrates how the density of a SCF varies with pressure and temperature. The plot is generalized and presented in terms of reduced parameters:

$$P_r = \frac{P}{P_c} \qquad \rho_r = \frac{\rho}{\rho_c} \qquad T_r = \frac{T}{T_c} \qquad (2.4)$$

where the subscript 'c' indicates the critical parameter for pressure, density, and temperature. Around the critical point, a SCF will undergo large changes in density as a result of small changes in pressure. This phenomenon can be explained using the isothermal compressibility of a fluid (K_T).

$$K_T = -\frac{1}{\rho}\left(\frac{\partial \rho}{\partial P}\right)_T \qquad (2.5)$$

The isothermal compressibility is inversely proportional to the density times the partial derivative of the density with respect to pressure at constant temperature. The slope of isotherms near the critical point is high and goes to infinity at the critical point. This characteristic of supercritical fluids becomes less pronounced as the pressure or temperature get higher than the critical values.

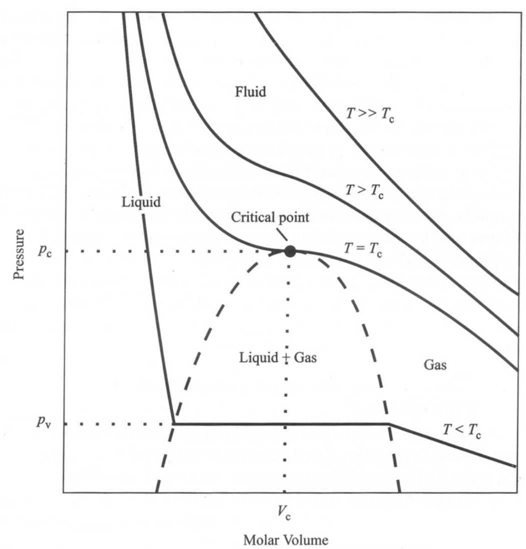


Figure 2.6. Phase diagram of a pure component as a function of reduced pressure and reduced temperature.

CO_2 is more attractive than other supercritical solvents that have been considered in part because of its properties near the critical point (T_c=304 K, P_c=72.8 bar). The density of supercritical carbon dioxide decreases significantly with increases in temperature. At its critical pressure, CO_2 has a density of 930 kg/m^3 at 272 K, at 304 K the density is

530 kg/m^3. This density decrease is more pronounced than traditional organic solvents like toluene that drops from 890 to 870 kg/m^3 over the same temperature range. Surface tension of CO_2 drops but only slightly as a result of an increase in temperature. At 272 K the surface tension of CO_2 is 0.004 N/m and at 304 K it has decreased only slightly to 0.002 N/m. Viscosity decreases from -0.0465 to -0.048 cP. In comparison, water has a density of 1000 kg/m^3, a surface tension of 0.072 N/m, and viscosity of 1 cP at STP. The diffusivity of supercritical CO_2 is an important parameter for many solubility dependent processes. The diffusivity of scCO_2 is not as low as it is for a liquid but it is higher than dilute gases. At 40^{o}C the diffusivity of organic liquids is roughly 1x10^{-5} cm^2/s one order of magnitude lower than the self-diffusivity of CO_2. In general the diffusivity of scCO_2 increases with temperature and decreases with pressure.

As a lubricant carrier for MWF applications, scCO_2 has a number of important advantages related to its solvency capabilities. As a tunable solvent, CO_2 has the potential to dissolve a wide range of lubricant classes. Water can only dissolve specifically modified lubricants. Further, for CO_2 systems, the amount of dissolved lubricant can be carefully dialed in by controlling the pressure. But in order to design stable mixtures in CO_2, it is necessary to first describe the high-pressure phase stability characteristics of mixtures.

2.3 Phase Behavior

The phase behavior described above applies to pure compounds only. For mixtures, complex behavior is more likely. Phase equilibrium lines or isotherms cannot generally be extrapolated assuming a simple weighted average based on percent composition. For common solutes, the phase behavior of mixtures has been studied and cataloged. Using the molecular properties of constituents, it is possible to describe the phase behavior of most mixtures. An understanding of this phase behavior is important for engineering applications in which phase separation can lead to a loss of process function.

Two general classes of binary mixtures have been defined for the case where a molecule is dissolved in a supercritical fluid. In the first, a solute with critical parameters slightly above those of the supercritical fluid, and molecular weight close to that of the fluid is added to change the fluid's solvency properties or act as a reagent in a chemical reaction (Clifford 1999). In the second class, a larger, nonvolatile molecule is added to the fluid to impact improved solvency. Phase diagrams for both classes of mixtures can be represented on three-dimensional diagrams with the pressure and temperature on the x- and y-axes as a function of changing mole fraction of the two components on the z-axis. Figure 2.7 depicts two-dimensional projections of these binary mixtures. The two curved vapor-liquid equilibrium lines (solid) in each plot are for each of the pure components and would be found at either end of the z-axis (e.g., where each component exists in its pure form). The dotted line connecting the two critical points is the projection of the critical line for the mixture over the range of mole fractions. Types I, V, and VI assume that the critical point for the mixture always exists where as Types II, III, and IV do not (hence the dotted lines that do not connect and disappear above the top of the plot). In some cases the behavior is complex and the critical point of the mixture is actually below that of one of the pure components (as in II, IV, V, and VI).

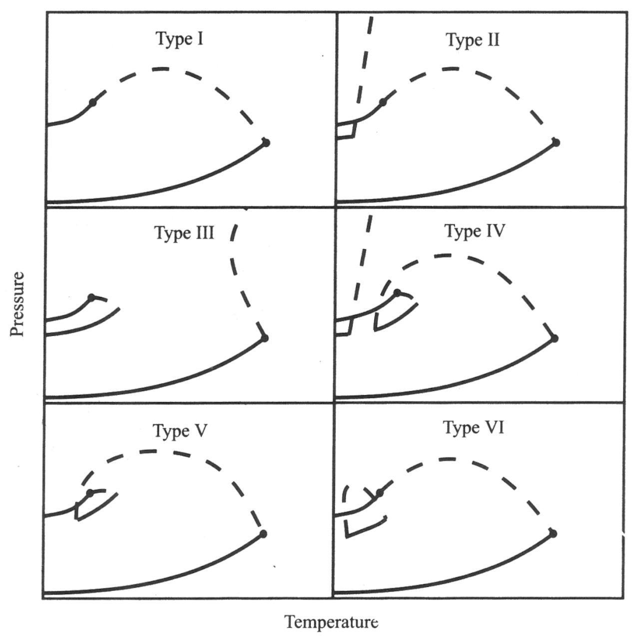


Figure 2.7: Types of phase behavior observed for binary mixtures of supercritical fluids. Adapted from (Clifford 1999).

The dependence of molecular structure on solubility in CO_2 is evident from the phase behaviors described above. In general, the functional groups, polarity, and molecular weight of a solute determines its solubility in a supercritical solvent. $scCO_2$ has a tendency to dissolve nonpolar and low molecular weight molecules. Relatively nonpolar hydrocarbons such as benzyaldehyde, hexanol, glycerol, and acetates; fluorocarbons; sugar acetates; and high vapor pressure compound are all very soluble in $scCO_2$ (Moyler 1988). Slightly polar molecules with one carboxylic or two hydroxyl groups such as saturated lipids up to C12, decanol, water, and oleic acid are somewhat soluble in CO_2. Highly polar substances such as sugars, proteins, waxes, inorganic salts, citric and malic acids, and amino acids are relatively insoluble in CO_2 (Mukhopadhyay 2000).

An understanding of the phase characteristics of lubricant mixtures in $scCO_2$ is important for the proper design of CO_2-based MWFs. Lubricants are often large macromolecules with nonpolar structure that are only marginally soluble in CO_2. A description of the mixture type is necessary to select appropriate operating conditions.

2.3.1 Equations of State

Equations of state (EOS) are used to describe the relationship between intensive variables (pressure, volume, and temperature) and system composition for liquids and vapors and if complete enough can describe the solubility behavior of mixtures without the need for exhaustive experimentation. The ideal gas law, perhaps the simplest example of an EOS, effectively describes real gas behavior under high dilution. More complex models have been developed that are useful over a wider range of operating conditions. Some models are overly demanding from an experimental or numerical standpoint to be generally useful. Polynomial equations that are cubic in molar volume offer a good balance between accuracy of representation of phase behavior and ease of use.

The first cubic EOS was proposed by Van-der-Waals in the late 19th century. Since then, several hundred cubic equations of state have been developed. Two EOS that have been applied extensively for high-pressure work include those of Peng-Robinson and Redlick-Kwong. Ultimately the selection of an appropriate EOS depends on 1) the phases in which the modeled compounds exists over the range of system conditions of interest, 2) the state variables that are known and, 3) the number of components that are present in a mixture.

The Peng Robinson Equation (PR EOS) (Peng and Robinson 1976) is widely used in high pressure applications and improves on models before it because 1) all EOS parameters are expressed in terms of the critical constants, 2) it has good accuracy near the critical point, and 3) mixing rules employ only one binary interaction parameter (independent of temperature, pressure and composition). In general, cubic equations of state rely on the additives of two semi-empirical parameters to the ideal gas law (parameters a and b) that are used to approximate repulsion and attraction between molecules and to account for material volume respectively. One version is shown in Equations 2.6-2.8:

$$P = \frac{RT}{V-b} - \frac{a(T)}{V(V-b)+b(V-b)} \qquad (2.6)$$

where: $a(T) = \left(0.457235\frac{R^2 T_c^{\,2}}{P_c}\right)\alpha(T)$ (2.7) and $b = 0.077796\frac{RT_c}{P_c}$ (2.8)

where P, V, R, T, P_c and T_c are pressure, molar volume, ideal gas constant, temperature, critical pressure and critical temperature respectively. The α(T) is calculated using Equation (2.9 and 2.10):

$$\alpha(T) = \left[1 + \kappa(1 - \sqrt{T/T_c})\right]^2 \qquad (2.9)$$

where $\kappa = 0.37464 + 1.54226\omega - 0.26992\omega^2$ (2.10)

and $\omega = -1.0 - \log_{10}\left[\frac{P^{vap}(T_r - 0.7)}{P_c}\right]$ (2.11)

where ω is the acentric factor which describes deviation from ideal behavior resulting from differences in molecular structure (Equation 2.11). Simple spherical molecules like argon have a ω value of zero. The acentric factor can be used to show the three-parameter theorem of corresponding states that states all fluids having the same value of ω, when compared at the same T_r and P_r will have the same compressibility (Z) and deviate from idea-gas behavior to the same degree.

In order to use equations of state for mixtures with more than one type of molecule, compositional dependence terms must be included. In the absence of an easy-to-use exact solution to the phase equilibrium for mixtures at all pressures and temperatures, semi-empirical mixing rules can be employed. Such mixing rules have been refined over decades to produce accurate predictions of multicomponent phase behavior. Van Der Waals mixing rules are the most commonly used modification to standard EOS for multicomponent systems. These are typically referred to as one-fluid mixing rules because they assume that that the equation of state for a mixture is the same as for a hypothetical pure fluid whose constants can be averaged as a function of composition.

For mixtures of two components, the conventional van der Waals mixing rules can be used to calculate “a” and “b” for the PR EOS where x_i and x_j are the mole fraction of molecules *i* and *j* as in Equation 2.12.

$$a = \sum_{i=1}^{n}\sum_{j=1}^{n} x_i x_j a_{ij} \qquad b = \sum_{i=1}^{n} x_i b_i \qquad a_{ij} = (a_{ii}a_{jj})^{0.5}(1 - k_{ij}) \tag{2.12}$$

where the sums extend over all components and a_{ii} and b_i indicate the pure component values for component *i,* and k_{ij} is the binary interaction parameter between molecules. Note that for simple mixtures of like molecules, e.g. alkanes, the interaction parameter can be assumed to be zero. For non-ideal mixtures, mixing rules may be required. Van Der Waals mixing rules are effective for nonpolar and some slightly polar systems. For highly nonideal mixtures, quadratic mixing rules are inadequate.

For mixtures involving CO_2 and an industrial lubricant, the interaction parameter will be non-zero and can change with temperature. Van Der Waals mixing rules have been used with the Peng-Robinson EOS to describe the high-pressure phase behavior of some lubricant compounds in CO_2. The interaction parameters for most common MWF lubricants in CO_2 have yet to be reported.

2.3.2 Solubility in Practice – Supercritical Fluid Extraction

Extraction of food oils was one of the early industrial uses for supercritical carbon dioxide. The mild critical temperature of CO_2 allowed for separation without decomposing the oil (Snyder and King 1994) avoiding the need to use organic solvents, with potentially toxic properties effectively dissolves a large number of bio-based fatty organic compounds. These compounds are a mixture of triglycerides, diglycerides, monoglycerides, free fatty acids and glycerin molecules and some minor components such as gums, flavonoids, and other volatiles, which are responsible for the flavor and smell of different oils (Stoldt et al. 1996).

As the use of supercritical fluid extraction of natural oils has grown, so too have the studies published investigating the solubility of plant lipids in CO_2. Some of these studies have looked at pure triglyceride mixtures or mixtures of fatty acids. For example, Bharath found that the solubility of triglyceride mixtures in CO_2 decreases with total carbon number in the compound (Bharath et al. 1993). When studying mixtures of natural lipids in CO_2 researchers have assumed the bulk properties of the primary fatty acid in the system to simplify modeling efforts. Reverchon modeled soybean oil as a pure component because it consisted of more than 80% linoleic acid esters (Reverchon and Sesti Osseo 1994). Using this approach, his group found that the solubility of soybean oil in $scCO_2$ is influenced more by pressure than by temperature.

Less work has focused on mixtures of mineral oils in CO_2. The large distribution of molecules in refined mineral oil makes them less suitable for experimental or modeling efforts as the data cannot be easily generalized in terms of oil properties. The most significant body of work focused on $scCO_2$ and petroleum processes to date involves the treatment of the coal shale stands, but this is of limited applicability as it deals primarily with unrefined petroleum (Greibrokk et al. 1992).

2.3.3 Lubricant Solutions in Supercritical Fluids

The solubility of lubricating compounds in CO_2 has been investigated in limited cases for two applications: industrial degreasing and refrigeration cooling cycles. Degreasing has traditionally been carried out using organic solvents but in the early 1990's CO_2 was seen as a promising alternative for cleaning manufactured parts. The initial research focused primarily on vessel design and optimization of mass transfer for maximum grease removal rather than lubricant solubility characteristics.

The phase behavior and viscosity of several synthetic lubricants have been investigated for the cooling circuits of automobiles. CO_2 has been proposed as an alternative refrigerant to chlorofluorocarbons and its hydro-fluorocarbon substitutes that have high global warming potential (Liu et al. 2005). In automobile air conditioning systems, the refrigerant and the oils that lubricate the shaft and bearings in the compressor must be mixed. Hauk and Weider looked at the solubility of three synthetic lubricants: polyolester (POE), polyalkylene glycol (PAG), and polyalphaolefin (PAO) (Hauk and Weidner 2000). Of these, PAG and PAO are also potential lubricants for MWF applications as previously mentioned. More importantly, the vapor-liquid equilibrium and importance of temperature in affecting solubility are generally useful for predicting how other lubricants are going to behave in high-pressure CO_2.

Figure 2.8 presents a phase diagram of the solubility pressure for the mixture of PAG and CO_2 over the full range of compositions from (Yokozeki 2007). The data points represent measured values and the lines represent model approximations. Above each of the curves where data is plotted, the mixture exists as a single-vapor phase homogenous solution. Each curve represents a constant temperature or isotherm. The plot shows how solubility pressure increases with temperature. As temperature is increased, the mixture must be pressurized ever higher to produce a stable solution.

The data and modeling estimates on the left hand side of Figure 2.8 represent the data for the liquid phase. This liquid phase exists when more PAG is present than CO_2. As pressure is raised, larger amounts of CO_2 will dissolve in the PAG until we exceed the solubility limit for CO_2 in PAG at around 40% w/w at 278 K. For intermediate compositions there exists a miscibility gap where a completely dissolved lubricant and CO_2 mixture is not possible under the pressure conditions typically used in a laboratory. Here a Vapor-Liquid-Liquid equilibrium (VLLE) line appears representing the pressure above which liquid CO_2 will form when the conditions are subcritical. Note that no VLLE, exists for supercritical conditions. For the data recorded at 373.15 K and 313.15 K (both above the 304.15 K critical temperature) no VLLE line is present.

On the right hand of the plot is the data and model results for the vapor phase CO_2 capacity to solubilize PAG. The steep slope suggests that CO_2 cannot dissolve PAG as well as PAG can dissolved CO_2. This is reasonable since CO_2 is a fluid and does not have the same molecular density of a liquid.

The phase behavior of multi-component mixtures in CO_2 can become complex with multiple phases possible and each component existing in each component. Understanding this behavior is important for a number of applications. For chemical reaction and synthesis it is important to know in which phase the reactants and products exist. From a design perspective, understanding such behavior is essential in order to know whether changes in pressure or temperature will result in the formation or separation of distinct phases. For delivery of CO_2-based MWFs, describing, controlling and taking advantage of this high-pressure behavior will be an important step toward designing effective CO_2-based MWFs.

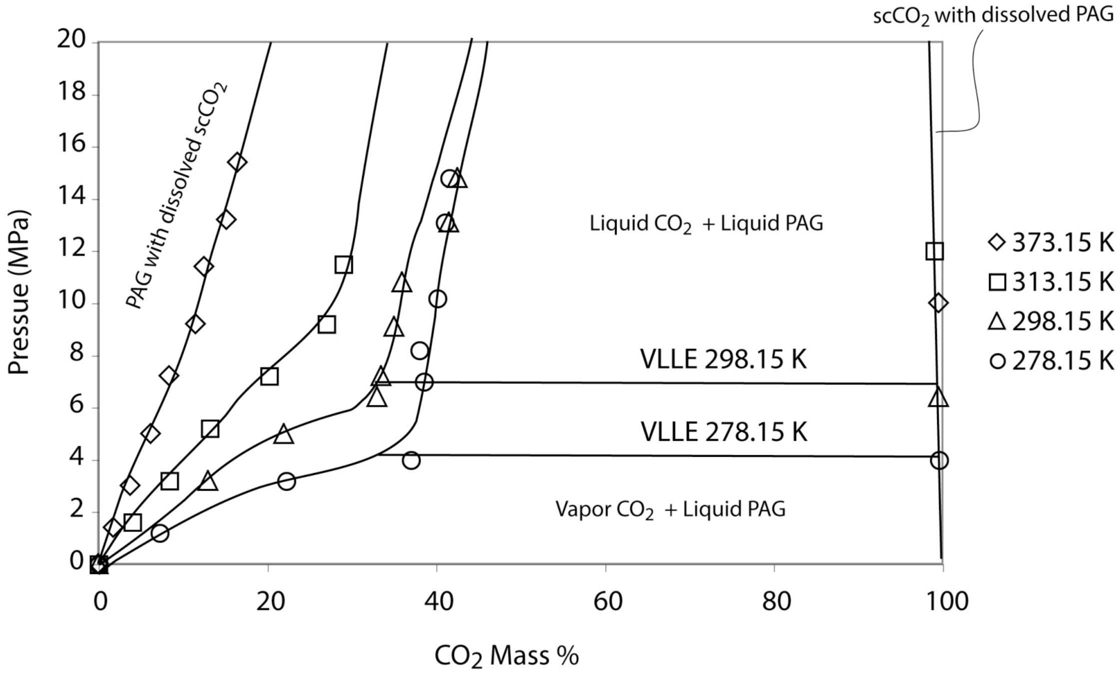


Figure 2.8: Pressure composition diagram for PAG-CO_2 as a function of CO_2 mass percent in mixture. Adapted from (Yokozeki 2007)

2.3.4 Rapid Expansion of Supercritical Solutions

Conventional surface coating processes are mostly based on the principle of spray atomization (Hoy and Donohue 1990). Atomization occurs when a fluid passes through a nozzle at high speed. Shear forces act on the fluid as it moves at high velocity through still air causing the fluid to break down into liquid filaments and ultimately droplets. The viscosity of the fluid must be low enough to achieve adequately high flow rates for spray atomization and so solvents are typically added to lower the fluid viscosity. Volatile organic compounds (VOCs) have traditionally been added for this purpose. In an effort to reduce the emissions of VOCs from their spray coating applications, Union Carbide developed the UNICARB process around 1989 for spraying polymer paint coatings (Schrantz 1989). In the UNICARB process, atomization occurs at the nozzle outlet rather than downstream as in conventional spray processes. In this case, atomization is driven by the expansive forces created when the high-pressure gases shoot out of the nozzle. The

UNICARB process also produces a wider angle and parabolic shaped spray profile compared to conventional spray processes. The particle size of the droplets is uniform throughout the cross section of the spray profile. Traditional spray processes produce smaller particle size toward the outside of the spray because of the higher shear forces present there. The Neilson group found that the fan shaped spray could be made smaller or larger depending on the geometry of the nozzle (Nielsen et al. 1991). The UNICARB process lowered the amount of VOCs released and produced a more uniform particle size distribution resulting in a more uniform and aesthetically pleasing coating finish.

A third spray process has been developed using $scCO_2$ called Rapid Expansion of Supercritical Solutions (RESS) (Debenedetti et al. 1993). The RESS process works by expanding a solute/CO_2 mixture at high pressure through a nozzle to lower pressure. In RESS expansion forces do not cause the solute atomization, rather the solubility drop through the nozzle causes the solute molecules to aggregate into particles. Because the solubility characteristics of CO_2 can be changed easily, even a slight pressure drop can cause a solute to precipitate. This decompression process through a capillary or pinhole nozzle provokes a chemical separation that quickly produces monodisperse particles (Franklin et al. 2001). The time required for phase separation is typically on the order of 10^{-5}-10^{-6} s (Tom and Debenedetti 1991). The spray profile looks more like a traditional spray process although the solute droplets form very close to the nozzle outlet as in the UNICARB process. The RESS process has been employed for many coating processes that require precise particle sizes or delicate treatment of solutes. The cooling potential of CO_2 sprays has also been considered in the context of particle formation.

The thermodynamics and processes that cause a solute to precipitate during the RESS process have been investigated extensively. As a result of the initial temperature and pressure drop through the nozzle, the solution crosses the cloud point (or equilibrium) curve and as solute begins to precipitate out of solution. As the temperature and pressure continue to fall, the solution can remain in the metastable region or split into two phases. After the solution has passed out of the nozzle, the solute is generally no longer soluble in the CO_2 and has all become frozen particles of solute. Figure 2.9 presents a schematic of the three spray processes as well as phase diagrams for the UNICARB and RESS process (adapted from (DeSimone and Tumas 2003)).

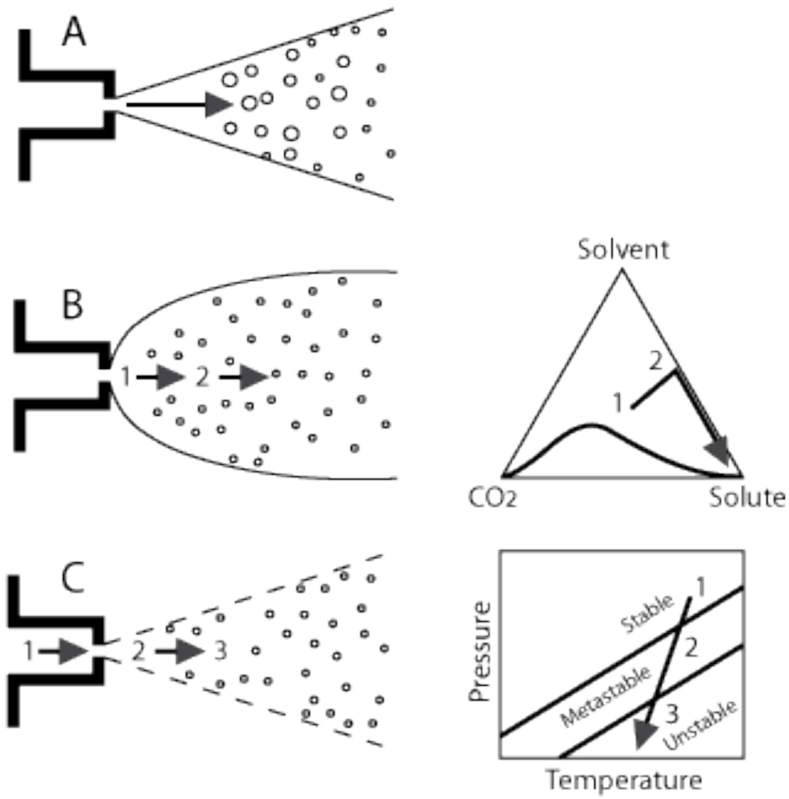


Figure 2.9: Schematic representation of the spray atomization of solutions (A) conventional spray process, (B) UNICARB process, (C) RESS process. Adapted from (DeSimone and Tumas 2003)

The Carbonell group (Chernyak et al. 2001) summarizes many of the nozzle geometry characteristics, concentration, as well as the temperature and pressure considerations important for designing a CO_2 spray process. He suggests that of all the design variables, nozzle geometry is the most important. For capillary and orifice nozzles, the precipitate morphology depends more on the length-to-diameter ratio of the nozzle than on its diameter. Low L/D ratios, also known as pinhole orifices, produce spherical submicron precipitate shapes. Large L/D, as in a capillary nozzles, produce fibers or elongated precipitates. The solute/ CO_2 concentration can also have an effect on the particle morphology. Liu found that a decrease in solute concentration brought a decrease in particle size (Liu and Nagahama 1997). In the RESS process the temperature of the nozzle can have a significant effect in determining when the solute precipitates out. If the temperature of the nozzle is higher than the temperature in the pressure vessel then the solution will split prior to entering the nozzle and the particle size will be larger. The opposite occurs if the temperature of the nozzle is lower than the bulk fluid (Chernyak et al. 2001).

Small changes in the pre-expansion pressure do not greatly affect the precipitation characteristics. Larger pressure changes have been found to affect particle morphology but no consistent trends have been found among different studies (DeSimone and Tumas 2003).

The delivery of solutes in sprays of CO_2 is a fundamentally different spray process than conventional sprays based on atomization and this could have important implications for MWF applications. The delivery of lubricant frozen lubricant particles could influence both lubricating and cooling potential of MWF sprays based on RESS. The discussion on system operating parameters above is considered in terms of spray cooling potential in the next section.

2.3.5 Spray Cooling

Sprays of CO_2 have not been studied extensively in the context of heat removal. Efforts to model the RESS process have often included temperature because this can have an important impact in the particle formation process, though the explicit heat removal capacity of sprays was not explored (Henczka et al. 2006). Work conducted by Reverchon et al used hydrodynamic models to predict the temperature drop that occurs in CO_2 sprays (Reverchon and Sesti Osseo 1994). This work concluded that almost all of the temperature drop occurring during the RESS process happens in the post expansion space, not in the nozzle. The study also found a reverse proportionality between the temperature drop and the CO_2 temperature in the vessel. Figure 2.10 shows one of the temperature profiles for a CO_2 spray modeled in the Reverchon work. Later work has confirmed the Reverchon results indicating that most of the temperature drop occurs several mm from the exit of the nozzle (Franklin et al. 2001).

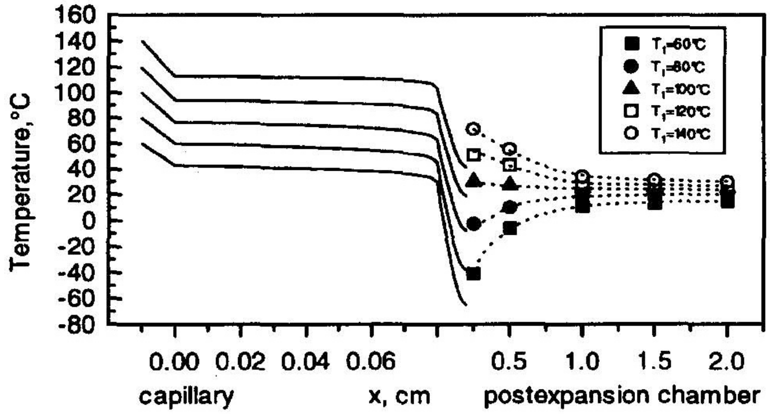


Figure 2.10: Calculated and measured temperatures along the expansion path for a spray of CO_2 as a function of pre-expansion temperature and distance through the nozzle Adapted from (Reverchon and Sesti Osseo 1994).

Measurement of the heat removal potential of sprays has been attempted in other systems. In these systems, the heat removal capacity of sprays has been shown to be comparable to cooling provided by impinging jets or immersion in a pool of a heat transfer fluid (Sehmbey et al. 1994). Most of this work, has been performed using water or fluorinated heat transfer fluids, compounds that are liquids at standard temperature and pressure (Aguilar et al. 2001). Much of the interest has been in overcoming the critical heat flux (CHF) problems associated with liquid heat removal fluids. When these fluids boil on a hot surface, they form vapors with significantly lower heat transfer coefficients that can impede heat removal. The design work has focused on particle size, particle velocity, particle flux, and identification of a spray efficiency metric that accounts for the limitations of phase transitions in spray cooling applications (Ruey-Hung et al. 2002). Few papers have focused on the heat removal potential of impinging jets of gases because of their inherently lower molecular density.

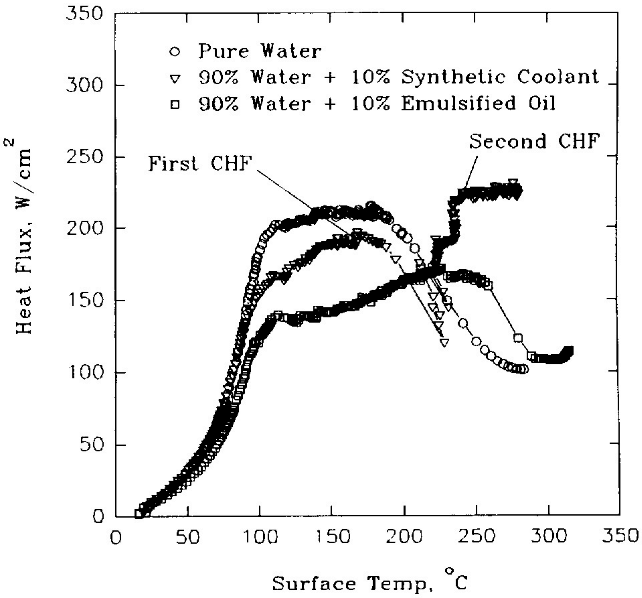


Figure 2.11: Heat removal potential of several MWF compared to pure water as a function of surface temperature.

Um et al. studied the heat removal potential of sprays of several water based MWFs (Um et al. 1996). Using a specially designed probe, sprays of synthetic and soluble oil MWFs were compared to straight water. They found that CHF will produce an appreciable plateau in the heat removal of MWF sprays as the temperature of the metal probe is increased (Figure 2.11) demonstrating the diminishing returns of water based coolants. They also demonstrated the zero-sum nature of MWFs by showing that cooling potential is decreased as oil is added to the mixture. Their results that water > synthetic > semi-synthetic is consistent with later results (Bittorf et al. 2006).

Inasmuch as the cooling potential of water-based MWF has been studied independently of CO_2 spray operations, no work has been conducted to understand how the heat removal potential of CO_2 sprays compare to sprays of water. Major questions exist about the interaction between cooling potential and both solute concentration and CO_2 spray system parameters. Addressing these questions will be important to full capitalize on the spray characteristics of CO_2 sprays in MWF applications.

2.4 Life Cycle Analysis of MWFs

Life cycle assessment (LCA) is a systematic methodology for quantifying the materials and energy flows required by a process or product over its entire life. LCA results can provide objective input into the design process that can be weighed subjectively against other design specifications. This is particularly important when trying to reduce the effective environmental footprint of a process or product. In the case of MWF, there has been a significant interest in moving toward more environmentally friendly MWFs but few efforts have been made to evaluate all the impacts of MWF over the life cycle. Most efforts to reduce the environmental impact of MWF have involved the substitution of petroleum oils with vegetable oil.

A LCA of two MWF systems was conducted by Zimmerman where the impacts of a petroleum-based aqueous fluid and a rapeseed-based aqueous fluid were compared (Zimmerman 2003). In that study environmental burden trade-offs between the petroleum and bio-based fluids were found. On the one hand, the bio-based fluids had a lower global warming potential (GWP) than petroleum-based MWFs. However, bio-based MWFs required pesticides and fertilizers for crop production that caused the bio-based MWFs to have a higher ozone depleting potential, (ODP) and greater consumption of energy. Some of the key assumptions in that study were that 1) the tool wear, failure, and machining energy rates for both MWF systems were identical and 2) additives impacts could be ignored because they comprised a small mass fraction of the overall fluid and would have similar impacts in different fluids. The study concluded that although trade-offs exist in switching from petroleum to vegetable oils, operational choices made by facility managers would impact most which fluid had the greatest overall life cycle impacts. For instance, the fluid replacement rate would have a significant impact on the relative overall life cycle impacts. Also, the in-use, pumping practices of the plant and the end-of-life treatment processes would have a significant impact on the energy and water emissions over the life cycle.

As with MWF, relatively few LCAs have been performed on technologies that use CO_2 as a feedstock. Blowers and Titus performed a life cycle inventory comparing semiconductor chip manufacturing using supercritical CO_2 instead of ultra pure water as a rinsing solvent (Blowers and Titus 2004). The study looked at material inputs of pure CO_2, co-solvents added to the CO_2, and energy required to compress, heat, and cool the CO_2. Using chemical modeling, the authors estimated the material and energy requirements for the start-up, purging, cleaning/stripping, and flushing steps of the chip stripping process. The authors reported that the energy needs for the CO_2 system were much lower than the ultra pure water system. The data for the ultra pure water production, however, were not determined by the authors directly and merely reported from a reference. The authors discussed issues such as the transportation of the CO_2 vs. ultra pure water in a qualitative fashion and acknowledged that their study was limited in scope. The paper concluded that a more in depth LCA was necessary for scCO_2 applications in industrial settings.

Overcash et al. (Overcash et al. 2007) performed a detailed assessment of industrial carbon dioxide production. The purpose of their study was to evaluate the principal processes in which CO_2 is commercially produced as a byproduct. The study identified three primary sources of industrial liquid carbon dioxide in the US: a byproduct from ammonia synthesis, a byproduct from the hydrogenation of hydrocarbons in petroleum refining, and from natural gas wells. The life cycle energy consumption and emissions from each of these processes indicated that the energy and emissions from each of these processes is dramatically different with the ammonia synthesis having the highest impact and natural gas wells having the lowest. The study brought up important questions about allocation since in all cases CO_2 is a byproduct. CO_2 can only be economically recovered in certain processes but these processes have different life cycle emissions. Further, since CO_2 is a commodity chemical that is bought and sold in large volumes, averaging the life cycle impacts of these flows many not provide an acceptable approximation for most commercially available CO_2.

Before decisions regarding CO_2-based MWF can be made on a large scale, the life cycle implications should be compared to those of conventional fluids. The existing research looking at a switch to bio-based MWF and CO_2 markets provide some of the background necessary for a more detailed life cycle assessment.

2.5 Summary

The environmental, public health, economic, and performance limitations of aqueous MWFs have been well documented. MWF are an expensive part of metals manufacturing and advances in MWF formulation and delivery approaches have the potential to reduce some of these impacts. But the industry has been slow to adopt some of these technologies. Work in minimum quantity lubrication has been met with general acceptance in manufacturing though technical challenges still exist, high among them is adequate heat removal in machining without water.

CO_2 has been shown to be a successful alternative solvent to water in a number of industrial applications. Its solubility potential can be easily controlled by varying the temperature and pressure. Equations of state models have been refined to accurately predict high pressure phase behavior. A number of studies have explored the high-pressure phase behavior of CO_2 and the spray conditions that are created if these solutions are delivered out of a nozzle. Spray cooling processes have been described for a number of heat transfer fluids including conventional MWFs and the in several models and the limitations of conventional MWFs with regard to heat transfer have also been reported.

A life cycle of the CO_2 production process shows that CO_2 is commercially obtained as a waste product of numerous industrial operations and so its environmental costs are relatively low. Life cycle assessments of vegetable based alternatives to conventional MWFs suggest that a number of tradeoffs are created when switching from petroleum to bio-based formulations.

Based on this analysis, it appears clear that CO_2 is a viable carrier for MWF formulations that could be used to reduce many of the occupational and environmental health impacts of water-based fluids. Before functional CO_2-based MWFs can be developed commercially, a number of research questions must be explored to compliment the existing understanding of MWF function and delivery of MWF in CO_2. These areas are:

1 - Sprays of $scCO_2$ and lubricant have the potential to more effectively penetrate the cutting surfaces in machining and reduce cutting forces. However, the best way to de-

liver these sprays and the differences in lubricant delivery mechanisms between conventional and high-pressure gas MWF delivery needs to be explored.

2 - A significant drawback to air-based minimum quantity systems is their inadequate cooling potential. The cooling gains that are possible when using higher-pressure CO_2 delivery remain to be demonstrated.

3 - Tool wear is well known to be temperature dependent but no existing work has systematically explored the connection between tool temperature and MWF in the application of gas-based MWFs. The tool life effects associated with a switch to high pressure gas-based MWF should be explored.

4 - A number of common MWF bulk lubricants are used by the industry and the solubility of only two of these (PAG and PAO) in CO_2 is well documented in the literature. A comparative study of lubricant solubility and a detailed evaluation of soybean oil, TMP Ester, or lubricant mineral oil in $scCO_2$ should be conducted.

5 - A life cycle evaluation of MWF and CO_2-based technologies is needed to determine whether a switch to CO_2-based MWF would be a clear environmental benefit. A full life cycle assessment should be performed to understand the overall impact reductions associated with a move away from water-based MWFs and any associated gains that could come from the use of CO_2.

The development of CO_2 based MWFs is a logical 'next-step' that will capitalize on existing knowledge of CO_2 and has the potential to significantly improve on existing MWF systems. This work will fill the knowledge gaps listed above by drawing from and building upon basic science research in surface chemistry, lubrication, and phase behavior to develop a body of applied knowledge that can be used to implement the new MWF technology.

CHAPTER 3

Methods

This chapter describes the methods used to achieve the objectives of this research. The experimental approach is based on literature reports of existing methods along with novel experimental setups. To deliver CO_2-based MWF with precision control of pressure, temperature, and nozzle geometry, a special bench scale delivery device was designed and built. The device was later modified and expanded into a larger portable version that was used to deliver most of the CO_2-based MWF used in this work. These devices are discussed in section 3.1. In Section 3.2, the method to reproducibly record the machining energy required in thread cutting is described. The development of a novel temperature flux probe is discussed in Section 3.3. Along with an experimental setup that could be used to carefully control spray nozzle offset and distance, the probe was used to evaluate the most important system parameters for the delivery of cooling using CO_2-based MWFs. Finally, a single point turning operation was used to evaluate tool life under a range of MWF and cutting conditions. This method, described in Section 3.4, provides a detailed understanding of how CO_2 sprays affects tool temperature and life in a large-scale machining operation.

3.1 Delivery of CO_2-based MWF

The major focus of this research is to develop a CO_2-based MWF. At the outset of this work, no examples existed in the literature, though work in related areas (e.g. solubility of oils, spray coating using CO_2) did provide guidance in the development of the CO_2 MWF spray process undertaken herein. The past work of the DeSimone group provided an understanding of how high pressure vessels and pumps operate (DeSimone 2002). The work of the Carbonell group provided experimental schematics needed to understand the development of CO_2-based spray systems (Chernyak et al. 2001). The work of Debandetti applying the RESS process was highly useful for designing and testing several nozzle geometries (Debenedetti et al. 1993).

The preliminary system was a bench scale prototype suitable for small-scale trials. The system consisted of a pressure booster, a six-way valve, a high-pressure vessel, a solenoid valve, and a computer with a data acquisition card (Figure 3.1 A. Tank of Food-Grade Carbon Dioxide; B. Check Valve; C. Pressure Booster; D. Pressure Gauge; E. Six-Way Valve; F. Oil Inlet; G. Fixed-Volume Coil; H. High-Pressure Vessel; I. Heating Element; J. Thermocouple; K. Pressure Transducer; L. Computer; M. Solenoid Valve; N. Nozzle; O. Tapping Torque Machine Tool; P. Workpiece; V1-V3. Pin Valves). The pressure booster (HIP, Erie PA) was used to raise the pressure of the CO_2 from tank pressure (~45 bar) to supercritical pressures (>73 bar). Soybean oil was then added via the six-way valve (Valco, Houston TX) and the mixture was allowed to mix in the pressure vessel using a magnetic stir bar. The vessel was also heated to supercritical temperatures (>31^{o}C) using a cartridge heater in the vessel body. The high-pressure vessel was connected to a solenoid valve that was computer controlled. The outlet from the solenoid fed to a 0.03” ID nozzle that delivered $scCO_2$-based MWF to the cutting zone.

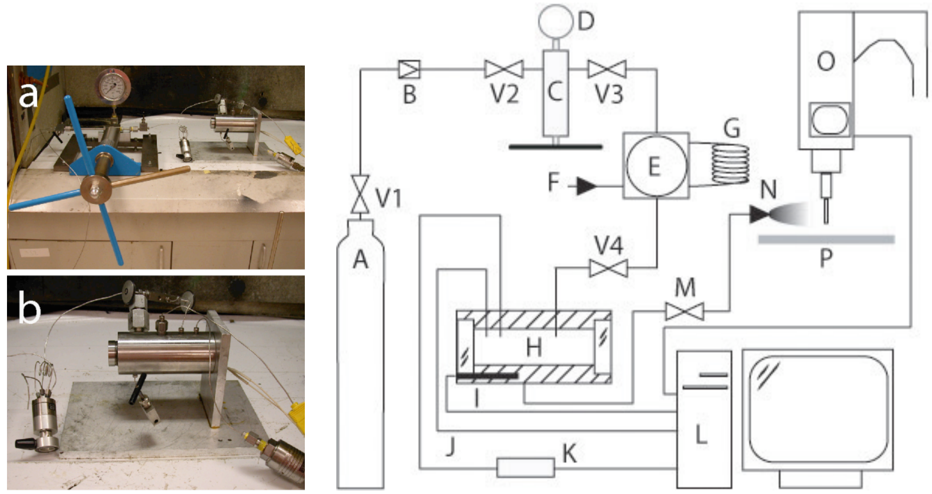


Figure 3.1: $scCO_2$-based MWF testbed. (Left) a. $scCO_2$-MWF system showing pressure booster and high-pressure vessel; b. close-up of high-pressure vessel; (Right)

A second system was then built that was larger, automated, and portable. The system was assembled on a cart and is depicted in Figure 3.2 (A. cylinder of food-grade CO_2, B. cooling unit C. pump, D. one-way valve, E. high pressure vessel, F. heating element, G. soybean oil, H. pressure transducer, I. thermocouple, J. computer, K. data acquisition device, L. nozzle, M. lathe, V1 and V2 are valves). Food grade CO_2 (Cryogenic Gases, Detroit, MI) was pre-cooled using a constant temperature chilled bath (Julabo, Seelbach, Germany) and compressed from ~47 bar (out of the tank) to supercritical pressures >72.8 bar using a Thar Technology (Pittsburgh, PA) P50 Pump. The high pressure gas was transferred to a 1 L high-pressure vessel (High Pressure Equipment, Erie PA). The 1 L vessel contained soybean oil (Cargill, Minneapolis, MN) and the inlet CO_2 was bubbled up through the liquid phase oil. The temperature in the vessel was controlled by a band heater. The outlet from the vessel removes fluid phase CO_2 and oil and delivers it through low inner diameter tubing serving as a nozzle to direct the spray to the machining operation. Either a hand pin valve or a solenoid valve could be used to control the flow of the spray out of the nozzle. The system was cart mounted with the exception of the CO_2 tank that was mounted near the machine tool. A computer was used to monitor the operating conditions in the high-pressure vessel using LabView software (National Instruments, Austin, TX).

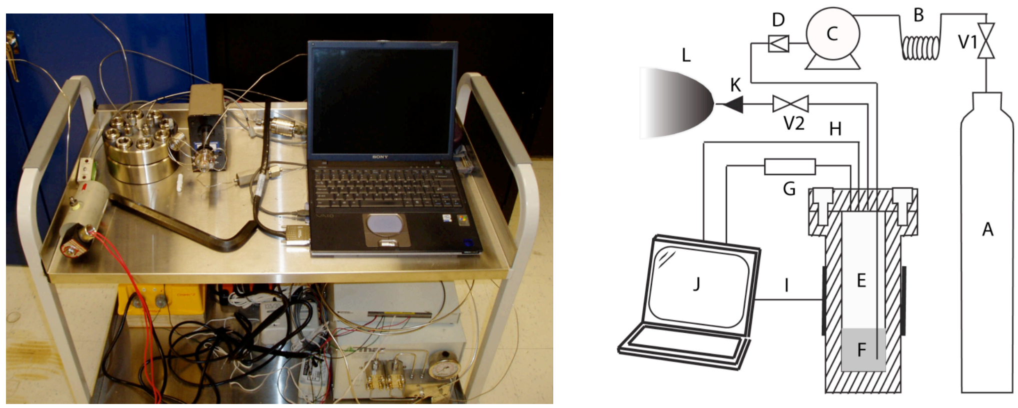


Figure 3.2: Second prototype of $scCO_2$-MWF system. (Left) Image of cart-based system that can be wheeled up next to machine tools for experimentation. (Right) Schematic of $scCO_2$-MWF delivery system.

3.2 Machining Forces in Tapping

The performance of MWFs has often been measured using the tapping process. In tapping, threads are cut in predrilled and prereamed holes in the presence of MWFs. The power required to thread a hole is recorded and compared to a calibration curve in a computer controller to produce an estimated force reading. This force is sensitive to MWF composition and over numerous repetitions, can provide valuable data regarding differences in MWF performance. Tapping is a relatively slow process and so the effects of lubricants in a MWF are much more important in tapping than the effects of cooling or chip removal.

The method used in this work was a variation on ASTM D 5619, the Standard for Comparing Metal Removal Fluids Using the Tapping Torque Test Machine (ANSI 2000), with modification made to account for the use of a MWF evaluation testbed that permits multiple cutting tests on a single workpiece (Zimmerman et al. 2003b). Tests were run on a MicroTap Mega G8 (Rochester Hills, MI) machine tool using uncoated high speed steel taps with 60o pitch and three straight flutes (Emuge, Northborough, MA). The tests were performed at a cutting speed of 1000 RPM on a 1018 cold rolled steel workpiece with 240 M6-sized holes (Maras Tool, Schaumburg, IL). This combination of tool geometry and machining speed were found in (Zimmerman et al. 2003b) to give the greatest resolution between MWFs when other size holes, coatings, and machining speeds were considered. The workpiece and tools were all used from the same lot for all tests to minimize variations caused by material differences from one lot to the next.

MWF performance is indicated as percentage efficiency in the tapping operation. A commercially available reference fluid (C225, Chrysan Industries, Livonia, MI) was used as a reference fluid serving as an internal control for all MWF experiments. Percent efficiency was calculated by dividing the average tapping torque observed for each experimental MWF by the average tapping torque observed for the reference fluid under the same experimental conditions. This relative measure of performance was selected to minimize the impact that inconsistencies in the work place material and tool wear can have on the results. Tapping torque efficiency above 100% indicates improved performance in the tapping torque test relative to the reference fluid.

3.3 Spray Cooling Potential

An experimental test bed was developed to evaluate the cooling potential of CO_2 sprays with five adjustable independent process parameters: pressure vessel temperature, pressure vessel pressure, nozzle geometry, distance between probe and nozzle, and offset between probe and nozzle (Figure 3.3a). The parameters were selected based on literature methods for spray analysis. The vessel temperature and pressure were expected to affect the expansion properties of CO_2. Nozzle geometry restricts the expanding gas and also affects fluid velocity as well as solute precipitation processes. Nozzle geometry was controlled by varying the length to diameter ratio (L/D ratio) of the nozzles. High pressure tubing with an inner diameter of 0.152 mm was cut to various lengths to create the nozzles. The distance and offset allows optimization of the spatial positioning of the nozzle relative to the cutting zone and to investigate how cooling and particle formation vary in the spray field.

The heat removal rate of CO_2 sprays was determined using a specially designed probe (Figure 3.3b). The probe consists of a 12.5 mm diameter 99.9% purity copper rod (McMaster-Carr) with one 20 mm long side cut down to 3 mm diameter (Figure 3.3c). The 12.5 mm side was kept at a constant temperature using a cartridge heater (Tempco, Wood Dale, IL). The 3 mm side was fitted with three K-type thermocouples (Omega, Stamford, CT) and encased in high temperature thermal shock epoxy (Epoxies, Etc.

Cranston, RI). The exposed tip of the copper rod was placed in the flow field of the CO_2 (Figure 2d) spray and the temperature drop across the thermocouples was recorded using a data acquisition device (National Instruments, Austin, TX). The heat flux was calculated using Equation 3.1:

$$q = h \cdot (T_1 - T_2) = k \cdot \frac{\Delta T}{\Delta x} \qquad (3.1)$$

where q is the heat flux (W/m^2), k is the thermal conductivity of the copper (385 W/m^{o}C), T_1 is the temperature of the constant temperature body (K), T_2 is the temperature of the copper at the probe tip (K), ΔT is the change of temperature through the copper rod (K), and Δx is the length of the copper rod (m). Changes in q reflect changes in the velocity, density, viscosity, specific heat, and thermal conductivity of the fluid at the tip of the probe.

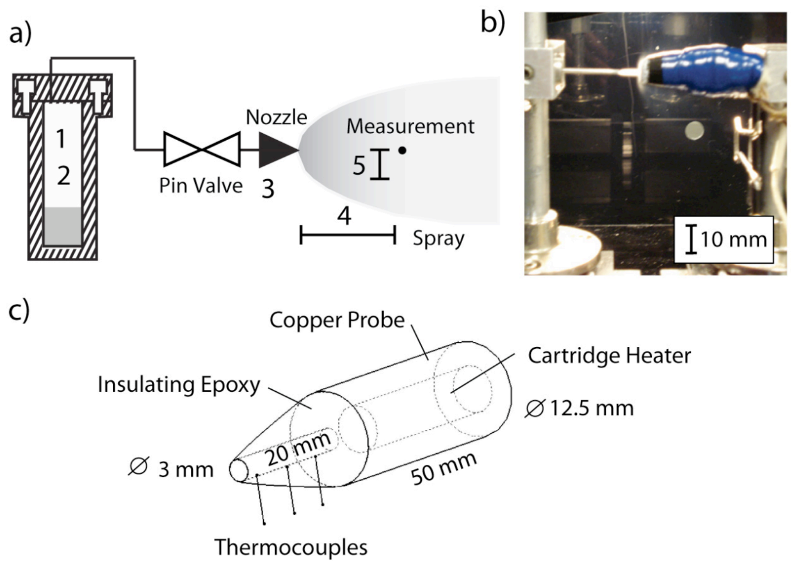


Figure 3.3: a) Experimental setup of the spray cooling capacity experiments. Numbers correspond to the process variables that were varied to find optimal cooling conditions: 1) CO_2 vessel temperature, 2) CO_2 vessel pressure, 3) nozzle geometry, 4) distance between nozzle and probe, 5) offset between nozzle and probe. b) photograph of heat flux setup with nozzle and probe. c) rendering of heat flux probe.

The probe was used over a range of temperatures. In machining processes, the surface temperature of the cutting edge is high (500 - 1000 ^{o}C) but it falls off rapidly away from the cutting zone as heat is dissipated into the workpiece or tool. In single-point continuous cutting operations the cutting edge can be assumed to generate heat at a relatively constant rate. The probe was designed to produce a constant heat flux and rated to 500 ^{o}C.

The surface area of the probe (7.1 mm^2) was small enough to be completely covered by the CO_2 spray but large enough to ensure that heat transfer from the sides of the copper through the epoxy were much lower than the heat transfer through the horizontal length of the probe. The biot number of the copper in the probe was calculated and found to be much less than 0.1 indicating that the convective heat flow at the surface is dominant over conductive flow through the copper (Holman 1997).

3.4 Tool Life in Orthogonal Cutting

Tool life can be significantly affected by MWFs and so measuring it is an important performance indicator in MWF design. Turning is often used for tool life tests because it is a continuous operation in which the tool is in contact with the workpiece and the geometry of the process is close to orthogonal simplifying modeling efforts. The speed and feed of the process can also be easily adjusted to provide the desired level of wear. A standard for tool life testing using turning can be found in ISO 3685 1993 (ISO 1993).

A Lodge and Shipley 10/25 BC 30 HP CNC lathe was used to perform machining tests. The images of the tool wear were taken using an OPTEM International 100X zoom digital camera. The wear measurements were made using PG1000 v1.0 software. Measurements were made of the wear at its deepest point on the wear land. The wear land is defined as the worn portion of the tool near the cutting edge.

Several types of workpieces and tools were used for the tests. Two hard materials were selected because the difference in tool life observed between MWFs is most dramatic in challenging machining operations. Workpieces of compacted graphite iron (CGI) (12.7 cm tubular) were cut using Kennametal (Latrobe, PA) SPG422 KD100 polycarbonate diamond (PCD) tipped inserts in a CSRPL164D tool holder. Titanium (6Al4V) 15.24 cm round workpieces were supplied by Metal Shorts Incorporated (Seattle, WA). A Kennametal #MCGN R 164D tool holder was used with CNGP432FS Grade K313 inserts.

Experiments were performed in triplicate to ensure the reproducibility of the results and to permit statistically significant comparison between different cutting conditions and the effects of MWF classes. The measurements were made on a workpiece with continually changing diameter so though the time between measurements was kept approximately the same, it varied between tests. For this reason, standard deviations for the recorded data could not be tabulated in a meaningful fashion. Literature reports of wear data almost always show only one experiment or duplicates that can be confusing and difficult to interpret. For this work, regression analysis was performed between the data points and the mean of the regression lines for several points over time was used to provide an average representation of the wear under each set of conditions.

To further account for variation that could arise from the varying cutting times, experiments were randomized so tools would not stay warm in between cuts. By ensuring that all tools reached room temperature and that the cutting times were randomly distributed between the experimental conditions, experimental confounding factors were minimized.

CHAPTER 4

Feasibility of MWF in CO_2

Although machining facilities worldwide are considering moving toward the use of minimum quantities of lubricants delivered in sprays of air, no work has been reported on the use of supercritical carbon dioxide as an alternative gas carrier. In principle, CO_2 should be an effective lubricant carrier that could provide excellent cooling and chip clearing when expanding out of a nozzle. In practice, however, it had not been attempted. This chapter describes early efforts to evaluate and characterize the performance of CO_2-based MWF. Unlike water-based MWFs, CO_2-based fluids require a novel high-pressure delivery device. To meet this need, one was custom-built and its development is described in Section 3.1. Further, a tapping torque test in combination with this custom delivery system was used to evaluate reductions in machining forces when using several benchmark fluids relative to soybean oil in CO_2. Finally, scanning electron microscopy was used to evaluate the surfaces of the metal chips produced in the tapping tests to related the force data as a function of fluid spray conditions to changes in surface roughness and to aide in mechanistic interpretation of the results.

4.1 $scCO_2$-based MWF Testbed Development

Water-based MWFs are chemically complex but relatively simple to store and deliver. MWF can be stored in liquid containers, often barrels or sumps, and delivered to the cutting zone via pumps. By contrast, CO_2-based MWFs are chemically much simpler than water-based alternatives, containing only CO_2 and a lubricant, but require a delivery system that is marginally more complex than conventional water-based delivery system. To address this challenge, an experimental delivery system and testbed was developed that relied on commercially available food-grade CO_2 and lubricant oil to produce and analyze the performance of sprays of $scCO_2$-based MWFs.

$scCO_2$-based MWF mixtures leaving the spray nozzle were composed of approximately 10% soybean oil and 90% CO_2. The initial spray mixture was created by removing fluid from the bottom of the vessel that represented an oil phase saturated with CO_2. Later work focused on the delivery of oils dispersed in the $scCO_2$ by withdrawing fluid from the top of the vessel. For reference several semi-synthetic and straight oil fluids were prepared to benchmark the performance of $scCO_2$-based MWFs (Table 4.1).

The benchmark fluids used to compare with the $scCO_2$-based MWF were based on naphthenic mineral oil (D.A. Stuart, Warrenville, IL) and soybean oil (Cargill, Minneapolis, MN). Soybean oil was selected because it had been shown to have the highest performance in previous tapping tests (Clarens et al. 2004b). The semi-synthetic formulations were based on recommendations provided by a commercial MWF supplier. The MWFs were produced in the desired concentration in deionized water. The oils were stabilized in water using a combination of anionic, nonionic surfactant, and a coupler. It was necessary to use different emulsifier packages for mineral oil and vegetable oils (Zimmerman et al. 2003b). These differences were relatively minor. Food grade CO_2 with a dip tube was provided by Cryogenic Gases (Detroit, MI). All components were used as delivered from the manufacturer and were subject to the same handling and storage conditions.

Table 4.1: MWF Formulations (All percentages are by weight) Listed Surfactants were Tagat V20 Nonionic Surfactant (Degussa-Goldschmidt Chemical Corp., Hopewell, VA), Tomadol 91-6 Nonionic Surfactant (Tomah Corp., Milton, WI), and Dowfax 3B2 Anionic Surfactant (Dow Chemical, Midland, MI).

Component	$scCO_2$	Mineral Oil in Water	Mineral Oil	Soybean Oil in Water	Soybean Oil	Soybean Oil in $scCO_2$
Soybean Oil				0.72%	100%	10%
Mineral Oil		0.72%	100%			
Tomadol 91		1.56%				
Tagat V20				1.38%		
Dowfax 3B2		0.14%		0.21%		
Coupler		0.07%		0.10%		
$scCO_2$	100%					90%
Water		97.50%		97.59%		

The sprays of $scCO_2$- and water-based MWF could be delivered to the cutting zone for evaluation as seen in Figure 4.1. It was found that this method of applying the $scCO_2$ MWF at a rate of 2 grams of CO_2 and 0.2 grams of oil was as facile and significantly cleaner than applying water based fluids at a rate of 5 mL/s at a standard pres-sure used in industry (1.4 bar).

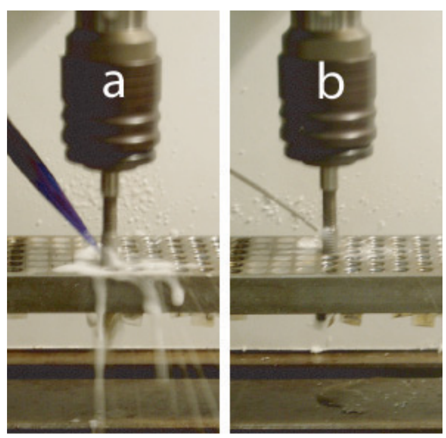


Figure 4.1: Images of tapping experiments using spray application of MWF micro-emulsion (a) and rapidly expanding supercritical carbon dioxide solution (b)

4.2 Performance Evaluation Using the Tapping Torque Test

Figure 4.2 provides the average tapping torque efficiency and 95% confidence interval values calculated for the >30 independent and randomized trials performed for each MWF.

The data reveal that soybean oil is a better lubricant than mineral oil in the tapping process, either in straight oil or emulsified form, as previously observed in (Clarens et al. 2004b). In addition, the data support the well-documented and intuitive fact that straight oils perform better in tapping processes than semi-synthetic emulsions. It is noteworthy that $scCO_2$ (without oil) had a statistically indistinguishable performance relative to the mineral oil microemulsion (0.75% w/w oil-in-water). The naphthenic mineral oil microemulsion is similar to base semi-synthetic MWFs used widely in industry.

Most importantly, the data reveal a pronounced synergy between soybean oil and CO_2. In over ten years of testing MWF formulation using the tapping torque test, a performance of 125% relative to the reference fluid has never before been observed. It was observed that the soybean oil + $scCO_2$ system performs on average approximately 10% better than straight soybean oil, 20% better than the soybean oil semi-synthetic emulsion, and 30% better than straight $scCO_2$. This unprecedented result confirms that the combination of soybean oil and $scCO_2$ performs better than either can alone. The performance of straight soybean oil can be improved by using $scCO_2$ for enhanced delivery of chilled, high velocity, oil particles. Using $scCO_2$ also delivers more efficient quantities of oil to the cutting zone, representing less than 20% the amount of oil delivered during a typical tapping operation.

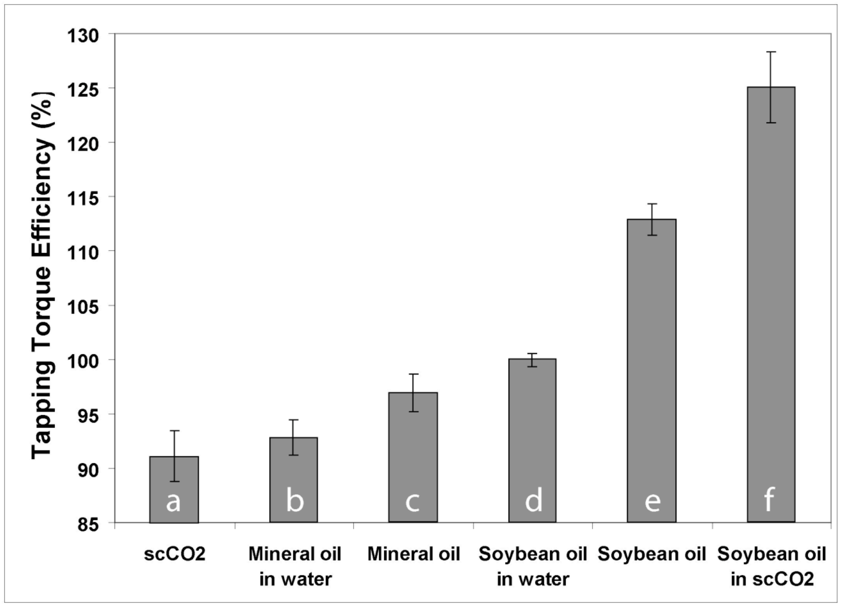


Figure 4.2: Tapping torque efficiency for straight oil, water-, and $scCO_2$-based MWFs. Letters correspond to electron microscopy images in Figure 4.3.

To corroborate these results from the tapping torque test and to provide more direct evidence of enhanced lubrication properties offered by MWFs based on soybean oil dissolved in $scCO_2$, scanning electron microscopy images of the back surfaces of chips produced during the tapping process were analyzed. Figure 4.3 provides representative images of the chip surfaces produced by the different MWF systems, with each image corresponding to the tapping torque data provided in Figure 4.2. The electron microscopy images provided in Figure 4.3. show that there is significantly more metal-to-metal contact in the tapping experiments characterized by lower values of tapping torque efficiency (e.g. mineral oil microemulsions) compared to experiments characterized by higher values of tapping torque efficiency (e.g. mixtures of $scCO_2$ and soybean oil).

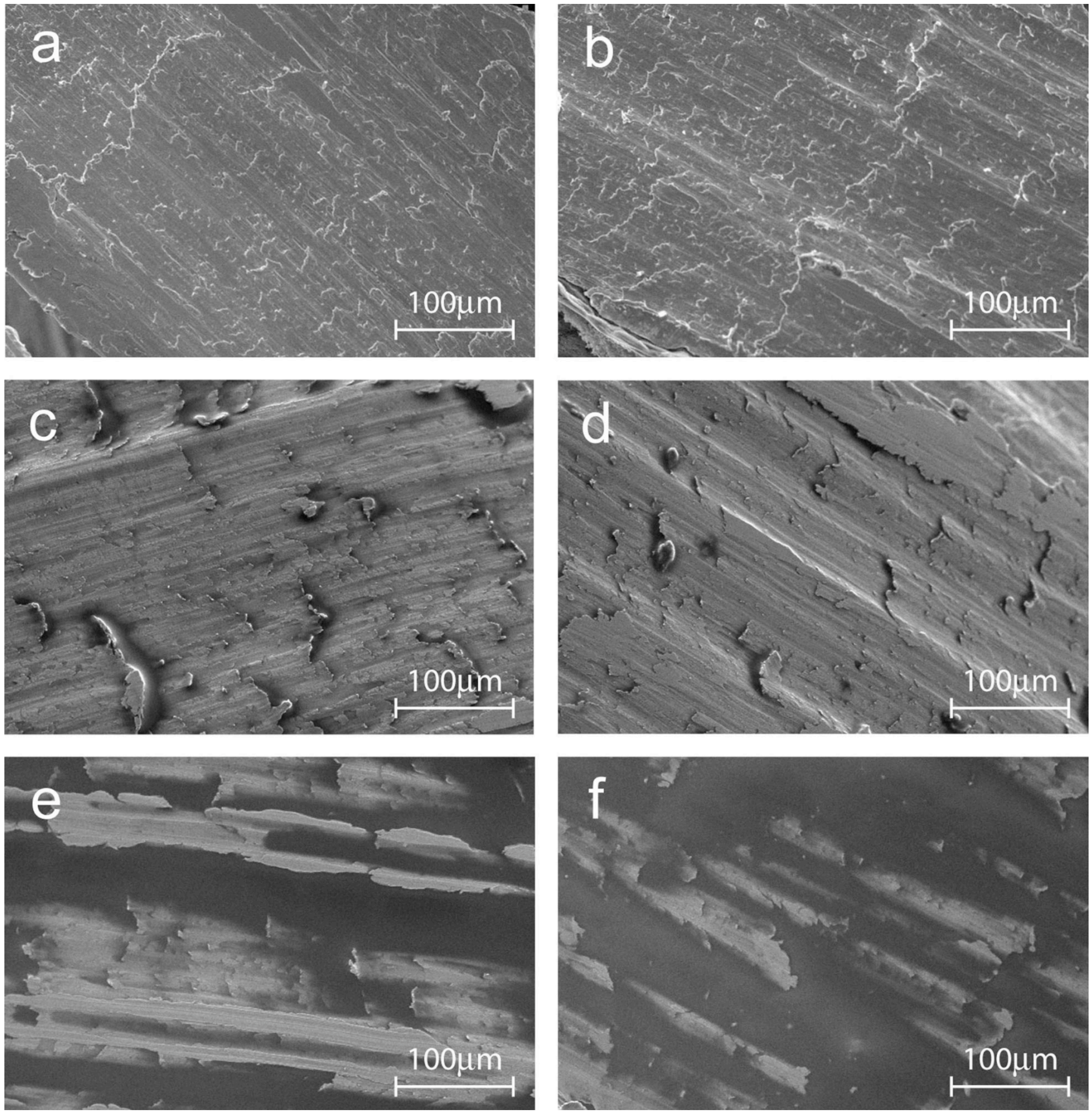


Figure 4.3: Magnified Images of Chip Surfaces Cut from 1018 Cold Rolled Steel During Tapping Using (a) $scCO_2$ Alone; (b) Mineral Oil in H_2O; (c) Straight Mineral Oil; (d) Soybean Oil in H_2O; (e) Soybean Oil Alone; and (f) Soybean Oil in $scCO_2$. Letters correspond to tapping torque efficiency data in Figure 4.2.

The two fluids most ineffective at reducing torque (straight $scCO_2$ and mineral oil semi-synthetic emulsion) produced chips with similar surface characteristics (Figures 4.3a and 4.3b). In these chips, the metal was ground down flat with no indication that lubricant separated the tool from the workpiece. The striations and scratches on the chip surface suggest poor lubrication in the presence of these fluids. For the two moderately effective fluids (straight mineral oil and soybean oil in water), the images show some surface asperities that indicate lubrication was reaching the cutting zone and permitting the metal to be removed without as much contact between the tool and the workpiece (Figures 4.3c and 4.3d).

The correlation of chip surfaces and tapping torque efficiency also holds for the two MWFs with the best performance (straight soybean oil and soybean oil in $scCO_2$). These microscopy images (Figures 4.3e and 4.3f) indicate much less contact between the chip and workpiece than the other experiments (Figures 4.3a-4.3d). For soybean oil in $scCO_2$, the contact area is isolated to only a few elevated relief zones on the chip surface that have not been ground down due to ineffective lubrication. Because the soybean oil-in-CO_2 results (Figures 4.2f and 4.3f) are readily distinguishable from the use of soybean oil alone (Figures 4.2e and 4.3e), it is plausible to suggest that the pressure of the $scCO_2$ coupled with its ability to lower the surface tension of soybean oil might serve to more effectively carry soybean oil deeper into the cutting process than conventional aqueous and straight oil MWF applications at moderate pressures. This penetration serves to minimize contact between chip and workpiece and results in lower tool-chip friction and lower observed torque in the tapping operation.

4.3 Conclusions

This chapter described the development of an experimental setup to deliver $scCO_2$-based MWF and the tapping torque tests that were performed to evaluate the performance of the new fluids. The $scCO_2$-based fluids consisted simply of $scCO_2$ and soy-bean oil above its solubility limit. The mixture was forced out of the bottom of a vessel by the pressure difference between the vessel and the atmosphere creating a spray of dry ice particles and frozen oil. Machining performance tests indicated that the $scCO_2$-based MWF performed significantly better than straight oil soybean and petroleum MWFs, and better than water-based MWF emulsions based on these oils. Analysis of the chips produced during form these experiments demonstrated that observed tapping torque values were highly correlated with evidence of chip-workpiece friction based on the microscopic images of the workpiece surface after the machining operation.

Taken together, the data indicate the feasibility of exploring a new class of MWF based on oils sprayed or dispersed in $scCO_2$. Additional work described in the following chapters explores the application of this technology to other machining operations. The spray characteristics of $scCO_2$-based MWFs were not explored here but are discussed in Chapter 5.

Chapter 5

Evaluation of Cooling Potential and Tool Life

The recent academic and industrial interest in the use of minimum quantities of lubricant delivered in air sprays has focused on cooling potential (Davim et al. 2006; Dudzinski et al. 2004). Air and lubricant sprays do not cool as well as emulsion floods which leads to shorter tool life and machining tolerances that may not meet specifications. Sprays of supercritical carbon dioxide produce dry ice that can effectively remove heat although to date, little research has been reported on the heat removal potential of scCO_2 sprays. No recent reports exist on the use of scCO_2 or other high-pressure gases to reduce tool temperature and mitigate wear.

This chapter describes a connection between heat removal potential of scCO_2 sprays and tool life extension. The heat removal delivered by emulsion floods and mists is compared to that of CO_2 and other high-pressure gases. Nozzle geometries, system setup and operating parameters are manipulated to demonstrate how the cooling capacity of these sprays can be increased. Turning tests were performed for two recalcitrant materials, compacted graphite iron and 6Al4V titanium, to connect heat removal capabilities with expected impact on tool wear rates for several MWF systems. Measured tool temperatures were combined with models of the cutting process to compare with predictions of tool life. The potential of CO_2 to suppress wear by inhibiting oxidation on the workpiece surface as a compliment to its cooling capacity is also explored.

It is demonstrated that tool life improvements associated with reduced flank wear are possible using high-pressure gases which provide more effective localized heat removal on the tool flank. The results demonstrate the importance of scCO_2 delivery angle in a turning process. For effective control of flank wear using $scCO_2$, sprays must be applied directly to the flank face of the tool. These results are corroborated using a heat removal model. At higher cutting speeds, the cooling potential of the $scCO_2$ sprays tested was not sufficient and so dual nozzles were tested. It was found that by applying $scCO_2$ on both the tool rake and flank faces, tool life extensions are achievable at higher cutting speeds.

5.1 Cooling potential of high-pressure gas sprays

Gases have a much lower molecular density than liquids so it follows that their ability to conduct heat away from solid surfaces is lower. Before the 1950s, Shaw reports that several research groups attempted to use sprays of carbon dioxide and nitrogen as metalworking fluids in machining operations (Shaw 2005). This is the only known discussion of CO_2 use in machining prior to the current work. The researchers noted that when delivered on the flank face it was possible to get significant improvements in tool life when using sprays of CO_2 or N_2 instead of water-based coolants.

Shaw noted that when spraying liquid CO_2, dry ice forms and the latent heat involved in its sublimation can effectively remove heat from the tool. For sprays of nitrogen the study speculated that nitrides were forming to assist in the lubrication at the cutting surface, a reasonable assumption based on more recent studies (Sopunna et al. 2006). The researchers further suggest that surface reaction mechanisms inhibiting oxidation at the surface would also reduce machining forces and tool wear. Though metal oxides typically exhibit lower coefficients of friction than metals (e.g., steel and copper (Bhushan 2002)) the formation of metal oxides can lead to accelerated wear. Metal oxides have a relatively low tensile and shear strength when compared to metals so that when two contacting surfaces are in relative motion, fracture will occur in the oxide rather than at the interface. This leads to large amounts of material transfer, galling, and high wear rates. These studies and conclusions suggested that both cooling and lubrication are important functions in sprays of CO_2 and N_2 in machining.

Despite early interest in the use of gases for cooling and wear reduction, the efforts reported in Shaw have not been further developed and for the past 60 years almost all work in machining has focused on liquid heat removal fluids, predominantly water.

This lack of understanding about the role of high pressure gases as coolants in manufacturing That has motivated the present study highlighted in this chapter investigating the cooling potential of gas sprays in CO_2.

5.1.1 Benchmarking the cooling of MQL sprays to conventional flood coolants

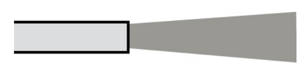
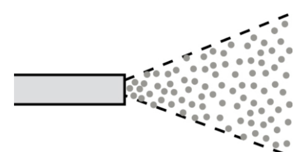
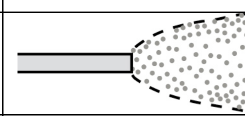
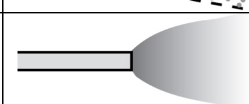
Floods (or jets) of heat transfer fluid, often water, are typically regarded as the most effective way to remove heat from solid surfaces. In MWF applications, floods of water-based emulsions are the industry standard for processes that produce significant amounts of heat. In a move to reduce the volumes of liquid used, the heat removal capacity of liquid sprays (or mists) has been studied and compared to the cooling provided by impinging flood jets of liquid (Sehmbey et al. 1994). Sprays are being used increasingly in heat transfer applications to provide cooling without the large volumes of fluid. In electronic applications, for instance, sprays are being used increasingly as chip size has decreased and heat generation has increased. Most of the work on spray cooling to date has focused on water as a heat transfer fluid because it is inexpensive and safe.

Sprays of water are limited, however, by the phase change that can occur when the water hits a hot surface. When water vapor forms on the surface above 100 ^{o}C, the heat transfer is slowed. Critical heat flux (CHF) is the widely studied phenomena in which phase change on a heated surface impedes heat transfer to a liquid fluid (Um et al. 1996). For flood systems with high flow rates, mass transfer dominates and phase change does not pose a significant technical limitation.

In spray systems where fluid flux is lower, CHF can become problematic. CHF can be minimized in spray systems if operating conditions are selected properly. For liquid sprays, Kim et al. provides an overview of the approaches that have been attempted to overcome critical heat flux limitations and to produce improved cooling in water sprays (Kim 2007). Flow rates and impinging angles can be varied to improve the spray cooling efficiency. Other work, mostly in biomedical and electronics applications, has focused on nozzle geometry, flux, and droplet diameter as ways to minimize CHF and increase cooling potential.

For aqueous MWFs, CHF has been recognized as a performance limitation, particularly in the implementation of minimum quantity sprays delivered in air. To explore the CHF phenomena and understand how sprays of high-pressure gas-based MWF compare, a series of tests were performed under the conditions commonly found in manufacturing settings using the specially designed heat removal probe discussed in Chapter 3. A flood of semi-synthetic emulsion was tested as a benchmark fluid along with two sprays in air, one of lubricant and one of emulsion. For comparison, two high-pressure gas based sprays were also considered: $scCO_2$ + lubricant and N_2. The MWF systems considered are listed in Table 5.1.

Table 5.1. MWF systems evaluated for cooling potential.

MWF	Lubricant		Coolant		Profile
	Composition	Flow (g/s)	Composition	Flow (g/s)	
Emulsion flood (or jet)	petroleum semi-synthetic emulsion	0.05	Water	1	
Air + lubricant spray (mist)	soybean oil	0.01	Air (6 bar)	1	
Air + Emulsion spray (mist)	petroleum semi-synthetic emulsion	0.005	Air (6 bar) + Water	1	
$scCO_2$ + lubricant	soybean oil	0.001	CO_2 (130 bar)	1	
Nitrogen	None	NA	Nitrogen (130 bar)	1	

The results, shown in Figure 5.1, indicate that flood jets of emulsion are able to remove all the heat produced by the probe as illustrated by the as seen in the emulsion flood line. Emulsion sprays exhibited the development of a pronounced critical heat flux above a surface temperature of 150^{o}C. The gases each had an approximately linear increase in heat removal above 150^{o}C as a function of surface temperature with heat removal properties of the gases increasing in the order $scCO_2$ > N_2 > air + lubricant. For these experiments CO_2 and N_2 were applied at high pressure (130 bar) and air was applied at lower pressure (6 bar) to simulate the cooling capacity of conventional air + lubricant MQL sprays, which are applied using 'line' air from centralized air compressors. The emulsion + air spray was also applied using 'line' air to simulate common industrial practice.

An impinging jet of emulsion flood will remove enough heat to avoid CHF limitations if the flow is high enough to dissipate all of the heat generated in the operation. The spray of air + emulsion did exhibit a pronounced CHF plateau and although its heat removal capacity was higher than the other sprays at 350°C, linear extrapolation of the results for the spray of $scCO_2$ + lubricant suggests that, at temperatures above 400°C, it could surpass the cooling potential of an emulsion spray by a significant amount.

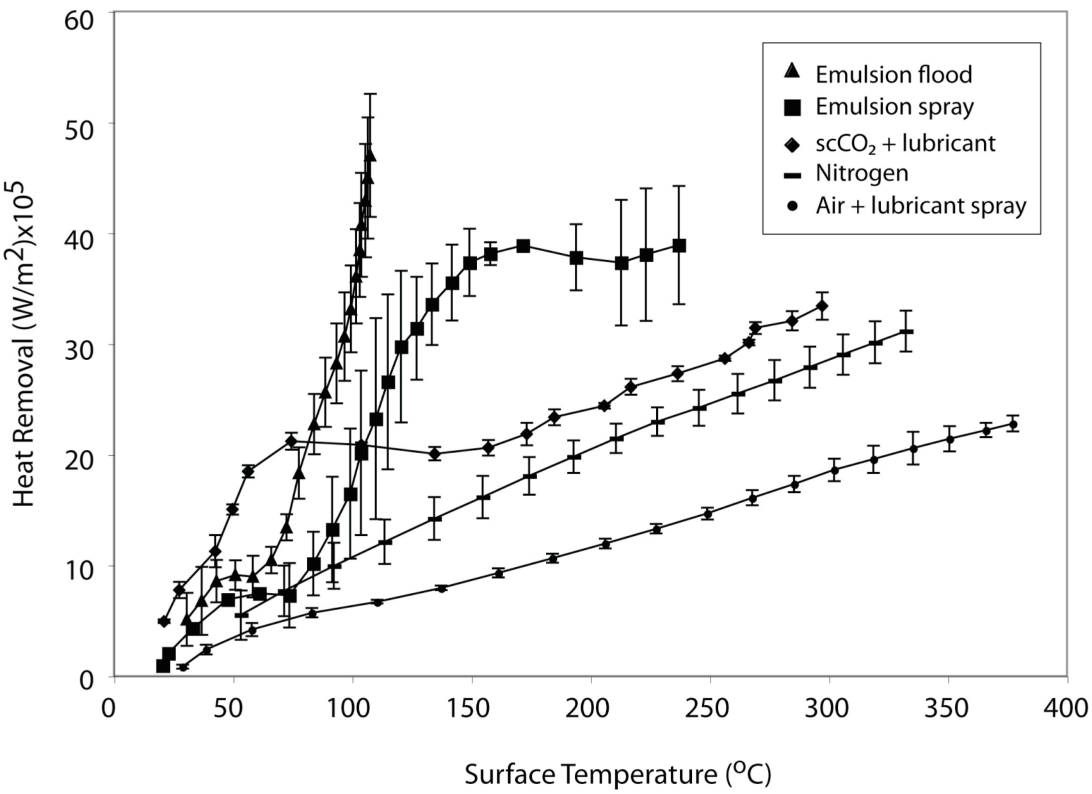


Figure 5.1. Influence of heat removal as a function of probe surface temperature

5.1.2 Maximizing the cooling potential of CO_2-sprays

The CHF literature for water based systems suggests that operating conditions, particularly fluid flux and impinging angle, can be used to minimize heat transfer losses. To determine whether gas-based sprays are similarly dependent on system operating parameters, an experiment was performed to maximize the cooling capacity of $scCO_2$ and $scCO_2$ + lubricant sprays. The experiment varied five independent process parameters: pre-expansion $scCO_2$ temperature, pre-expansion $scCO_2$ pressure, nozzle geometry, distance between probe and nozzle, and offset between probe and nozzle (Figure 3.3). The parameters were selected based on literature methods for spray analysis with the methods to test each discussed in Chapter 3. High and low values for each parameter were selected and a full factorial experimental design was used to measure independent and interaction effects among the variables and the cooling potential of the sprays. An analysis of variance (ANOVA) was performed on the results that showed each variable was independently significant at influencing the heat removal potential of $scCO_2$ sprays. Table 5.2 lists the significance and partial η^2 for the data. A significance value below 0.05 indicates that there is 95% certainty that the independent variable has an effect on the dependent variable. Partial η^2 is a measure of the effect size. The closer to unity, the larger the effect. The results suggest that distance, vessel pressure, impinging offset, and L/D ratio all have an important effect on the cooling potential of CO_2 sprays. The temperature in the vessel is also important but somewhat less so than the other variables. No interaction effects between the variables were found to significantly influence the cooling potential of the sprays so these are not reported here.

Table 5.2. ANOVA results for cooling potential of CO_2 sprays

Independent Variable	Significance	Partial η^2
Distance	0.000	1.000
Vessel Pressure	0.001	0.998
Impinging Offset	0.001	0.997
L/D Ratio	0.002	0.997
Vessel Temperature	0.019	0.962

The results of the spray tests for $scCO_2$, $scCO_2$ + lubricant, emulsion spray and emulsion flood (Figure 5.2) indicate that operating conditions for $scCO_2$-based MWF can be selected to remove heat as well or better than conventional water-based emulsions at a probe temperature of 100 ^oC. Probe temperature is distinct from the surface temperature reported in Figure 5.1 and the results in Figure 5.2 were recorded at a surface temperature of 60-70 ^oC (varied with heat flux but in all cases lower than the CHF point). 100 ^oC was selected because although the contact between a tool and workpiece can reach up to 1000^oC, much of the bulk of the tool is at a temperature closer to 100^oC. In addition, recording heat flux at higher temperatures can damage the probe over time resulting in experimental error when extensive data collection is required as in Figure 5.2.

The results presented in Figure 5.2 show the heat removal of $scCO_2$ systems for all combinations of the five input parameters. The results are ordered from lowest to highest heat removal. The results highlight the important role of operating conditions and of lubricant in the heat removal process. At higher heat removal rates, the $scCO_2$ with and without lubricant diverge with the $scCO_2$ + lubricant cooling at a rate that was almost 100% higher than the same spray conditions without lubricant. The synergistic nature of the $scCO_2$ + lubricant spray is likely attributed to the cooling capacity effects provided by the lubricant that stores the cold generated during the expansion for $scCO_2$ and delivers it to the probe. This capacitance cooling effect associated with rapid expansion of super-critical solutions had not been previously reported in the literature.

Unlike the experimental results in Figure 5.1 where only a single flow rate was reported for each condition as in Table 5.1, here a range of values was tested. An emulsion mist was tested at fluid flow rates ranging from 0.005 g/s to 0.05 g/s. For the emulsion flood, the fluid flux (flow per area) was found to be more significant than flow rate and so the upper limit in this bar is the higher flux of 12 g/mm^2 sec and the lower limit is set by lower flux of 6 g/mm^2 s.

As shown under optimal conditions, sprays of $scCO_2$ + lubricant remove heat more effectively than a spray or flood of emulsion under the experimental conditions tested here. In the context of MWF design, this conclusion is significant because water-based emulsions demonstrate the opposite behavior. For conventional MWF emulsions composed of lubricant and water, additional lubricity comes at the expense of more effective cooling. This zero-sum constraint of MWF has been demonstrated by several researchers to manifest itself in the form of lower CHF levels for formulations containing higher concentrations of lubricant (Bittorf et al. 2006).

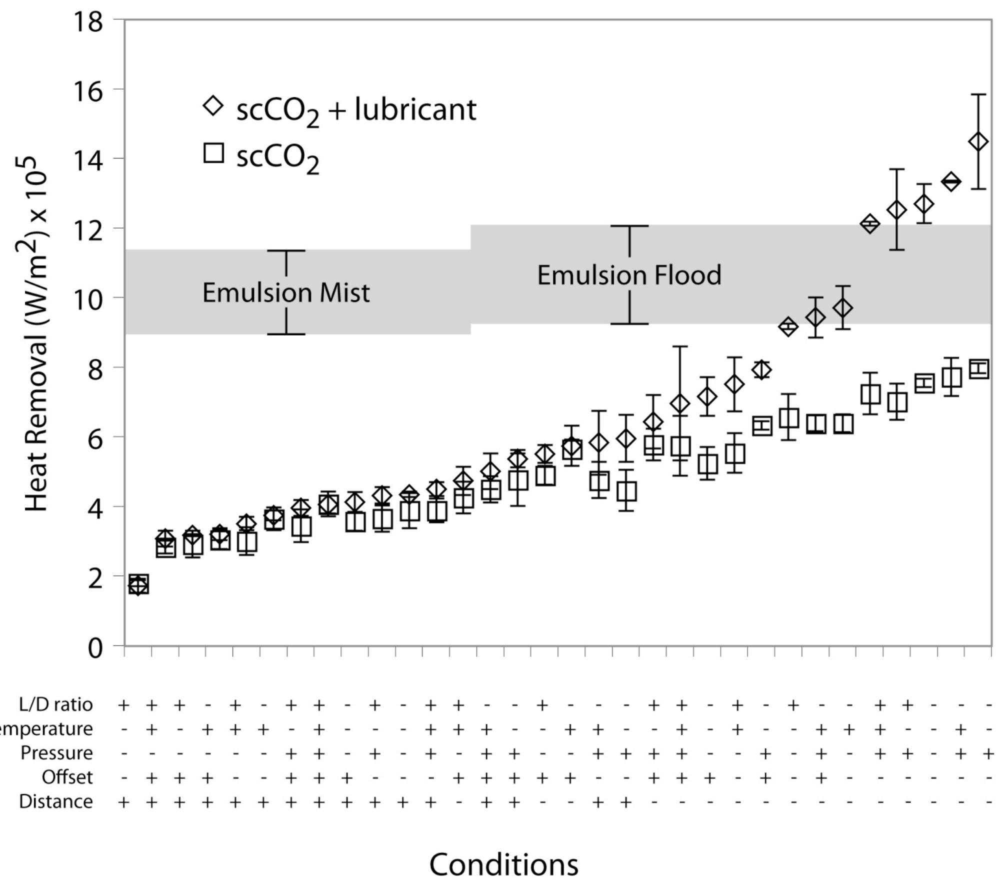


Figure 5.2. The heat removal capacity of scCO2 sprays with and without oil compared to water-based MWFs. (- indicates a low value and + a high value for a parameter)

5.2 Cooling in the tool bulk and on the tool surface

In cutting, the heat generation occurs due to the friction between the workpiece and tool and from the deformation of the material in the chip as discussed in Chapter 2. Both of these regions are expected to be inaccessible to conventional MWFs. The tool/chip and the tool/workpiece interfaces are not easily reached by conventional MWF emulsions, so tools are flooded with coolant to draw out the heat and reduce the temperature in the bulk of the tool (Byers 2006). This approach is effective at reducing the temperature at the cutting surface when large amounts of emulsion flood can be delivered. Emulsion or lubricant sprays in air do not remove heat from the bulk of the tool as effectively, which is a problem if minimum quantity processes are to be adopted on a broad scale without reconsidering how they are used to remove heat from a tool. Gas-based coolants, such as $scCO_2$, have the potential to effectively access the confined area in the workpiece/tool interface and remove heat without CHF limitations. However, the low molecular density of $scCO_2$ suggests that it will not remove heat from the bulk of the tool as effectively as a liquid flood of MWF emulsion.

To understand how molecular density, critical heat flux, and other spray parameters will influence heat removal from a cutting tool, a model was developed using the physical properties of the MWFs and several heat transfer relationships. The heat transfer was modeled as a flow across a flat plane. MWF are either delivered as impinging jets from the top of the tool (normal to the surface) or as tangential sprays along the rake or flank face of the tool (Figure 5.3). Models of impinging jets are complex and do not provide for straightforward comparisons between different fluids, particularly when some are gases and others liquids (Kim 2007). Heat transfer along a flat plane is a classic and better studied heat exchange problem involving the flow of a liquid parallel to the heated surface. The relationships associated with this problem can be used to estimate the convective coefficient (h_x) and to develop a greater understanding of cooling potential of MWF sprays in practice.

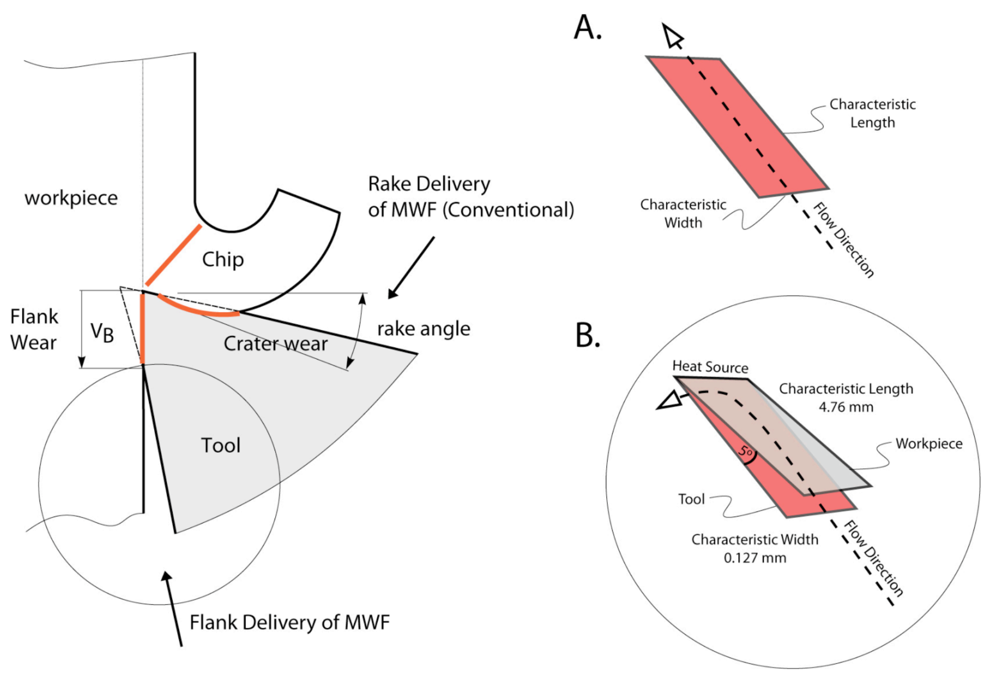


Figure 5.3. Schematic of cutting process with geometry defined for heat transfer analysis with heat generation regions in orange. A. flat plate heat transfer, B. heat transfer from orthogonal cutting tool.

A series of dimensionless number correlations have been reported to analyze the heat transfer problem for a flat plate. One of the most common employs the Nusselt number which is a ratio of convective heat transfer to conductive heat transfer from a surface. Empirical relations have been published to describe the Nusselt number in terms of the Reynolds number (ratio of inertial to viscous forces) and the Prandlt number (ratio of viscous to thermal diffusive rate) for different geometries. For convective heat transfer along a heated flat plate the widely employed empirical relationship is:

$$Nu = 0.332 \mathrm{Re}^{1/2} \mathrm{Pr}^{1/3} \qquad (5.1)$$

The Nusselt number can be written as:

$$Nu = \frac{h_x L}{k} \qquad (5.2)$$

where h_x is the convective heat transfer coefficient (W/m^{2}K) along the flat surface, L is the characteristic length (m), and k is the thermal conductivity of the fluid (W/mK).

The Prandlt number can be written as:

$$\mathrm{Pr} = \frac{C_p \mu}{k} \qquad (5.3)$$

where C_p is the heat capacity for the fluid (J/kgK), μ is the dynamic viscosity of the fluid (Pa·s), and k is the thermal conductivity of the fluid.

The Reynolds number for the flow can be calculated by:

$$\mathrm{Re} = \frac{\upsilon L}{v} \qquad (5.4)$$

where υ is mean fluid velocity, L is the characteristic length, v is the kinematic viscosity (m^2/s). Using these relationships and data from the National Institute of Standards and Technology (NIST) *Book of Thermophysical Properties of Fluid Systems (Lemmon et al. 2005)*, the convective heat transfer coefficient for water, water vapor, CO_2, and N_2 was estimated by combining equations 5.1-5.4 and solving for h_x using equation 5.5.

$$h_x = \frac{0.332 \mathrm{Re}^{1/2} \mathrm{Pr}^{1/3} k}{L} \qquad (5.5)$$

For a surface temperature of 200°C (average for the range commonly observed in machine tools), the convective heat transfer was estimated based on the difference in temperature between the solid surface and the coolant times the convective heat transfer coefficient.

To produce a model with results as relevant to the MWF systems of interest, four different fluids were considered. Pure water was modeled because MWF emulsions are >97% water by mass. Water vapor was considered because at low flows of emulsion or when CHF becomes a problem, the heat transfer capacity of saturated water vapor is of interest. CO_2 and N_2 gas sprays were modeled to estimate the cooling potential of high pressure gases. The results of the analysis are provided in Table 5.3.

Table 5.3. Results of convective heat transfer analysis for several MWF carriers.

Variable	Symbol	H_2O	H_2O vapor	CO_2	N_2	Units
Kinematic viscosity	*u*	8.0E-07	2.1E-05	8.5E-06	1.6E-05	m^2/s
Thermal conductivity	*k*	0.62	0.03	0.02	0.03	W/mK
Heat capacity	*Cp*	4.18	2.08	0.86	1.04	J/gK
Velocity*	*v*	6	6	100	100	m/s
Prandlt #	*Pr*	5.41	1.02	0.76	0.72	
Reynolds #	*Re*	35670	1391	55765	29715	
Nusselt #	*Nu*	110.1	12.5	71.6	51.3	
Characteristic length	*L*	0.00476	0.00476	0.00476	0.00476	m
Coolant Temperature	*T*	30	100	-40	20	^oC
Heat transfer coefficient	h_x	14237	66	256	281	W/m^2K
Convective heat transfer**	*q*	2420290	6600	61440	50580	W/m^2

*Velocity estimates were obtained from (Khan and Dhar 2006)
** Heat transfer calculation assuming solid surface temperature of 200^{o}C

The results for the convective heat transfer shown in Table 5.3 suggest that water cools about 40-50 times better than gases but that high-pressure jets of CO_2 and N_2 remove heat about 8-9 times better than water vapor. If water vapor forms in the cutting zone as one would expect from the CHF results, then high-pressure gases will more effectively remove heat at the cutting surface. CO_2 is slightly less effective at convective heat transfer than N_2 according to the heat transfer coefficient calculations but CO_2 cools much more when it is sprayed out of a nozzle due to the Joule-Thompson effect and the lowering of the gas temperature that this causes. The Joule-Thompson effect describes a gas' tendency to change temperature during an isentropic expansion. Ideal gas laws do not uniquely describe changes in volume and pressure for real gases. A Joule-Thompson coefficient (μ_{JT}) captures the behavior of real gases. Both N_2 and CO_2 will cool when sprayed out of a nozzle at the pressures and temperatures described here but CO_2 will cool much more significantly. At standard temperature and pressure CO_2 has a μ_{JT} of 1.093 K/bar while N_2 has a μ_{JT} of 0.214 K/bar. The lower temperature in the CO_2 spray results in a higher heat transfer rate than for N_2 supporting the experimentally measured data from Figure 5.1. The absolute values of the heat transfer from this analysis and the results in Figure 5.1 are different because the geometry of the model system is different than the experimentally measured system. The trends, however, are consistent in that cooling occurs in the following order: water > CO_2 > N_2 > water vapor.

5.3 Tool wear results

For most types of cutting under normal operating conditions, wear occurs primarily on the rake and flank faces of the tool (Figure 5.2). The rake face of the tool receives the majority of the wear as chips slide over the surface and remove material forming a crater (Shaw 2005). The flank face experiences the same type of forces associated with the heavily loaded sliding surfaces but the forces on the flank face tend to be lower. Since the flank face has an impact on the tolerance of the final part, it is typically monitored closely during machining to prevent damaged parts. Tools fail when the crater and material between the flank wear and the crater wear becomes thin enough to break off. Tools are typically replaced well before this when an established flank wear limit has been achieved to avoid poor part quality and tool failure in production.

5.3.1 Spray direction effect

Previous studies have shown that spray direction of flood coolant can have a moderate impact on the temperature profiles in a tool during cutting but that effective cooling is possible using emulsion flood delivery from either the flank or the rake face of the tool (Shaw 2005). This follows the earlier discussion on the effective bulk heat removal from tools that is possible by flood coolants. For sprays or emulsion or lubricant in air, the probe experiments from Figure 5.1 suggest that these MWF are not as effective at heat removal and may not remove heat from the bulk of the tool effectively if sprayed from the rake face. To test this hypothesis a series of turning experiments were performed using compacted graphite iron (CGI) cut using polycrystalline diamond tools (PCD). CGI is a highly abrasive material that must be cut using expensive PCD tools because other tool materials wear too quickly. PCD is very strong and will last much longer than carbide tools but is very temperature sensitive and requires adequate cooling and lubrication.

PCD was selected for this work because it fails easily without sufficient cooling. Many MQL sprays do not sufficiently control the wear in PCD tools for CGI cutting operations leading to rapid tool deterioration.

The results of the CGI-PCD experiments are presented in Figure 5.4. The lathe was run at a speed of 738 sftm (square feet per minute), at a feed rate of 0.0134 inch/revolution and a depth of cut of 0.005 inch. The tests represent duplicate trials under each condition with results typically not deviating more than 10% between trials. For clarity only one trial is plotted. Delivered from the flank face, sprays of air + lubricant and air + emulsion produced significant tool life extensions relative to dry cutting (left plot in Figure 5.4) when tool life is defined as the time it take the tool to reach the wear limit. A flank wear limit of 0.15 mm was plotted to indicate the wear level a manufacturer typically chooses to replace a tool in this type of an operation. The results confirmed the hypothesis that sprays of $scCO_2$ + lubricant from the rake face of the tool are unable to provide enough cooling to extend the life of the tool. The results (shown on the right of Figure 5.4) show that from the rake face, flank wear develops in approximately the same fashion as it does on dry tools. Sprays of $scCO_2$ + lubricant were then tried from the flank face of the insert. When applied from the flank face, sprays of $scCO_2$ + lubricant reduced flank wear by approximately 50% when compared to the air + emulsion or air + lubricant spray for 10,000 seconds of cutting. An emulsion flood was not tested in this experiment because the industrial partner interested in this process could not use flood MWFs because they interfered with the process operation.

The experiments show clearly that nozzle placement relative to the cutting zone matters. Sprays to the rake face result in rapid tool failure whereas sprays to the flank face control flank wear effectively, better, in fact, than conventional coolants. This result supports the idea that improved localized cooling in cutting can have significant effects on tool life. Applied from the rake, sprays of $scCO_2$ do not extend the life of the tool much beyond that which would be expected under dry conditions. Applied from the flank, sprays effectively penetrate the cutting zone dissipating heat leading to lower wear rates.

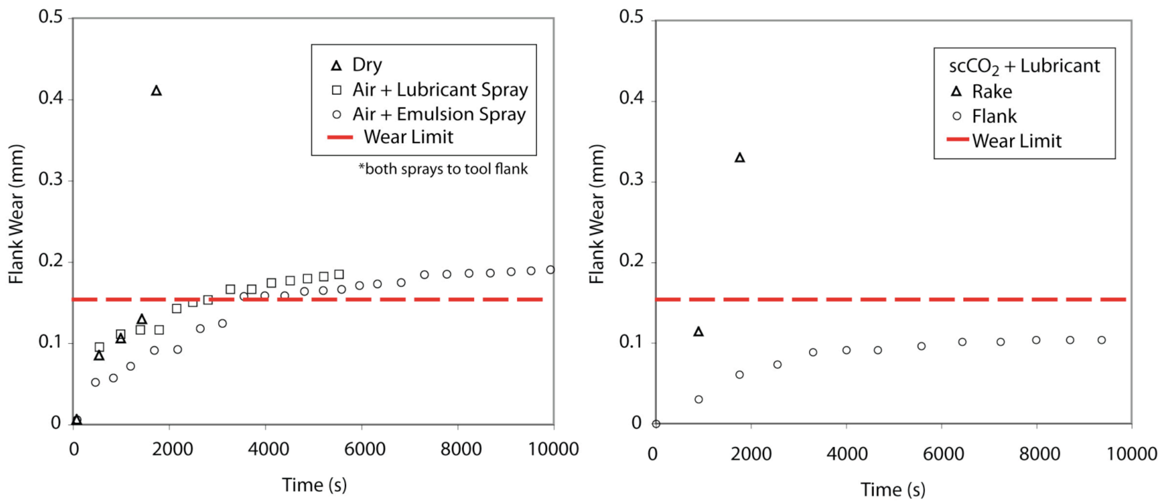


Figure 5.4. Tool life tests from single point turning of compacted graphite iron.

5.3.2 Tool wear comparison between MWF-classes

To further explore the idea that localized cooling using high pressure sprays of $scCO_2$ could effectively control tool wear, a separate study was conducted using another tough-to-cut material: Titanium (6Al4V). Eight different fluids were tested in turning and compared to each other and to the results from dry cutting. Titanium was selected because it is well known to cause rapid tool wear driven primarily by the large amounts of heat generated when it is cut and its low thermal diffusivity. K313 carbide tools were used because they are a commonly used tool material and the wear mechanisms that dominate in K313 are representative of other carbide types. The turning operation was conducted using the following conditions: speed = 150 sftm, feed rate = 0.008 inch/revolution, and depth of cut =0.005 inch. The nine different cutting conditions are listed in Table 5.3. The wear results are shown in Figures 5.5-5.7.

The tool wear results for conventional fluids (Figure 5.5) show clearly that a switch from conventional flood coolants to sprays of air + lubricant or air + emulsion results in a dramatic decrease in tool life. The difference in tool life between emulsion spray and emulsion flood is 2 to 3 fold lower as the tool wears considerably faster when sprayed with 0.01 g/s of emulsion mist versus 1 g/s of emulsion flood. The presence of an air spray in the emulsion spray does not effectively compensate for the lower MWF flow rate relative to the emulsion flood.

Table 5.4. MWF systems evaluated in tool flank wear tests when turning of 6Al4V Ti using K313 carbide tools.

MWF	Lubricant		Coolant	
	Composition	Flow (g/s)	Composition	Flow (g/s)
Emulsion flood	petroleum semi-synthetic emulsion	0.05	Water	1
Air + lubricant spray	soybean oil	0.01	Air (6 bar)	1
Air + emulsion spray	petroleum semi-synthetic emulsion	0.005	Air (6 bar) + Water	1
scCO_2	None	NA	CO_2 (130 bar)	1
scCO_2 + lubricant	soybean oil	0.001	CO_2 (130 bar)	1
Nitrogen	None	NA	Nitrogen (130 bar)	1
CO_2	None	NA	CO_2 (13 bar)	0.1
Argon	None	NA	Argon	1
Dry	None	NA	None	NA

In production, manufacturers impose wear limits on tools to prevent the possibility of a failure or damaged part. In this work, wear limits also facilitate tool life modeling. Imposing a wear limit of 0.15 mm, CO_2 and flood coolants are the MWF systems most likely to extend the life of the tool past 10 minutes. To quantify the advantage associated with the lower wear rate, regression analysis of the tool wear data was used to estimate the mean time to failure for several fluids. It was assumed that the first 100 seconds of cutting corresponded to the break-in period and these data were not included in the regression. The mean time to failure for tools to reach 0.15 mm of wear was 100 s for air + emulsion, 900 s for emulsion flood, and 1400 s for scCO_2 + lubricant.

The wear rate for scCO_2-based coolants (Figure 5.6) is 2 to 4 times lower than it is for floods and sprays of emulsion (Figure 5.5) after 300 s of cutting. Both scCO_2 and scCO_2 + lubricant wear at a low rate with only a small, if any, difference between sprays of scCO_2 and sprays of scCO_2 + lubricant. This result is potentially contrary to the conclusion in Figure 5.2, namely, that dissolved lubricant can improve the cooling potential of scCO_2 sprays. Alternately, the tool wear results obtained using the turning tests do not have the resolution needed to record the effects of these differences in heat removal.

5.3.3 Tool wear reductions by oxidation inhibition

In order to explore the potential that tool life advantage was attributed to chemical passivation of the cutting zone rather than strictly cooling potential, several other gases including CO_2 at a lower pressure (13 bar) were tested. Published reports of CO_2 use in cutting had suggested that the CO_2 worked by reducing oxidation rates on the cutting surface (Shaw 2005). If this is the mode of action then reduced tool life results should be evident even at lower pressures of CO_2. The results suggest that low pressure CO_2 does have some tool wear reduction potential, e.g. the wear was not as severe as in the tests for dry or MQL results, but the wear was approximately 75% higher than for higher pressure scCO_2 sprays after 300 s. This suggests that even though the presence of an inert gas in the cutting region could assist in reducing wear, the improved cooling capacity provided by higher pressure sprays of scCO_2 are primarily responsible for the improved tool life.

To determine whether other high-pressure industrial gases would work as effectively as CO_2, sprays of Argon and Nitrogen were tested at the same high pressure (130 bar). The results, shown in Figures 5.6 and 5.7, reveal that other gases at high pressure perform approximately as well as lower pressure CO_2 (13 bar). This supports the general conclusion that by excluding oxygen from the cutting zone, wear rates are suppressed. For the trial in which more oxygen is provided to the cutting zone via high-pressure air sprays with emulsion or lubricant, the wear rates are much higher than emulsion alone or even dry conditions. The comparable results between lower pressure CO_2 and higher pressure Ar and N_2 suggest that CO_2 is a more efficient heat transfer fluid than other gases.

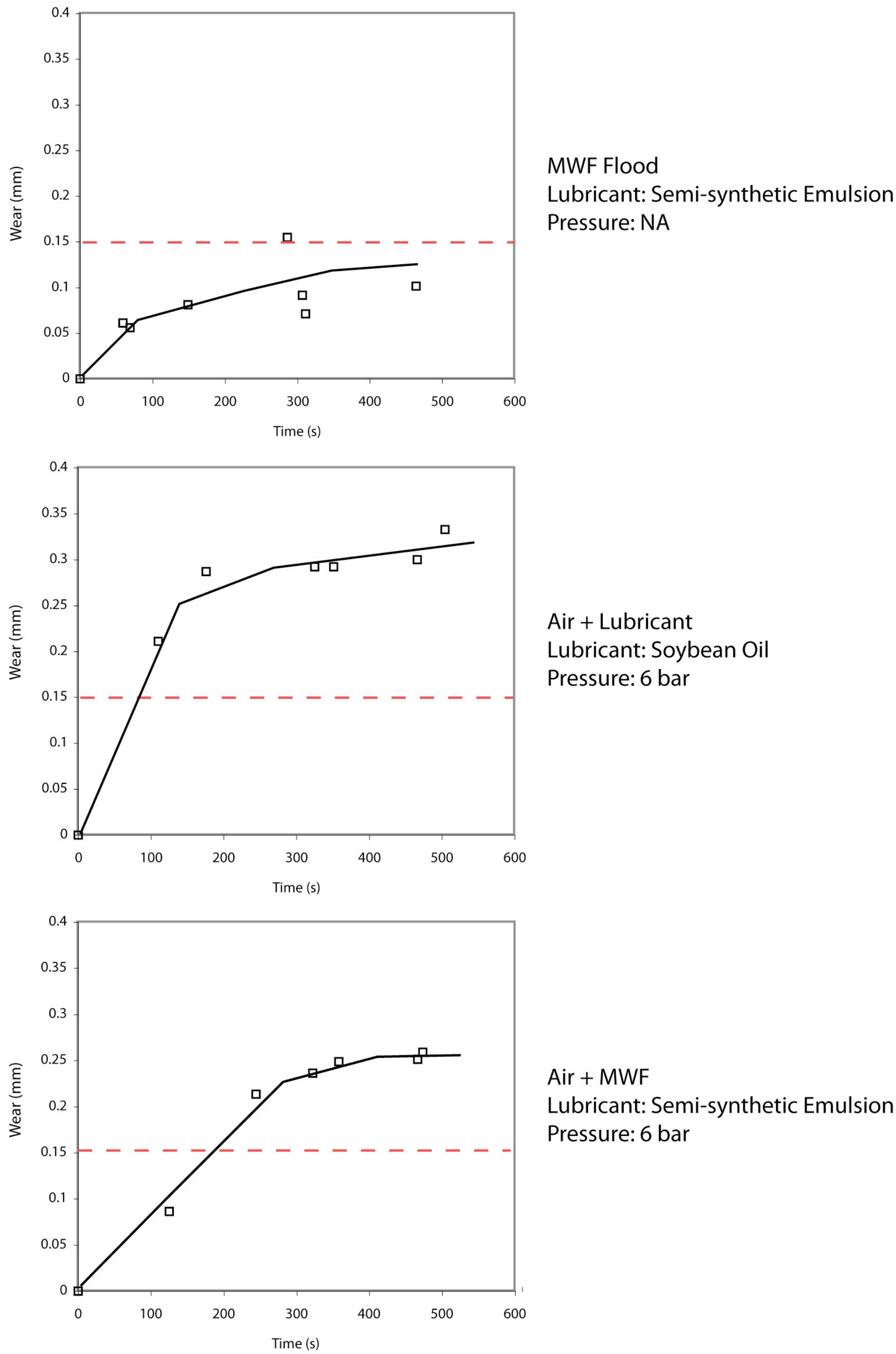


Figure 5.5. Wear results for conventional or MQL sprays of MWF.

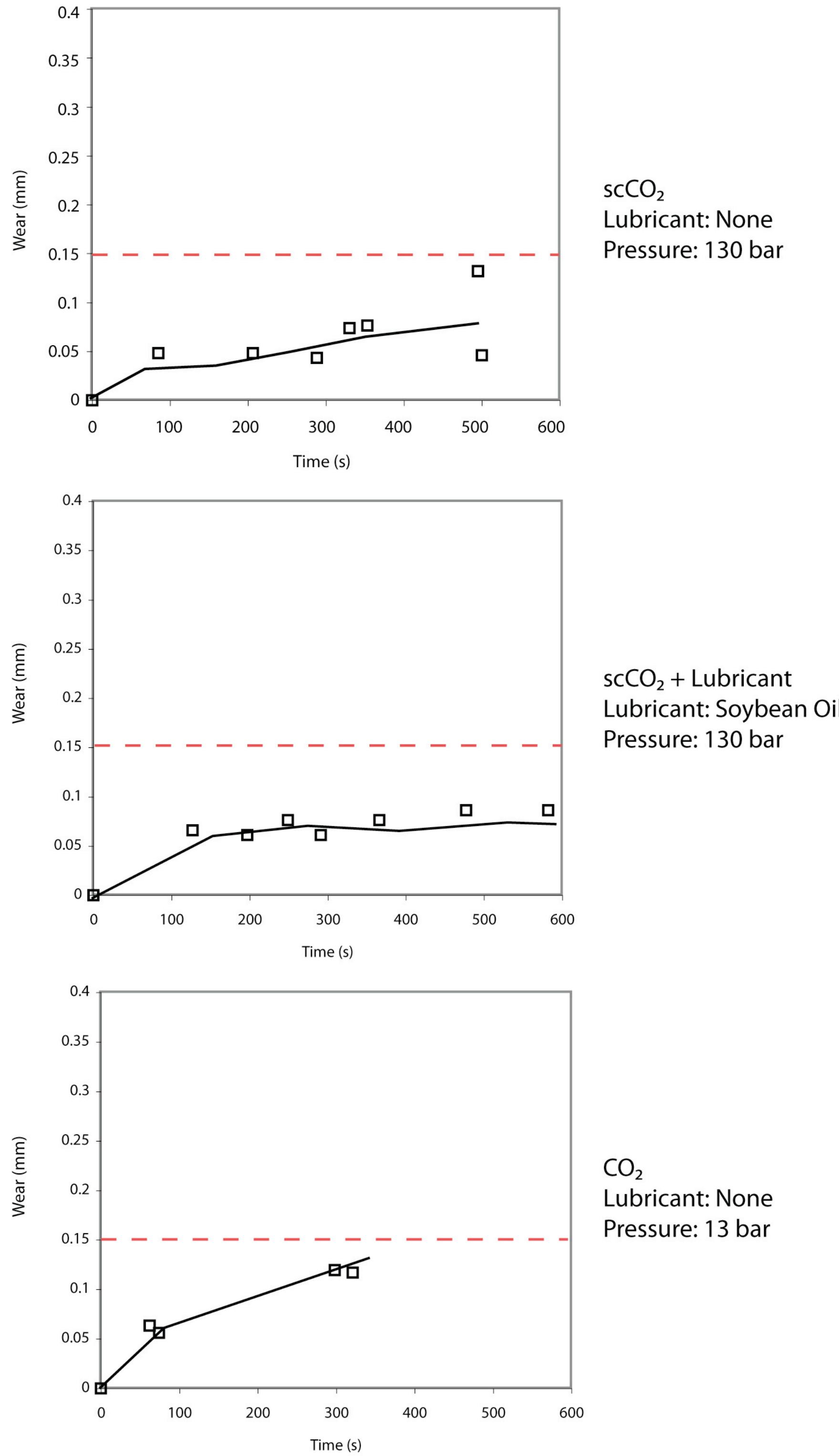


Figure 5.6. Wear results for CO_2-based MWFs.

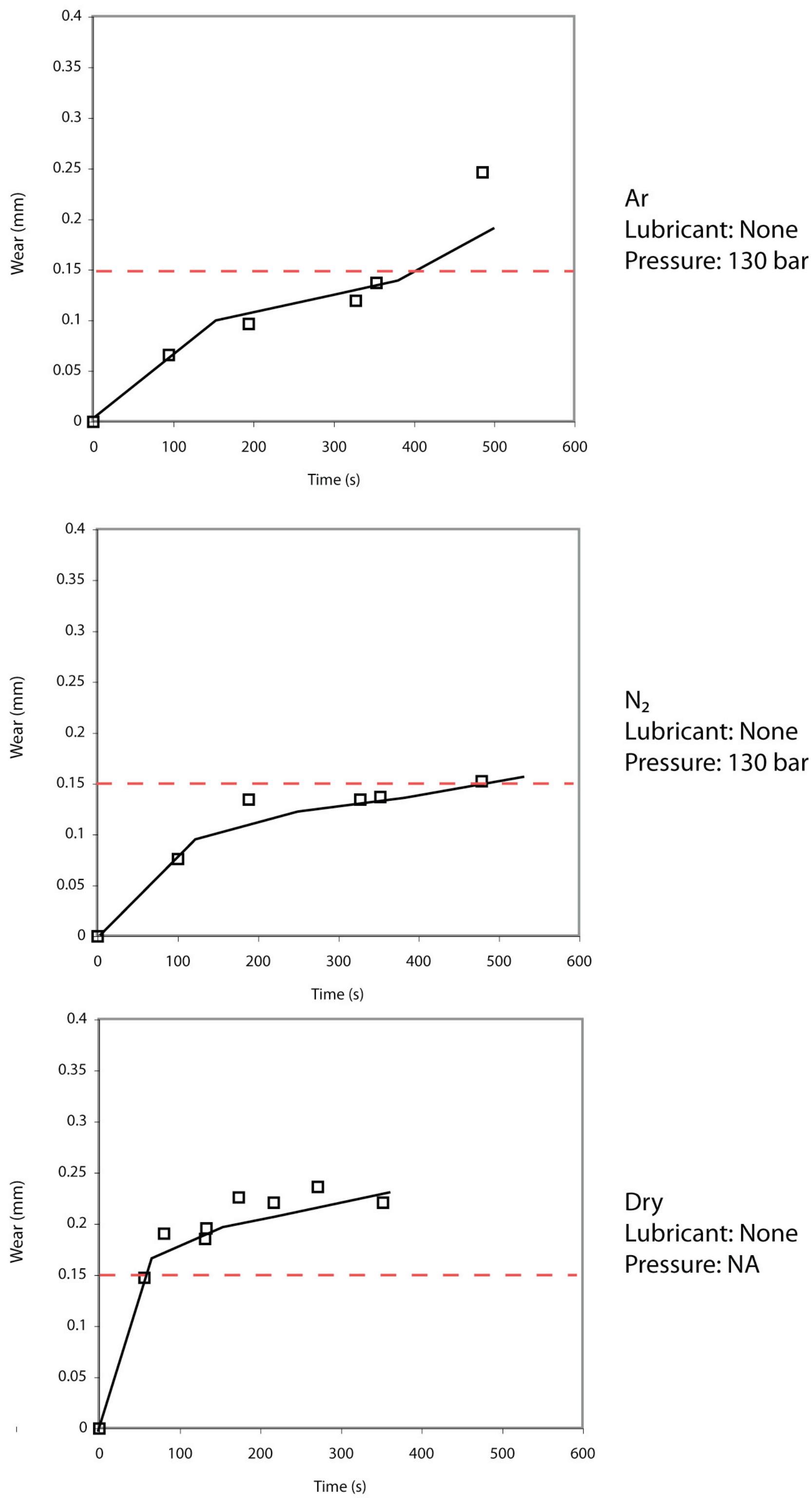


Figure 5.7. Wear results for high pressure gases and dry cutting.

Table 5.5. Time to reach wear limit using linear regression of experimental cutting results. Average time ($\bar{x}$) to wear limit is reported for tools cut using each MWF.

System	Time (s)			
	x_1	x_2	x_3	$\bar{x}$
Emulsion flood	230	2000	875	*1035*
Air + lubricant	230	87	10	*109*
Air + emulsion	570	267	570	*469*
$scCO_2$	8800	1100	600	*3500*
$scCO_2$ + lubricant	722	8000	859	*3194*
CO_2	450	457	-	*454*
Argon	330	467	1180	*659*
Nitrogen	1467	400	600	*822*
Dry	240	104	95	*146*

5.3.4 Measuring the tool temperature in turning

To corroborate the probe heat removal results in Figure 5.1, the tool temperatures for the titanium turning tests were recorded. Although, the results from Figure 5.1 are useful for understanding heat removal potential in cutting, other factors such as the MWF's ability to penetrate the cutting zone can affect its cooling potential.

To allow an estimate of surface temperature, the tool holder was retrofitted with a thermocouple to directly measure the temperature of the insert during cutting. The approach allowed for consistent, real time measurements of the bulk temperature rise in the insert during cutting. The thermocouple was located 4.7 mm from the cutting edge. The positioning of the thermocouple is depicted in Figure 5.8:

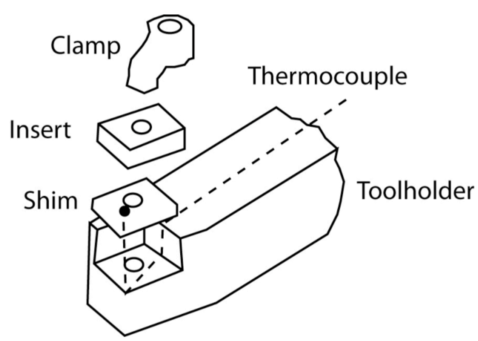


Figure 5.8. Thermocouple placement for temperature measurement in turning tests.

The results, shown in Figure 5.9 demonstrate that significant differences can be seen in insert temperature as a function of MWF used. In the first 30 seconds of the turning operation, the temperature of a dry cutting process increases approximately 50^{o}C higher than a tool cut in the presence of an emulsion flood. In between, the temperature removal of the fluids reflects the results observed in the heat removal probe experiments. Air + lubricant cools the least effectively followed by high-pressure nitrogen, CO_2, and MWF emulsion spray. These differences in tool temperature are consistent with the probe results presented in Figure 5.1 and provide a basis to calculate the difference in temperature between MWFs. By subtracting the tool temperature under a given cooling condition from the tool temperature under dry cutting conditions a ΔT is determined.

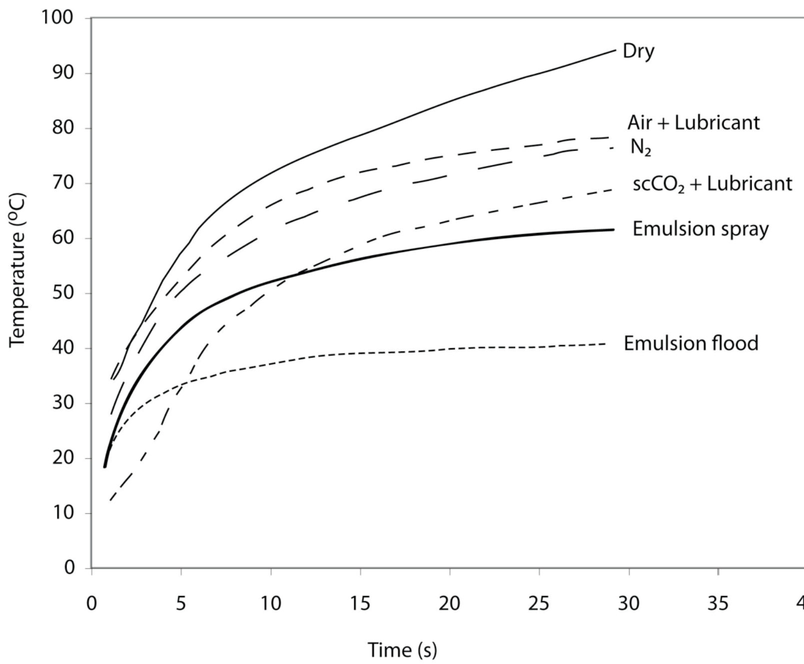


Figure 5.9. Measured insert temperature when cutting using several MWF systems.

5.3.5 Estimation of cutting edge temperature

Using estimated values of the temperature at the cutting edge and the ΔT measured in the laboratory, temperature estimates can be made for the contact between the tool and titanium workpiece under each of the cutting fluid conditions. To estimate surface temperature from insert temperatures, a model described briefly here (for further description see (Shaw 2005)) was used that assumes that temperature generation in machining is constant based on a steady state approximation of heat generation from two sources: the shear plane where material is being deformed and the chip/tool contact area where friction is generated as the chip leaves the cutting zone as shown in Figure 5.10. The schematic also shows how typical isotherms would appear during a cutting operations and the location of the thermocouple used here (Shaw 2005).

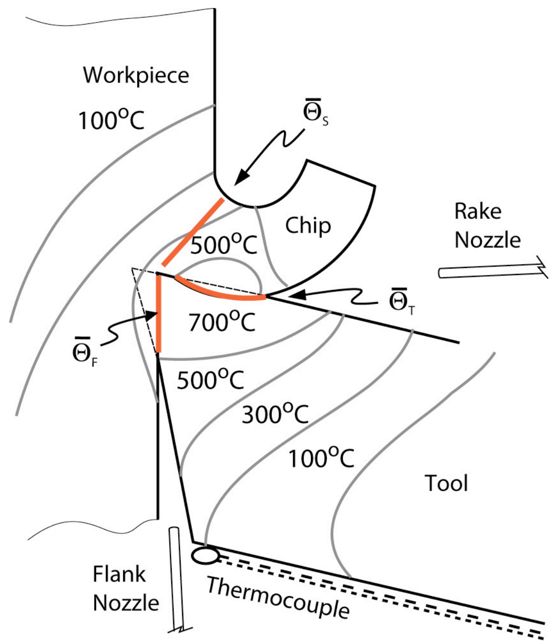


Figure 5.10. Image of cutting zone showing the location of the heat sources (Θ_S = shear zone, Θ_T = rake zone, Θ_F = flank zone), representative temperature gradients, and location of the thermocouple.

A smaller amount of heat is generated from friction between the tool and workpiece but this is typically neglected next to the heat generated from the shear deformation (Θ_S) and the chip/tool contact area (Θ_T). When cutting titanium, two confounding factors related to heat transfer accelerate tool wear. The first is that titanium does not conduct heat as well as many other common metals and so excessive heat accumulation can occur regionally in the tool. The second is that the hard chips do not deform and move along the surface of the tool as readily as other metals resulting in higher forces on the top of the tool and higher frictional temperature on the Θ_T face. Both of these factors can lead to high surface temperature on the flank face even though the heat is generated in other parts of the cutting process.

To estimate the shear and tool/chip temperatures the following series of equations can be applied. The shear plane temperature can be estimated by:

$$\bar{\theta}_s = 0.754 \frac{(1-R_1)q_1\left(\frac{t\csc\phi}{2}\right)}{k_2\sqrt{L_1}} + \theta_o \qquad (5.6)$$

where R_1 is the fraction of energy leaving in the chip that can be estimated using the thermal conductivity of the tool and workpiece (Boivineau et al. 2006), q_1 is the frictional energy flowing to the chip, ϕ is the shear angle, k_2 is the thermal conductivity of the tool W/m·K, t is the chip thickness, L_1 is a function of the diffusivity of the workpiece material, the strain in the chip, and the machining forces, and Θ_O is the room temperature in ^{o}C. The mean temperature (^{o}C) along the chip surface on the tool face can then be calculated by:

$$\bar{\theta}_T = \bar{\theta}_S + \frac{0.377(R_2 q_2)a}{k_2\sqrt{L_2}} \qquad (5.7)$$

where R_2 is the fraction of energy entering the tool, q_2 is the frictional energy that will be dissipated at the chip-tool interface, L_2 is a calculated using thermal diffusivities and cutting forces. The equations are solved iteratively as many of the variables, such as thermal conductivity, are temperature dependent. For the system used in this work, material values for titanium (heat capacity, thermal conductivity, and density) were obtained from (Boivineau et al. 2006) and tool geometry was obtained from the manufacturer. Forces were measured and used to calculate L_1 and L_2. The calculated value for temperature at the tool/chip contact Θ_T = 679 ^{o}C assuming dry cutting conditions.

Having calculated Θ_T, it is possible to estimate the temperature in the tool in the presence of different MWF using the experimental data reported in Figure 5.9. The values for the other conditions were determined using the measured ΔT values from Figure 5.9. To account for the likely scenario that ΔT on the flank surface is some $f(\Delta T)$ at the thermocouple position, a function, α, was defined to determine the impact it would have on the temperature driven wear model. The calculated temperature in the tool and the sensitivity function α were then used to evaluate the relationship between tool temperature and heat induced diffusive flank wear.

5.4 Temperature driven tool wear mechanisms

Tool wear is a complex phenomenon driven by numerous factors that influence surface temperature including: 1) the material properties of the tools and workpieces such as conductivities, diffusivity; 2) physical properties of the cutting operation such as the surface finish and tool geometry; and 3) operating conditions such as cutting speeds and feed rates. Under certain combinations of conditions, tools will wear excessively. At the speeds and feed rates commonly seen in metals manufacturing, abrasive and diffusive wear tend to dominate. Abrasive wear occurs when small pieces of the tool break off forming chips that slide or roll along the cutting surface under pressure. Diffusive wear occurs when solid-state diffusion from the tool to the workpiece causes degradation tool. Figure 5.10 shows the high temperature contacts between the tool and chip on the rake face between the tool and workpiece on the flank face. For high speeds and high temperatures diffusive wear dominates. Previous studies using tungsten-carbide-cobalt (WC-Co) carbide have shown that a material transition occurs in the tool at higher temperatures (Mathew 1989). Around 700 ^{o}C it becomes more likely that the Co is able to move through the dislocations in the WC matrix making solid state diffusion more problematic from a tool life perspective (Arsecularatne et al. 2006). Based on these reports, tool life can be expressed as a function of tool temperature and system specific coefficients:

$$\frac{dW}{dt} = De^{-E/R\theta_T} \qquad (5.8)$$

where $\frac{dW}{dt}$ is the wear rate, D is a constant associated with the tool and work material, E is the process activation energy, R is the gas constant and Θ_T is the temperature on the face of the tool. From this equation it is clear that as the tool temperature decreases, wear rate decreases proportionally.

The data for the titanium turning tests and the temperature measurements were plotted and the data was fit using the model described by Equation 5.8. The results, shown in Figure 5.11, demonstrate that the data fit a linear regression when plotted in terms of the exponential relationship in Equation 5.8. The relationship between tool temperature and tool wear does a good job of predicting the tool life extension possible for conventional ‘wet’ MWF systems as shown by the lower line in the figure. Surprisingly, the ‘dry’ MWF systems, e.g. those delivered in MQL, dry, or high-pressure gas, did not appear to fit the same model prediction observed for the conventional ‘wet’ coolants. A separate model was fit for the ‘dry’ MWFs and as expected, the slopes of the two lines are very similar. Slope, in this model, is a physical parameter that determines the activation energy for Co to diffuse through the carbide tool thus resulting in tool wear. It should not change as a function of MWF if tool material and workpiece material are kept constant as they were here. The intercept of the two model predictions is different. In practical terms this suggests that ‘dry’ coolants permit the tool to run at higher temperatures with comparably lower levels of wear than those provided by ‘wet’ coolants. In this case wet coolants are defined as emulsion flood, emulsion spray, and lubricant spray and dry coolants are defined as $scCO_2$, $scCO_2$ + lubricant, Ar, N_2, CO_2, and dry. The diffusivity constant D is larger for the dry lubricants suggesting that wear would occur at a higher rate.

As mentioned above, the slope of the regression lines in Figure 5.11 represents the activation energy (E_a) for Co to diffusive through the tungsten matrix in the tool. As cobalt diffuses out of the tool and is carried away on the workpiece or chip, the tool wears since cobalt is the binder that holds together the harder tungsten carbide grains. The experimentally determined results for the activation energy were on par with reports from other work. Crosskey et al report an activation energy of 288 kJ/mole (Crosskey and Gutierrez-Miravete 2007) and Jiang et al. reports 114 KJ/mole both for carbide tools on titanium (Jiang and Shivpuri 2005). The value found in this work is 211 kJ/mol.

A function was used to determine the sensitivity of the modeled result to the estimated surface temperature. The measured temperature change (ΔT_M) was expressed as a $f(\Delta T)=\alpha\Delta T_M$ and E_a was estimated for $f(\Delta T)=\Delta T_F$, the difference in temperature on the flank surface. Since $\Delta T_F \propto \Delta T_M$ and $|T_F| > |T_M|$ it is reasonable to assume that $\Delta T_F > \Delta T_M$. The results suggest that if ΔT_F is slightly higher than ΔT_M ($\alpha=2.3$), as expected, then the results approach the lower limit for E_a of 114 KJ/mole. When ΔT_F is lower than ΔT_M ($\alpha=0.7$), the results approach the upper limit for E_a of 288 KJ/mole. The close sensitivity of the experimental E_a with published values calculated under similar conditions suggests that the model is an accurate representation of the wear mechanisms for this system.

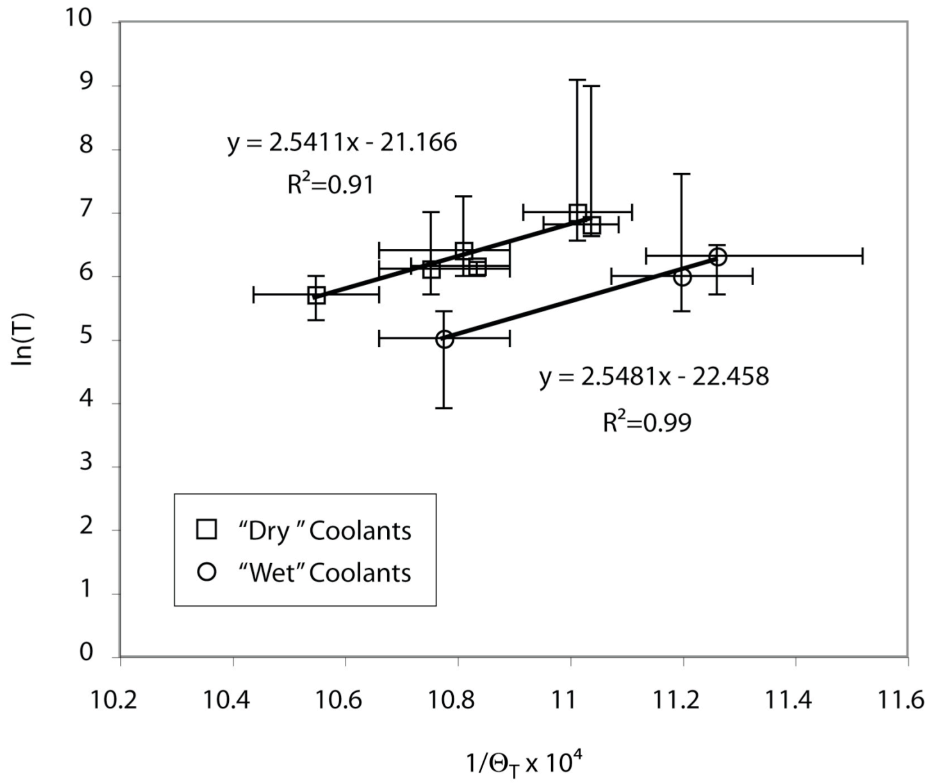


Figure 5.11. Correlation between tool life and insert temperature showing separation between conventional 'wet' MWFs and 'dry' MWFs.

5.5 Heat Removal at Higher Material Removal Rates

The results of this work showed that sprays of $scCO_2$ reduce flank wear more effectively than flood coolants. This is a dramatic advancement over other existing MQL sprays that perform significantly worse than conventional emulsion floods. To fully characterize the potential of $scCO_2$-sprays to improve manufacturing processes, it was necessary to evaluate their performance at a high material removal rate. Manufacturers refer to material removal rates as the general metric by which processes can be evaluated. Higher material removal rates with constant tool wear lead to increased productivity. For turning operations, material removal is proportional to speed.

One of the primary manufacturing limitations of high strength materials is that cutting speed must be intentionally slowed. The results described above were collected using an average cutting speed based on the tool manufacturers specifications to ensure controlled and reproducible wear rates. To capture the full potential of $scCO_2$-based MWFs it is necessary to consider their performance at higher speeds.

Cutting speed has been known for many years to be the primary variable influencing tool wear (Taylor 1907). The exponential relationship between wear and cutting speed is captured using the Taylor tool life relationship:

$$C = VT^n \tag{5.8}$$

where C and n are constants, V is the cutting speed, and T is the time to reach a specified wear limit. As discussed in the Chapter 2, n is largely determined by the tool material and for carbide tools is usually 0.2. C represents the cutting speed required to achieve the set wear limit for one unit of time.

A plot of tool life results and speed using liquid nitrogen (LN_2) and emulsion flood from the literature are plotted with a Taylor model approximation in Figure 5.12 (Venugopal et al. 2007). Low temperature (i.e. cryogenic) MWFs, such as LN_2, have been proposed to overcome the accelerated tool wear at higher speeds. The Veugopal et al. results confirm that wear rates follow an approximately log-linear decrease with increasing cutting speed as predicted by Taylor. The experimental results also suggest that as speeds increase, the benefits of LN_2 become less significant. At high speeds, tools wear quickly regardless of coolant efficacy. The definition of high speed varies from system to system and though the Venugopal et al. data was collected using 6Al4V Titanium and carbide tools, the grade was different and the cutting geometry were different making direct comparison of the data difficult. The general conclusions that the tool life improvements provided by MWFs are lower at higher speeds and that wear should follow a log-liner decrease are generally applicable to all MWF systems.

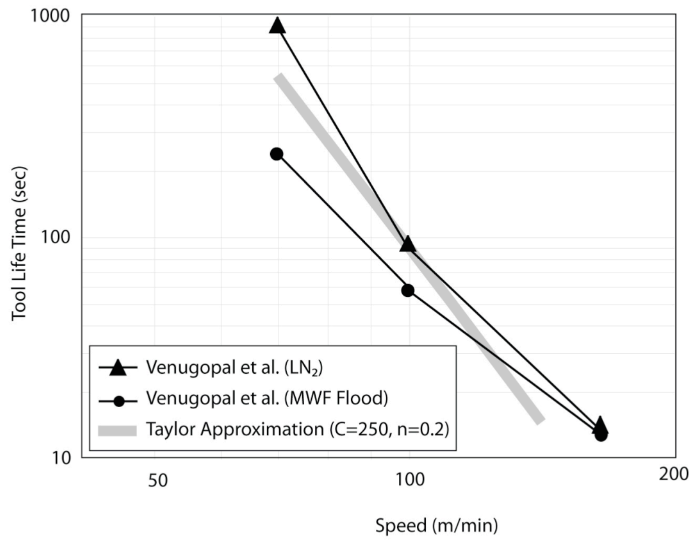


Figure 5.12. Taylor Tool Life prediction of literature data for titanium cutting using liquid nitrogen and flood emulsion showing the diminishing benefits provided by MWF at higher cutting speeds. Adapted from (Venugopal et al. 2007).

To determine the extent to which $scCO_2$-based coolants will decrease at higher speeds for CO_2-based coolants, $scCO_2$ + lubricant and emulsion Flood were used on the 6Al4V titanium alloy cut at 62 m/min cutting speed, a 25% increase over the conditions used to date for cutting titanium. The results show the same type of decrease in tool life with increasing speed as predicted by Taylor (Figure 5.13). At higher speeds, the difference between a $scCO_2$ + lubricant spray to the flank face only increased the tool life from 150 to 300 seconds. At these high speeds the spray of $scCO_2$ provide am improvement over MWF flood but the improvement is less extensive than the 1000 second improvement at a cutting speed of 42 m/min.

Recognizing that at higher speeds, heat generation rates are greater than the rate at which a single nozzle can cool, the experimental setup was modified to deliver $scCO_2$ via two nozzles, one from the flank and one from the rake face of the tool. The results, plotted in Figure 5.13 show that using a nozzle to both tool faces, tool wear may be more effectively controlled at higher speeds. This result, suggests that by incorporating two or more CO_2 nozzles or by increasing flow rates the cutting operation can ensure high tool life extensions under harsh machining conditions.

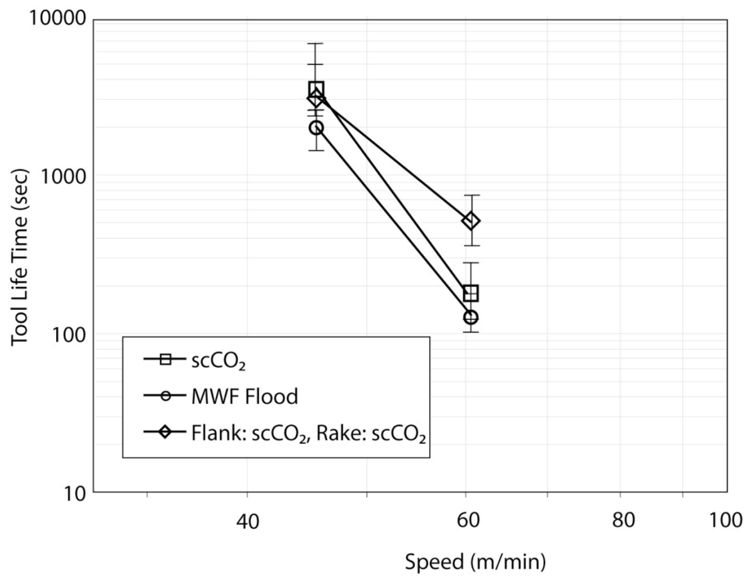


Figure 5.13. Taylor plot of experimental results showing that at higher speeds single nozzles of $scCO_2$ could have diminishing benefits unless multiple nozzles are used in which case tool life can be extended considerably.

5.6 Summary and Discussion

Sprays of $scCO_2$ and $scCO_2$ + lubricant were found to control flank wear significantly better than sprays of air + emulsion or air + lubricant. The wear rates of tools cut in the presence $scCO_2$ were lower than those obtained using floods of water based emulsions. The results were replicated on two difficult-to-machine systems: compacted graphite iron cut with PCD tools and 6AL4V titanium cut with carbide tools.

To explain the mechanism by which CO_2-based MWF reduce tool wear relative to emulsion floods or sprays in air, two models were used along with additional experiments. First, a model of heat removal over a flat plate was developed to characterize the cooling potential of $scCO_2$ sprays relative to conventional MWFs. It showed that under very high flow conditions, water-based emulsions remove heat more effectively than gas-based MWF although the formation of water-vapor near the cutting surface at lower flows can be a major impediment to effective heat transfer. This critical heat flux limitation of water-based coolants was observed experimentally using controlled laboratory experiments on a heat probe. To understand the operating conditions that influence heat removal potential of CO_2 sprays, several parameters were varied including the nozzle geometry, distance and offset between the spray and the heated source, temperature of the gas, and pressure of the gas. All were found to have a statistically significant effect on heat removal. It was concluded that by controlling operating conditions, CO_2-based MWF can remove heat as well as water-based MWF.

To evaluate the influence of scCO_2 spray cooling in machining, experimental trials were conducted on the single point turning of the PCD-CGI system. In these tests the importance of spray application direction in cutting became clear. scCO_2-based coolants provided significant reductions in flank wear when applied from the flank face but did not control flank wear as effectively as water based coolants when delivered from the rake face. This result indicated that scCO_2 was acting by effectively penetrating the flank face of the tool and delivering cooling locally to the heat source. To better understand this process, a second model was used to predict the heat-induced tool wear. The results of this analysis showed that temperature and wear rates of conventional 'wet' MWFs gas-based MWF cannot be used to accurately predict the results obtained using scCO_2 and other 'dry' MWFs. Tools cut using these 'dry' MWFs achieved higher temperatures during machining but wear rates were lower because the impact on the flank face was mitigated through the improved penetration of gas-based MWFs.

To determine whether the enhanced cooling provided by scCO_2 was solely responsible for the improved wear rates, several other high-pressure gases were tested. Both argon and nitrogen were tested using the same experimental conditions and it was found that they controlled wear more effectively than sprays of air + emulsion and air + lubricant. However, these gases did not cool as effectively as high pressure CO_2 and also resulted in higher wear rates. This result suggested that inhibiting oxidation at the cutting surface will lead to reduced wear but that improved cooling is also necessary to effectively control wear better than conventional floods of emulsion.

The results of the experimental and modeling efforts showed some very clear advantages possible using scCO_2-based MWFs, namely that they more effectively control flank wear in turning by penetrating the cutting zone and removing heat. But these results also exposed a limitation in the experimental conditions because the CO_2 flows tested did not effectively reduce the temperature through the entire bulk of the tool. For higher material removal rate conditions where the increased machining speeds result in higher temperatures, CO_2-flow rate could be a limiting factor. To evaluate this hypothesis, turning tests were conducted at the upper limit of speeds commonly reported for titanium cut with carbide tools. Consistent with the Taylor tool life equation, a log linear decrease in tool life and the importance of MWFs results from the increase in speed. To overcome the more rigorous high speed conditions, two sprays of scCO_2 were applied to the cutting zone, one on the flank and one on the rake. The results showed a significant increase in tool life at higher speeds using the dual-nozzle delivery system suggesting that multiple nozzles or even larger flows of CO_2 could be used to extend the scope of CO_2-based MWFs.

The general result that high-pressure sprays to the flank effectively reduce tool wear is not entirely novel. Several papers have reported on the use of high-pressure sprays on conventional water-based MWF in cutting (Ezugwu et al. 2007; Kovacevic et al. 1993). Researchers have found good improvements in tool life when using these high-pressure sprays of water-based coolants at pressures of 100-200 bar, as high as those reported in this work, though magnitude of the improvement cannot be directly compared quantitatively with the results in this work because a milling testbed was used instead of turning.

The successful delivery of high pressure water-based MWF by other research groups confirms the general conclusion of this chapter that more effective cooling in turning processes can assist in lowering tool wear but it presents many questions that are not addressed in the literature. The first question is that the delivery of high-pressure sprays of water can interfere with machining function as the forces produced by such a high-pressure jet of water-based fluid are significant (Ezugwu et al. 2007). At best, the use of high-pressure water jets requires that a machine operator learn how to modify system operating parameters to account for the forces generated by the high pressure sprays of MWF. More likely, new machines would be required to handle the higher-pressure sprays of MWF. The second question deals with the environmental and occupational implications of dramatically increasing the flow rate of water-based MWFs. At a minimum this would increase the energy consumption required to deliver MWF and likely increase the other environmental and occupational health impacts of MWF. Both the technical and environmental barriers to the high-pressure delivery of water-based coolants could outweigh any tool life improvements making high-pressure gas-based MWF more attractive. In Chapter 6, the overall life cycle impacts of MWFs are explored to understand how aqueous flow rates and MQL delivery conditions can impact the environmental emissions and energy consumption of water, air, and CO_2-based MWFs.

CHAPTER 6

Life Cycle Emissions and Energy Comparison

A high performance alternative to conventional MWFs is not generally viable in a manufacturing setting if the environmental impacts of the fluid are much higher than those of conventional systems. Carbon tetrachloride, for example, is one of the best know MWFs available but its carcinogenic properties make it impractical in any machining operations. Water-based MWF systems produce mists and hazardous waste that are increasingly problematic for manufacturers facing stricter government oversight on occupational health or toxic releases. Carbon dioxide can eliminate some of the problems associated with water-based MWFs, though it is a potent global warming gas that is being increasingly scrutinized by the environmental community. This chapter explores the life cycle impacts of MWFs to facilitate an informed comparison of the environmental impacts of bio-based, MQL, and $scCO_2$-based MWF options.

The chapter begins by describing the model development and the data acquisition conducted for the life cycle inventory. Each of the life cycle stages including material production, use, and disposal is described. Then the model presents the results of the life cycle study in terms of eight impact factors including global warming potential and energy-use. The impacts are considered with respect to a detailed sensitivity analysis that includes user-defined operating conditions such as flow rate and oil concentration. The chapter concludes with a discussion of the qualitative factors such as safety and human toxicity, factors that are difficult to quantify in the context of a traditional LCA assessment but that would significantly influence the MWF selection process.

6.1 Introduction

Water-based MWFs have been widely cited in the literature for their negative environmental and health impacts (Figure 6.1). A search of approximately 500 articles on the topic of metalworking showed that three quarters of the articles reported human health, contamination, and worker safety as a keyword. Ecological toxicity, water use, and fugitive emissions were also reported in a number of cases. The health concerns exist due to the misting of water-based MWFs, which leads to pulmonary exposures of chemical additives, surfactants, and bio-aerosols among manufacturing workers. An authoritative catalog of these health concerns was first documented by OSHA in 1998 and led to the recommendation to significantly reduce standard workplace mist concentrations (OSHA 1998). The ecological toxicity concerns associated with MWFs exist due to their chemical content (e.g., chlorinated fatty acids and chelating agents), their ability to carry metals through waste treatment plants, and other treatment issues such as biochemical oxygen demand and oil content. The United States Environmental Protection Agency has recognized the problem and passed the Metals Products and Machinery Rule in 2003 to begin to improve disposal standards at metals manufacturing plants (EPA 2003).

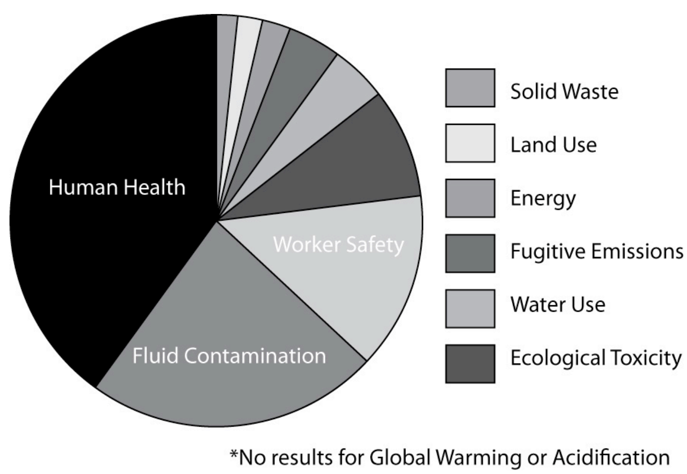


Figure 6.1: Relative interest in the environmental and health impacts of MWFs as reported in the academic literature. Developed by performing a search for the terms "Metalworking Fluid and 'X'" where 'X' is the exact term used in the plot. 9 databases (ArticleFirst, General OneFile, ISI Web of Science, Mirlyn, OAIster, ProQuest, Readers Guide Abstracts, Wilson Select Plus, and Engineering Village) were searched with a total of 635 articles selected as relevant. The articles represent only those published 1/1/80 and the day the search was conducted, October 24, 2007.

These environmental and health concerns have led to the development of environmentally adapted lubricants (EALs). EALs are defined by the European Union as lubricants that have high biodegradability and low toxicity with performance equal to or better than conventional alternatives (D.Theodori et al. 2004). In MWFs, the EAL concept has so far been synonymous with the substitution of petroleum-based lubricants with vegetable-based lubricants in conventional water-based formulations (Honary and Boeckenstedt 1998). Recently manufacturers are starting to have success applying Minimum Quantity Lubrication (MQL) strategies involving low-volume sprays of petroleum-based oil delivered in compressed air. In principle MQL systems deliver oil exactly at the rate the oil is consumed by the process while in reality the excess is typically carried out with the metal part and is hardly noticeable in a practical sense (Filipovic 2006). External MQL sprays that are not delivered through the tool can generate mists that require control strategies similar to water-based MWFs, although these mists do not contain chemical additives or microbial by-products and are more easily controlled due to their low volume of application (Andersen et al. 2004).

The MQL approach eliminates large volumes of aqueous waste and can be applied in a manner that results in essentially a mist-free work environment (Stoll et al. 2007). MQL also eliminates the maintenance and disposal operations associated with water-based MWFs (Silva et al. 2005), which significantly reduces both cost and environmental impact (Adler 2006). Therefore MQL can solve the most important environmental and health issues associated with today's water-based MWFs. However, lubricant-in-air MQL technology cannot be universally applied since it does not provide sufficient cooling for all manufacturing operations (Furness et al. 2006).

This dissertation has explored the feasibility of using minimum quantity sprays of lubricants dissolved in supercritical carbon dioxide. $scCO_2$ effectively dissolves lubricants and the rapid expansion of the supercritical solution (RESS) out of a nozzle forms chilled microparticles of lubricant. This rapidly expanding CO_2 spray provides a cooling function that permits the benefits of MQL to be extended to a greater number of manufacturing operations.

Although all EALs promise to reduce the impacts of conventional MWFs, the technologies are relatively new and face technical and economic barriers to implementation. The relative environmental emissions of these systems also have yet to be quantified in the literature. Therefore this research effort to better understand the relative environmental emissions of benchmark EAL technologies, so that future investments in infrastructure, time, and effort can be evaluated in context with the relative environmental emissions of competing approaches.

6.2 Definition of MWF Systems Considered

Three representative EAL technologies were selected for comparison in this work (Table 6.1):

1) A microemulsion of rapeseed oil-in-water
2) A dispersion of mineral oil-in-compressed air
3) A solution of rapeseed oil-in-supercritical CO_2

In this chapter, these MWF are compared with a benchmark microemulsion of mineral oil-in-water that has been extensively researched in the literature (Zhao et al. 2006; Zimmerman et al. 2003a). This formulation includes water, oil, and an emulsifier system comprised of a mixture of nonionic and anionic surfactants (Clarens et al. 2004b). All water-based MWFs include other proprietary additives that are not required in MQL systems such as corrosion inhibitors, defoaming agents, and biocides. Such additives are not included in the life cycle emissions model but are discussed qualitatively in the discussion section of this chapter. The compositions of the benchmark microemulsion, along with the composition of the three alternative EALs, are listed in Table 6.1.

Table 6.1. Metalworking fluid classes considered in this study. EAL = Environmentally Adapted Lubricants, MQL = Minimum Quantity Lubrication, RESS = Rapid Expansion of Supercritical Solutions. Formulations are in weight %.

Class	Conventional	EAL	EAL,MQL	EAL,MQL,RESS
Components	**Petroleum oil in water**	**Rapeseed oil in water**	**Petroleum oil in air**	**Rapeseed oil in $scCO_2$**
Comments	microemulsion benchmark	bio-based microemulsion	nozzle mixes oil in high pressure air	oil dissolved in $scCO_2$ sprays at high velocity
Oil	0.75	0.75	1	1
Anionic Surfactant				
sodium petroleum sulfonate	0.3			
alcohol sulfate		0.25		
Nonionic Surfactant				
diisopropanol amine	0.4			
ethoxylated glycerol ester		1.25		
Water	98.55	97.75		
Compressed Air			99	
CO_2				99

6.3 Development of LCA Model

A visual representation of the life cycle analysis (LCA) scope for the water-based, air-based, and CO_2-based MWFs is provided in Figure 6.2. For the comparative LCA model, the service of a MWF provided to one machine tool for one year was selected as the functional unit. It was assumed that the number of parts produced per unit time did not vary depending on the MWF type selected. The machining time selection of one year was based on the production schedule used at a major automotive power-train facility in Detroit, MI. It was assumed that a schedule of 102 hours/week and 42 weeks/year is representative of the machine times used at other large metals manufacturing facilities.

Most manufacturing facilities are moving away from the use of centralized distribution systems because of high maintenance costs and because these systems are difficult to modify as production lines change. Auxiliary processes such as filtration and continuous circulation that are required to maintain a large volume of water-based MWF in a centralized system were not included since MQL systems are not centralized, and only in large factories are water-based systems centralized.

The LCA model quantifies the environmental emissions and energy use associated with the products and processes used to produce, deliver, and dispose each MWF. The reference country for the analysis is Germany since data regarding bio-based oil and surfactant production were available and complete in the literature. Water production and electricity generation were based on German data. Impacts associated with the transportation of MWFs from production facilities to use facilities were excluded because they were expected to be negligible and similar for both volumes used and distances shipped for each MWF system. Impacts from the transportation of carrier fluids (e.g. high pressure CO_2 and air, water) were assumed to be small because these commodity chemicals are typically produced and consumed within close proximity. A schematic of the systems and the boundaries of the study is provided in Figure 6.2.

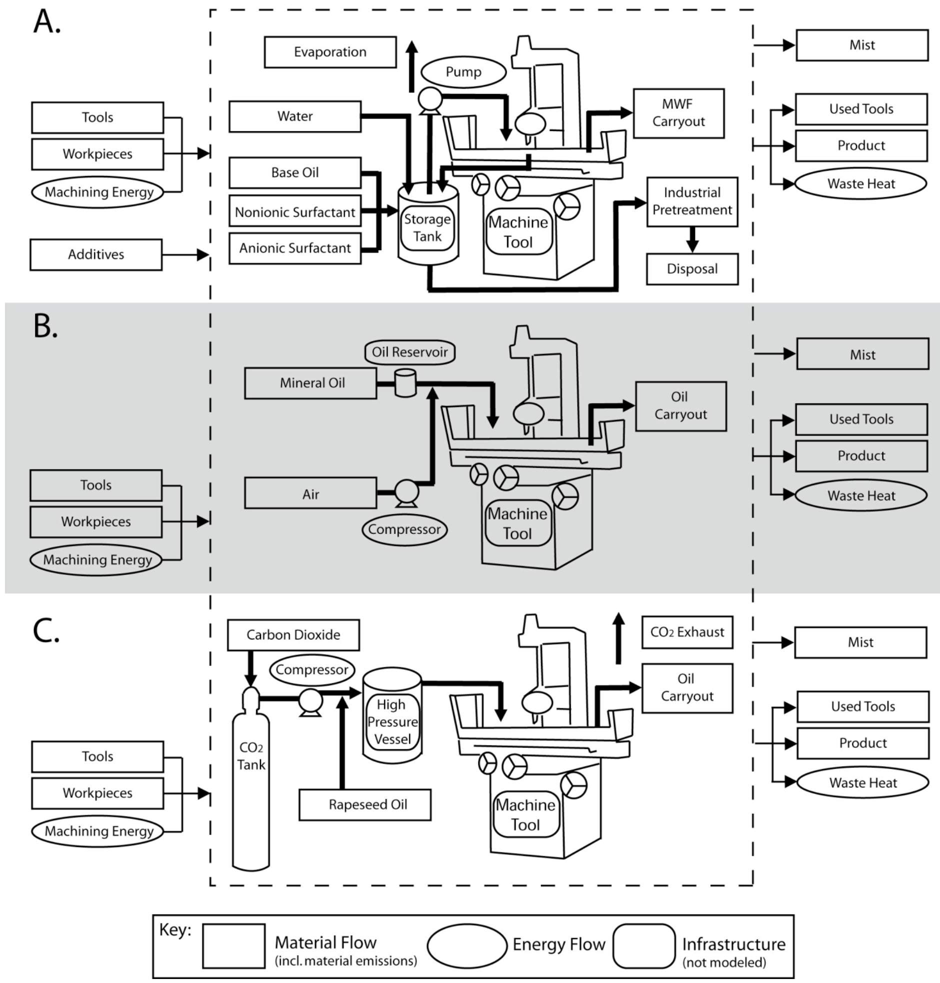


Figure 6.2. Schematics of MWF systems considered in this research: A. microemulsion of petroleum oil or rapeseed oil in water, B. petroleum oil in air, C. rapeseed oil in CO_2. Dotted lines bound components or processes included in the life cycle model.

6.3.1 MWF Production

Each of the four MWFs is comprised of lubricant oil and a lubricant carrier (water or gas). Emulsifiers are used to stabilize the oil in water-based systems and are not required in gas-based systems. Either petroleum-based oil or bio-based oil can be carried in water or gas. Presently, petroleum oil dominates air-based MQL systems and $scCO_2$ systems have been primarily developed using bio-based oil. The production of lubricant and carrier materials is discussed below. The overall material and energy flows for the petroleum and bio-based compounds are presented in Figure 6.3 and Figure 6.4 respectively.

Petroleum-based Lubricant and Surfactants: The benchmark MWF contains mineral oil and surfactants based on petroleum feedstocks. Producing these components requires the distillation of crude oil and the processing of distillation products. Since crude oil refinement creates several by-products, the emissions of this process were allocated using a mass percentage, based on 1.9 liters of lubricating oil produced per barrel (159 liters) of crude oil (McManus 2001). Sodium petroleum sulfonate is an anionic surfactant produced by reacting linear alkyl benzene with sulfur. Diisopropanolamine is a nonionic surfactant made by reacting propylene oxide and ammonia. Environmental emissions from the production of sodium petroleum sulfonate and diisopropanolamine were estimated from (Berna et al. 1995) and respectively (Postlethwaite 1995).

Vegetable-based Lubricant and Surfactants The processes required to convert rapeseed and corn crops into lubricant oil and surfactants include the production of diesel for farm equipment, the production of fertilizers and pesticides for farming, and the distillation of crude oil for process chemicals used to purify the bio-based components. Rapeseeds (also known as canola) are produced through seedbed preparation, sowing, fertilizing, pesticide application, growth, and harvesting (McManus 2001). The seeds are converted to oil through drying, storing, crushing, and refining. Alcohol sulfate is an anionic surfactant made from coconut oil (Hirsinger and Schick 1995) and polyethoxylated glycerol ester is a nonionic surfactant made by reacting glycerol with straight chain alcohol ethoxylates (Schul et al. 1995).

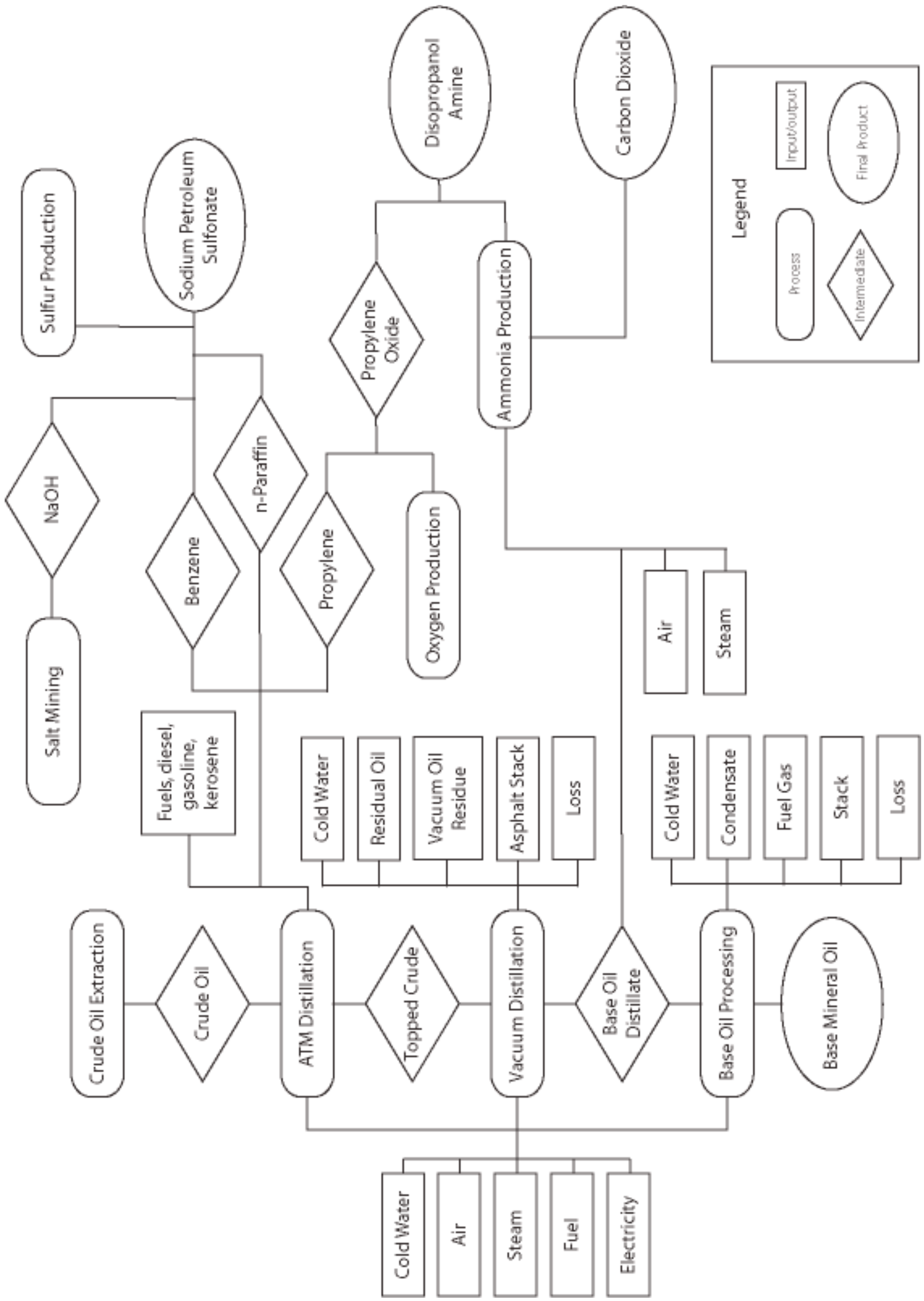


Figure 6.3. Schematic for the production stages of the oil and emulsifier system for petroleum-based products in MWF systems. Adapted from (Zimmerman 2003)**.**

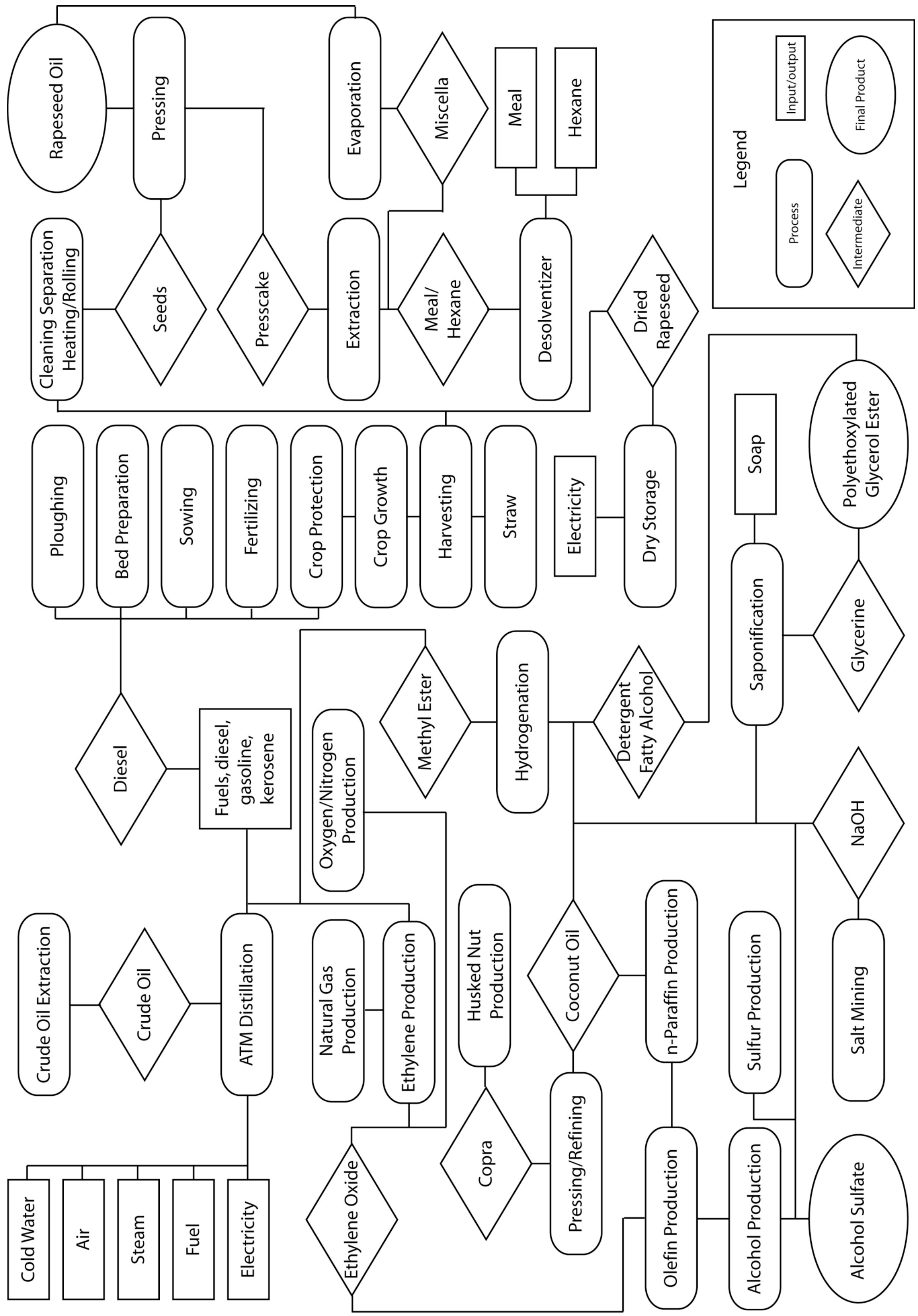


Figure 6.4. Schematic for the production stages of the oil and emulsifier system for bio-based semi-synthetic metalworking fluid components. Adapted from (Zimmerman 2003).

Lubricant Carriers: The production of water by municipal water distribution systems was accounted for using German data sources (Frischknecht and Jungbluth 1996). The CO_2 used in industrial processes is typically recovered as a saleable waste product from the steam reforming of hydrocarbons as required to produce hydrogen (Overcash et al. 2007). Most of this hydrogen in used to produce ammonia (Kirk-Othmer 2006) so emissions and energy consumption were therefore accounted for considering the production of CO_2 as a byproduct of ammonia production using a price allocation. The price allocation is selected here since CO_2 can be produced using other significantly different processes, and the use of CO_2 for MWF is unlikely to influence the market for CO_2. For all results it was assumed that CO_2 was obtained from ammonia synthesis (unless otherwise noted) and a cost allocation was used for CO_2 with other components allocated on a mass basis. A mass allocation for CO_2 is presented and a discussion on the allocation impacts on the analysis results is provided.

6.3.2 Life Cycle Phases

Use Phase: MWFs are delivered to manufacturing processes by pumping them from a reservoir attached to the tool. The pumping energy is a significant factor in the analysis, and depends heavily on the MWF application rate which can vary greatly in practice (Sheng and Oberwalleney 1997). For this reason, emissions and energy consumption for this work are reported explicitly as a function of flow rates typical of industrial practice. The production of the MWF delivery equipment (e.g. pumps, compressors, tanks) was not considered since these environmental impacts are relatively small compared to the use phase, and the equipment is reasonably similar across all systems being compared here (Olner 1996).

The electricity consumption for pumping or compressing the fluid during delivery to the workpiece was directly accounted for in the analysis. The electricity utilized to operate the pumps for MWF distribution was modeled using data describing the average emissions from the European power grid. For instance, this grid was assumed to emit approximately 137 g CO_2 emissions from the generation of 1 MJ of electrical energy (Frischknecht and Jungbluth 1996).

The electricity consumption rates for the aqueous, MQL, and CO_2-based fluids were calculated using equations 6.1 and 6.2. A single machine tool using aqueous MWFs requires an individual pump to circulate the fluid from a 55 gallon tank to the cutting zone (Equation 6.1). Air or CO_2 must be brought up to operating pressures using a compressor before use (Equation 6.2).

$$W_p = \frac{gh}{\eta} \text{ where } h = \frac{P_o - P_i}{pg} \tag{6.1}$$

$$W_C = \frac{c_p T_i}{\eta}\left[\left(\frac{P_o}{P_i}\right)^{\left(\frac{\gamma}{\gamma-1}\right)} - 1\right] \tag{6.2}$$

The work to pump the aqueous fluid was calculated as a function of the force of gravity (*g*), the liquid head (*h*), the pump efficiency (η), the inlet and outlet pressure (P_i and P_o), and the density of water (ρ). The work to compress the gas (W_c) is a function of the specific heat of the gas (cp) thjbze inlet Temperature (T_i), the adiabatic efficiency of the compressor (η), the inlet and outlet pressures (P_i and P_o) and the specific heat ratio (γ).

During use, MWF deteriorates and is also lost to evaporation, leaks, spills, mist, and residue on chips and workpieces (Skerlos and Zhao 2003). Due to the large variability that can be observed between similar manufacturing facilities, the energy and emissions results are reported as a function of the consumption rate of the fluid. For water-based MWF systems, this is a bulk liquid replacement rate (usually liters per week) and for MQL this is a flowrate (grams of oil or liters of air per minute) and a lubricant flowrate (milliliters per hour) (Itoigawa et al. 2006).

End-of-Life For MQL systems, the MWF is a single-use product where the gas volatilizes and the oil is carried out on the manufactured workpiece at relatively low flow rates. Therefore no disposal treatment operations were considered for the MQL systems. For water-based systems, the MWF is a re-used product that it is collected and recycled until it fails (or is replaced on a schedule) after a period of weeks or months (Zimmerman et al. 2004). In this analysis, two options were considered: disposal directly to a municipal wastewater treatment plant and disposal by evaporation followed by incineration. Significantly extending the useful life of the water-based MWFs using advanced recycling technology based on continuous membrane filtration was also considered (Skerlos et al. 2001b).

Waste-water Treatment: Most MWF are treated through a combination of industrial and municipal wastewater treatment processes. Preliminary stages of treatment involve separation of oils through flocculation or foaming processes. After discharge to the municipal water system, biological treatment and polishing steps can be used to reduce the concentration of organics and metals in the wastewater stream. Wastewater treatment is by far the most commonly encountered EOL technology and was therefore modeled as the nominal scenario in this analysis (Taylor et al. 2003).

Incineration: Separation and collection of oily sludge from the MWF waste for incineration can offset some electricity production but the air emission impact factors associated with that process are then allocated to the MWF.

Filtration: Microfiltration was modeled by assuming that introduction of a weekly filtration operation on a tank of MWF would reduce the replacement frequency from 6 times/year to 1 time/year. The energy to run the microfiltration operation was added to the use-phase energy loads for these fluids. At the end of life, the fluids were disposed of via wastewater treatment.

Part Cleaning In many industrial applications metal parts are cleaned to remove oily MWF residue before painting or assembly. This cleaning process typically takes place using organic solvents or aqueous mixtures involving detergents, both of which can have an environmental impact. Cleaning was not included in this analysis, however, because the authors assumed that part cleaning is driven primarily by downstream use (Lorincz 1994). If parts must be degreased prior to painting, for example, they will be cleaned regardless of the MWF used. Several studies have reported that workplaces using MWFs delivered in air produce cleaner workplaces and cleaner parts than those using aqueous fluids (Furness et al. 2006). Although the same has been observed for CO_2 parts, both of these technologies are new enough that it would be difficult to generalize about the reduced cleaning loads in a meaningful way. Assuming that cleaning processes are the same for all MWF systems is therefore a conservative assumption that, if included in the analysis, could further support the conclusion that a switch away from water-based fluids is environmentally preferable.

6.4 Results

The environmental emissions associated with the use of MWFs were characterized according to seven categories: water use, toxic emissions to water, solid waste, land use, nonrenewable energy consumption, global warming potential, and acidification. Water consumption was expressed as kg/yr and included all the water integrated into the MWFs or used in production processes. Aquatic toxicity was calculated by normalizing to Pb equivalents and summing the concentration of Cr(III), Cu(II), Pb(II), Ni(II), Zn(II), and Cd(II) as effluent to water (Cheng et al. 2005). These metal ions are leeched to the MWF from machine tool and workpiece alloys. The normalization was performed using the EC50 concentrations (concentration affecting resulting in a 50% acute mortality of aquatic test species) reported in the literature as an aggregate of arthropod and plant toxicity (Haye et al. 2007). Solid waste production was expressed without capturing any differences in the hazard of the waste. Land use represents all the cultivated land used to produce the agricultural feedstock in the MWF components. Nonrenewable energy was expressed as MJ and represents the sum of coal, natural gas, and petroleum required to produce a MWF component or operate a MWF delivery system. Global warming potential (GWP) was expressed as CO_2 equivalents over a 100 year time horizon and forcing factors for methane and nitrous oxide were used to normalize the data. Acidification was measured in terms of SO_2 emitted.

The results are presented in Figure 6.5. It is observed that for water-based MWFs, a switch from petroleum to rapeseed oil lubricants can produce modest reductions in GWP and acidification but these reductions are associated with increases in energy, solid waste, and land use. The reduction in GWP for rapeseed oil is associated with sequestered CO_2 from growing the oil seed. This reduction is overcome by increased non-renewable energy required to farm and process the rapeseed oil and to produce the surfactants causing further CO_2 emissions. The reduction of GWP is significant in a relative comparison between the two water-based fluids (~60% reduction) but not too significant in an absolute sense (reduction equivalent to about ~10% of the emissions from an average U.S. automobile for one year). The categories listed in Figure 6.1 that are most often cited as significant MWF concerns are largely unchanged in the switch from mineral oil to vegetable oil MWFs.

In contrast to the relatively minor differences between rapeseed oil and mineral oil MWFs delivered in water, Figure 6.5 illustrates that switching from water-based to gas-based MWFs results in a significant reduction in environmental emissions for the key categories listed in Figure 6.1. The switch from water-based to gas-based MWFs results in major reductions in water use, toxic emissions to water, and solid waste. Gas-based MWFs do release approximately 800 kg more GWP per year than conventional mineral oil in water MWFs. But this increase is likely to be smaller in large manufacturing facilities where the circulation pumps and coarse filtration systems produce large energy loads. In relative terms, an increase of 800 kg of CO_2 is less than 20% of the GWP released by the average US automobile when driven 12,000 miles per year. To further contextualize these emissions, the GWP of MWF are compared to other emissions from metals manufacturing and found to be small. If it is assumed that an average machine tool consumes 30 kW (in reality, machine tool energy loads vary considerably and this number is intended solely to provide a ballpark estimate), that would produce 70 times as much CO_2 per year than a CO_2-based MWF (Narita et al. 2006) (assuming an emissions factor of 136 gCO_2/MJ for the German grid (Frischknecht and Jungbluth 1996)).

The result that gas-based MWFs have lower environmental emissions than water-based MWFs in most impact categories is robust to different end-of-life options that can be considered for water-based fluids. As shown in Fig. 6.5, the environmental emissions from water-based MWFs can be reduced significantly by microfiltration recycling. Overall, however, the gains made by microfiltration are smaller than the gains made by moving from emulsified MWFs to the MQL systems considered here. Incineration of the waste to recover the embedded energy does reduce the energy requirements over the life-cycle but overall it is not an improvement because it does not reduce water use or aquatic toxicity and it significantly increases GWP and acidification. The results indicate that extending the MWF usable life using filtration reduces the magnitude of all impact areas relative to the other end of life schemes (Figure 6.6). The disposal reduction provided by filtration was assumed to be 6 fold but this was conservative and microfiltration technologies have the potential to increase useable life of aqueous MWFs even more. Wastewater treatment can result in unintended discharges to streams causing them to exceed permitted levels of metals or fats oils and greases. By reducing the amount of MWF discharged annually, filtration reduces both production and disposal costs. Incineration does offset some of the primary pumping energy but it is markedly unfavorable in all other impact areas.

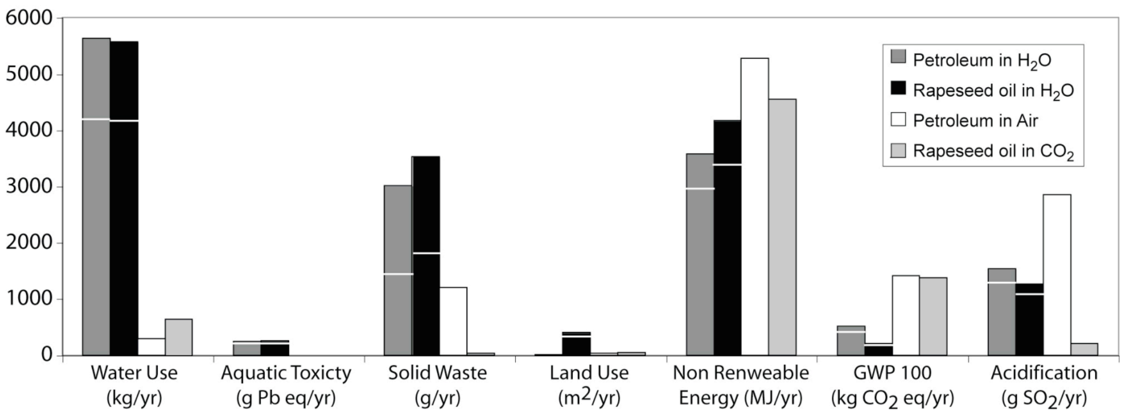


Figure 6.5. Life cycle impacts for the four MWF systems evaluated in this work based on expected application conditions. White lines for aquatic systems represent approximate reductions possible if implementing microfiltration recycling.

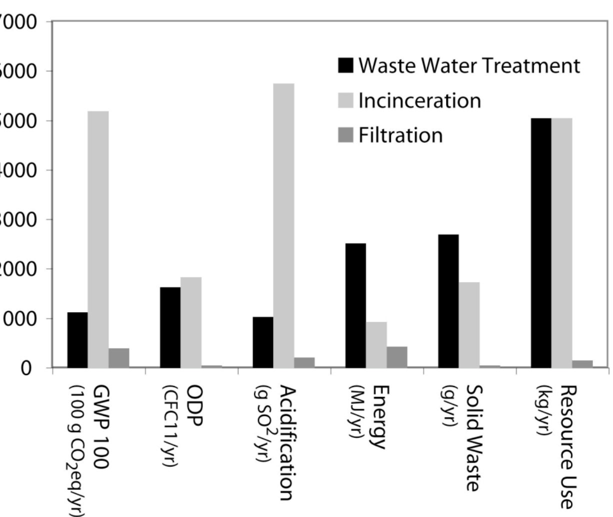


Figure 6.6. End of life impacts for the two water based MWFs for wastewater treatment incineration and filtration of MWF in use to extend the life of the fluid.

Two other impact factors were calculated but not presented in the final analysis because the impacts for all systems were small. Pesticide use was calculated from values presented in LCA databases for canola and corn production. The overall usage to produce the oils used in the study were <1 g per year. Ozone depletion potential (ODP) was calculated as equivalents of CFC 11 where CFC 12, 13, 14 and HCFC 21 were included. The values here were also on the order of a g/year suggesting that both the differences and magnitude of differences between systems would not significantly contribute to the impacts.

The results shown in Figure 6.5 are based on MWF use estimates gained from typical applications but can change significantly depending on and at the discretion of factory operators and machinists. Operating flowrates, pressures, and replacement intervals (for water-based MWFs) all have a significant impact, for instance, on energy consumption as shown in Figure 6.7. The largest and smallest reasonable values and appropriate scales to consider have been selected for this analysis. The general conclusion is that it is possible to run any of the systems in a way that it is much better or much worse than the alternatives selected. However, it should be noted that for some machining operations very low flow rates do not provide adequate cooling and lubrication. Generally speaking, the gas-based MWFs are more effective delivery approaches for oil at low flow rates in machining than water-based MWFs.

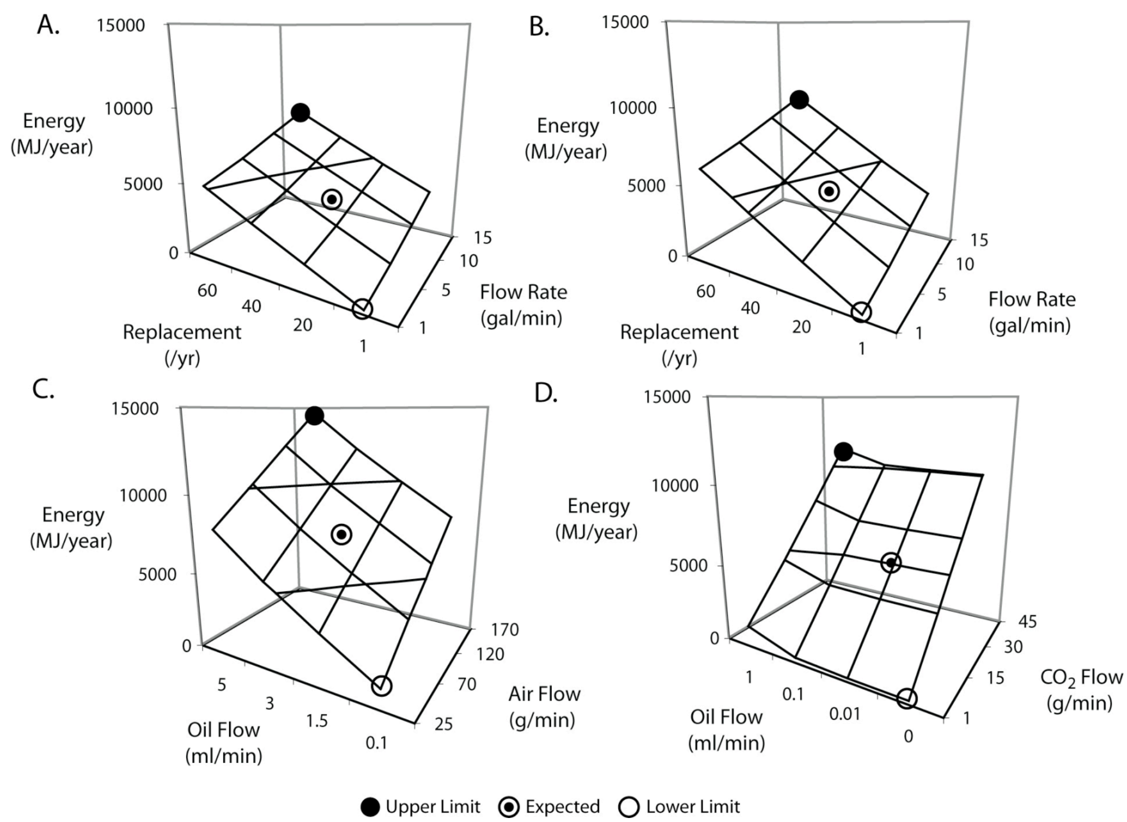


Figure 6.7. Nonrenewable energy requirements for the production and use phase for 4 MWF systems: A. petroleum in water; B. rapeseed oil in water; C. petroleum oil in air; and D. rapeseed oil in CO_2 as a function of operating parameters: flow rate; replacement frequency; oil flow. Upper and Lower limits represent heavy and light use of the MWF while expected values represent normal operating conditions.

For the petroleum in air system, increases in the air compression and oil flow rates can drive up the life cycle energy requirements of the fluid. This is in contrast to the $scCO_2$ system, which generally consumes much less oil, but for which energy per unit of CO_2 flowrate is higher due to the energy embedded in the ammonia synthesis process which produces CO_2 as a by-product. Other production processes for CO_2 are possible and these are discussed in the next section. The energy requirements of the air and $scCO_2$ compressors are significantly higher than the energy requirements of the emulsified MWF pumps but the mass flows of air or $scCO_2$ are much lower than the flow of water. Therefore the energy requirements for delivering the gases are on the same order of magnitude as that for delivering water. The results suggest that the energy loads for all four MWFs are comparable but that for MQL and $scCO_2$-based MWFs, modest reductions in flow rates can produce large energy efficiency gains. Such gains seem likely given that both technologies are relatively new.

A sensitivity analysis was performed to better characterize the MWF systems included in the study and understand the effects of model inputs on the results. A range of values was selected for each model parameter as shown in Table 6.2.

Table 6.2. Model input values used in the sensitivity analysis. Flows of individual components can be determined by combining these numbers with those from Table 6.1

	Low	Expected	High	Unit
Petroleum oil in H_2O	1	5	10	Gal/min
	9.7E5	4.8E6	9.7E6	kg pumped/yr
	0	24	50	Replacements/yr
	190	4548	9475	kg produced/yr
Rapeseed oil in H_2O	1	5	10	Gal/min
	9.7E5	4.8E6	9.7E6	kg pumped/yr
	0	24	50	Replacements/yr
	189.5	4548	9475	kg produced/yr
Petroleum in Air	0.1	1	2	Oil ml/min
	23	231	462	Oil kg/yr
	2	3	5	Air pressure (bar)
	2.0E5	3.4E5	5.5E5	KJ/yr
Rapeseed oil in CO_2	0	0.1	1	% w/w oil in CO_2
	0	3.85	77	Oil kg/yr
	0.1	15	30	CO_2 g/min
	26	3855	7711	CO_2 kg/yr

*Air delivered at a constant flow rate of 60L/min

To understand how the operating conditions influence all of the impact factors, the model was run for each of the operating conditions listed in Table 6.2. The results are shown in Figure 6.8. For the lower limit, the results suggest that air-based MQL systems, even at low flow rates, have a large impact, primarily from the energy required to compress the large amounts of air typically used. Through proper maintenance and infrequent replacement, aqueous MWFs have the advantage that they can be internally recycled within a process effectively reducing the impacts. But the smallest impacts across all impact factors under the lower limit in the sensitivity analysis are from the CO_2-based MWFs. CO_2-based MWFs in many processes (such as the one described in Chapter 5) require very little lubrication and so all of the impacts under these conditions came from a small flow of CO_2. Under worst-case conditions and most conservative case, the results of the general conclusion of this study holds i.e., gas based MWF tend to have lower impacts across the board.

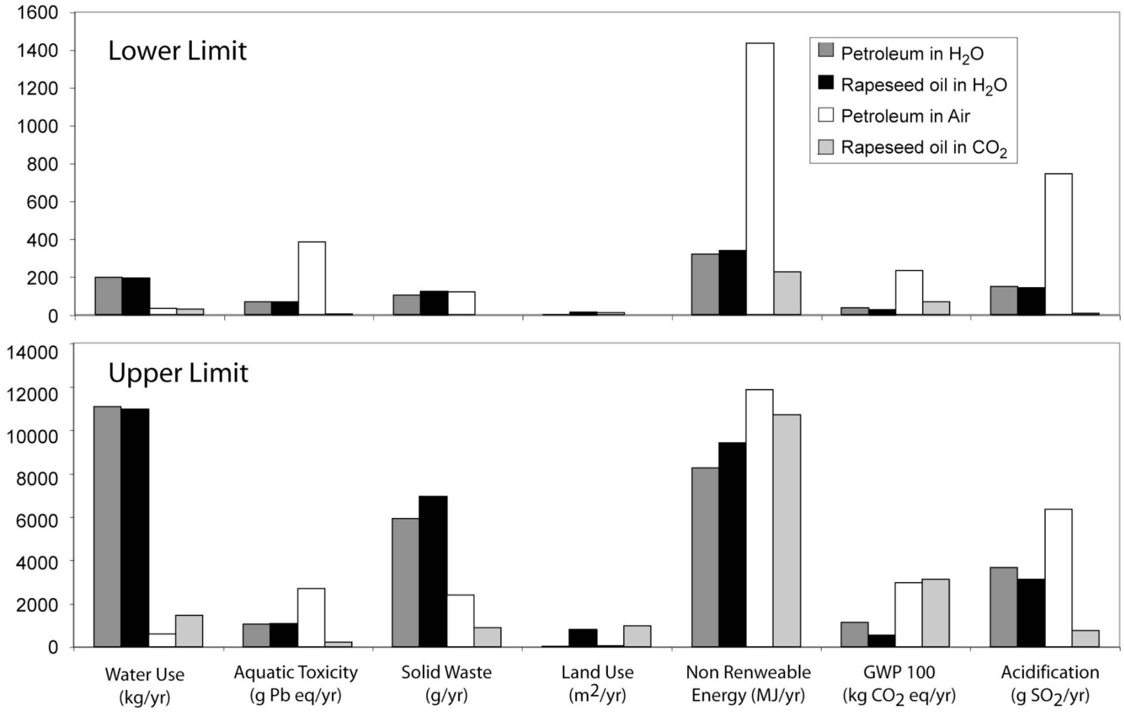


Figure 6.8. Lower and upper operating conditions for life cycle impacts for the four MWF systems. Operating conditions can affect which MWF system performs the most favorably.

The results should be interpreted recognizing that variations in these systems are possible. For example, petroleum oil can be delivered in CO_2 rather than water or air. In light of the possible variations and the sensitivity analysis selecting operating conditions such that MWF is delivered in the precise quantities needed to operate the process without excess seems the most prudent approach for reducing impact.

Figure 6.9 presents the emissions differences associated with delivering rapeseed oil in water, air, and CO_2 at the baseline flowrates that would be typical of practice today (the nominal values shown in Fig. 6.5). The results indicate that in all impact areas except water use, GWP, and energy, MWFs delivered in CO_2 have the lowest emissions. The amount of water, GWP, and energy associated with the MWFs delivered in CO_2 are almost entirely dependent on the allocation assumptions used in the methodology. For this analysis a price-based allocation of emissions from the ammonia synthesis process was utilized for CO_2 production. A mass-based allocation for CO_2 would increase the numerical values significantly, while a marginal price-based allocation would decrease the numerical values significantly as discussed further below. Overall the results suggest that delivery of minimum quantities of lubricant in gas carriers, regardless of the feedstock, in gas carriers, is the most effective way to reduce environmental impacts.

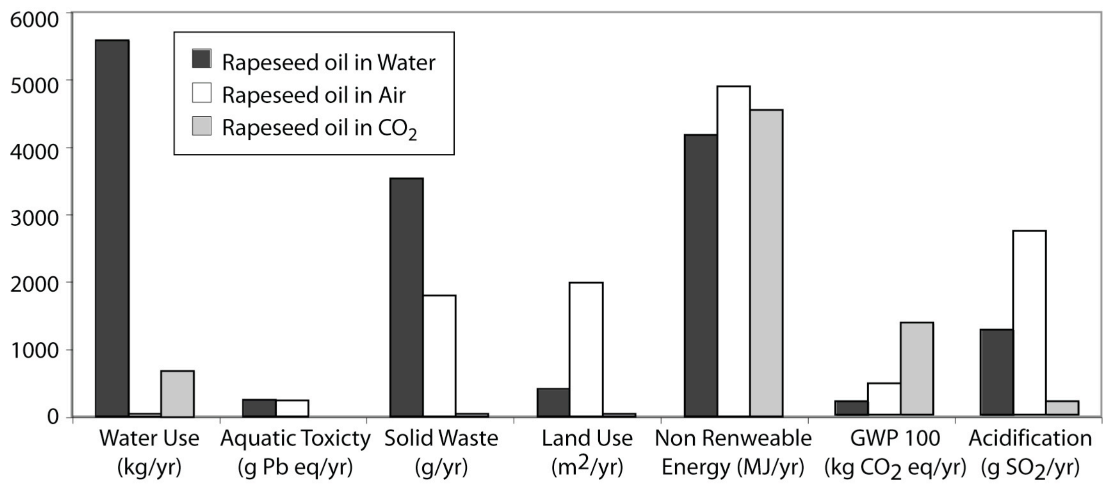


Figure 6.9. Life cycle impacts for rapeseed oil delivered in water, air, and CO_2.

6.4.1 CO_2 Impact Allocation

The allocation of environmental impacts for all feedstocks used in this analysis was performed on a mass basis. Mass assignment of impacts is the straightforward standard used in most life cycle studies. In certain situations mass allocations can be inappropriate. For example, when small volumes of toxic substances are produced as a byproduct in an otherwise benign process or when environmental footprint is not proportional to molecular weight (e.g. methane has a lower molecular weight than carbon dioxide but higher global warming potential). When performing the allocation for CO_2, a mass allocation seemed unreasonable because most CO_2 used in industrial processes is a byproduct in the production of ammonia, a much more desirable and valuable commodity. Figure 6.10 shows the primary sources for industrial CO_2.

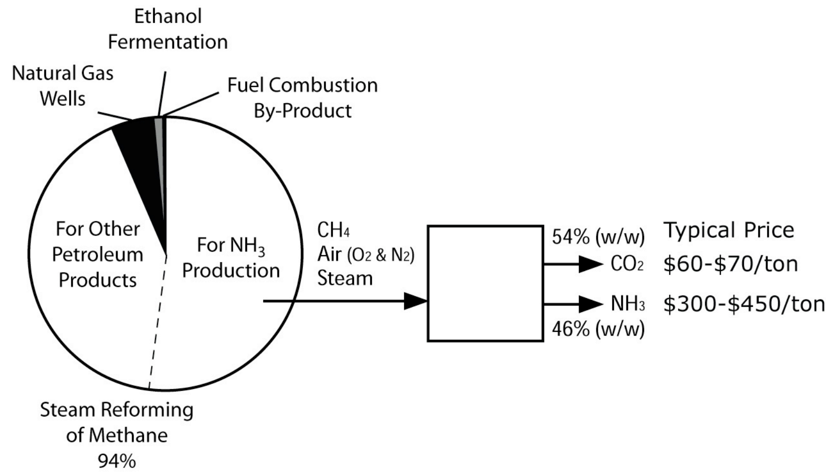


Figure 6.10. Allocation of impacts to carbon dioxide as an industrial feedstock. Most of the CO_2 produced in industry is a byproduct of the steam reforming of hydrocarbons and most of the hydrogen made from this process is used to make ammonia.

Economic: An economic allocation can be performed and was the one of choice for evaluating the impacts of CO_2 in the steam reforming of hydrocarbons to make ammonia. This process is one of many industrial processes that produces CO_2 as a byproduct but the one from which most CO_2 is ultimately recovered. In most others it is not economical to collect the CO_2 byproduct, but if it were, the price of (and emissions allocated to) CO_2 would be lower still. By using market data averaged from 1990-2002, a financial allocation accounts for the relative abundance of both CO_2 and NH_3 and assigns impacts reflecting the market's valuation of each commodity.

Mass: As mentioned above, the impact allocations for all feedstock other than CO_2 were conducted on a mass bases to be consistent with LCA methodology. For comparative purposes a mass allocation was performed of the impacts associated with CO_2 production from ammonia synthesis. The results are presented in Figure 6.11. On a mass basis, the impacts associated with the rapeseed oil-in-CO_2 go up by over a factor of two in energy and GWP. In all other impact areas, however, the allocation influence is negligible.

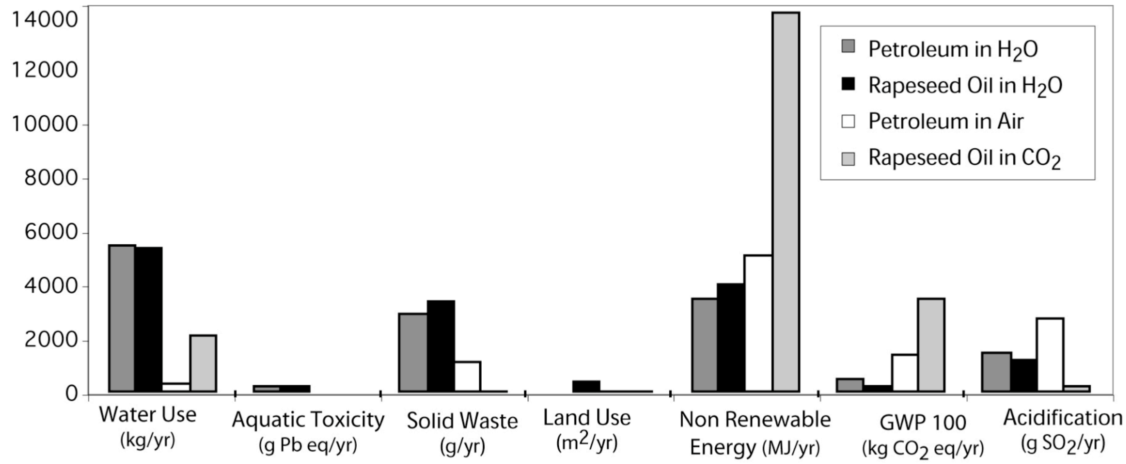


Figure 6.11. Life cycle impacts for the four MWF systems evaluated in this work based on expected operating conditions using a mass allocation of impacts to carbon dioxide.

The case for using an economic allocation becomes more apparent when comparing the production emissions from several different manufacturing processes that produce CO_2 as a byproduct. Table 6.3 lists the three major processes by which commercial CO_2 is made. The data illustrate that large variations exist between production routes with ammonia having the largest footprint. Assigning price allocation to the emissions factors for ammonia production captures both the differences in emissions factors and the variability in the CO_2 market associated with the different processes through which it is produced. This was deemed preferable compared to the mass allocation approach which does not.

Table 6.3. Select production emissions for the three processes that generate most industrial CO2. The GWP 100 and Water Use are reported with no allocation. The energy is allocated on a mass basis for the unit operations in which CO_2 is made. Adapted from (Overcash et al. 2007)

Imapct	Units	Ammonia	Hydrogenation	Geologic deposits
GWP 100	g CO_2eq / kg	424.5	27.9	149.6
Water Use	kg / kg	1.018	0.158	0
Energy	MJ / kg	3.6	-1.6	-0.2

6.4.2 *Alternative Gas Carriers*

Substituting another gas for CO_2 may be desirable from a technical standpoint but are unlikely to reduce the environmental impacts of the fluids. The use of high-pressure nitrogen (N_2) jets could be a viable substitute for CO_2, with only slightly lower cooling potential. But the life cycle emissions of high-pressure nitrogen are substantially higher than CO_2. N_2 is produced predominantly through the cryogenic distillation of liquid air, a highly energy intensive process (ETH-ESU 2003). Production of 1 kg of CO_2 requires 0.8 MJ/kg (using a price allocation) and produces 60 g of CO_2eq (not including the kg of CO_2 released to the environment). In contrast, 1 kg of N_2 requires 2.4 MJ/kg and produces 280 g CO_2eq. If both systems were used identically, N_2 would have a life cycle energy consumption over two times higher than that of CO_2-based MWF and CO_2 emissions would be comparable, with these impacts are driven almost entirely by the manufacturing energy required to make N_2.

For machining operations that do not require lubrication, sprays of CO_2 alone are possible but again here, the environmental impacts of the fluids are not significantly changed by omitting rapeseed oil from the formulation (as shown in Figure 6.12). With the exception of land use and small levels of other emissions, the flows of rapeseed oil in CO_2-based fluids do not substantially drive the impacts of these fluids.

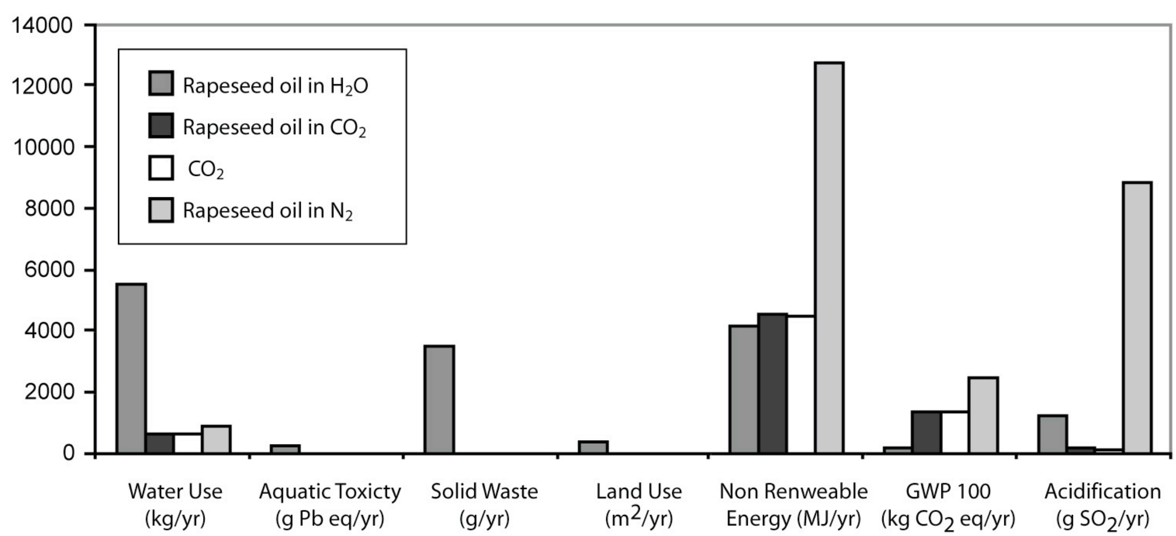


Figure 6.12. Life cycle emissions associated with alternative gas carriers or MWF with no oil relative to water based delivery.

6.5 Discussion

Regardless of allocation approach, ultimately it is necessary for the practitioner to decide if the use of the waste CO_2 as a MWF carrier is an appropriate approach to reducing solid waste, toxic emissions to water, land use, and acidification as shown in Figure 6.5. In this decision-making process, the practitioner must also consider issues listed in Figure 6.1 that are difficult to quantify and not included in Figure 6.5. As a result, the question we consider in this section is whether more qualitative issues such as worker health and safety, manufacturing performance, and ease-of-maintenance, and manufacturing performance would reinforce the conclusion from Figures 6.3 and 6.5 that gas-based MWFs are a more sustainable solution to meeting cooling and lubrication needs in manufacturing than water-based MWFs. Here each of these issues is discussed separately:

6.5.1 Worker Health and Safety

The move to EALs has been driven in large part by a desire to create safer workplaces (Lucke 1996). The inhalation of water-based MWF mists over time has been shown to be responsible for serious health risks . As a result the National Institute for Occupational Safety and Health (NIOSH) has set limits for workplace exposure to MWF mists on a mass per volume basis.

However, it is important to note that not only is the mass of mist per volume of factory air important, the content of the mist also matters. Water-based MWF mists can harbor bacteria, as well as their byproducts, and contain surfactants, biocides, and defoamers. None of these materials are present in gas-based MWF mists which contain only oil. This is notable since it has been shown that surfactants and biocides impair lung function at concentrations at least ten times lower than oil (Table 6.4) (Krystofiak and Schaper 1996). More importantly, it has been shown that factory mist can be nearly eliminated in gas-based MWF systems, especially if these MWFs are delivered through the tool (Furness et al. 2006). In any case the mists produced from gas-based MWF systems are easier to control if needed than water-based systems using existing ventilation and filtration systems already in place in many manufacturing settings (Sheehan and Hands 2007).

On the basis of this evidence, it can be argued that MWF systems based on gas are a better solution than water from the standpoint of worker health. The safety picture is somewhat more complicated. This is because the immediate safety concerns associated with the MWF alternatives are markedly different. Water-based fluids can cause dermatitis and other skin irritations. They also tend to accumulate oily sludge on and around the factory over time. Spills can also be a regular workplace hazard. These safety issues are relatively common and do not exist with gas-based MWFs. However a much less likely but more serious safety issue exists with the possibility that air or CO_2 lines or tanks could rupture, causing rare but serious acute hazards for workers if facility and operating procedures are not designed and adhered to properly.

Table 6.4. Respiratory toxicity of common metalworking components. Adapted from (Krystofiak and Schaper 1996)

Component	Class	$RD_{50}P^A$	Post exposure recovery	Required in gas-based MWF
Sodium petroleum sulfonate	surfactant	103	poor	no
Boramide	corrosion inhibitor	129	yes	no
Triazine	biocide	137	poor death within 24-72 hrs	no
Petroleum oil	lubricant	3188	moderate	yes (or vegetable alternative)

$^A RD_{50}P$ is a measure of the mist concentration that results in pulmonary irritation

6.5.2 *Ease of Maintenance*

Recirculated water-based MWFs are known to become contaminated by hydraulic oils, grease, dirt, and other debris (Skerlos et al. 2001b). This impacts their performance and leads to functional deterioration and break-down. In addition, water-based MWF ingredients such as biocides and defoamers (not considered in Figures 6.3 and 6.5) lose their efficacy over time and must be replaced typically at a rate faster than the bulk MWF. These factors taken together will increase the environmental emissions associated with the water-based MWFs relative to the gas-based MWFs which carry none of these concerns.

One issue that exists with all MWFs is the possibility that unintended fugitive emissions can occur through uncontrolled or unexpected pathways. These losses are particularly important when the MWF is being stored in large reservoirs (e.g., water based fluids can spill or leak, a CO_2 tank could be left open overnight and found empty in the morning, etc). There is little basis for calculating the frequency of these events though the magnitude of such emissions is lessened when individual MWF systems are associated with a single machine tool (such as those modeled in this work) because tank sizes are smaller and the transmission losses are negligible.

6.5.3 Manufacturing Performance

In the results, it was assumed that all MWFs have comparable machining performance and lead to identical tool replacement rates (Rakic and Rakic 2002). In practice this is highly unlikely. In fact one motivation for developing $scCO_2$ MWFs was that oil-in-air MWFs are not applicable to certain severe machining operations using advanced materials such as titanium and compacted graphite iron. In some cases, tool life increases ranging from 100-1000% can be realized as shown in this work when using $scCO_2$-based MWFs relative to alternative air-based MQL or water-based MWFs. In this case, the environmental emissions associated with the life cycle of tools are reduced by a factor ranging from 2 to 10 times. However, it should also be noted that the usual response to this type of gain in tool life performance would be for the manufacturer to increase the machining rate so that parts can be produced faster (a rebound effect). This is especially the case when machining is the rate-limiting step to increased revenue generation for a company.

There are several other performance criteria to consider that include, for instance, issues such as dimensional accuracy and workpiece surface finish. These are both strongly dependent on the quality of lubrication and cooling functions of MWF, and if these quality tolerances are not achieved, the parts must be re-made with associated environmental emissions. This is especially significant to consider in the comparison of MQL systems described in this paper. A significant drawback to mineral oil-in-air MQL systems in some machining operations is that they do not cool the workpiece sufficiently, which can lead to dimensional accuracy outside desireable tolerance limits. $scCO_2$-based fluids extend the applicability of MQL systems in this regard as they are capable of producing cooling on par with traditional aqueous fluids.

6.5.4 *Pulling it all Together*

As illustrated in Figures 6.3 and 6.5, and supported with the more qualitative discussion in this section, it appears that a switch from water to gas-based MWF systems is a strong move in the direction of sustainable manufacturing. Table 6.5 summarizes 14 environmental, occupational health, maintenance, economic, and performance metrics that have been discussed in this chapter. The table illustrates the potential for significant improvements in these factors associated with a switch from water-based to gas-based MWFs. In 10 of the 11 areas of concern, a switch to gas-based MQL presents at least a possibility of significant improvement over current water-based systems. In 6 out of 10 of these areas, the improvement is very likely.

Table 6.5. Expectation that a switch from water- to gas-based MWF systems will affect a positive change in 14 impact areas:

Impact Factor	Improvement Unlikely	Improvement Possible	Improvement Likely
Ecological Toxicity			✓
Human Toxicity			✓
Tool Wear		✓	
Nonrenewable Energy	✓		
Solid Waste			✓
Water Use			✓
Fluid Contamination			✓
Worker Safety		✓	
Friction Generated		✓	
Fugitive Emissions		✓	
Component Replacement			✓
Acidification		✓	
GWP 100	✓		
Land Use			✓

In the field of pollution prevention and sustainable engineering, it is rare that technology solutions present themselves without trade-offs. In the case of switching from water-based to gas-based MWFs, this is almost the case. Significant reductions in aqueous/solid waste, occupational health risks, and maintenance are achievable at the cost of relatively small increases in GWP and non-renewable energy for single machine-tool systems as modeled in Figure 6.2. This cost is even less when considering centralized water-based MWF systems, or the ten or so additives required to stabilize these fluids. While water-based MWF systems have undergone intense optimization over at least the past 6 decades, gas-based MWF systems have only recently been studied in depth and applied in manufacturing operations. Given their relative positions on the experience-efficiency curve, it is expected that significant efficiency and performance improvements in gas-based MWF systems are still possible relative to conventional water-based systems.

Chapter 7

Conclusions and Future Work

Metalworking Fluids are used widely in the manufacturing sector even though they entail a host of occupational and environmental health impacts. These impacts, such as respiratory health effects on workers during use and aquatic toxicity after disposal, have driven a recent interest in alternative technologies to conventional fluids. Sprays of lubricants delivered in minimum quantities directly to the cutting zone have proven to be a viable alternative to conventional flood coolants. Minimum quantity lubrication (MQL) dramatically reduces the amount of aqueous waste produced by an operation and early industrial results suggest that misting and infrastructure cost are also reduced. The use of MQL sprays seems to be the most effective way to improve the environmental sustainability of MWF systems.

A more sustainable MWF system will not gain widespread acceptance if it does not perform as well or better than conventional water-based MWFs. The first barrier for MQL technologies is the dramatically lower cooling potential of air relative to water. Tools and workpieces cannot be cooled as effectively using sprays of 'line' air from the factory compressors resulting in accelerated tool wear and parts that are out of specification. The second barrier to MQL's potential is that air and lubricants do not readily mix and so complex delivery mechanisms are required to aerosolize the lubricants. Both of these barriers could be overcome if lubricants were delivered in sprays of CO_2. At high pressures, CO_2 is an effective solvent that will solubilize many common lubricants. When sprayed out of a nozzle, the CO_2 forms dry ice, which cools surfaces more effectively than a spray of air. The goal of this research was to understand the feasibility of MWF delivered in CO_2. To achieve this goal, three major research tasks were performed in this dissertation:

Task 1: Design a CO_2-based MWF formulation, evaluate the capabilities of such a system to replace conventional water-based fluids and benchmark the effects on cutting forces

Task 2: Develop the knowledge needed to maximize the spray cooling potential of CO_2-based MWF and describe the effects on tool life

Task 3: Quantify the life cycle impacts of CO_2-based MWFs relative to conventional, bio-based, and MQL alternatives

In Task 1, a prototype was developed that allowed for the delivery of MWF lubricants + CO_2 at a range of temperatures and pressures. $ScCO_2$-based MWF were sprayed through interchangeable nozzles to produce dry ice and frozen oil. The functional mechanism and potential advantages associated with CO_2-based MWF were then explored with the following conclusions:

- Tapping tests revealed that sprays of $scCO_2$ + lubricant dramatically reduced the energy required in a cutting process. The improvement which was higher than that of soybean oil or CO_2 alone indicating that a synergy exists between lubricants and CO_2 in the thread cutting process.
- In high-pressure $scCO_2$-based MWF systems, two phases can generally be delivered, a CO_2-rich phase or a lubricant-rich phase. The distinction is described in Appendix A and for the tapping work, all experiments were run using the lubricant-rich phase of the solution.
- The CO_2 + lubricant formulation (even from the lubricant-rich bottom phase) delivered much less oil than straight oil with dramatically higher performance suggesting that CO_2 is a more efficient lubricant carrier than air or water at the same levels of performance.
- SEM images of the chip surfaces suggest that CO_2-based MWF function, at least in part, by more effectively penetrating the contact region between the chip and

the tool. This result is consistent with the prevalent understanding of MWF function.

The primary obstacle to widespread adoption of air-based MQL systems is that they do not cool as well as water. The purpose of Task 2 was to explore the cooling potential of high pressure gas sprays relative to conventional MWFs and characterize the implications on tool wear. Tool wear is known to be highly temperature dependent and for hard materials, ineffective heat removal leads to low tool life and ineffective process function.

- High-pressure sprays of CO_2 and CO_2+lubricant were found to reduce flank wear significantly better than sprays of air + MWF or air + lubricant. Even though sprays of CO_2 were found to be less effective at bulk cooling, CO_2-based MWFs reduced heat-driven tool wear as effectively or moreso than conventional flood coolants.
- Spray direction is an important parameter when delivering gas-based MWFs. The less effective cooling potential of gases mandates that sprays be directed at the wear surface or they will not provide the cooling necessary to mitigate tool wear. This result indicated that CO_2 cools by penetrating the flank face of the tool and removing heat locally.
- Several important operating parameters were found to control the heat removal potential of CO_2 sprays including the nozzle geometry, distance and offset between the spray and the heated source, temperature of the gas, and pressure of the gas. Of these, all but gas temperature had a large effect on heat removal.
- Tests performed on titanium showed that CO_2 and other gases reduce tool flank wear by effectively removing heat at the cutting surface even though the temperature in the tool is higher than it is for conventional water-based coolants. High pressure argon, nitrogen, and low pressure CO_2 also mitigate tool wear but high pressure CO_2 cools the most effectively. The results suggest that this is not a chemical passivation effect but a cooling effect.
- Although CO_2 and CO_2 + lubricant were found to have different cooling potential, only small differences in tool life were found. The CO_2-rich phase of CO_2 + lubri-

cant does provide effective cooling for processes where heat removal is important for controlling tool life.

- The tool life tests were performed on titanium where diffusive wear predominates but other types of wear exist at other speeds. At higher speeds, sprays of CO_2 on both the flank and rake faces resulted in effective heat removal and provided better tool life than either conventional or CO_2-based coolants alone.

Increasing environmental scrutiny has been placed on conventional water-based MWFs as well as on processes that emit significant amounts of carbon dioxide. To understand the tradeoffs that could be associated with a switch to CO_2-based MWF, in task 3 a life cycle model was developed to quantify the life cycle emissions and energy consumption of CO_2-based MWFs relative to several other environmentally adapted lubricants such as petroleum with vegetable-based components and sprays of minimum quantities of lubricant in gas rather than water. These systems were compared to a conventional oil-in-water semi-synthetic emulsion. A summary of the assessment is listed here:

- Switching to gas-based MWFs reduces most of the impacts associated with conventional MWFs. In particular, gas-based MWFs reduce solid waste by 60% (~3 kg to 1 kg), aquatic toxicity by 80% (300 g Pb-eq to <50 g Pb-eq) and can effectively eliminate occupational health concerns. The increases in GWP associated with gas-based MWFs are small relative to other manufacturing processes.
- Compared to air based delivery, carbon dioxide has a lower overall impact because CO_2 is a more effective coolant and does not require the large volumes needed with air. Both gases have higher GWP and energy consumption than water-based MWFs but the absolute magnitude of these increases is small compared to the reduction of more significant environmental burdens in other impact areas.
- The use of bio-based MWF instead of petroleum-based components produced marginal tradeoffs between energy, land use and global warming potential. Much more dramatic reductions were possible by switching to gas based MWF systems.

- For water-based systems, implementation of a microfiltration recycling unit can reduce the life cycle impacts in many categories to be on par with gas based systems.
- User-defined operating conditions can have a dramatic impact on the overall life cycle emissions of MWFs though gas based MWF have the lowest overall impacts over a wide range of operating conditions.

7.1 Recommendation for Future Research

Though the results of this work set the stage for the development of novel MWFs that are petroleum and water free, further research in several key areas is necessary to deploy this technology onto the manufacturing floor.

Through-tool delivery of CO_2-based MWFs

This work demonstrated that sprays of CO_2 can produce effective heat removal directly to the cutting zone. To maximize these benefits, the nozzle must be placed close (<5 cm) to the cutting zone. For some machining processes such as turning and face milling, this constraint is easily met as the operations are generally exposed and accessible by the small CO_2 nozzles. For other processes, such as drilling and slot milling, the cutting zone is not readily accessed. In these processes, it becomes difficult to deliver effective cooling and lubrication to the confined regions of the cutting zone and in fact, the high-pressure spray of CO_2 can actually impede chip removal through flutes. For these processes, traditional machining has relied on through-tool delivery of water-based coolants through holes built into the tool. This sort of through-tool delivery is being used widely for air and lubricant MQL systems though this application is problematic as the capillary forces on the machine tool spindle readily force lubricants to the delivery tube walls. Both of these factors 1) the widespread use of through-tool delivery and 2) the importance of nozzle proximity to the cutting zone for CO_2-based MWF suggests that through tool delivery of CO_2-based coolants is an important next step in developing the technology.

Nozzle optimization for temperature control on the machine floor

Sprays of CO_2 and lubricant were found to effectively reduce temperatures at the tool/workpiece interface but insufficiently reduce the temperature in the bulk of the tool. For interrupted cutting or short processes this is reasonable but it can be problematic if a part is to be machined for enough time that temperature increases can begin to affect tolerances. In MQL-based systems, this has been a dramatic problem and complex controllers have been developed to account for thermal expansion by modifying cutting parameters in real time to compensate. For machining using CO_2-based MWF, it should be possible to effectively control temperatures using properly positioned nozzles of CO_2 and high pressure air. To determine the best way to control temperature in optimal nozzle placement, finite element techniques may be used.

Evaluate the effect of tool life improvements on the life cycle impacts

The life cycle assessment described in Chapter 6 was performed using the assumption that tool wear rates are constant for all MWF systems. This conservative assumption was made to account for the wide variety of tool materials and cutting applications. But the experimental results of Chapter 5 suggest that CO_2-based MWF could produce lower tool wear rates. Many tool materials have high embedded energy values or are coated with materials that have disproportionately large environmental burdens. These impacts could influence the conclusions of the life cycle assessment and lower the impacts of high performance fluids like those based on $scCO_2$. When more generalized tool wear data is available for CO_2-based fluids, the life cycle model should be expanded to include it. This could coincide with additional life cycle work looking at the life cycle costing of the different MWFs.

Develop a family of 'green' additives for CO_2-based MWFs

This work explored two component systems containing only oil and CO_2. For many machining operations, this binary mixture has the potential to adequately provide the cooling and lubrication necessary for proper function. For other, difficult to machine operations, extreme pressure (EP) additives can be included to reduce wear and machining forces. Such boundary lubricants were not included in this work but could significantly increase the applicability of CO_2-based MWF.

When CO_2-based MWF go from two to three or more components, the phase behavior will become significantly more complex. Certain compounds, typically intermediate molecular weight organic compounds, have been found to increase the solvency power of CO_2. Cataloging the interaction effects between lubricants and additives, both synergistic and detrimental, will be an important step in achieving the ultimate goal of fully functional MWFs.

Completely describe the relationship between phase behavior and machining performance

For all of this work, soybean oil was used because it is the most effective common MWF lubricant alone and in CO_2. The relative composition of oil and CO_2 in a spray was found to have a much greater impact on the performance of a CO_2-based MWF than the type of lubricant. Other lubricants have different phase behavior in CO_2 and these phase characteristics should be explored in the context of machining performance.

In Appendix A, efforts to characterize the phase behavior of lubricants in CO_2 are described. As mentioned above, different phases were used to provide the lubrication needed in the thread cutting process in Chapter 4 and the cooling needed in the turning process in Chapter 5. A major research effort is needed to describe the influence of machining process, operating conditions, metal/tool combinations and delivery approaches on the effectiveness of CO_2-based MWFs. Indeed the tuneability of CO_2-based MWFs is one of their most important features for manufacturing and this potential, like its cooling capacity and lower environmental impact, needs to be further explored.

Appendices

Appendix A

Solubility Characteristics of Metalworking Lubricants in CO_2

Carbon dioxide is an attractive MWF carrier in part because of its ability to dissolve lubricants. To fully leverage this capability it is necessary to understand how MWF lubricants dissolve in CO_2 and how their phase behavior can be applied for maximum machining performance. The machining tests described in this thesis were performed using binary mixtures of soybean oil and carbon dioxide. Soybean oil was selected initially because CO_2 has been employed as a replacement solvent in soybean oil extraction and the solubility behavior of the mixture has been well studied (Reverchon and Sesti Osseo 1994). Soybean oil has also been tested in machining and found to work better than all other lubricants, petroleum or vegetable based (Clarens et al. 2004b).

Inasmuch as the early tests described here relied on soybean oil, a significant focus of the research became to understand the solubility behavior of other lubricants in CO_2. The expectation was that more highly soluble oils would result in better machining performance. The solubilities of numerous MWF lubricants were explored to develop a library of data for common MWF lubricants. These data could also be used to design functionally complete MWFs containing the necessary additives. This analysis determined that even though significant differences in lubricant + CO_2 solubility were found, the machining performance results were not linearly correlated with solubility. Instead, the performance of CO_2-based MWF was found to depend more on the phase composition of the spray than on differences in relative solubility.

The results of the effort to characterize MWF lubricant solubility in CO_2 are described in this appendix. The general conclusion is that optimal performance of CO_2-based MWFs requires the delivery of the appropriate high-pressure phase: liquid phase for lubricant intensive machining processes and vapor phase for cooling intensive processes. Based on the five classes of base lubricants evaluated, soybean oil was found to the most effective at reducing machining forces.

A.1.1 MWF function in machining

As the two primary functions of metalworking fluids, cooling and lubrication have differing levels of importance for different machining processes. Table A.1 lists common machining operations and the predominant function of MWF for that process. In reality, processes do not discretely require one or the other entirely and the distinction between lubrication intensive processes and cooling intensive processes would be better described using a scale (Figure 2.3). Even within the same process, lubrication may be more important at low speeds while cooling is more important at high speeds. For the purposes of this discussion, operations are listed as those that primarily require cooling and those that primarily require lubrication. Categorizing machining operations in this manner allows for some experimental justification for selecting only three machining processes to gather information about a wide range of metals machining operations.

Table A.1 lists the machining tests that were used to explore the function of CO_2-based MWFs. To measure the effect that CO_2-based MWF have on cooling intensive processes, a turning operation was used as described in Chapter 5. To evaluate the role that CO_2-based MWF has on operations that require lubrication, a tapping process was used as discussed in Chapter 4. In this chapter, additional results from these two methods are presented along with a third method based on metal forming. In many metalworking operations, material is not actually removed but deformed into the desired shape. The role of CO_2-based MWFs was explored in this operation using a forming modification of the thread cutting process to expand into machining processes that primarily require lubrication.

In the next section, the thread forming process is introduced; thread cutting and turning were introduced in Chapter 3. Two methods to evaluate the solubility of lubricant compounds in CO_2 are described first.

Table A.1. Relative importance of cooling and lubrication in different machining processes and operations testing in this research.

Predominant Function of MWF	Common Operations	Tested Operation
Lubrication	Stamping	
	Drawing	Thread Forming
	Rolling	
	Broaching	
	Tapping	Thread Cutting
	Grinding	
Cooling	Milling	
	Turning	Turning
	Drilling	

A.1.2 Methods

Analysis of high-pressure fluid phase equilibria is a mature research area, with well-defined methods. Two of these methods were adapted for this research 1) a bulk extraction method to screen MWF lubricants for solubility in CO_2 and 2) a static method for assessing detail equilibrium phase behavior at high pressure. Finally a new MWF evaluation method using the thread forming extension of the tapping torque test was developed and also used in this study.

A.1.2.1 Solubility screening in CO_2

Acquiring a complete set of high-pressure solubility data over a range of compositions in CO_2 is an involved process so a preliminary screening method was utilized to efficiently evaluate the compatibility of numerous lubricants in CO_2. Adapting a method developed by Bray et al., a 1 L high-pressure vessel (High Pressure Equipment, Erie PA) was modified with a wire rack to accommodate 36 glass test tubes (Bray et al. 2005). Samples were weighed into the test tubes and CO_2 was flowed through the vessel at a known rate (2 g/min) and vented using a backpressure regulator to a fume hood. Each set of extractions was run for 4 hours. A standard of known molecular weight and composition (linoleic acid) was run during each trial to serve as a reference control between experimental runs. Experiments were run at three pressures: 100, 200, and 300 bar.

By running the samples together in the same vessel it was possible to ensure that all compounds were subjected to the same pressurization and depressurization conditions. In cases were more than 36 samples were to be tested, the samples were randomly divided into groups to be run in triplicate at each pressure. Because most of the interest in

MWFs is focused on low temperature solubility, experiments were run at 35°C. The percent extracted was determined by gravimetric means and error was calculated using the standard deviation of the triplicate samples.

A schematic of the experimental setup is shown in Figure A.1. Food grade CO_2 was chilled and compressed at a set flow rate using a Thar Technology (Pittsburgh, PA) P-50 high-pressure pump. A computer was used to monitor the operating conditions in the high-pressure vessel using LabView software (National Instruments, Austin, TX). In Figure A.1: A. Canister of food grade CO_2, B. valve, C. cooling coil, D. high pressure pump, E. one-way valve, F. high pressure vessel, G. band heater, H. test tubes in rack, I. back-pressure vessel, J. pressure transducer, K. thermocouple, L. computer, M. data acquisition device.)

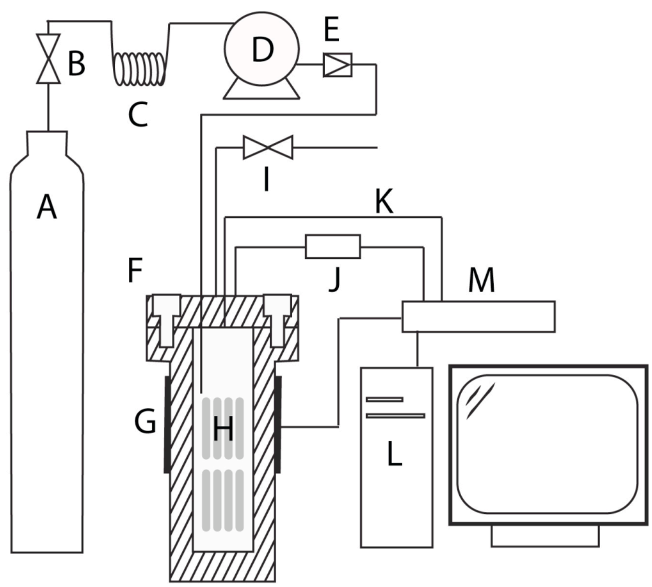


Figure A.1. Schematic of high-pressure solubility screening setup.

Bulk extraction studies are useful for determining relative solubility between lubricants but the method has some limitations. Mass transfer is assumed to be comparable between lubricants when in reality different molecules likely diffuse through CO_2 at different rates. In addition, there could be interaction effects between lubricants dissolved in the CO_2 that could synergistically contribute to the solubility of some lubricants. The ability of a particular lubricant to dissolve into this cocktail of components could be different than its ability to solubilize into pure CO_2. For these reasons, it was necessary to develop more detailed solubility data for CO_2 and several of the more promising lubricant classes.

A.1.2.2 High pressure phase equilibrium measurements

The solubility of compounds in CO_2 has been determined via several methods that can be broadly described as either static or dynamic. In static systems, a known amount of solute and solvent is added to a variable volume vessel and the phase behavior is determined via visual inspection. In dynamic systems, a supercritical fluid flows continuously through a vessel containing the solute. The flow rate and decompression of the CO_2 are closely monitored and the effluent concentration of solute can be determined using chromatography or other analytical methods. A static system was used for this work because the data were more conducive to fitting using predictive models and most of the components required for the experimental setup were readily available.

The static method was carried out as follows: a known amount of CO_2 and solute were added to a high-pressure cell with a variable volume piston attached and a window for viewing. The mixture was pressurized to form a single homogeneous phase and then equilibrated with mixing for ~20 minutes. After this equilibrium period, the volume of the piston was slowly increased until a phase separation occurred. This phase separation was monitored visually, by observing the bubble or cloud point through the sapphire windows in the view cell, or directly measured by recording the inflection point in the pressure record of the vessel during the volume increase process. Each condition was repeated a minimum of two times to ensure experimental accuracy.

The experimental setup, illustrated in Figure A.2, consisted of food grade CO_2 which was compressed from a tank through a cooling coil into a high pressure syringe pump (Isco LC-5000). After passing through a check valve, the CO_2 was fed into a 6 mL high-pressure view cell with two sapphire windows. A light source was placed next to one window and a digital camera (Allied Vision, Guppy) was placed on the other. Inside the high pressure vessel was a magnetic stir bar that was driven by an exterior stir plate. From the bottom of the vessel, a short high-pressure line ran to a variable volume piston (HIP 62-6-10). Both the piston and the vessel were maintained at constant temperature via heating elements. The pressure and temperature of the system were monitored using LabView software and a data acquisition device attached to a PC. The solubility experiments were all performed at 35°C and a range of pressures. For Figure A.2: A. Canister of food grade CO_2, B. cooling coil, C. syringe pump, D. one-way valve, E. high pressure view cell, F. pressure transducer, G. thermocouple, H. heating element, I. stir plate, J. digital video camera, K. variable volume piston, L. computer with data acquisition, V1-3. valves.

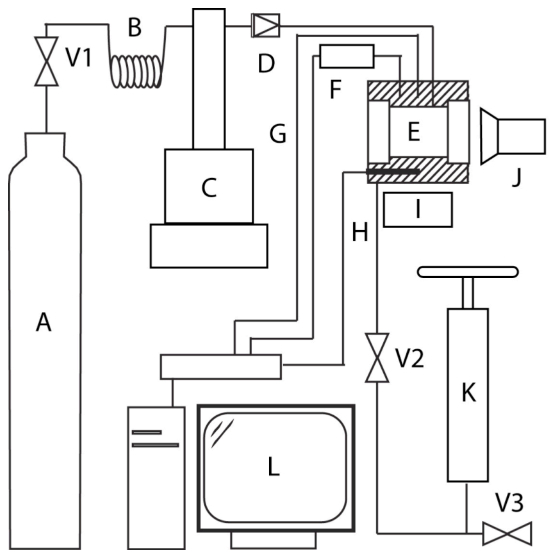


Figure A.2. Schematic of high-pressure solubility setup.

A.1.2.3 Thread forming methods to evaluate MWF performance

The tapping torque test was extended to perform thread forming experiments as a method to evaluate the performance of extreme pressure additives in machining. In thread cutting (described in Chapter 3), material is removed from predrilled holes to produce a threaded hole. In thread forming, a different geometry tool is used in slightly larger predrilled holes to deform the metal into threads (Figure A.3). The results of the two processes are identical: holes with threads of a standard size. The metalworking processes by which the threads are achieved are very different. In thread forming, the tool is shaped to plastically deform the metal to shape it into threads. Localized forces are much higher during the process and the threads are harder. For extreme pressure additive evaluation, thread forming was preferred because the high pressure necessary for EP activation could be created easily as function of cutting speed. At lower speeds EP additives did not register an impact in the test and at higher speeds their presence was obvious as they reduced cutting forces. The method was not only useful for measuring EP activity, it provided an effective bench scale operation to evaluate MWF performance in forming.

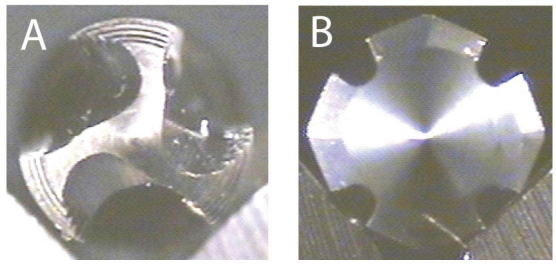


Figure A.3. Axial images of taps A. cutting and B. forming.

Thread forming tests were carried out using a MicroTap Mega G8 (Rochester Hills, MI) capable of 700 N cm maximum torque. ANSI 1018 cold rolled steel workpieces with thickness 10 mm were pre-drilled and pre-reamed with 175 holes of 5.6 mm diameter. High-speed steel M6 taps of identical geometry (60° pitch and 4 straight flutes) were used. A forming speed of 750 RPM was tested. Each new tap was broken in by tapping 20 holes at 300 rpm. For each fluid, thread forming was performed on 25 holes. The forming torque efficiency was calculated by normalizing average torque over the 4-8 mm traveling distance to that obtained from the benchmark fluid with error bars calculated following the same procedure as in described for thread cutting in Chapter 3.

A.1.3 Solubility Results

The overarching goal of the solubility work was to evaluate the phase behavior of the most common MWF lubricants in high pressure CO_2 and to use these results to inform lubricant selection for CO_2-based MWF applications. The experimental approach used to achieve this goal involved an initial survey of 15 different lubricants followed by more in depth binary phase behavior studies of 4 lubricants representing the major lubricant classes: petroleum-based, vegetable based, polyalpha olefins and polyalkalyene glycols. Using literature values for physical-chemical properties of the tested lubricants some general rules of thumb were established between several of the properties and solubility in CO_2.

The fifteen lubricants considered in the analysis are listed in Table A.2 along with reported viscosity and average molecular weight (MW) data. Molecular weight was listed because smaller molecules tend to dissolve better in CO_2 than larger ones. Viscosity was included to illustrate the correlation between viscosity, molecular weight and solubility in synthetic lubricants. For synthetic polymeric compounds, molecular weight and viscosity are proportional so even though MW is not always reported for commercial lubricants, viscosity can serve as an effective surrogate indicator of solubility.

Table A.2. Lubricants considered in this work along with reported viscosity and molecular weight information that was correlated with solubility results to inform selection.

Class	Type	Commercial Name	Average MW	Viscosity (40°C)
Petroleum-based	Naphthenic mineral oil	Hydrocal 100	-	109
	Paraffinic mineral oil	DA Stuart	-	-
Vegetable-based	Soybean oil	Cargill Alkali Refined	925	39
	Canola oil	Cargill AP 75	932	-
	Sunflower oil	Cargill	928	-
	Trimethylolpropane (TMP) trioleate ester	Uniquema Priolube. 1427	946	44
Synthetic	Polyalkylene glycol (PAG)	Dow 50-HB-100	520	19
		Dow 50-HB-260	970	53
		Dow 50-HB-660	1700	130
		Dow 75-H-1400	2500	-
		Dow 50-HB-3520	3380	700
	Polyalpha olefin (PAO)	Spectrasyn 2	990	-
		Spectrasyn 6	1040	31

A.1.3.1 Bulk Extraction Results

The results of the bulk lubrication solubility studies showed dramatic differences between the solubility of base lubricants in CO_2. The results are shown in Figure A.4. Mineral oils tended to be the most soluble and vegetable oils the least. Some synthetics, e.g., PAOs, tended to be highly soluble, while others, e.g., PAGs, had a range of solubilities. For all lubricants, solubility increased at higher pressures of CO_2.

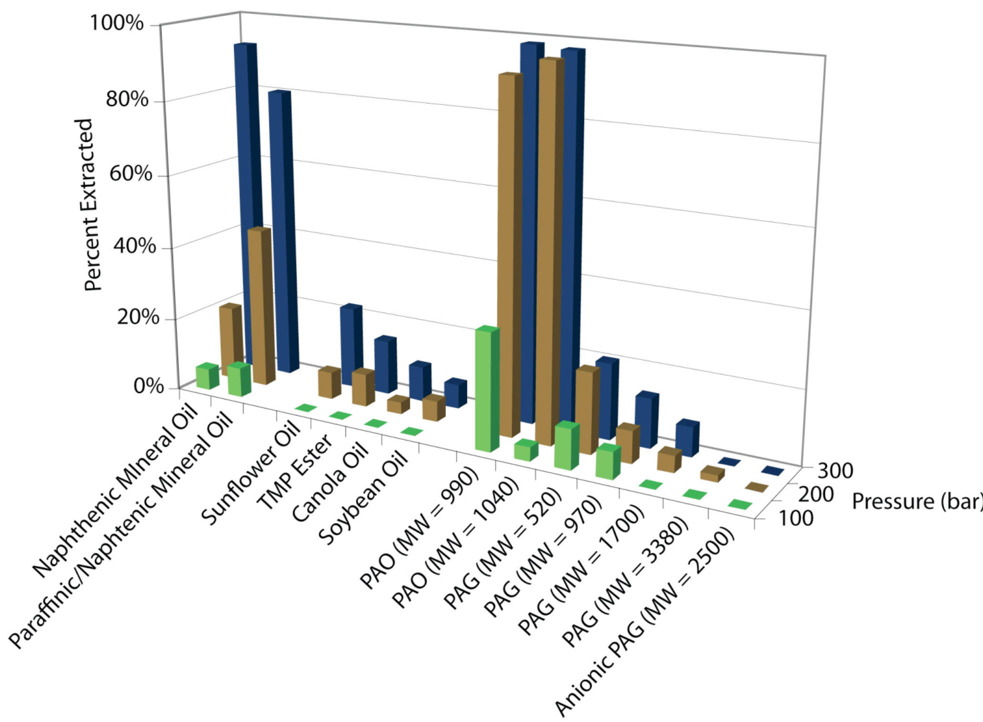


Figure A.4. Bulk extraction of 15 representative lubricants in $scCO_2$ for three pressures.

The two most common vegetable oils for MWF applications, soybean and canola were tested and found to have relatively low solubility with moderate solubility at higher pressures. Trimethylol propane ester trioleate (TMP), a vegetable oil derivative used commonly in MWF formulations, was tested and found to be moderately more soluble than canola or soybean oils, although the differences are small. This is consistent with the small differences in MW between the vegetable oils. The degree of saturation of the constituent fatty acids affects the bulkiness of the vegetable oils which in turn can influence solubility. TMP is a synthetic triglyceride made with oleic acid and it is the most saturated of the triglycerides tested making it the least bulky molecule. Sunflower oil is a highly saturated vegetable oil composed primarily of shorter length fatty acids, would lead to higher solubility in the $scCO_2$. Sunflower oil was tested and found to be the most soluble, and though it is expensive and not commonly used in MWF applications, it could be employed if solubility was a limiting factor to achieving effective lubrication.

Qualitative molecular structure as represented by the bulkiness and size of constituents of the lubricants was found to correlate well with lubricant solubility for the other classes of lubricants. The mineral oils were all very soluble in $scCO_2$ as the pressure was raised. These oils are complex mixtures, however, containing compounds ranging in size from C15-C35, benzene, xylenes, ethyl benzene and a wide variety of others. The smaller, more volatile molecules will selectively partition out leaving the bulkier molecules behind making them suboptimal candidates for evaluation using the steady-state dynamic method for solubility analysis. For the synthetic lubricants, molecular structure and size was also an effective predictor of solubility. For the series of PAG compounds investigated, the smaller PAG molecule, the greater was the solubility.

Polarity of the compound was also found to play a role. Between the two classes of synthetics at higher pressures, the PAOs were highly soluble in $scCO_2$ and more so than PAGs. PAO is a simple nonpolar hydrocarbon and CO_2 tends to dissolve nonpolar solutes. PAGs are co-polymers with approximately the same ratio of ethylene and propylene oxides, the later being polar making them less soluble.

Within each of the two groups of synthetic lubricants, molecular weight was an effective predictor of solubility. Several PAGs were tested with molecular weights ranging from 520-3250. For all synthetic lubricants, molecular weight was proportional to viscosity and inversely proportional to solubility. The least soluble synthetic compound and one with the highest viscosity and MW, an anionic modified PAG developed for aqueous MWF applications did not dissolve at all in $scCO_2$. The results, shown in Figure A.5 show that the lower the molecular weight of the lubricant, the higher its solubility.

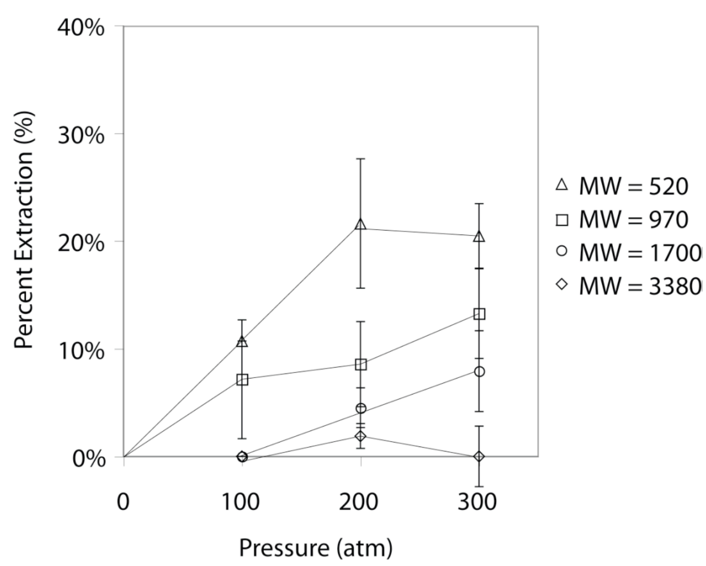


Figure A.5. Bulk extraction results for 4 PAG lubricants showing how lower molecular weight results in higher solubility for synthetic lubricants in CO_2.

For most lubricant mixtures, however, molecular weight is generally not reported due to the distribution of compounds in a mixture or the propriety nature of the product. Additionally, most lubricants of interest have low vapor pressures so this was not generally useful for predicting solubility in $scCO_2$. Instead, viscosity, widely reported in the material safety data sheets for industrial lubricants was found to be an effective predictor of solubility in synthetic polymeric compounds. For synthetic lubricants, viscosity is typically proportional to molecular weight via a log liner relationship. So using viscosity as a surrogate predictor of solubility in CO_2 for synthetic lubricants is an appropriate method. The results for the PAG, which is arranged from least viscous to most viscous from left to right, illustrate this trend most clearly.

A.1.3.2 Phase Behavior

To further understand the behavior of MWF lubricants in high pressure CO_2, detailed phase solubility studies of four of the representative lubricants were performed. These tests were time intensive so the results from the bulk extraction tests were used to select the most promising lubricants to further evaluate. Napthenic mineral oil DA Stuart), soybean oil (Cargill Alkali Refined), TMP Ester (Uniquema), and PAG (Dow, 10-HB-100) were selected for detailed evaluation. The results, shown in Figure A.6, provide a plot of the solubility pressure limit as a function of composition. The curve provides the phase boundary between CO_2 dissolved in the lubricant (to the left of the curve) and lubricant dissolved in CO_2 (to the right of the curve). The plotted data are experimental results and the lines are model predictions. All the experiments were run at 35 ^{o}C. For MWF applications, low temperature mixtures with higher oil solubility are desirable so higher temperature isotherms were not considered.

The results show that all the lubricants have a high capacity to dissolve CO_2. When delivering sprays from the liquid phase, sprays of soybean oil or PAG are most likely to result in synergistic performance because these lubricants have the highest capacity for dissolving CO_2. Mineral oil was the least capable of dissolving CO_2 and at 30 mol% CO_2 would not form a single-phase mixture. In effect the lubricants were found to dissolve CO_2 in approximately the following order: soybean oil ≅ PAG > TMP Ester > mineral oil.

The vapor solubility composition can be determined by the data on the right hand side of the curve. The curves for the four lubricants have approximately the same slope suggesting that the performance differences will not be dramatic when delivering vapor phase mixtures of CO_2 + lubricant. The 'miscibility gap' in the middle of the diagram where the curves extend above the maximum plotted pressure exists for a concentration range where mixtures of CO_2 and the lubricant cannot exist as a single phase under reasonably achieved pressures. The miscibility gap is a physical phenomenon that occurs for many high pressure combinations and is larger for some solutes e.g., mineral oil, than for others e.g., soybean oil.

The results for PAG and soybean oil were consistent with published data for those components in equilibrium with CO_2. The results for these systems are plotted along with published data from (Ndiaye et al. 2006; Yokozeki 2007). No published results for the solubility of TMP Ester and lubricating mineral oil were available in the literature.

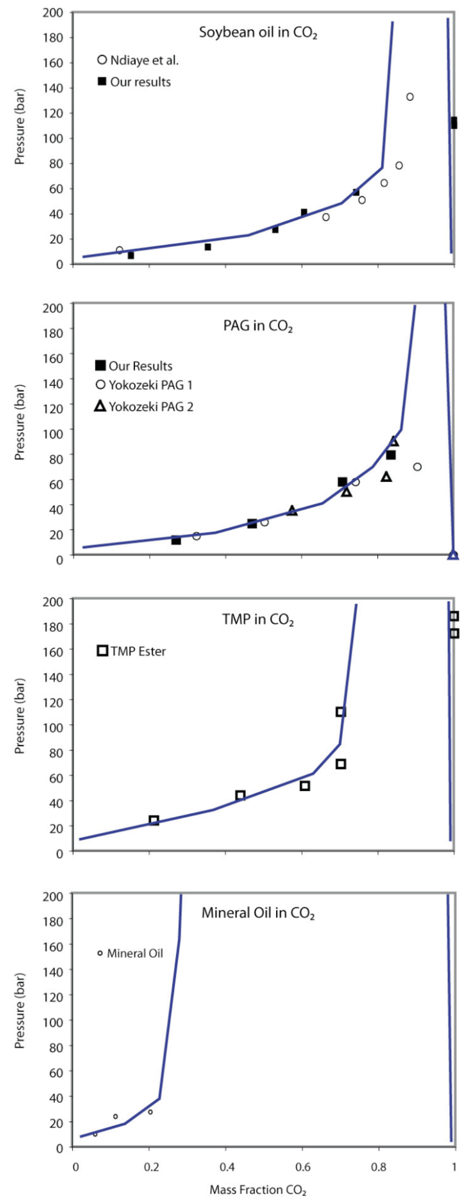


Figure A.6. Binary phase solubility for four common MWF lubricants in CO_2.

Interpretation of the solubility data and its implications for machining must be done in the context of a discussion on how MWF are delivered in CO_2. All the work in this thesis was performed in high-pressure vessels with lubricant present in large excess. CO_2 was continually pumped into the vessel at the rate CO_2-MWF was being sprayed out. Maintaining the lubricant in excess ensured that lubricant would not run out during a machining operation and that a uniform delivery of CO_2 + lubricant would be delivered to the cutting zone. At temperatures or pressures below the critical point of CO_2, three phases would form in the vessel as in Figure A.7.A. CO_2 would exist as a vapor and liquid (liquid 1) and the lubricant (liquid 2) would be a separate liquid. Some CO_2 would dissolve into the lubricant and some lubricant would dissolve into the CO_2 liquid and some into the vapor. Upon reaching supercritical conditions the mixture would form two homogenous phases (Figure A.7.B). The vapor phase would be CO_2 rich but contain some dissolved lubricant. The liquid phase would contain mostly lubricant with some CO_2 dissolved. For steady state operation, CO_2 was pumped into the vessel and the mixture was removed via either a port on the top of the vessel or a port on the bottom. At a given pressure, the composition of the vapor phase can be determined using the results on the right side of the plots in Figure A.6. The composition of the liquid phase can be determined via the results and model predictions on the left side of the plots.

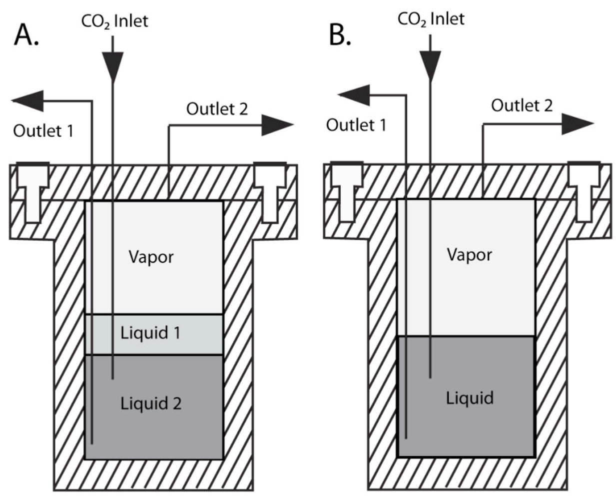


Figure A.7. Schematic of CO_2-MWF vessel showing phase behavior under A. subcritical and B. supercritical conditions.

A.1.4 Performance Results

The machining performance of the five MWF base lubricants was tested to correlate their performance with the solubility data. The results for three different machining operations are discussed in the following sections. The data indicate that for some processes, e.g., cooling intensive process, it is more desirable to deliver lubricant from the vapor phase and in others, e.g., lubrication intensive processes, delivery from the liquid phase produces the best results. For lubricant intensive processes, such as tapping, the solubility of the lubricant is important to predict the performance of lubricant + CO_2 mixtures. For cooling intensive processes, the concentration of lubricants in CO_2 was similar and performance differences were not observed between lubricant classes.

A.1.4.1 Thread Cutting

The four oils tested for solubility in this work plus a PAO were evaluated using the tapping torque test as straight oils and dissolved in CO_2 in the vapor phase. All experiments were run at a pressure of 170 bar and 35 ^{o}C. The results for the straight oil, presented in Figure A.8.A, show that there are significant differences between the oils when tested alone in thread cutting. Soybean oil performs the best consistent with previous data in which soybean oil was found to perform better than canola or TMP Ester. PAG performed better than the straight oil reference fluid used to normalize the data (tapping torque efficiency = 100%). Straight mineral oil does not perform as well as the reference fluid and PAO performs almost 20% worse than the reference. For these tests, approximately 700 μL of lubricant were used per test.

The same five oils were then tested as vapor phase solutions in CO_2. The performance differences in CO_2 are lower, ±8% between all the oils as opposed to ±30% between the best and worst straight lubricant. The oils more or less have the same performance ranking as straight oils when they are added as dissolved oils with the exception of the PAO and the mineral oil. The PAO was unusual in that it performed much better in CO_2 than straight, likely because of its high solubility. Soybean oil was the highest performance oil followed by TMP Ester and PAG. During these experiments, the total lubricant delivered per test was approximately 1 μL.

When compared to the data presented in Chapter 4, several important observations can be made. In that chapter, thread cutting results reveal that CO_2 dissolved in lubricant will perform up to 10% better than the lubricant alone. The cutting results in Figure A.8, show that sprays of soybean oil dissolved in the vapor phase do not perform as well as sprays of CO_2 dissolved in the lubricant. The sprays of vapor phase soybean oil still perform significantly better than a reference soluble oil even though much less oil is being delivered. When comparing several key MWF classes with soybean oil, the data suggest that even though its solubility is substantially lower, soybean oil still performs the best.

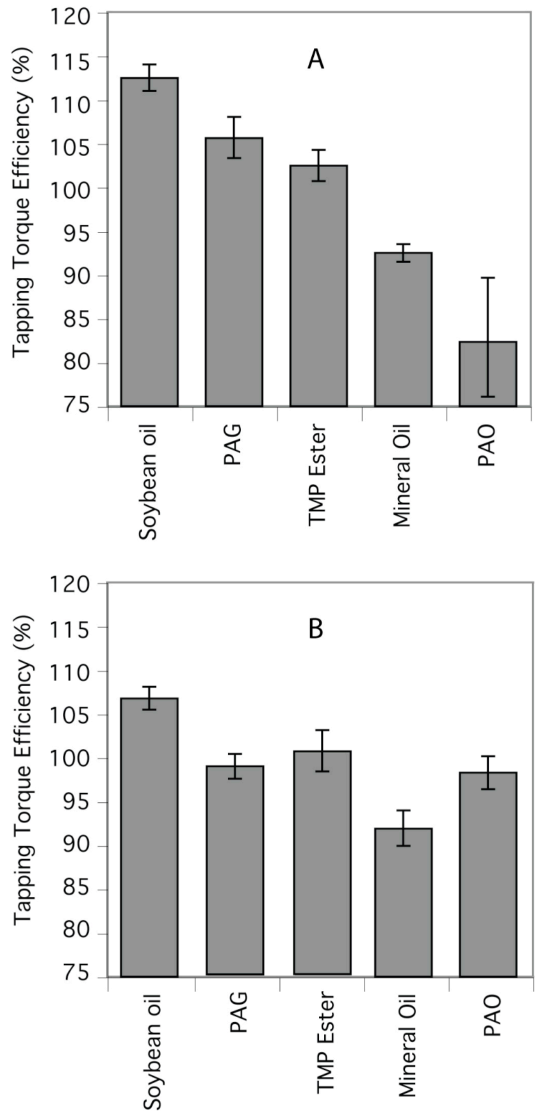


Figure A.8. Thread cutting data for five representative MWF lubricants as straight oils and in CO_2.

A.1.4.2 Thread Forming

Experiments were conducted using the thread forming test to further explore the differences between vapor and liquid phase lubricant + CO_2 mixtures in machining. Like other forming operations, thread forming is known to be lubrication intensive. The results shown in Figure A.9 show a dramatic decrease in performance for lubricants dissolved in CO_2. Spray conditions that produced 98% efficiency in cutting here produced 60% efficiency in forming. For these tests, PAG was selected to ensure that the trends being observed were not unique to soybean oil and because it was found to be nearly as effective as soybean oil in the thread cutting tests. Here, the reference fluid was straight PAG because the soluble oil used in the cutting tests would not provide enough lubrication to obtain a reasonable baseline. Consistent with the results presented in Chapter 4, the fluid phase lubricant with CO_2 dissolved performed over 10% better than lubricant alone. As discussed in Chapter 4, this increase in performance is likely due to better penetration of the CO_2 in PAG into the contact zone between the chip and the tool to reduce cutting forces and wear. The general conclusions that performance is driven primarily by whether the liquid or fluid phase MWF is delivered are strongly supported by these results.

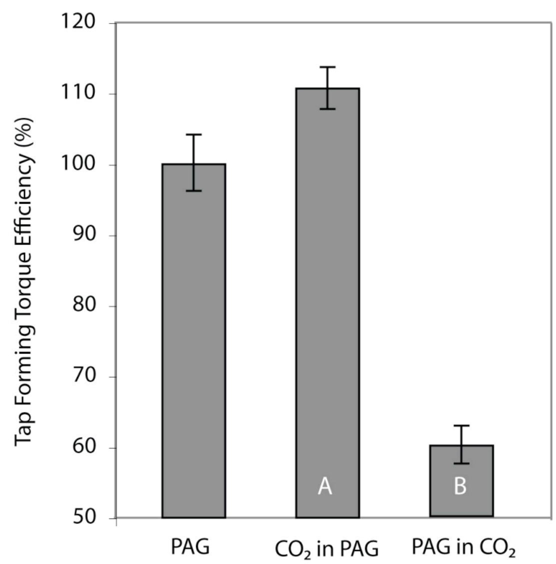


Figure A.9. Thread Forming results when cutting using straight PAG and A. PAG in vapor phase CO_2 and B. CO_2 dissolved in liquid phase PAG.

A.1.4.3 Turning

The two machining operations described above were performed for operations that are lubrication intensive. The results show that for processes that require heavy lubrication, (e.g., thread forming), application of liquid phase oil + $scCO_2$ reduces machining forces better than lubricants alone. To test the other end of the machining spectrum in which cooling is more important than lubrication, turning tests were conducted as described in Chapter 5 using sprays of CO_2 dissolved in liquid phase soybean oil and sprays of soybean oil dissolved in supercritical CO_2. The results (Figure A.9) show that sprays of supercritical phase CO_2 with lubricant dissolved reduce tool life much more effectively than sprays of lubricant with CO_2 dissolved. This effect is likely due to the cooling potential described in Chapter 5. For sprays of CO_2 dissolved in lubricant, it appears that the lower percentage of CO_2 in the spray does not produce enough cooling to affect a significant decrease in tool wear. Sprays of the lubricant rich liquid phase cannot remove heat well enough to reduce tool wear.

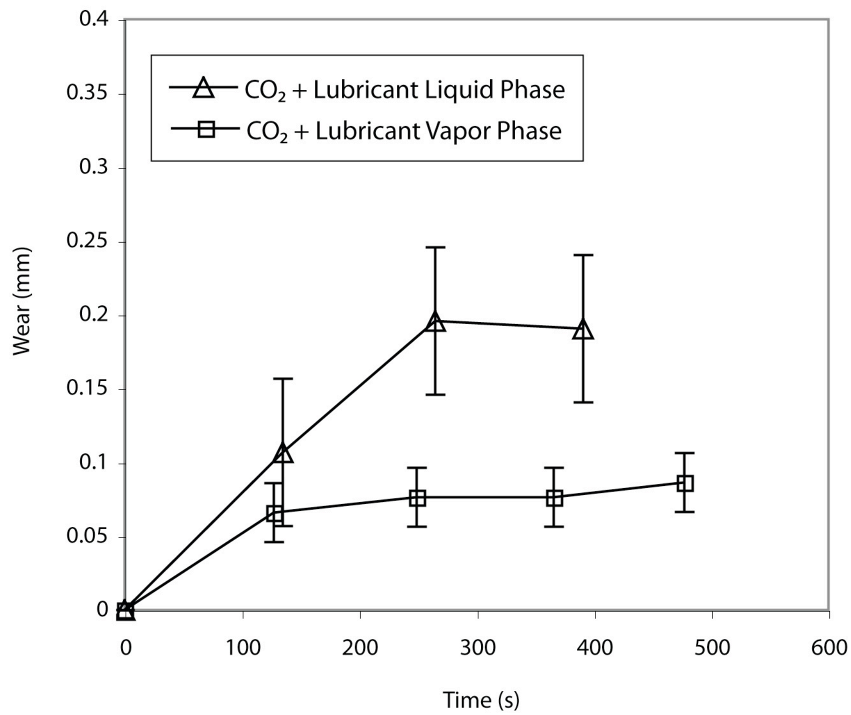


Figure A.10. Tool wear results for titanium cutting with CO_2 + soybean oil liquid phase and vapor phase.

A.1.5 Discussion

This work demonstrates that the phase behavior of CO_2 and lubricants must be evaluated for designing CO_2-based MWFs that are machining application specific. For processes that require extensive lubrication, it is preferable to deliver liquid phase CO_2 + lubricant. The combination shows better performance than straight lubricant in forming operations. For operations that are more cooling intensive, it is preferable to deliver sprays of vapor phase CO_2 with lubricant dissolved in it. This dual functionality with the same MWF formulation could be an advantage for reconfigurable manufacturing operations that need to change among various processes regularly.

This work also investigated the performance of several common MWF classes to determine how their solubility affects machining performance. The results indicate that machining performance of a straight oil is an effective predictor of performance when the lubricant is dissolved in CO_2. Soybean oil is the most effective MWF lubricant tested both alone and in CO_2. Though vegetable oils are infrequently used in manufacturing setting because of their high cost, the low volumes of soybean oil spread by this process, especially when vapor phase CO_2 is sprayed with lubricant, suggest that the new technology could make vegetable-based lubricant more affordable to many manufacturers.

Though soybean oil is the most effective lubricant tested in CO_2 and alone, the solubility of lubricants was an effective predictor of machining performance for all lubricants. As vapor phase sprays of lubricant dissolved in CO_2, the four lubricant classes tested had comparable solubility. As liquid phase mixtures of CO_2 dissolved in lubricant, the four lubricant classes had varying degrees of solubility that correlated well with machining performance. Effective delivery of CO_2-based MWFs will require consideration of supercritical phase behavior, lubricant solubility, and lubricant performance.

Appendix B

United States Patent Application

Metalworking Lubricant Formulations Based on Supercritical Carbon Dioxide

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(54) **METAL WORKING LUBRICANT FORMULATIONS BASED ON SUPERCRITICAL CARBON DIOXIDE**

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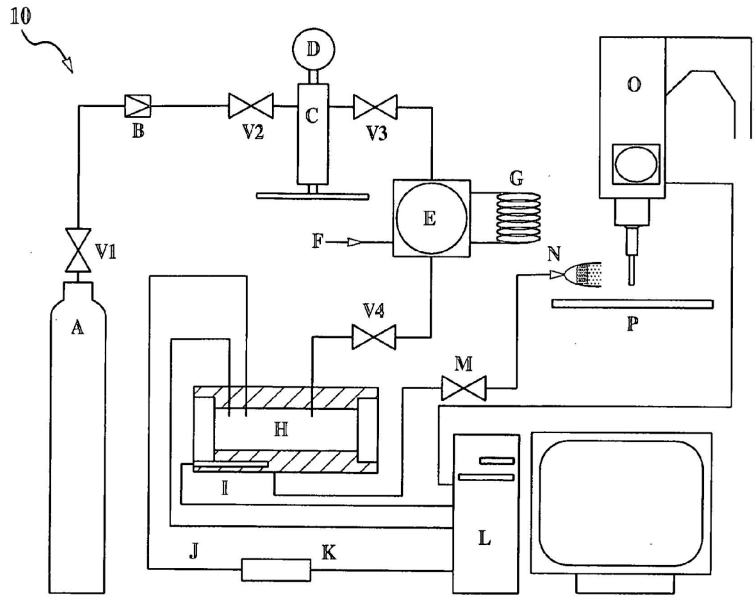
Publication Classification

(51) **Int. Cl.**
C10M 169/04 (2006.01)

(52) **U.S. Cl.** **508/154**

(57) **ABSTRACT**

A method for lubricating a metal workpiece during a metalworking process includes delivering supercritical carbon dioxide to the workpiece during the metalworking process. The supercritical carbon dioxide acts as a lubricant, coolant, chip evacuator, and/or carrier for another lubricant or corrosion inhibitor.


10
D
C
B
V2
V3
V1
A
E
G
F
N
O
P
V4
M
H
I
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K
L

FIG. 1

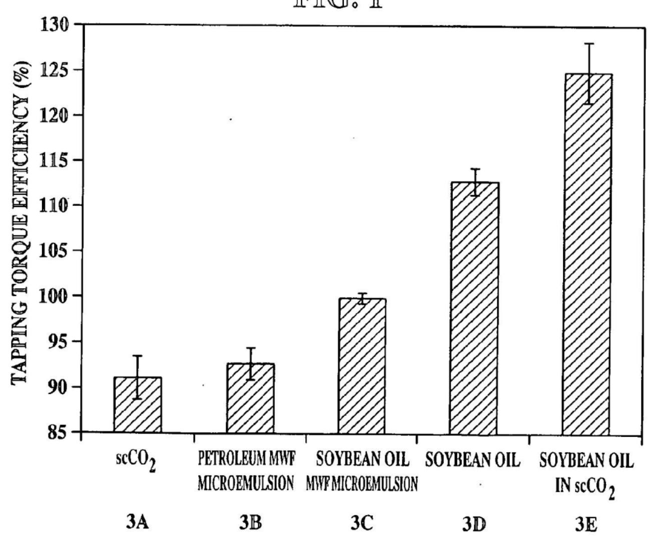
TAPPING TORQUE EFFICIENCY (%)
130
125
120
115
110
105
100
95
90
85
$scCO_2$
PETROLEUM MWF MICROEMULSION
SOYBEAN OIL MWF MICROEMULSION
SOYBEAN OIL
SOYBEAN OIL IN $scCO_2$
3A
3B
3C
3D
3E

FIG. 3

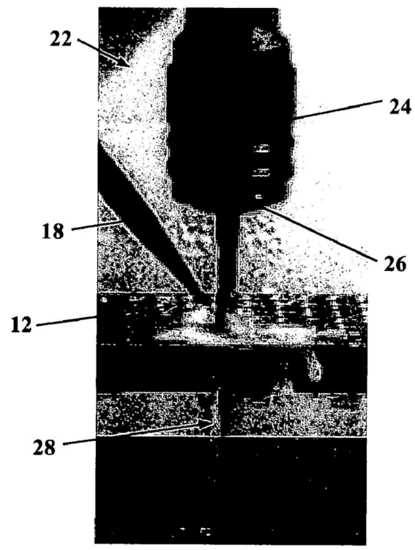

FIG. 2A

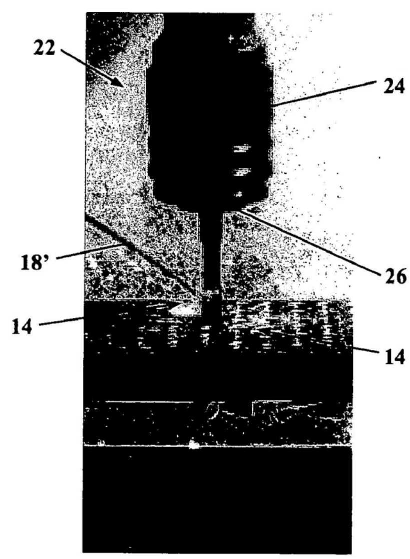

FIG. 2B

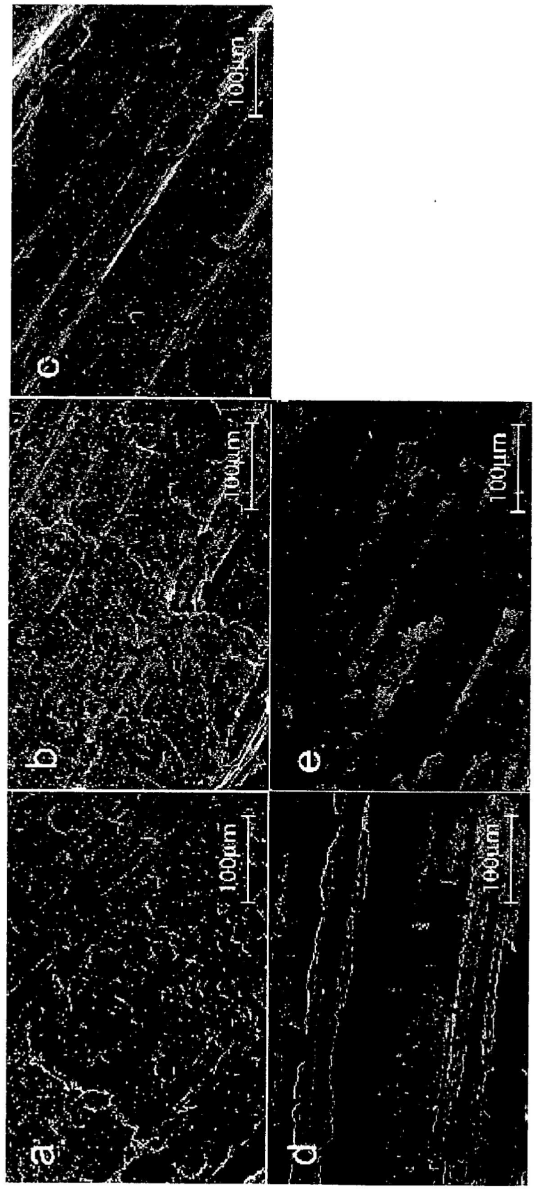

FIG. 4

METAL WORKING LUBRICANT FORMULATIONS BASED ON SUPERCRITICAL CARBON DIOXIDE

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit of U.S. Provisional Patent application Ser. No. 60/676,531 filed on Apr. 29, 2005.

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT

[0002] This invention was made in the course of research supported by a grant from the National Science Foundation (NSF), Grant No. DMII 0093514; and from the National Science Foundation (NSF)/Environmental Protection Agency (EPA), Grant No. RD 83134701. The U.S. Government has certain rights in the invention.

BACKGROUND

[0003] The present disclosure relates to metalworking, and more particularly to lubricants for metalworking.

[0004] Metalworking Fluids (MWFs) lubricate and cool metal during various metalworking processes (some non-limitative examples of which include cutting processes, forming processes, etc.) and are useful for proper process function. Specifically, MWFs increase tool life, substantially ensure proper surface finish, permit faster manufacturing rates, and reduce energy consumption during machining. They are typically oil in water emulsions, where the oil lubricates and the water cools the cutting zone. However, the mixture of oil and water has the potential to makes MWFs an environmental and occupational health concern. This may be due, at least in part, to the metals, organic constituents, and microorganisms that may accumulate in these fluids and to the aerosols that may form when they are sprayed in large excess onto machining processes. The aerosols that may form from these oily solutions reduce the air quality in the workplace and may, in some cases, potentially have acute and/or chronic skin and lung impacts on workers. The oil in water emulsions tend to degrade over time as a result of microbial attack and hard water ion accumulation, which may pose a waste treatment problem, particularly if the mixture contains toxic additives. Thus, the MWFs may become a hazardous waste problem when they reach the end of their useful life. Many environmental and health concerns potentially associated with MWFs may be substantially eliminated if the lubrication could be provided in minimal quantity using a solvent other than water.

[0005] As such, it would be desirable to provide metalworking lubrication in the minimal necessary quantity using a non-water solvent. Such an alternative solvent may advantageously reduce or eliminate the problems associated with water-based MWFs and, subsequently, the need for traditional MWF maintenance or treatment systems such as pumps and separation systems. Further, delivery of minimal quantity lubrication may conserve resources, maintain more consistent high quality process operation, and reduce life cycle emissions, while substantially aiding in removal of health risks and spoilage concerns potentially associated with traditional water-based MWFs.

SUMMARY

[0006] A method for lubricating a metal workpiece during a metalworking process includes delivering supercritical carbon dioxide to the workpiece during the metalworking process. The supercritical carbon dioxide acts as a lubricant, coolant, chip evacuator, and/or carrier for another lubricant or corrosion inhibitor.

BRIEF DESCRIPTION OF THE DRAWINGS

[0007] Objects, features and advantages of embodiments of the present disclosure will become apparent by reference to the following detailed description and drawings, in which:

[0008] **FIG. 1** is a schematic diagram showing an experimental setup incorporating an embodiment of the present disclosure;

[0009] **FIG. 2A** is a photograph of a tapping torque test using water-based MWFs;

[0010] **FIG. 2B** is a photograph of a tapping torque test using $scCO_2$-based MWFs according to embodiment(s) of the present disclosure;

[0011] **FIG. 3** is a chart depicting tapping torque efficiency for the following water-based MWFs and $scCO_2$-based MWFs: $scCO_2$ alone (**3**A); petroleum MWF microemulsion (**3**B); soybean oil MWF microemulsion (**3**C); soybean oil alone (**3**D); and soybean oil in $scCO_2$ (**3**E);

[0012] **FIG. 4***a* is a scanning electron micrograph (SEM) showing a magnified image of a chip surface in a piece of 1018 cold rolled steel cut with $scCO_2$ alone;

[0013] **FIG. 4***b* is a SEM showing a magnified image of a chip surface in a piece of 1018 cold rolled steel cut with petroleum MWF microemulsion;

[0014] **FIG. 4***c* is a SEM showing a magnified image of a chip surface in a piece of 1018 cold rolled steel cut with soybean oil MWF microemulsion;

[0015] **FIG. 4***d* is a SEM showing a magnified image of a chip surface in a piece of 1018 cold rolled steel cut with soybean oil alone; and

[0016] **FIG. 4***e* is a SEM showing a magnified image of a chip surface in a piece of 1018 cold rolled steel cut with soybean oil in $scCO_2$.

DETAILED DESCRIPTION OF THE EMBODIMENTS

[0017] The present inventors have unexpectedly and fortuitously found that supercritical carbon dioxide ($scCO_2$) may be used as an effective lubricant and lubricant carrier in metalworking processes/operations, such as, e.g., cutting and forming. Further, $scCO_2$ provides better basic lubricity in metalworking than does water and $scCO_2$ alone has been found to have lubricity substantially similar to that of basic semi-synthetic metal working fluids (MWFs), at least in one machining application. Lubricants such as straight oils, i.e. oils without the addition of water, are among the best known lubricants for most processes. Yet, the present inventors have also found that the combination of $scCO_2$ and lubricants is advantageously synergistic, i.e. the lubricity measured from the combination provides substantially better lubricity than the lubricity of either when measured alone. This has also been found to be true even if less oil is applied to the system when delivered in $scCO_2$. For example, improved performance has been found (with the $scCO_2$ delivery system) comparing the same oil with and without the $scCO_2$ delivery system but, advantageously, those improved results have been found with lesser amounts of the same oil when used with the $scCO_2$ delivery system. Still further, the present inventors also contemplate that method(s) according to embodiment(s) herein may also advantageously clear chips (chip evacuation) during cutting processes, reduce tool wear, provide corrosion resistance, and improve surface finish in certain systems.

[0018] Although supercritical CO_2 is becoming an important constituent in the pharmaceutical industry and semiconductor industry, and in chemical engineering extraction processes, etching processes, and cleaning processes, to date $scCO_2$ has not been shown to have advantageous use in the metalworking industry. As shown herein, $scCO_2$ lubricants and/or $scCO_2$-based lubricant fluids may be added to a cutting region in substantially controlled quantities, thereby improving efficiency and recovery, and reducing the amount of raw materials needed to make the fluids. Thus, the use of $scCO_2$ may be seen as a new class of micro-/nano-lubrication technology that may be compatible with all metal cutting and forming operations. It is also within the purview of the present disclosure to add more oil (i.e. not limited to micro-/nano-lubrication) to the metalworking zone, if desired.

[0019] Still further, novel dispensing method(s) as disclosed herein substantially create a supercooling effect (e.g. via dry ice), in addition to the substantially enhanced delivery of lubricants (when one or more additional lubricant(s), e.g., oil, are used as the lubricant in conjunction with the $scCO_2$). For machining operations in which the cooling requirements are greater than those met using the dry ice cooling, the $scCO_2$ system may optionally be coupled with a spray of compressed air or nitrogen or other inert gas as a pressure released cooling spray to provide additional cooling.

[0020] It is to be understood that, when the supercritical CO_2 formulation(s) of the present embodiment(s) reach the metalworking zone, they are no longer supercritical; yet the lubricant(s) are very finely dispersed and thus able to reach the metalworking zone (e.g. cutting zone) better than it/they otherwise could had the formulation not originally been supercritical. The greater pressure release also generally leads to more cooling per mass of lubricant delivered than with non-supercritical formulations.

[0021] As described more fully herein, it is to be understood that the present disclosure is not intended to be limited to any machining and/or forming operations; i.e. the tapping process described is but one example of many machining operations for which embodiment(s) of the present compositions are contemplated as being useful. Further, it is to be understood that the present disclosure is not intended to be limited to any single formulation/composition of the lubricants of the present embodiment(s). It is contemplated as being within the purview of the present disclosure that, in addition to $scCO_2$ alone, many oils, esters, fatty acids, flourinated oils, block co-polymers, surfactants, ionic liquids, and other compounds may be suitable for use in $scCO_2$-based lubricants of the present embodiment(s), either as oils dissolved or dispersed in $scCO_2$, or emulsified using surfactants designed for emulsification in CO_2 systems. It is also contemplated as being within the purview of the present disclosure that secondary additives may optionally be added to lubricants of the present embodiment(s). Some classes of secondary additives that are generally useful in metal machining operations are corrosion inhibitors, extreme pressure additives, boundary lubricants, and/or antiwear additives, recognizing that some types within these individual classes may not be soluble in CO_2 and, thus, may not be useful for this application. Yet further, it is to be understood that the method(s) and compositions/formulations of the present embodiment(s) may be useful for metal cutting (non-limitative examples of which include drilling, boring, turning, milling, tapping, broaching, thread forming, planing, shearing, punching, reaming, and/or the like), as well as for metal forming (non-limitative examples of which include stamping, drawing, rolling, extruding, forging, and/or the like).

[0022] As used herein, the term "metalworking" is meant to encompass all metal working operations, examples of which are metal cutting and metal forming. "Cooling, ""coolant," or like terms are meant to encompass the phenomenon of cooling of the metal workpiece due, at least in part, to rapid expansion of the carbon dioxide at/adjacent the nozzle. The lubricant composition(s)/formulation(s) described herein are meant to include any such lubricants, in addition to $scCO_2$ itself, that are dissolved and/or dispersed and/or emulsified by any suitable means in $scCO_2$.

[0023] As discussed in more detail hereinbelow, the SEM images shown in **FIGS. 4**_a_-**4**_e_ and the tapping torque data shown in **FIG. 3** are well correlated. The ground surfaces are indicative of higher friction; higher friction equates with higher torque; and higher torque equates with lower tapping torque efficiency. The comparison of **FIG. 3** and **FIGS. 4**_a_-**4**_e_ clearly shows this relationship. As such, from the data shown herein, it may be seen that the tapping torque efficiency is a reliable indicator of lubricity potential.

[0024] Further, method(s) of embodiment(s) herein also advantageously clear chips (chip evacuation) during cutting processes, thereby allowing deeper penetration of the lubricant(s) of the present embodiments. Such chip evacuation may be due, at least in part, to the pressure of the present method(s). It is to be understood that the deeper penetration of lubricant(s) may also be due to the very fine dispersion and high pressure of the carbon dioxide release, allowing very small droplets to reach deeper into the cutting and chip evacuation zones. Additionally, $scCO_2$ has a lower surface tension than water and is known to reduce the surface tension of fluids in which it is dissolved, further increasing the penetrating ability of lubricants delivered in CO_2.

[0025] Several vegetable-based formulations have been developed as alternatives to petroleum-based formulations. The tapping torque test is used to compare the performance of the new vegetable- and/or $scCO_2$-based lubricants to the petroleum- and water-based MWFs used today. It is believed that the data presented herein are the first to demonstrate the feasibility of CO_2-based MWFs.

[0026] Vegetable oils are desirable for use in MWF applications because they come from renewable feedstocks (which reduces dependence on foreign oil), they are less toxic during use and at the end-of-life, and they have been shown to be more stable and easier to recycle under field conditions. They may also be particularly suitable for medical applications (e.g. machining of medical products) since substantially no toxic materials are used, as well as for traditional operations. Vegetable oils have also been shown to be better lubricants than mineral oils. In addition, CO_2 is sequestered when the vegetable feedstocks are grown. While numerous feedstocks are available on the market, three common vegetable-based oils and two common petroleum-based oils were selected as illustrations for the experiments described herein. They are: naphthenic mineral oil, a 50/50 blend of naphthenic and paraffinic mineral oil, soybean oil, canola oil (75% oleic content), and a TMP Ester (a polyol ester made by reacting a mixture of nC8 and nC10 fatty acids with trimethylolpropane may be referred to as a "TMP" ester). The five oils were tested as straight oils, and as soluble oil and semi-synthetic MWFs, to understand the impacts of emulsification on base oil performance. Machining performance was evaluated using a modification to the standard tapping torque test (ASTM D 5619). MWF performance is expressed relative to a commercially available MWF using the metric "tapping torque efficiency." Higher efficiency indicates improved performance in the tapping torque test and has been shown to be a suitable metric for field performance (as discussed in further detail below).

[0027] Over 25 tapping torque experiments were conducted for each test fluid to establish a statistical estimation of the experimental error. The results indicate that as straight oils, all vegetable-based stocks perform significantly better than the mineral oils. This trend holds, although is much less pronounced, after the vegetable stocks are emulsified into soluble oil and semi-synthetic MWFs. The results also indicate that some vegetable oil-based stocks have a higher potential for lubricity than others, with data revealing that the soybean and TMP ester provide improved tapping torque efficiency relative to canola oil in emulsified MWFs. It is to be understood that the above experiments were run to show that vegetable-based MWFs (not formulated in $scCO_2$) perform as well or better than petroleum-based MWFs.

[0028] The research also produced stable dispersions of $scCO_2$ and soybean oil that can be utilized as MWFs. These dispersions can be sprayed on the cutting zone to apply lubricity locally with controlled quantity. In addition to providing lubrication, the rapidly expanding CO_2 provides superior cooling ability relative to water. Furthermore, the pressure release of CO_2 also provides a chip evacuation function previously achieved using water as the carrier for working constituents of the MWF.

[0029] The supercritical temperature and pressure of CO_2 (Tc=31.1° C. and Pc=72.8 atm) is easily achieved in industrial environments. Under these conditions, CO_2 is a good solvent for many materials, and it is to be noted that some vegetable-based oils are highly soluble in CO_2.

[0030] To test the feasibility of $scCO_2$-based MWFs, a dispersion of soybean oil in $scCO_2$ was developed and tested using the tapping torque method relative to soybean oil MWF microemulsion. **FIG. 1** illustrates an embodiment of an experimental setup **10** incorporating an embodiment of the present disclosure. It is to be understood that this is a non-limitative embodiment, and that some of the elements listed below may not be necessary and/or additional elements may be added, if desired. In **FIG. 1**, letter A represents a tank of food-grade carbon dioxide (Cryogenic Gases, Mich.); letter B represents a check valve; letter C represents a pressure booster (High Pressure Equipment, Pa.); letter D represents a pressure gauge; letter E represents a six-way valve (Valco Instruments, Tex.); letter F represents an oil inlet; letter G represents a fixed volume coil; letter H represents a high-pressure vessel; letter I represents a heating element; letter J represents a thermocouple (Omega, Stamford, Conn.); letter K represents a pressure transducer (Zook Enterprises, Ohio); letter L represents a computer; letter M represents a solenoid valve (Clark Cooper, N.J.); letter N represents a nozzle; letter O represents a tapping torque machine; letter P represents a steel work piece; and letters V**1**-V**3** represent pin valves.

[0031] In an embodiment of the setup **10**, CO_2 from tank A may be pressurized to supercritical pressures by pressure booster C. Oil via inlet F may be added to the pressurized CO_2 using the valve E, which may be any suitable valve or device. The mixture of pressurized CO_2 and oil may then pass into vessel H, which may be any device suitable to contain the pressurized mixture. Oil may exit the vessel H and pass through a solenoid valve M before being sprayed out of nozzle N and onto the metalworking region, such as a steel work piece P in a tapping torque machine O.

[0032] The computer L, which may be any suitable computing device, may be used to control actuation of the solenoid valve M and/or to record data from the tapping torque machine O. The computer L may also be used to monitor/control operating/environmental conditions inside vessel H. The computer L may receive temperature data from the thermocouple J and/or pressure data from a pressure-sensing device. The computer L may be in communication with a heating element I and a pressure transducer K, both of which may be in communication with the vessel H, whereby if the temperature or pressure inside the vessel H falls outside a predetermined range, the computer directs the heating element I and/or the pressure transducer K to correct the environmental conditions to correspond with the predetermined range.

[0033] In another embodiment of an experimental setup **10**, oil may be added to, and mixed with pressurized CO_2 in the vessel H instead of, or in addition to oil added via the oil inlet F to valve E. In such an embodiment, a stir-bar may be included in vessel H to facilitate mixing of the CO_2 and oil.

[0034] **FIG. 2A** illustrates a tapping torque test using water-based MWFs **12** delivered via nozzle **18**, and **FIG. 2B** shows the same test utilizing $scCO_2$-based MWFs **14** delivered via nozzle **18'**. The tapping torque test of **FIGS. 2A and 2B** is performed with a tapping torque test tool **22** having a lock nut **24** and a specimen nut **26**. Excess water-based MWF **28** is visible in **FIG. 2A**, whereby the test shown in **FIG. 2B** using scCO2-based MWF **14** generally has no such excess fluid. It is to be understood that the test illustrated in **FIG. 2B** may provide greater lubrication and potential to reduce application rates while delivering less fluid **14** volume to the metalworking region.

[0035] The chart of **FIG. 3** illustrates tapping torque efficiency for water-based MWFs and $scCO_2$-based MWFs. The results show that soybean oil in $scCO_2$ (**3**E) performs roughly 20% better than a soybean oil MWF microemulsion (**3**C), as discussed further hereinbelow. The dramatic increase in performance observed reached a level of performance in the tapping torque test previously not observed. Although CO_2 is inexpensive, nonflammable, environmentally benign, and can be easily removed from products, it has been shown to be a potential contributor to anthropogenic global warming. This drawback, it turns out, is relatively small in the proposed application because the majority of the CO_2 used in industry is a byproduct of other processes. In effect, the use of CO_2 in industrial processes actually takes advantage of an abundant waste stream rather than creating demand for another pollutant. Therefore, relative to existing hazards of MWF systems to human health and the environment, the incremental global warming potential of $scCO_2$ MWF technology is not substantially significant.

[0036] This disclosure teaches new method(s) to lubricate, cool, and/or evacuate chips in metalworking operations using supercritical carbon dioxide ($scCO_2$). Water-based metalworking fluids (MWF) have traditionally been used to perform these functions even though the use of water may lead to high economic, occupational health, and environmental costs. Carbon dioxide, above its critical temperature and pressure, is a tunable solvent that dissolves certain oils. This means that oil can be delivered to interstitial spaces previously inaccessible to water jets. The oil-in-CO_2 dispersion can be sprayed out of a nozzle at high speed to deliver the oil and form dry ice in the cutting zone, as shown in **FIG. 2B**. The rapid expansion of the CO_2 leads to cooling at cryogenic temperatures. This rapid expansion of CO_2 and/or solutions in CO_2 cool significantly as a result of the pressure drop and can reach temperatures below about −80° C. A uniform coating of the solubilized material forms on the spray surface as the CO_2 warms and volatilizes. Tapping torque efficiency measurements showed that the new $scCO_2$-based fluids perform up to 20% better than conventional aqueous fluids in terms of tapping torque efficiency. Scanning electron microscope (SEM) images of the chips produced in the tapping operation suggest that $scCO_2$ is a better lubricant delivery mechanism than water, as described further hereinbelow. Further, when delivered in $scCO_2$, straight oils show higher performance than when applied under conventional pressures.

[0037] To further illustrate embodiment(s) of the present disclosure, various examples are given herein. It is to be understood that these examples are provided for illustrative purposes and are not to be construed as limiting the scope of the disclosed embodiment(s).

EXAMPLES

Tapping Torque Test Method

[0038] The machining performance of the MWFs developed as disclosed herein was measured via the tapping torque test using a MicroTap Mega G8 (Rochester Hills, Mich.) machine tool at a machining speed of 1000 RPM on 1018 steel work pieces that were pre-drilled and pre-reamed with 240 M6 holes (Maras Tool, Schaumburg, Ill.). Tapping was performed using uncoated high-speed steel (HSS) taps (for 1018 steel), with 60° pitch and 3 straight flutes. MWF evaluations were carried out according to ASTM D 5619, the Standard for Comparing Metal Removal Fluids Using the Tapping Torque Test Machine with several modifications made to account for the use of a MWF evaluation test bed that permits multiple evaluations on a single workpiece. MWF performance is reported here as percentage tapping torque efficiency (%), which is an average torque measured during full tool engagement normalized to the average torque measured for a reference MWF. Higher efficiency indicates improved performance in the tapping torque test, and has been shown to be an adequate metric for field performance as discussed below.

Supercritical Carbon Dioxide Test bed

[0039] An experimental test bed was designed by the present inventors to make $scCO_2$-based MWFs and apply them to the cutting region of a tapping torque machine. Referring again to **FIG. 1**, as previously described, a schematic diagram of the experimental setup is generally designated as **10**.

[0040] The CO_2 was boosted from ~700 psia to supercritical pressures >1070 psia by the pressure booster C. Oil was added to the mixture via the inlet F using a 6-way valve E, and the mixture was stored in a high pressure vessel H. The 25 mL volume vessel H had two sapphire windows for viewing the mixture. The mixture traveled through the pressure vessel H outlet and passed through an automated solenoid valve M before spraying out the nozzle N and onto the tapping torque cutting region. A personal computer L was used to monitor the operating conditions in the high-pressure vessel H, to control the actuation of the solenoid valve M, and to record the data from the tapping torque machine O.

[0041] The $scCO_2$-based fluids were applied to the cutting zone simultaneously with the engagement of the tapping tool into the blank workpiece surface. The valve M was opened for 2 seconds to allow the machine O to carry out the entire tapping process while being sprayed with the MWF mixture. For each test using the CO_2 fluids, the vessel H was brought to approximately 1500 psia and 35° C., and the contents of the vessel H were allowed to equilibrate for three minutes. As stated hereinabove, photographs of the cutting process using water- and $scCO_2$-based MWFs are shown in **FIGS. 2A and 2B**, respectively. In both cases, the valve M was released for the duration of the tool engagement. It is seen in **FIG. 2A** that the aqueous process, delivered under 20 psig, delivers an excess of MWF **12**. The setup of **FIG. 2B**, while delivering less fluid **14** volume, provides greater lubrication and the potential to reduce oil application rates even lower through process optimization. After the cut, the pressure in the vessel H was typically around 900 psia, and more CO_2 was fed into the vessel H to return the pressure to approximately 1500 psia. Additional oil was added after every six tapping experiments.

Formulations

[0042] The water-based MWF formulations were developed using soybean oil and mineral oil. The water-based formulations are based on a formulation provided by a commercial MWF supplier. A tapping torque efficiency of 100% represents the tapping torque efficiency of a soluble oil MWF purchased from such a commercial MWF supplier. The MWFs were first produced in concentrated form, and then were diluted to a working concentration in deionized water. This formulation procedure is consistent with the manner in which aqueous MWFs are prepared and utilized in practice. The compositions used for each of the aqueous formulations, as well as the formulations according to the present embodiments, are presented in Table 1.

TABLE 1

Component	$scCO_2$	Mineral Oil in Water	Soybean Oil MWF microemulsion	Soy-bean Oil	Soybean Oil in $scCO_2$
Soybean Oil			0.72%	100%	1%
Mineral Oil		0.72%			
Tomadol 91 (Nonionic Surfactant)		1.56%			
Tagat V20 (Nonionic Surfactant)			1.38%		
Dowfax (Anionic Surfactant)		0.14%	0.21%		
Coupler		0.07%	0.10%		
$ScCO_2$	100%				99%
Water		97.50%	97.59%		

[0043] Both of the water-based formulations were made with an anionic and/or nonionic surfactant, but the structure and the amount of surfactant was modified slightly between oils to achieve a stable emulsion. Both water-based formulations contained coupler as a secondary emulsifier.

[0044] The $scCO_2$-based formulation was made by injecting soybean oil into a high pressure vessel H at concentrations comparable to those in the water-based fluids. The contents of the vessel H were stirred using a stir bar, and the pressure and temperature were maintained above the critical values for CO_2. All of the fluid components were used as delivered from the manufacturer and were subject to the same handling and storage conditions. The base oils used in the formulations were a petroleum-based naphthenic oil and a soybean oil (Alkali Refined Soybean Oil, Cargill Inc., Minneapolis, Minn.). The surfactants for the aqueous formulations were Tagat V20 (a glycerol fatty acid ester-based surfactant commercially available from Degussa-Goldschmidt Chemical Corporation, Hopewell, Va.), Dowfax 3B2 (a disulfonate surfactant commercially available from Dow Chemical, Midland, Mich.), and Tomadol 91-6 (an alcohol ethoxylate surfactant commercially available from Tomah Corporation, Milton, Wis.).

[0045] Although not shown in **FIG. 3**, tests were also run according to the "Tapping Torque Test Method" described herein on 1018 high speed steel (HSS) using deionized water alone as the lubricant. The results of this test showed a tapping torque efficiency of about 50%.

Experimental Results and Discussion

[0046] Referring now to **FIG. 3**, the results of the tapping torque studies show that a soybean oil in $scCO_2$ dispersion (as depicted at **3**E) performs roughly 20% better than a soybean oil MWF microemulsion (as depicted at **3**C) in terms of tapping torque efficiency. Supercritical CO_2 alone (as depicted at **3**A) performs roughly as well as a conventional semisynthetic mineral oil in water MWF (as depicted at **3**B), and better than water alone. A soybean oil MWF microemulsion (at semi-synthetic MWF oil concentration 0.75%) performs as well as a mineral oil at the same level of a conventional soluble oil (3.4% oil) (not shown). Straight soybean oil, as depicted at **3**D, produced improved tapping performance up approximately 12% over the reference fluid (the reference fluid is a soluble, mineral oil-based oil used in industry, with wax added for additional lubrication). The reference fluid is not shown in the figures, but results in 100% tapping torque efficiency.

[0047] If soybean oil is delivered to the cutting zone using $scCO_2$ as the carrier, the performance of the fluid increases dramatically. The performance of the soybean oil-in-$scCO_2$ fluid is significantly better than soybean emulsified in water or even straight soybean oil. This suggests that, in addition to applying the lubricant and cooling the cutting region, the $scCO_2$ has tribological benefits that make the cutting process more efficient. In order to help investigate this phenomenon of enhanced lubrication properties offered by MWFs based upon soybean oil in $scCO_2$, scanning electron microscope images of the chips produced during the tapping process were taken.

[0048] Referring now to **FIG. 4**, generally speaking, **FIGS. 4***a*-**4***e* show that the chips produced in the presence of straight soybean oil and soybean oil in $scCO_2$ have less contact with metal surfaces upon exiting the workpiece. The similarity in the surface morphology between **FIGS. 4***d* and **4***e* suggest that as the oil dispersion in the $scCO_2$ fluid shoots out of the nozzle, it is penetrating the chip exit zone and filling void spaces on the backside of the chip to effectively carry load and prevent chip-tool contact.

[0049] As stated above, each of **FIGS. 4***a*-**4***e* corresponds with one of **3**A-**3**E, respectively. Representative electron microscopy images provided in **FIG. 4** clearly show that there is much more metal-to-metal contact in the tapping experiments characterized by lower values of tapping torque efficiency (e.g., petroleum MWF microemulsion, as shown in **FIG. 4***b*, and soybean oil microemulsion, as shown in **FIG. 4***c*) relative to experiments characterized by higher values of tapping torque efficiency (e.g., mixture of $scCO_2$ and soybean oil, as shown in **FIG. 4***e*). For instance, the petroleum-based microemulsion shows wear scars from the cutting process that have been ground down flat into the surface of the chip, as shown in **FIG. 4***b*. The image also indicates striations and scratch marks that are indicative of poor lubrication and metal-to-metal contact. This friction means that more torque must be supplied to perform the tapping operation, resulting in a lower value of tapping torque efficiency as depicted at **3**B. In contrast, the $scCO_2$/soybean oil MWF shows much less contact between the chip and workpiece, as shown in **FIG. 4***e*. In this case, the contact area is isolated to a few elevated relief zones on the chip surface that have not been ground down due to the presence of effective lubrication. Since these results are clearly distinguished from the use of soybean oil alone, as depicted in **FIG. 4***d*, it is believed that the pressure of the $scCO_2$ and its ability to carry previously dissolved soybean oil deep into the cutting process, may serve to minimize contact between chip and workpiece. This advantageously results in lower friction and observed torque in the tapping operation.

[0050] One of many conclusions drawn from experiments discussed herein is that metalworking fluids made from soybean oil and delivered in $scCO_2$ perform significantly better than traditional oil-in-water emulsions and straight oil MWFs.

[0051] Although a few formulations were discussed herein for illustrative purposes, it is to be understood that the demonstrated novelty and/or synergy derived from utilizing scCO2 in combination with lubricants in dissolved, dispersed, and/or emulsified mixtures may be extended to numerous classes of oils, esters, polymers, waxes, and soaps that include, but are not limited to, the following examples: mineral oils, including at least one of napthenic oils, paraffinic oils, and mixtures thereof, vegetable oils, including at least one of soybean oil, rapeseed oil, canola oil, corn oil, sunflower oil, and mixtures thereof; esters, polymers, and/or glycols, including at least one of trimethylpropane esters, polyalkylene glycols, polymerized esters (e.g., monobasic/dibasic acid, fatty amine-based, sulfurized), ethylene oxide/propylene oxide copolymers, synthetic and natural polymers (hydrocarbon, fluorinated, chlorinated), and mixtures thereof; as well as combinations of any of the above.

[0052] In addition, the scCO2 lubrication system may include extreme pressure additives for additional lubrication in metal forming or cutting applications with or without primary lubricants that include, but are not limited to, chlorinated paraffins, chlorinated waxes, chlorinated esters, chlorinated fatty acids; sulfurized fats, sulfurized olefins, polysulfides, sulfur-chlorinated compounds, sulfurized sulfonates, phosphate esters, phosphate fatty acids, phosphate amines (e.g., alkyl or aromatic), and/or combinations thereof.

[0053] Embodiments of the present method(s) and/or composition(s) using supercritical carbon dioxide ($scCO_2$) are adapted to deliver oil lubricants, boundary lubricants, and extreme pressure lubricants in metalworking applications. The use of CO_2 as a lubricant and/or as a lubricant delivery system offers the following non-limitative advantages: improved efficiency and recovery of metalworking, reduction in the amount of raw materials needed to fabricate products; substantial elimination of many, if not all, drawbacks associated with traditional metalworking fluids (one example of which includes their potential for microbial contamination); substantial elimination of the need for biocides that may become a problem due to potential disposal and occupational hazards associated with exposure to biocides in the manufacturing setting; substantial elimination of auxiliary metalworking fluid additives such as chelating agents, which may cause disposal problems; compatibility with a wide variety of traditional and non-traditional base oils such as fluorinated oils and surfactants with high oxidative stability, durability and potential for reuse, vegetable oils with low life cycle burdens relative to fossil alternatives and petroleum-based oils with surfactants; and an efficient recovery system for the oils and/or surfactants using $scCO_2$ as the solvent, which may advantageously lead to a "dry manufacturing" environment in which aqueous and/or organic solvents are no longer necessary. A further advantage is that method(s) and/or composition(s) of the present embodiments may substantially eliminate the disposal of metalworking fluids altogether.

[0054] Other advantages include, but are not limited to, reduced/eliminated need for MWF plant circulation and maintenance; applications to otherwise difficult to machine metals, such as hard steels or titanium; and application to products used in medical applications (substantially no toxic materials are used).

[0055] While several embodiments have been described in detail, it will be apparent to those skilled in the art that the disclosed embodiments may be modified. Therefore, the foregoing description is to be considered exemplary rather than limiting.

What is claimed is:

1. A method for lubricating a metal workpiece during a metalworking process, the method comprising:

delivering supercritical carbon dioxide to the workpiece during the metalworking process.

2. The method as defined in claim 1 wherein a lubricant is mixed with the supercritical carbon dioxide before delivery to the workpiece.

3. The method as defined in claim 2 wherein the lubricant is selected from mineral oils, vegetable oils, esters, polymers, glycols, fatty acids, and combinations thereof.

4. The method as defined in claim 1 wherein the metalworking process is a cutting process, and wherein metal chips formed during the cutting process are evacuated during delivery of the supercritical carbon dioxide.

5. The method as defined in claim 1 wherein the workpiece is cooled during delivery of the supercritical carbon dioxide.

6. The method as defined in claim 1 wherein the delivery of supercritical carbon dioxide substantially accomplishes at least one of microlubrication or nanolubrication of the metal workpiece.

7. The method as defined in claim 1, further comprising delivering at least one of compressed air or inert gas as a pressure released cooling spray to the workpiece during the metalworking process to provide additional cooling.

8. A composition for lubricating a metal workpiece during a metalworking process, the composition comprising a mixture of a supercritical carbon dioxide carrier and a lubricant.

9. The composition as defined in claim 8 wherein the lubricant is selected from mineral oils, vegetable oils, esters, polymers, glycols, fatty acids, and combinations thereof.

10. The composition as defined in claim 8, further comprising at least one of an extreme pressure additive, a corrosion inhibitor, a boundary lubricant, an antiwear additive, or combinations thereof.

11. The composition as defined in claim 10 wherein the extreme pressure additive is selected from chlorinated paraffins, chlorinated waxes, chlorinated esters, chlorinated fatty acids; sulfurized fats; sulfurized olefins; polysulfides; sulfur-chlorinated compounds; sulfurized sulfonates; phosphate esters; phosphate fatty acids; phosphate amines, and combinations thereof.

12. The composition as defined in claim 8 wherein the lubricant is at least one of dissolved in the supercritical carbon dioxide, dispersed in the supercritical carbon dioxide, emulsified with the supercritical carbon dioxide, or combinations thereof.

13. A system for applying supercritical carbon dioxide during a metalworking process, the system comprising:

a source of carbon dioxide;

a pressure booster in fluid communication with the source of carbon dioxide;

a high-pressure vessel in fluid communication with the pressure booster;

a source of lubricant in fluid communication with the high-pressure vessel; and

a nozzle in fluid communication with high pressure vessel.

14. The system as defined in claim 13 wherein the system is adapted to provide at least one of lubrication, cooling, corrosion inhibition, or chip evacuation during the metal-working process.

15. The system as defined in claim 13, further comprising an automated solenoid valve in fluid communication with, and located between the high pressure vessel and the nozzle.

16. The system as defined in claim 13, further comprising a computer in communication with a heating element and a pressure transducer, the heating element and the pressure transducer in communication with the high-pressure vessel, the computer adapted to control one or more environmental conditions inside the vessel.

17. The system as defined in claim 16, further comprising a thermocouple in communication with the computer and adapted to monitor a vessel temperature.

18. The system as defined in claim 13, further comprising a solenoid valve in communication with, and located between the high-pressure vessel and the nozzle.

* * * * *

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