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10.5 Market driven emissions associated with supplying recovered carbon dioxide to sustainable manufacturing applications

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Abstract

This paper presents a life cycle assessment (LCA) framework for quantifying marginal emissions associated with the use of recovered carbon dioxide (CO_2) in sustainable manufacturing applications. A consequential LCA approach is applied to estimate marginal emissions from various steps in the recovered CO_2 supply chain such as capture, separation, and transport. These emissions are allocated to the CO_2 producer or the end user considering market forces, technology application, and product substitution. Additionally, a GHG accounting method is proposed that distinguishes between CO_2 generation and CO_2 emission to account for direct emissions from the recovered CO_2 supply chain. The approach is demonstrated in the context of a case study that considers using recovered CO_2 from an ammonia plant as an input to a machining process using supercritical CO_2-based metalworking fluid.

Keywords

Carbon Dioxide Reuse, Consequential Life Cycle Assessment, Green House Gas Accounting, Pollution Prevention, Technology Diffusion

1. INTRODUCTION

Carbon Dioxide (CO_2) is being widely considered as an environmentally benign substitute material in applications such as pharmaceutical production [1], polymerization [2], semiconductor manufacturing [3], metal component cleaning [4], and metals forming and machining [5]. The benefits of substituting existing process fluids with CO_2 are well known and include the elimination of numerous environmental concerns ranging from toxicity, to energy consumption, to water consumption. However, allocation methods used in traditional (attributional) life cycle assessment (LCA) may lead to gross overestimation of environmental impacts involving the use of recovered CO_2. Additionally, current greenhouse gas (GHG) accounting practices may place the burden of the reused CO_2 emission on these sustainable manufacturing technologies, especially in the event of a carbon tax introduction.

From a technology diffusion standpoint, overestimation of environmental impacts of using recovered CO_2 can act as a deterrent to its adoption, despite providing multiple environmental and health benefits. As a result this paper presents a framework to quantify the marginal emissions associated with the use of recovered carbon dioxide (CO_2) using a consequential life cycle assessment approach and a supporting greenhouse gas accounting methodology, so that the true environmental impacts from the use of CO_2-based process fluids in production systems can be assessed.

2. LCA AND GHG ACCOUNTING FRAMEWORK

2.1. Allocation and System Boundaries

A vast majority of the merchant CO_2 that is used today is recovered as a byproduct during the manufacturing of chemical products such as ammonia, hydrogen, and ethanol (hereafter referred to as primary market products) using chemical solvents, physical adsorption or membranes. Many of the plants that produce these primary market products simply release the CO_2 to the atmosphere without recovering it for sale in the merchant CO_2 market. In fact there are only about 100 plants recovering CO_2 in the United States, which is sourced and distributed in the merchant market by about five major companies. The limited supply of recovered CO_2 is due to relatively low demand for CO_2. As a result, marginal demand for CO_2 is unlikely to influence the production of the primary product such as ammonia or hydrogen.

A mass or volumetric allocation approach typically used in attributional LCA would suggest that recovered CO_2 should be allocated 50-90% of the environmental impacts associated with the production of the primary market product. This approach directly attributes environmental impacts to recovered CO_2 that were not *caused* by the recovery of CO_2. This both defies logic and deters use of recovered CO_2. Some studies have used a market price-based allocation [6] to address these issues, which results in lower impacts attributed to the recovered CO_2 since the price of CO_2 is significantly lower than that of the primary market product. The approach still does not lead to causal emissions being attributed to recovered CO_2, and faces additional problems identified by Overcash et al. [7] who noted that the demand and economic value of the primary market product and recovered CO_2 vary in manners irrelevant to environmental emissions. Thus, given that the demand for recovered CO_2 does not affect the production of the primary market products, a different approach is needed to estimate the real marginal emissions from the recovery of CO_2.

The allocation approach proposed in this framework is "market-based" and follows the approach outlined by Ekvall and Weidema [8]. The approach is rooted in consequential LCA (cLCA) methodology, which emphasizes the need to allocate emissions on a causal basis. In the case of recovered CO_2, a cLCA approach accounts only for the deployment and operation of marginal technologies employed by the producers of the recovered CO_2. The direct emission of the recovered CO_2 in the reuse application (e.g., machining process or soda drinks) is

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attributed to the primary market product that originally generated the CO_2. The cLCA methodology includes any significant differences in the environmental burdens from the transportation, use and waste management of CO_2, compared to the transportation, use and waste management of products and processes replaced by CO_2. We also expand the system boundary to encompass the production of other products or processes whose use is affected by the use of CO_2. For instance, the application of recovered CO_2 in manufacturing displaces traditional metalworking fluids and maintenance systems, and may extend tool life as well. The credit for the avoided impacts from the technologies displaced by CO_2 is

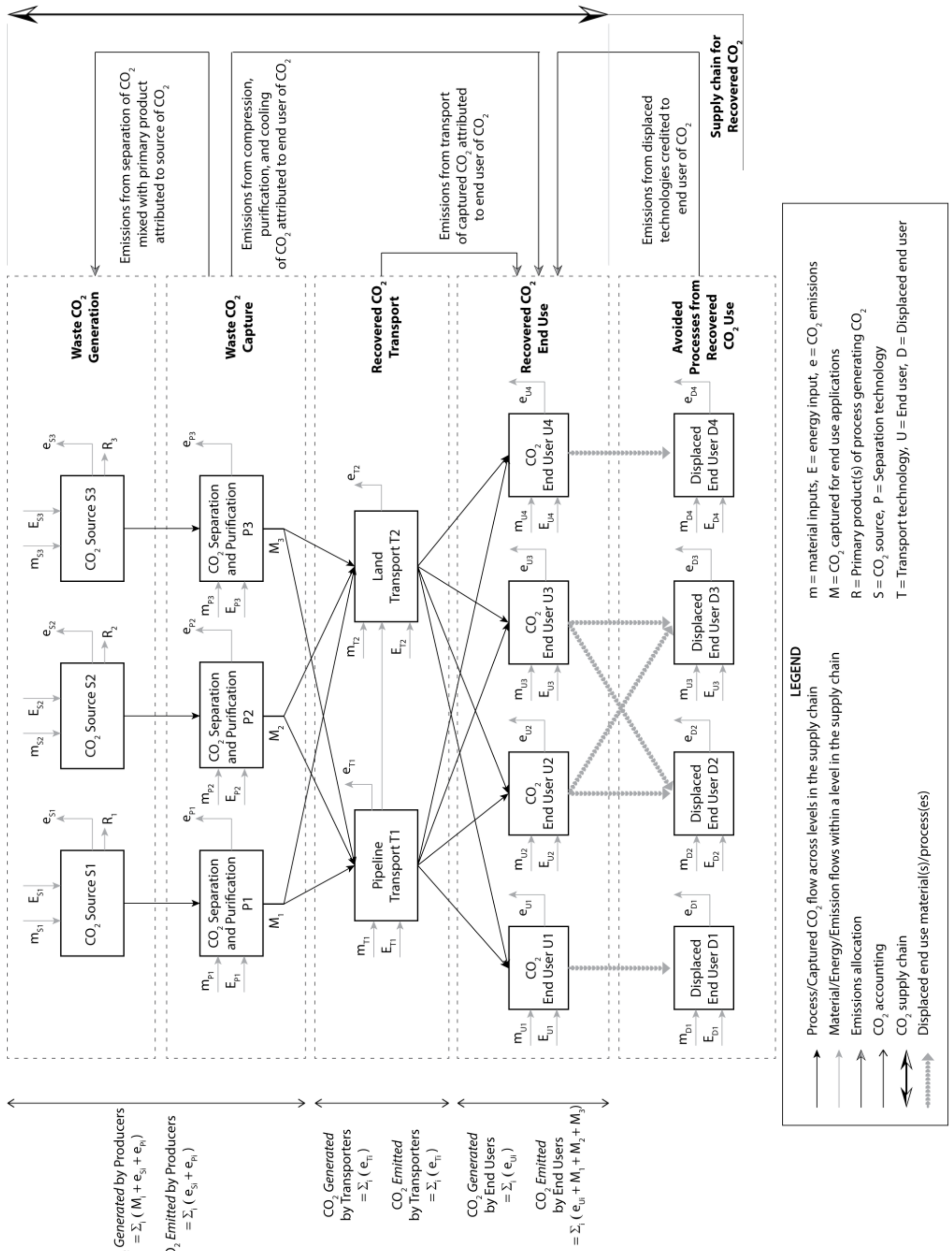

Figure 1: Recovered or waste CO_2 supply chain. Emissions allocations and greenhouse gas accounting methodology used in the framework are indicated.

given to the recovered CO_2 end user.

2.2. GHG Accounting

The World Resources Institute (WRI) and World Business Council for Sustainable Development (WBCSD) provide guidance for GHG accounting for businesses and organizations [9]. Companies first define their organizational boundary by using an ‘equity’ or ‘control’ based approach. Then there are operational boundaries within these organizational boundaries, which divide emissions into three ‘Scopes’. Scope 1 accounts for direct emissions that occur from operations owned or controlled by the company. Scope 2 accounts for emissions due to generation of electricity that is purchased by the company and its entities. Lastly, Scope 3 is an optional reporting category that encompasses all other indirect emissions (e.g., upstream production processes associated with materials used by a company). While the current WRI guidelines on operational boundaries clearly distinguish between direct (Scope 1) and indirect (Scope 3) GHG emissions from an organization, they do not distinguish between GHG generation and GHG emission. The WRI guidance document only mentions that (regulatory) compliance schemes are more likely to focus on the point-of-release of emissions. On this basis it is claimed that making a distinction between generation and release may not matter.

On the contrary, the cLCA approach inherently necessitates distinguishing between generation and emission of CO_2. Since Scope 1 does not distinguish between *generation* of GHGs and their *emission* into the atmosphere, we propose the definition of what we call here “Scope 0”, which accounts purely for generation of GHGs. Then Scope 1 is newly defined as the emission on GHGs. By these definitions, the total Scope 0 generation must equal the combined Scope 1 emissions from all points of CO_2 release if the CO2 is used in multiple applications. For organizations that emit all their generated CO_2, their Scope 0 and Scope 1 emissions are equal and WRI guidelines apply.

Based on the allocation approach outlined in the previous section, the global warming potential from the use of recovered CO_2 in a sustainable manufacturing application is the sum of its own Scope 0, Scope 2 and Scope 3 emissions. This revised approach can now serve as a more accurate accounting tool to separately account for CO_2 generation, emission, and avoided emissions. The proposed allocation and accounting method is explained in Figure 1.

3. LCA CASE STUDY

3.1. Background

Metalworking fluids (MWFs) are essential coolants and lubricants used in metal cutting and deformation operations such as turning, milling, grinding, and forming. In their most ubiquitous form, they are formulated as aqueous emulsions of mineral oils with at least a dozen other additives such as surfactants, biocides, corrosion inhibitors, and defoaming agents. Despite their widespread use today, aqueous MWFs have been known to have deleterious effects on human health such as dermatitis, cancer, respiratory disorders, and bacterial infections [10]. Untreated or improperly treated spent aqueous MWF waste can pollute the environment through release of toxic chemicals, BOD, and heavy metals. Aqueous MWFs along with their delivery, recycling, and waste management systems, are expensive and can constitute over 15% of a product’s manufacturing cost [11]. Aqueous MWFs also limit the material removal rate and tool life due to poor cutting zone penetration

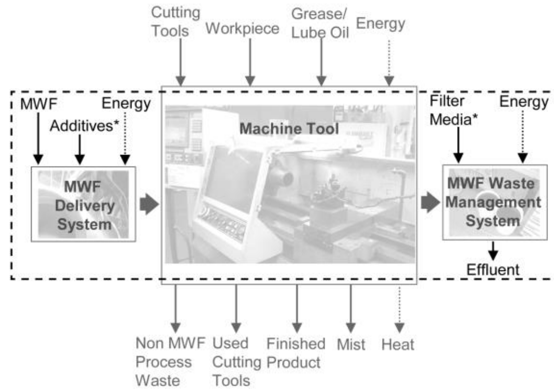

Figure 2: Flows marked in bold typeface fall within the LCA system boundaries indicated by the dotted line. Flows marked * indicate that data for proprietary materials such as extreme pressure additives or resins are not included in the analysis.

[12]. Thus, from a health, environmental, and cost standpoint, there is a need to replace aqueous MWFs with a more sustainable alternative. In this case study, aqueous MWFs thus serve as the displaced end-use technology. The alternate end-use technology is supercritical CO_2 ($scCO_2$) MWF, which is a rapidly expanding solution of lubricant in supercritical CO_2 directed at the tool-workpiece interface through a nozzle. $ScCO_2$ MWF has been shown to significantly increase tool life and material removal rates in numerous machining [13] and grinding applications. Additionally, $scCO_2$ MWF does not pose operator health risks or involve MWF waste management costs. The following sections evaluate the life cycle environmental impacts of applying $scCO_2$ using the cLCA framework discussed earlier. The results are compared with life cycle impacts of two alternatives to conventional MWF that have the potential to improve tool life: high pressure aqueous MWF and Liquid Nitrogen (LN_2).

3.2. Goal and Scope of LCA

The goal of this life cycle assessment is to estimate the marginal environmental impacts from the use of $scCO_2$ in machining and to compare the impacts with those of competing alternative MWF technologies in the market. Aqueous MWFs are assumed to be a 5% aqueous emulsion of semi-synthetic oil containing surfactants and biocides as per the formulation specified in Byers [14]. System boundaries used in the analysis are shown in Figure 2. Emissions from production of the machine tool and auxiliary machines such as MWF handling systems are excluded from the analysis. Emissions from wastewater treatment were found to be negligible and excluded from the analysis. For all MWFs, cradle-to-gate data on emissions, energy use, and water use were used for each component of the MWF considered in the analysis. Inventory data for CO_2 production from ammonia manufacturing was obtained from [7]. Emissions data from natural gas use at the ammonia plant were obtained from the Argonne National Lab GREET database [15]. Inventory data for U.S. average energy mix, vegetable oil in $scCO_2$ MWF, all components of aqueous MWFs, and materials used in aqueous MWF recycling and waste treatment were obtained from the SimaPro 7.3.3 database [16]. Energy emissions were calculated using the U.S. average energy mix. Emissions from transportation of compressed CO_2 and LN_2 were obtained from the NREL US LCI database [17]. Environmental impacts were evaluated for the following mid-point categories: 100 year global warming potential, Ozone depletion potential, photochemical smog formation potential, acidification potential, eutrophication potential, respiratory effects, ecotoxicity, total energy use, and fresh water use.

3.3. Functional Unit and Reference Flow

The functional unit is chosen as the service provided by a MWF system at a machine tool in a medium-size manufacturing facility in Detroit, MI machining Inconel alloy workpieces over a period of one year. Inconel is chosen as the workpiece material because of its recalcitrant machinability, which necessitates the use of MWFs with high heat removal capability (e.g., this rules out traditional minimum quantity lubrication as an option). It is assumed that the machine tool operates for two 8-hour shifts a day for 251 working days in a year with a utilization factor of 60%. The reference flow for the analysis is then the quantity of a MWF used at the facility over a period of one year.

3.4. CO_2 Allocation

In the ammonia manufacturing process, CO_2 is produced during a shift conversion reaction in which CO (produced along with H_2 from the reaction of methane with steam) is oxidized. This CO_2 has to be separated before the N_2 and H_2 present in the stream can react to form ammonia. Thus, the emissions inventory of the steps involved in CO_2 separation are allocated to ammonia. The separated CO_2 can be released into the atmosphere or compressed and refrigerated for being sold in the merchant market. Impacts from the production and maintenance of post-separation CO_2 processing and storage equipment are to be allocated to the end users of the merchant CO_2. In this case the end use is scCO_2 MWF in an Inconel cutting process. Impacts from the operation of post-separation CO_2 processing equipment to produce the reference flow amount of CO_2 used by the scCO_2 MWF are allocated to the cutting process.

3.5. Results and Discussion

Figure 3 illustrates how price-based allocation for CO_2 obtained as a byproduct of ammonia manufacturing can lead to over-estimation of environmental impacts of scCO_2 MWF by a factor of about 10. This overestimation is actually less than a mass-based allocation, which leads to an overestimation by a factor of 40 (this is because a mass based allocation attributes 54% of the impacts from ammonia production to CO_2 since ammonia only constitutes 46% of the process output by mass). Such over-of-magnitude overestimates can be expected to inhibit adoption of CO_2 applications in sustainable manufacturing. More generally, the results support the need for a market-based (cLCA) allocation approach for byproducts or co-products that do not impact the production of the main product(s) and have a significantly lower economic value than the main product(s). The results discussed in the following paragraphs assume a market-based allocation for the CO_2 used in scCO_2 MWF.

Figure 4 shows that a majority of the life cycle environmental impacts of scCO_2 MWF come from energy use for the compression and refrigeration of CO_2 at the ammonia plant. The nominal case in this analysis assumes that the manufacturing facility in Detroit, MI sources its CO_2 from the Lima, OH ammonia plant 250 km away through a local industrial gas supplier. As such, the impacts from transportation of CO_2 to the manufacturing facility contribute only about 25% to the total impacts in most impact categories except smog formation potential where it contributes to 60% of the total impacts. Impacts in the global warming potential, smog formation potential, acidification potential, and respiratory effects mid point metrics are strongly correlated to the distance of the ammonia plant from which the CO_2 is sourced.

CO_2 generated at the ammonia plant in the steam reformer and shift converter counts towards its Scope 0 emissions. The CO_2 in the steam reformer is emitted into the atmosphere at the ammonia plant, and constitutes its Scope 1 emissions. The CO_2 from the shift converter is captured at the ammonia plant, and eventually emitted at the manufacturing facility as spent scCO_2 MWF, thus constituting for the manufacturing facility's Scope 1 emissions.

Based on the allocation as well as GHG accounting method proposed in section 2, the CO_2 emitted from the manufacturing facility in the form of spent scCO_2 MWF is not counted towards the GWP of scCO_2 MWF. Figure 5 shows the GHG accounting for the ammonia plant and the manufacturing facility using scCO_2 MWF. The GHG emissions in Scopes 0, 2, and 3 of the manufacturing facility add up to the GWP potential of scCO_2 MWF (5114 kg CO_2 eq.). Additionally, since spent scCO_2 MWF only consists of CO_2 and trace quantities of lubricant, both of which are non-toxic substances requiring no additional treatment, the end-of-life impacts from the use of scCO_2 MWF

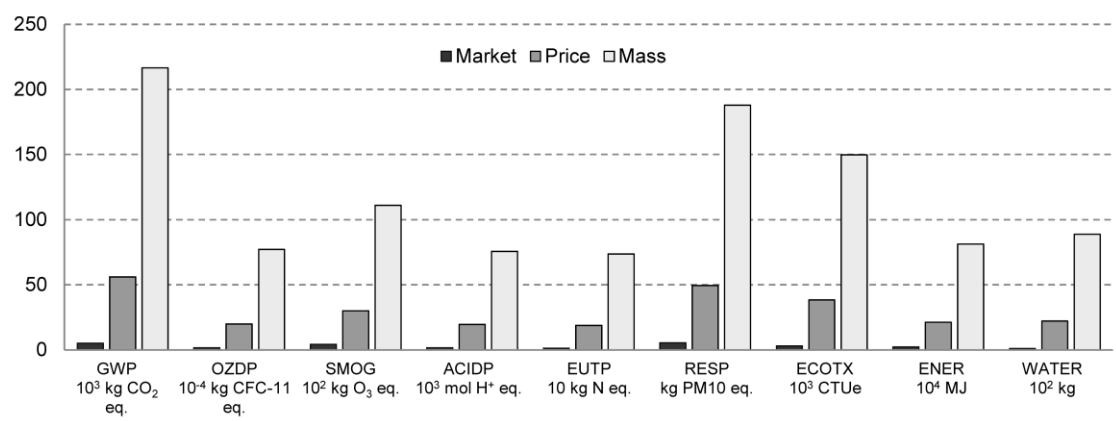

Figure 3: Comparison of different allocation methods for calculating the life cycle environmental impacts of scCO_2 MWF.

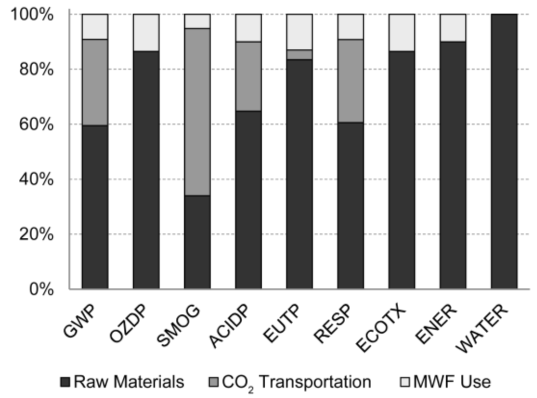

Figure 4: Breakdown of $scCO_2$ MWF environmental impacts by various stages in its life cycle. No significant end-of-life impacts observed for $scCO_2$ MWF.

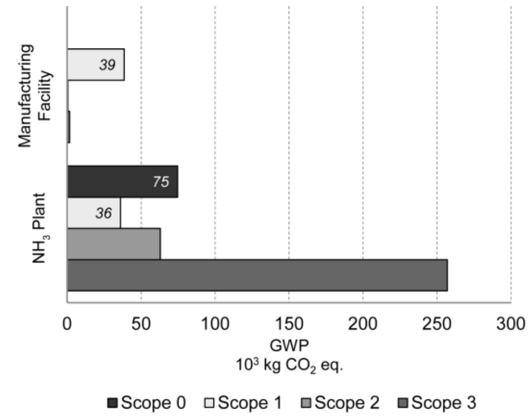

Figure 5: Application of the new GHG accounting method to the ammonia plant (CO_2 generator) and manufacturing facility (CO_2 emitter). All the CO_2 generated at the ammonia plant (Scope 0) is accounted for by the CO_2 emitted (Scope 1) at the plant and the manufacturing facility.

are insignificant.

Figure 6 compares the environmental impacts from $scCO_2$ MWF with high pressure aqueous MWF and LN_2 under the nominal operating conditions shown in Table 1. It is assumed that the aqueous MWFs are recycled weekly and disposed twice a year after proper primary, secondary and tertiary treatment of the spent MWF. The impacts shown for all MWFs do not include credits from the displaced conventional aqueous MWF end use. Avoided impacts from conventional aqueous MWFs, which are identical for all three MWFs are instead shown separately. These impacts should be subtracted from the impacts of each substitute MWF to estimate the marginal environmental impacts from the use of that substitute MWF.

It is observed that high pressure aqueous MWF has more than three times the impact of $scCO_2$ MWF in all categories. Most of the increased impact comes from the higher energy required to pressurize the water to about 11 MPa. The equipment, labor, and environmental compliance costs, as well as operator health and safety concerns associated with operating and maintaining conventional aqueous MWF systems still exist for high pressure aqueous MWF as they do for conventional aqueous MWF systems. While the analysis assumes that spent aqueous MWFs are properly treated before being discharged into the environment, this may not always be the case due the lack of specific regulations for MWFs. If untreated spent MWFs are released into the environment, they lead to high level of nutrient loading, human toxicity and ecotoxicity due to the presence of oils, biocides, and heavy metals.

Table 1: Values of key input parameters used in the LCA

PARAMETER	VALUE	UNITS
CO_2 flow rate	16	kg/hr
Vegetable oil flow rate	40	ml/hr
CO_2 Transportation Distance	250	km
Aq. MWF flow rate	1134	kg/hr
High pressure aq. MWF flow rate	3000	kg/hr
Aq. MWF sump size	100	gal
LN_2 flowrate	20	kg/hr
LN_2 Transportation Distance	925	km

LN_2 is produced using cryogenic air separation, which is an energy intensive process. This leads to higher environmental impacts compared with the other alternative MWFs. Transportation emissions for LN_2 are roughly 35% more than transportation emissions for CO_2, but the overall impacts are dominated by production of LN_2, and are thus strongly correlated with the flow rate of LN_2 MWF. The LN_2 MWF was assumed to be running without a lubricant.

It is important to differentiate and examine the environmental impacts of each MWF system from a qualitative perspective, as well as the quantitative perspective provided in Figure 6. For instance, global warming and ozone depletion are global impacts that have an adverse effect on the ecosystems worldwide regardless of the location of the emission source. Smog formation, acidification, eutrophication and ecotoxicity are more regional impacts. Even within each of these regional impacts, there is a qualitative difference between 1kg of pollutant emissions coming from a source such as an ammonia plant or a power plant that may be far away from populous areas, and 1 kg of the same pollutant emission coming from a source such as a transportation truck which causes a more localized impact on the air, water and soil quality. There could thus be a tradeoff between regional air quality and operator health and safety when selecting a MWF system.

The absolute value of the emissions should also be taken into account while assessing the relevance of a particular environmental impact. For instance the GHG emissions from $scCO_2$ MWF are comparable to an average person's annual personal driving GHG emissions, but all of the MWF systems considered here have several hundred times the average person's acidification or photochemical smog footprint. The decision to select a particular alternative MWF system thus has to put the quantitative LCA results in the context of a qualitative assessment of global, regional and human health impacts relative to the existing levels of pollution. These considerations should be made on a case-by-case basis beginning with the LCA results and approch provided here.

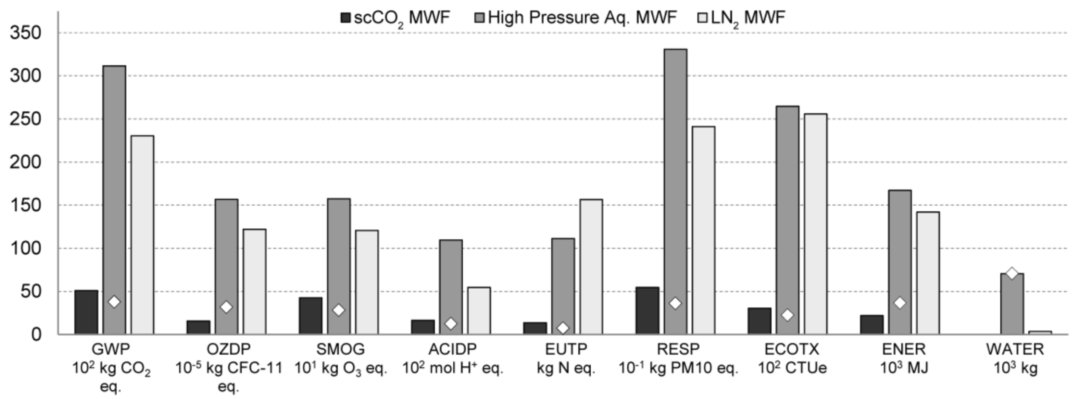

Figure 6: Life cycle environmental impacts of $scCO_2$, high pressure aqueous, and liquid nitrogen MWFs without displaced end use credit. Points along the high pressure aqueous MWF data represent values for conventional aqueous MWFs (displaced end use).

4. CONCLUSION

A market based allocation method consistent with consequential life cycle assessment frameworks is proposed for quantifying the market driven emissions associated with the use of recovered carbon dioxide in sustainable manufacturing applications. A greenhouse gas accounting method is also proposed that distinguishes between greenhouse gas generation and emission, thus

- creating a framework to assess and account for the true environmental impacts associated with utilizing recovered CO_2 to displace manufacturing processes that involve hazardous and energy intensive substances, and,
- eliminating barriers to the use of recovered CO_2 in such applications owing to previous problems of perception related to the use of mass-based and price-based allocation methods in assessing the environmental burdens of systems based on recovered CO_2 .

The approach is applied to estimate marginal emissions and environmental impacts from using CO_2 generated from an ammonia plant in a supercritical CO_2 metalworking fluid used at a manufacturing facility, while displacing the costly aqueous metalworking fluids that are harmful to operator health. The results indicate significant improvements machining productivity tool life and operator exposures may also come along with significant environmental improvements. Future work should focus on considering other end-use applications as well as understanding the local environmental impacts of recovered CO_2 systems.

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