Supporting Information for:

COMPARISON OF LIFE CYCLE EMISSIONS AND ENERGY CONSUMPTION FOR ENVIRONMENTALLY ADAPTED METALWORKING FLUID SYSTEMS

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Scope and Boundary of Life Cycle Model

This analysis compared the material production, application, and disposal of several metalworking fluid (MWF) systems. Impacts from the transportation of MWFs from production facilities to use facilities was excluded because it is negligibly similar for both volumes and distances shipped for each MWF system. Impacts from the transportation of carriers (e.g. CO_2 and water) were assumed to be small because these commodity chemicals are typically produced and consumed within close proximity.

MWF storage and delivery

Delivery of water-based MWF has traditionally occurred either from centralized distribution systems or from smaller tanks near the tool. 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 [1]. New gas-based MWF systems are designed to be stored next to the machine tool. To be consistent with both industry trends and between MWF systems in this analysis, it was assumed that each MWF is stored near the machine tool and delivered to the tool during use.

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 [2]. 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 [3]. 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.

Functional Unit

Machining time for one year was selected as the functional unit because it provided for the most internally consistent measure of MWF use. By necessity, it was assumed that the number of parts produced per unit time did not vary depending on the MWF type selected. The machining time selected for 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 a representative of the machine times used at other large metals manufacturing facilities.

Impact Categories

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 [4, 5]. 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.

Three 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. Eutrophication potential for the fluids was calculated as equivalents of PO_4^{3-} and found to be small <50 g/year for the aqueous MWF systems. 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.

Development of Figure 1

Figure 1 was developed by performing a search for the terms "Metalworking Fluid and 'X'" where 'X' is the exact term used in the plot. Two separate searches were performed, the first using the University of Michigan's general search tool which scans 8 databases (ArticleFirst, General OneFile, ISI Web of Science, Mirlyn, OAIster, ProQuest, Readers Guide Abstracts, Wilson Select Plus) and the second using Engineering Village. The magnitude of 'hits' for each search was similar using both searches. For each search, the titles were scanned and counted if they appeared to be on topic. In total 635 articles were selected as relevant. The articles represent only those published between 1/1/80 and the day the search was conducted, October 24, 2007.

Production

The life cycle data for the components included in the analysis were compiled from several sources with similar boundaries. The chemical compounds modeled for each component, with their respective primary and supplemental life cycle inventory (LCI) data sources, are listed by feedstock in Table S-1. The overall material and energy flows for the petroleum and bio-based compounds included in this analysis are presented in Figures SI-1 and SI-2 respectively.

Table SI 1: Life Cycle Inventory Data Sources for Metalworking Fluid components.

WATER	**Tap water** ETH [6]	**Demineralized** BUWAL database [7]	
CARBON DIOXIDE	**Commercial, hydrocarbon based** Bousted [8]		
BASE OIL	**Mineral Oil** McManus [9]	**Crude Oil** Bousted [8]	**Rapeseed Oil** McManus [9] Fertilizer Use [10, 11] Pesticide Runoff [12]
ANIONIC SURFACTANT	**Sodium Petroleum Sulfonate** Berna [13]	**Alcohol Sulfate** Hirsinger [14]	
NONIONIC SURFACTANT	**Dissopropanol Amine** Ethylene Oxide: Franke [15] Propylene: Bousted [8] Ammonia: BUWAL [7]	**Polyethoxylated Glycerol Ester** Linear Alcohol Ethoxylate: Schul [16] Coconut yield: Cassium [17] Glycerol: [18]	

Water

LC data for tap water in Europe was used as reported by the Association of Plastics Manufacturers in Europe [8].

Carbon Dioxide

The majority of the CO_2 that is used as an industrial feedstock is recovered in the steam reforming of hydrocarbons to make either ammonia or hydrogen[19]. LC data for CO_2 is based on the Bousted database [8]. See Allocation discussion below for more information on how impacts were assigned.

Petroleum-based oil

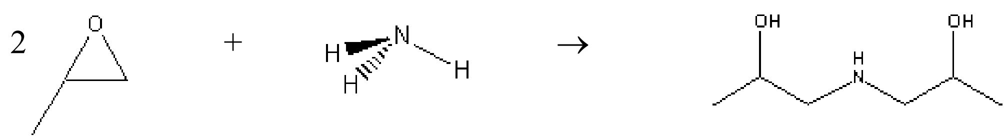
Naphthenic mineral oil. The base oil for the petroleum feedstock used in this study is a naphthenic mineral oil [20]. Life cycle data for the mineral oil was modeled as reported in BUWAL [7] and McManus [9]. The average yield for lubricating oil from crude oil in 2000 was 0.5 gallons (1.9 L) per 42 gallon (159 L) barrel, and the burdens associated with crude oil refinement were allocated by this mass percentage to the mineral oil.

Petroleum-based anionic surfactant

Sodium petroleum sulfonate. In petroleum-based MWFs, the anionic emulsifier most commonly used is sodium petroleum sulfonate (SPS) [21]. This component was modeled using life cycle inventory data reported for linear alkylbenzene sulphonates in Europe by Berna et al. [13].

Petroleum-based nonionic surfactant

Diisopropanol amine. Nonionic surfactants, such as fatty alkanolamides, are often used in combination with SPS in petroleum-based MWFs to form an anionic: nonionic surfactant mixture [22]. The nonionic surfactant component used for this model was a fatty amide based on diisopropanol amine (DiIPA). A mole of DiIPA can be synthesized by reacting 2 moles of propylene oxide with 1 mole of ammonia as shown in Equation SI-1:



Equation SI 1: Synthesis of Diisopropanol Amine, the petroleum-based nonionic surfactant considered in this work.

For estimation purposes, propylene oxide was modeled using data for propylene production from Bousted [8] and data reported for ethylene and ethylene oxide from an LCI describing the production of petrochemical intermediates in Europe [15]. First, the life cycle contributions associated with converting ethylene to ethylene oxide were determined. These energy and environmental emissions were then added to the life cycle inventory data for propylene to estimate the total life cycle energy consumption and emissions associated with the production of propylene oxide. The LC data for ammonia was used as supplied in the BUWAL 250 database [7].

Bio-based oil

Rapeseed oil. The life cycle model for rapeseed oil was developed based on data reported by McManus [9] with modifications for fertilizer use in Europe from the International Fertilizer Industry Association (IFA) [23]. According to the IFA, the average usages of nitrogen, phosphorous, and potassium fertilizers are 185 kg/hectare, 45 kg/hectare, and 48 kg/hectare, respectively.

The rapeseed oil production stages considered in the model were seedbed preparation, sowing, fertilizing, pesticide application, growth, harvesting, drying, storing, crushing, and refining. In this study, only the direct emissions and energy consumption of agricultural equipment during use (i.e., the acquisition and emissions related to the diesel fuel) were considered. For a field of 10,000 m^2 (1 hectare), approximately 60 kg of diesel is used to operate machinery for necessary agricultural processes (i.e., sowing, plowing fertilizing, harvesting, etc.) over the course of a season. The life cycle inventory of diesel was modeled using data reported by McManus [9].

There are several types of fertilizers, pesticides, and additives used to augment nutrients in the soil for improved crop yield. These include potash, magnesium, nitrate, and phosphorus fertilizers, herbicides, insecticides, and fungicides, as well as lime. Soil additive demands vary according to geographic location and were therefore estimated from values reported in the European Crop Protection Association Annual Report [10], in the European Commission report on Environmental Policy on Plant Protection Products [11], and by the International Fertilizer Industry Association report of fertilizer use by crop and country [23]. Emissions associated with pesticide use are dependent on the estimation of field runoff. Since the reported figures range from 0.5 - 10% by weight of the applied pesticide [12, 24], pesticide runoff was modeled at a mid-range value of 5% by weight of the pesticide applied.

It is expected that a 10,000 m^2 field will yield 3500 kg rapeseed and 7000 kg straw based on the developed country mean yield of rapeseed per hectare from 1990-2000 [25]. However, rapeseed is 85% dry matter and straw is 50% dry matter. Since the dry matter represents the useful product, impacts for all life cycle stages were allocated based on dry weight. Therefore, 10,000 m^2 of land was assumed to yield 2975 kg rapeseed and 3500 kg straw. Of the 2975 kg of rapeseed, 4 kg is needed to seed a 10,000 m^2 field [26] and this mass of product is cycled back into the agricultural process for future rapeseed oil production.

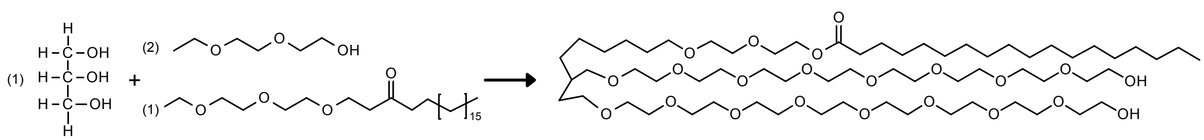
The balance of the rapeseed is sent to the mill for pressing, a process that separates the oil from the meal. Prior to pressing, the seeds undergo several steps of purification and conditioning prior to pressing including dehulling and enzyme deactivation for improved oil quality [9]. To obtain the maximum useful product, the oil is extracted using hexane as a solvent. While it was assumed that a maximum 0.75 kg of hexane is used per 1000 kg for extraction in accordance with the controlling Environmental Protection Act of the United Kingdom [27], a sensitivity analysis indicated that reducing the concentration of hexane to 0 did not have a significant affect on the total life cycle emissions and energy consumption associated with the bio-based MWF. On average, about 0.2% of this hexane is lost due to volatilization and residual in the oil while the balance is continually recycled [28]. It is assumed that solvent extraction, drying, and cooking produces about 1190 kg of oil and 1780 kg of meal, 40% and 60% of 2975 kg of rapeseed respectively [29]. Accordingly, only 40% of the impacts associated with these processes were attributed to the rapeseed oil.

Bio-based anionic surfactant

Alcohol sulfate. In the bio-based aqueous system, an alcohol sulfate (AS) synthesized from a fatty alcohol (based on petroleum or coconut feedstock) with an average chain length of C12-C14 was used as the anionic emulsifier. LC data for AS production in Europe was inventoried by Hirsinger [14].

Bio-based nonionic surfactant

Polyethoxylated glycerol ester. The nonionic surfactant used in the bio-based MWF emulsifier system was a polyethoxylated glycerol fatty acid ester (PGE). This surfactant was selected based on experimental results reported by the authors for the design of emulsifier systems for rapeseed oil [30]. PGE is made by reacting one mole of glycerol with three, different length, straight chain alcohol ethoxylates as shown in Equation SI-2. LC data for glycerol was obtained from [18]. LC data for alcohol ethoxylates was reported by Schul et al [16].



Equation SI 2: Reaction of glycerol with straight chain ethoxylates to make polyethoxylated glycerol ester, the bio-based nonionic surfactant modeled in this study.

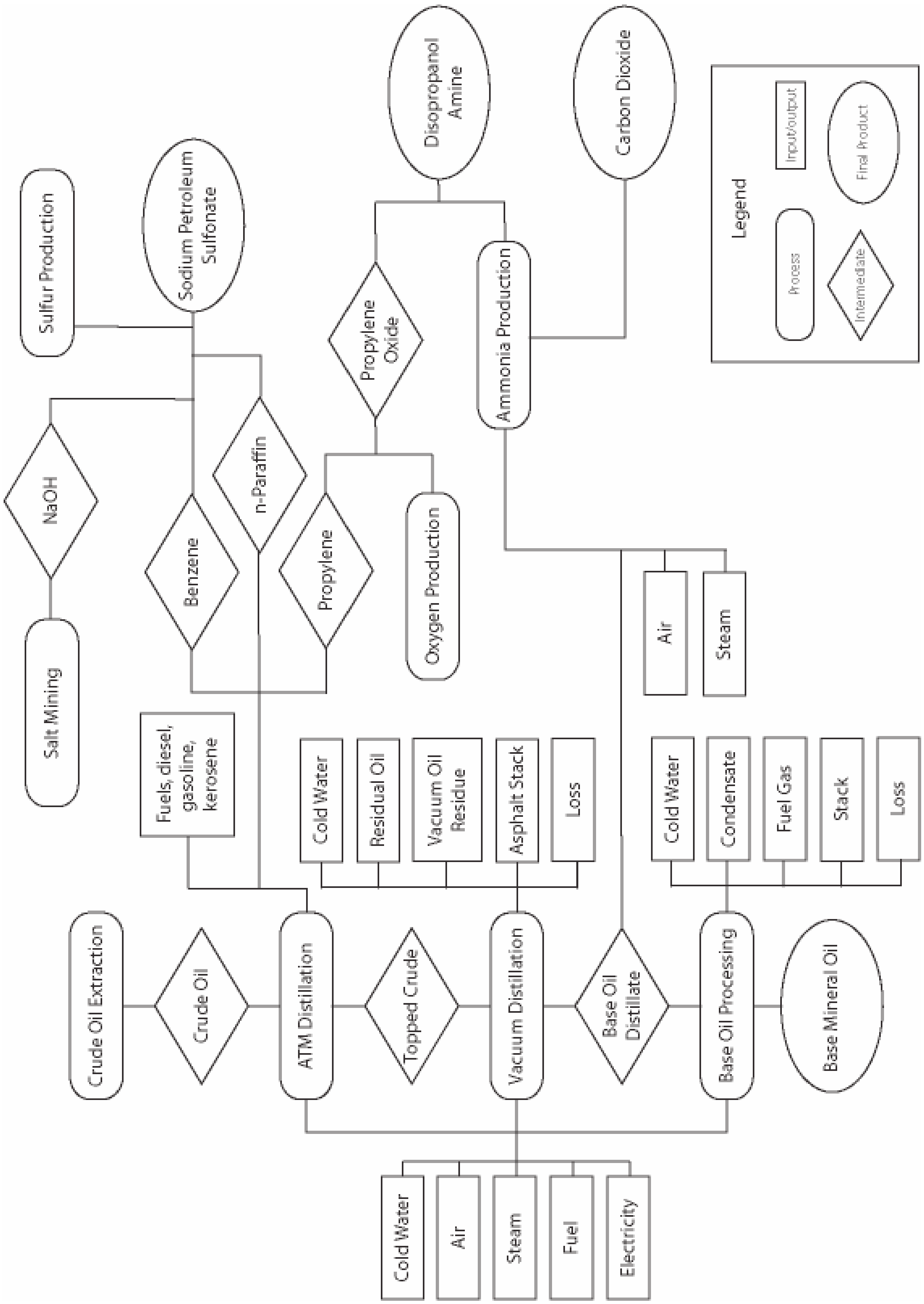


Figure SI 1: Schematic for the production stages of the oil and emulsifier system for petroleum-based products in MWF systems. Life cycle data sources are listed in Table SI-1.

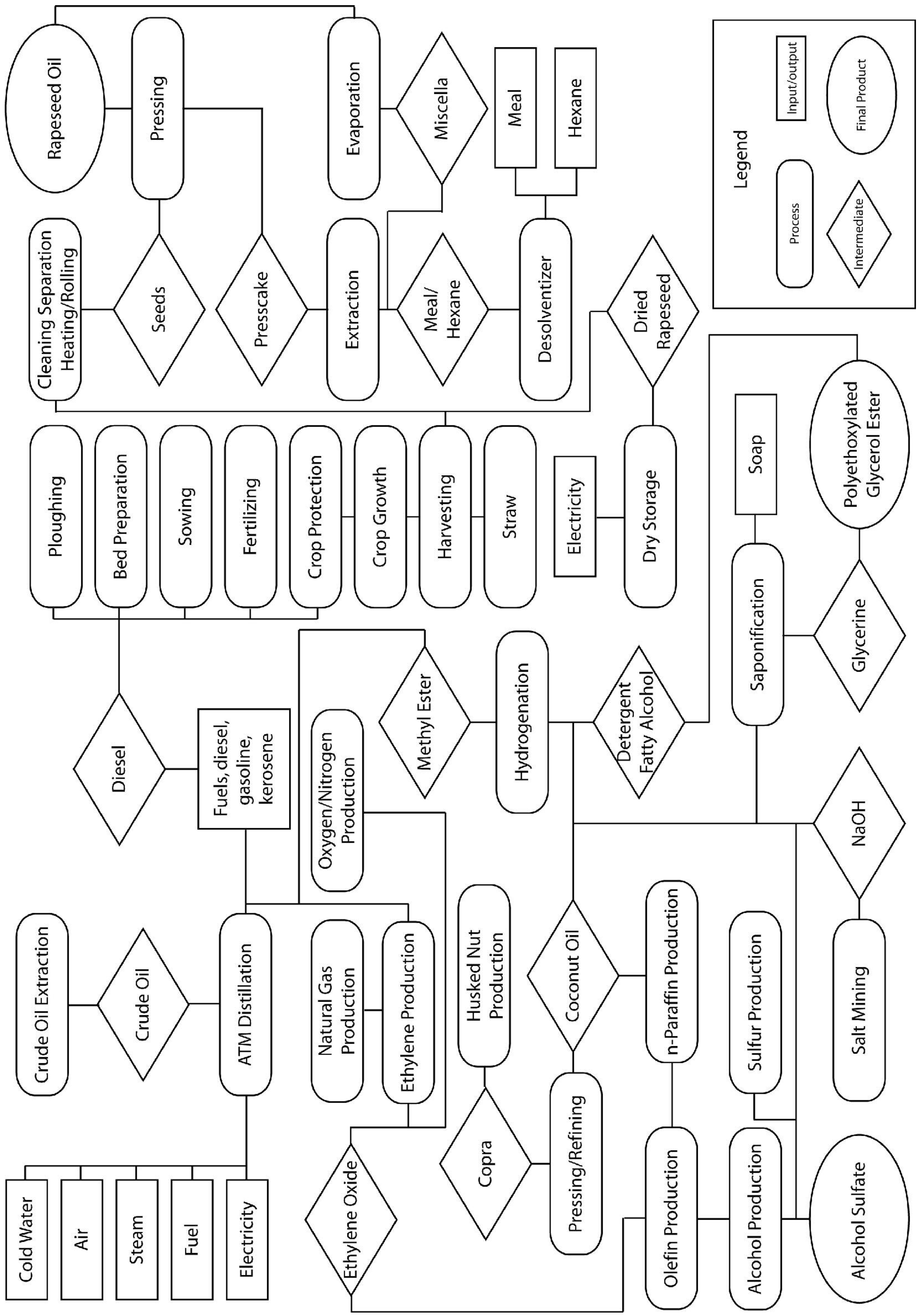


Figure SI 2: Schematic for the production stages of the oil and emulsifier system for bio-based semi-synthetic metalworking fluid components. Life cycle data sources are listed in Table SI-1.

Production Impact Comparison

When comparing MWF systems, particularly multi-component aqueous systems, it is useful to compare impacts based on individual components to illustrate the source of the environmental burden. Figure SI-3 compares the material production impacts for the two water-based MWFs broken down by component. The environmental emissions associated with the production of the MWFs delivered in gas were not broken down by component because they contain only two components: oil and carrier gas. Their production impacts are discussed in the context of the entire life cycle. The results suggest that surfactants dominate the impacts for four of the eight impact categories: GWP, acidification, energy, and solid waste. The rapeseed oil-in-water formulation has slightly lower GWP and acidification but requires more energy and produces more solid waste. The need for surfactants in both the aqueous systems means that though modest tradeoffs exist between petroleum- and bio-based fluids, neither system has a significantly lower impact than the other. A move away from aqueous systems would eliminate the burdens associated with surfactant production.

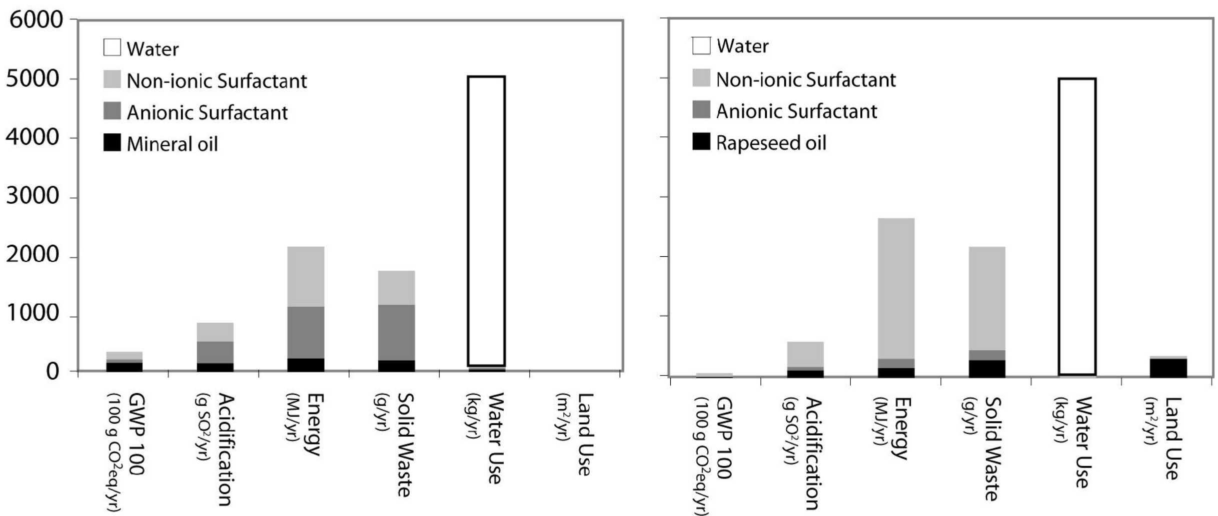


Figure SI 3: Production impact comparison for petroleum (left) and rapeseed (right) oil-in-water MWFs.

CO_2 Impact Allocation

The allocation of environmental impacts for all feedstock 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 (e.g. where small volumes of toxic substances are produced as a byproduct in an otherwise benign process) mass allocations can be inappropriate. 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 pricey commodity. Figure SI-4 shows the primary sources for industrial CO_2 based on [31].

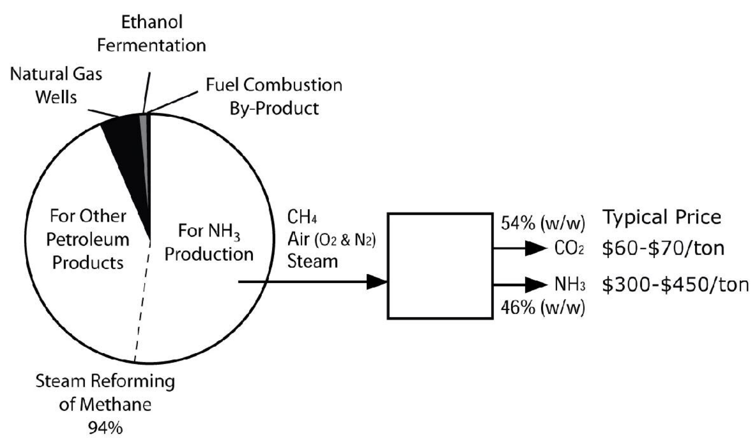


Figure SI 4: Allocation of impacts to carbon dioxide as an industrial feedstock. Most of the CO_2 produced in industry is a byproduct of the steam reforming of hydrocarbons and most of the hydrogen made from this process is used to make ammonia.

Economic

The authors chose an economic allocation for 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 it is not economical to collect the CO_2 byproduct, if it were, the price of 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.

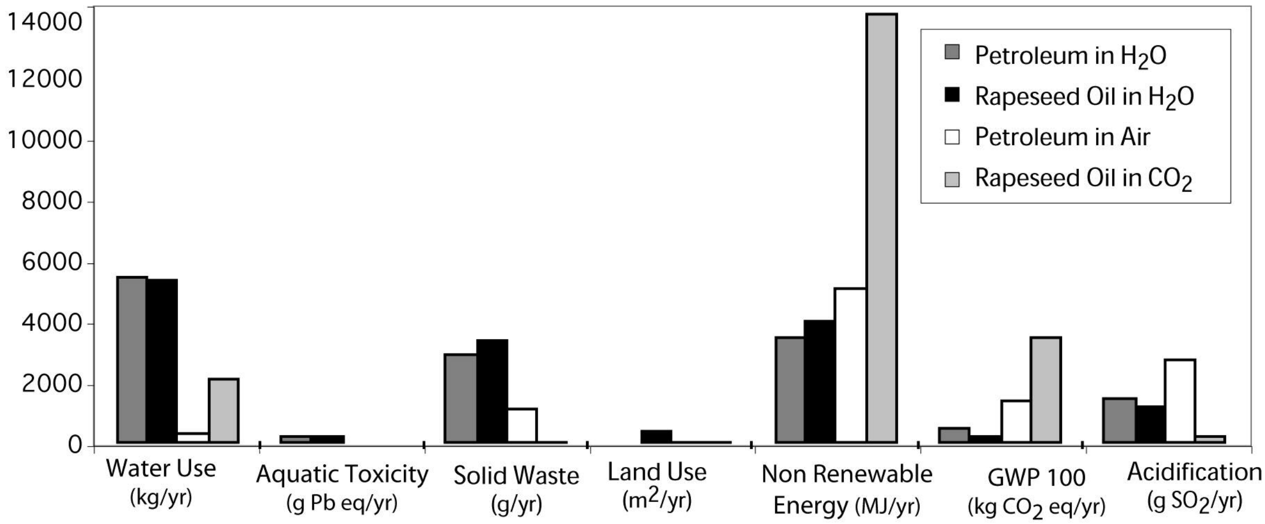


Figure SI 5: Life cycle impacts for the four MWF systems evaluated in this work based on expected operating conditions using a mass allocation of impacts to carbon dioxide.

Mass

The impact allocations for most feedstock performed in this analysis were conducted on a mass bases to be consistent with LCA methodology (Figure SI-6). For comparative purposes a mass allocation was performed of the impacts associated with CO_2 production from ammonia synthesis. The impacts associated with the rapeseed oil-in-CO_2 go up markedly in energy and GWP. In all other impact areas, however, the allocation influence is negligible.

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.

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 SI-2 lists the four 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. The authors believe that by assigning price allocation to the emissions factors for ammonia production they were able to capture both, the differences in emissions factors and the variability in the CO_2 market associated with the different processes through which it is produced.

Table SI 2: Select production emissions for the three processes that generate most industrial CO_2. 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 [32]

	Source	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

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 [6]. 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. 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.

From these analyses, one can draw the conclusion that CO_2 is a desirable solvent for MWF applications because 1) its environmental footprint is lower than many other industrial gases 2) it is already being produced in large quantities as a byproduct of other processes and 3) creating a new use for CO_2 before it is ultimately vented to the atmosphere while reducing other environmental emissions is a clear win-win scenario. The use of CO_2 in conjunction with bio-based oils makes them technically viable for a wide range of machining operations without dramatically impacting the life cycle impacts.

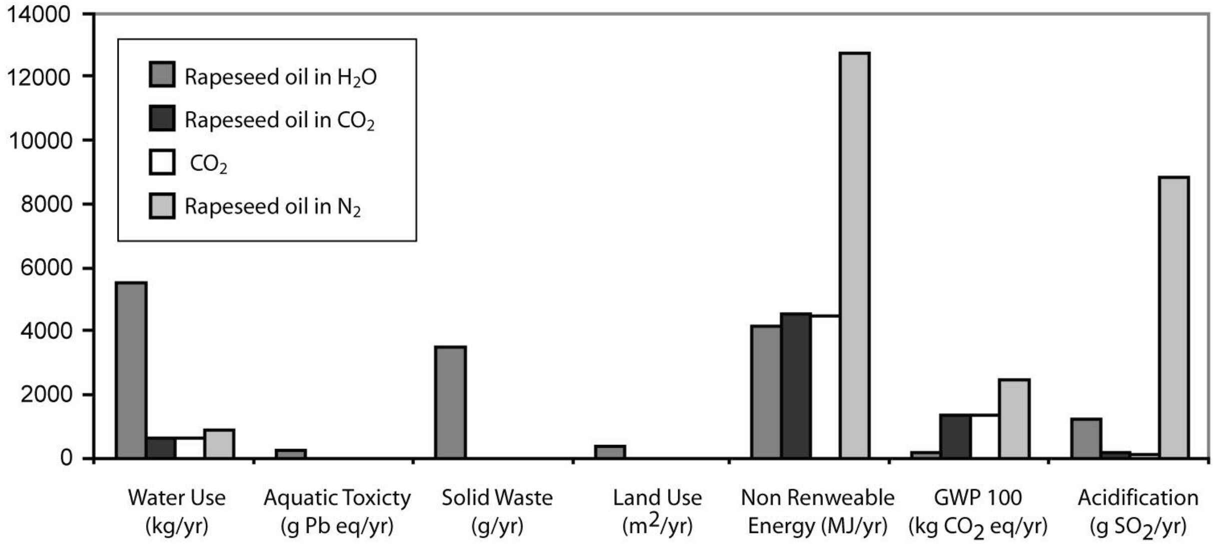


Figure SI 6: Life cycle emissions associated with alternative gas carriers or MWF with no oil relative to water based delivery.

Carriers Effects

Figure SI-7 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. 4). 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, however, are highly 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 increases the numerical values significantly, while a marginal price-based allocation would decreases the numerical values significantly. This sensitivity is further discussed in the supporting information. Overall the results suggest that delivery of minimum quantities of lubricant, regardless of the feedstock in gas carriers is the most effective way to reduce environmental emissions.

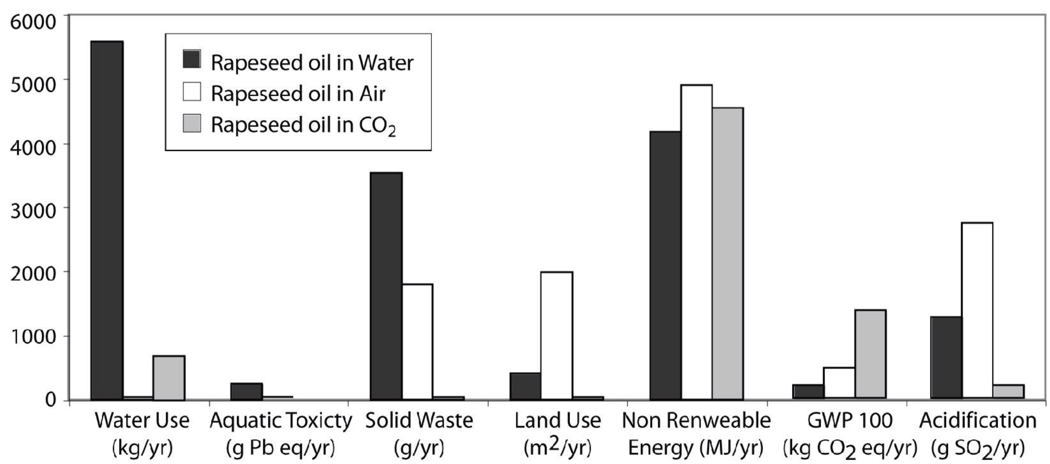


Figure SI 7: Life cycle impacts for MWF delivered in water, air, and CO_2 demonstrate that a switch to gas-based delivery can reduce many of the impacts associated with water-based delivery.

Use Phase

Energy

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 per MJ of electrical energy produced [33].

The electricity consumption rates for the aqueous, MQL, and CO_2-based fluids were calculated using equations 1 and 2. A single machine tool using aqueous MWFs requires an individual pump to circulate the fluid from a 55 gallon (208 L) tank to the cutting zone (Equation SI-3). A machine tool using an air or CO_2-based MWFs would require a compressor to bring the gas up to operating pressures (Equation SI-4).

$$W_p = \frac{gh}{\eta} \text{ where } h = \frac{P_o - P_i}{pg}$$ **Equation SI 3**

$$W_C = \frac{c_p T_i}{\eta}\left[\left(\frac{P_o}{P_i}\right)^{\left(\frac{\gamma}{\gamma-1}\right)} - 1\right]$$ **Equation SI 4**

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 (c_p) the 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).

Water-based MWFs - In service, water-based MWFs are circulated between tanks, and the machining operation. MWF is lost to evaporation, leaks, spills, mist, and residue on chips and workpieces. Various influences may also affect its properties. These factors include leakage from the hydraulic system of the machine tool ("tramp oil"), oils and greases introduced on the workpiece, chips of workpiece and tool, as well as other environmental influences such as microbial growth and the accumulation of hard water ions from "make-up" tap water. After use in the machining process, the MWF is allowed to drip back into the reservoir. From the reservoir, the MWF is continually monitored and cycled through maintenance procedures such as filtration. Even with careful monitoring and maintenance, the fluid condition eventually deteriorates to the point where the MWF fails and requires disposal (13). This time interval can be as little as 2 weeks or as long as 1 year or more.

Minimum Quantity Lubrication (MQL) – Air-based MQL fluids are typically delivered to the tool from a device located close to the tool. Air is compressed to 0.3-0.5 MPa and mixed with oil that is pumped (10-100 ml/hour) into the spindle where the two components mix. All of the oil is carried out on the workpieces or collected as mist in disposable air filters.

CO_2-based MWFs - The components are stored separately as CO_2 in a standard cylinder and the vegetable oil in a high-pressure vessel. During machining, a pump and heating coil is used to increase the pressure and temperature of the CO_2 flowing into the high-pressure vessel where it dissolves oil. This mixture is then sprayed onto the machining process in regulated quantities. As the mixture expands out of the nozzle, it cools to form a mixture of dry ice and oil before it contacts the cutting zone. The CO_2 then volatilizes into the gas phase and diffuses into the air surrounding the machine tool. A thin film of vegetable oil is left on the workpiece or tool. All CO_2 and oil is lost after one use in the machining process.

Evaporation and Leaks

During use, several pathways exist for aqueous MWF escape into the environment: 1) water-based MWFs are stored in vessels that can and do leak, 2) water will evaporate out of the mixture and must be replaced, and 3) aqueous MWFs are carried out on workpieces [34]. Each of these pathways can be difficult to estimate in a general sense. Leaks will exist in older or less clean manufacturing facilities. Evaporative losses will depend on the MWF storage tank surface area and factory conditions. Carry-out will vary according to the machining operation and the size and/or dimensions of the workpieces being made. To incorporate all of these factors, a fixed percentage (5%) of the tank volume was replaced during use [35].

End of Life

Three treatment scenarios were considered for aqueous MWFs:

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. Waste water treatment is by far the most commonly encountered EOL technology and was therefore modeled as the nominal scenario in this analysis.

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 [36].

The results indicated that extending the MWF usable life using filtration reduces the magnitude of all impact areas relative to the other end of life schemes (Figure SI-8). 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 energy required to dispose of MWFs but it is markedly unfavorable in all other impact areas.

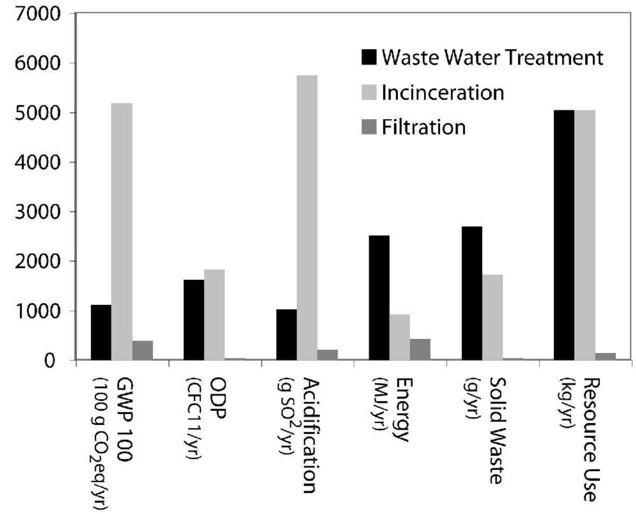


Figure SI 8: End of life impacts for the two water based MWFs. Filtration of MWF in use to extend the life of the fluid significantly reduces all of the environmental impacts.

Life Cycle Inventory

A life cycle inventory is provided in Table SI-3 that lists the results presented in Figure 3 of the manuscript broken out by life cycle stage.

Table SI 3: Life Cycle Inventory with data presented in Figure 3 broken out by life cycle stage. Prod. = production, Use = use phase, EOL = end of life.

	Petroleum in H_2O			Rapeseed in H_2O			Petroleum in Air			Rapeseed oil in CO_2		
	Prod.	Use	EOL	Prod.	Use	EOL	Prod.	Use	EOL	Prod.	Use	EOL
Water Use (kg/yr)	5624	8.6	0	5568	8.6	0	265	28.3	0	642	2.4	0
Ecotoxicity (g Pbeq/yr)	0.2	0.4	239	14.5	0.4	239	0.1	0	0	0	0	0
Solid Waste (g/yr)	1932	0	1077	2449	0	1077	1198	0	0	0	0	0
Land Use (m2/yr)	0	9.7	0	398	9.7	0	0	32.0	0	43.3	2.7	0
Non Renewable Energy (MJ/yr)	2400	1179	0	2993	1179	0	1388	3891	0	4220	330	0
GWP 100 (kg CO2eq/yr)	392	119	0	87.5	119	0	1022	393	0	309	33.5	1028
Acidification (g SO2/yr)	940	596	0	670	596	0	888	1966	0	23.8	167	0

Sensitivity Analysis

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. Use phase delivery characteristics were evaluated first Table SI-4 and these results are presented Figure SI-9. The influence of material production data on the analysis are presented in Figure SI-10.

Table SI 4. Model input values used in the sensitivity analysis.

	Low	Expected	High	Unit
Petroleum oil in H_2O	3.8	19	38	L/min
	974181	4870908	9741816	kg pumped/yr
	0	24	50	Replacement
	190	4548	9475	kg produced/yr
Rapeseed oil in H_2O	3.8	19	38	L/min
	974181	4870908	9741816	kg pumped/yr
	0	24	50	Replacement
	189.5	4548	9475	kg produced/yr
Petroleum in Air	0.1	1	2	Oil ml/min
	23	231	462	Oil kg/yr
	0.2	0.3	0.5	Air Pressure (MPa)
	206435	347004	550290	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

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 SI-3. The results are shown in Figure SI-9. For the lower limit, the results suggest that water based MWF can be operated in such a way as to reduce the environmental footprint below those of MQL systems in most impact areas. Through proper maintenance and infrequent replacement, aqueous MWFs have the advantage that they can be internally recycled within a process effectively reducing the impacts. Under worst-case conditions, the results of the expected results seem to hold, gas based MWFs tend to have lower impacts across the board. The results should be interpreted recognizing that variations in these systems are possible. Petroleum oil can be delivered in CO_2 rather than water or air, for example. In light of the possible variations and the sensitivity analysis two approaches seem to drive the largest impact reductions 1) choosing an MQL gas carrier suitable for the application (air for mild processes, $scCO_2$ for severe process) or 2) selecting operating conditions such that MWF is delivered in the precise quantities needed to operate the process without excess.

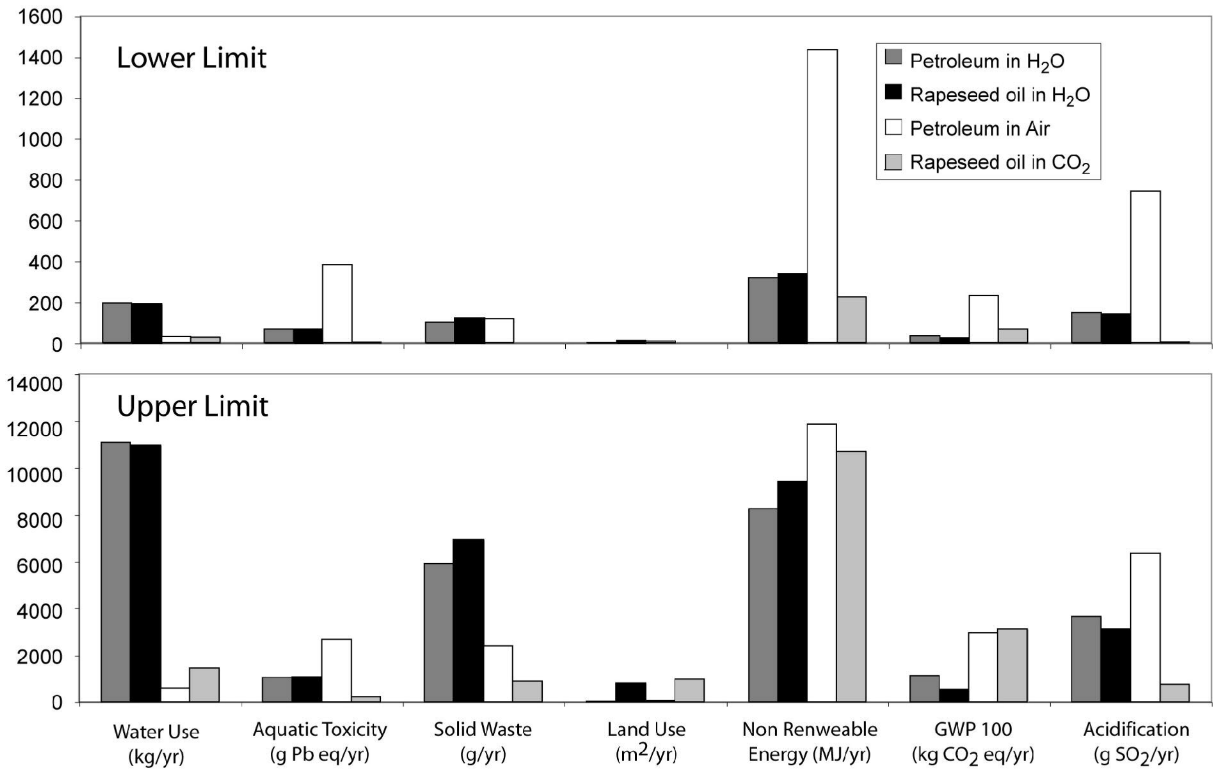


Figure SI 9. Lower and upper operating conditions for life cycle impacts for the four MWF systems. Operating conditions can affect which MWF system performs the most favorably.

To cross-reference the materials production impact data used in the analysis, the model was run using data form the ecoinvent database [37]. Minor differences were found for individual impact factors as would be expected when comparing across life cycle databases but overall the emissions factors corresponded well to order of magnitude resolution and smaller differences had little impact on the overall results of the analysis. Figure SI-10 shows how the model results appear using ecoinvent data. Some impacts such as nonrenewable energy increase substantially though the relative differences between MWF are consistent with those presented in Figure 3 of the manuscript.

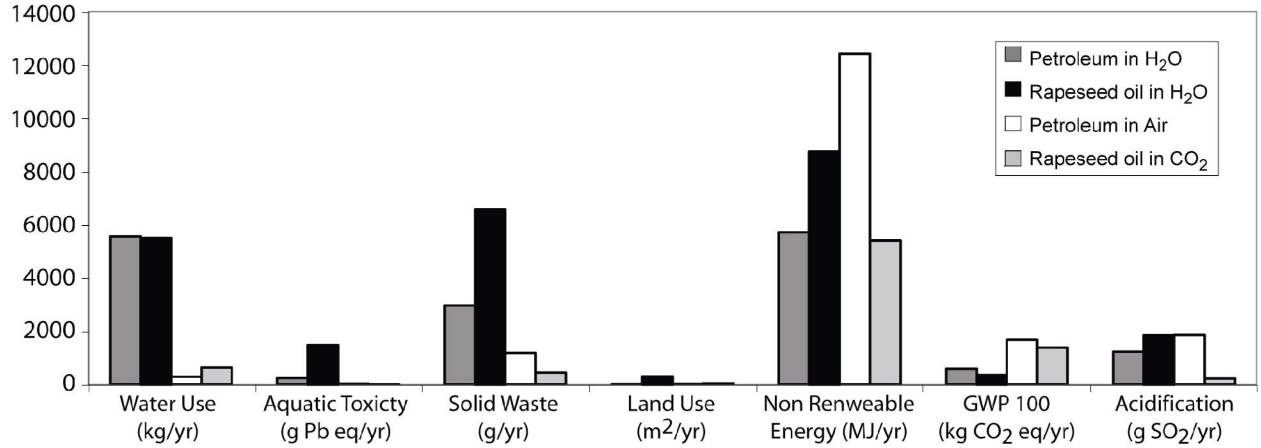


Figure SI 10: Model results using ecoinvent database values for materials production. The results suggest that the overall conclusions of the analysis do not change.

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