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Sustainability Analysis of Phase-Change Solvents for Post-Combustion CO_2 Capture

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Phase-change solvents is a solution to the energy penalty problem of post-combustion CO_2 capture. While the improved thermodynamic performance of processes using phase-change solvents is previously demonstrated, there is no research done on the environmental and health aspects of such processes. The purpose of this study is to bridge this gap with the help of combined life cycle and safety, health and environment hazard assessment. In terms of life cycle analysis, steam for the reboiler, CO_2 compression for transport and electricity consumption by the flue gas blower are the main contributors to the impact, however, in comparison with the conventional solvents, phase-change solvents will require additional electricity and reclaimer steam input due to phase-separation and potential increase of degradation compounds, the overall energy requirement is, however, smaller. The assessment indicated that phase-change solvent systems may experience additional problems of accumulation of harmful solvent degradation products due to the design of the process. The study highlights that in comparison with the conventional systems, phase-change solvent process might require additional safety equipment, but the overall environmental and health impact of the system is expected to be lower.

1. Introduction

Limiting global warming to 1.5 – 2 °C requires a widespread adoption of efficient carbon capture and storage techniques. Post-combustion CO_2 capture by chemical absorption is the most mature among the existing technologies, and one that has already been utilized by several industrial projects. However, the high energy requirement and associated costs of the process hinder this technology's diffusion and large-scale employment. Currently, research is focusing on identifying new solvent blends (Bernhardsen and Knuutila, 2017) and process designs (Xue et al., 2017) to address CO_2 capture by chemical absorption. Specifically, CO_2 capture systems utilizing phase-change solvents seem to have certain advantages over conventionally proposed solvents (i.e., MEA) for climate change mitigation (Liu et al., 2019). At certain temperatures, phase-change solvents generate two phases and one of them—water rich flow—is recycled back to the absorber, reducing the input to the energy-intensive stripping process (Aleixo et al., 2011). Phase-change solvents are regenerated at lower temperatures (Boulmal et al., 2017), thus, the energy required for the recovery process is decreased. The beneficial thermodynamic performance of phase-change solvent systems has been extensively investigated. However, to ensure an overall optimal performance of phase-change solvents, their safety for the environment and human health must be established. Few studies have addressed this issue from the safety perspective. Some research exists for conventional solvents. For instance, it has been reported that such phenomena as amine degradation (Vevelstad, 2013), vaporization (Zhang, 2013), aerosol formation (Khakharia et al., 2013) increase the emissions of solvent and degradation products and, therefore, pose danger to the environment and human health. Badr (2016) highlights the change in hazard effects depending on the operating conditions of the process. The existing research with conventional solvents thus indicates serious concerns in terms of safety and environmental impact.

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Operation of the carbon capture process with phase-change solvents requires a different process design and operating conditions, and therefore problems and the impact of the systems utilizing such solvents might differ from the ones reported for the conventional capture systems. For phase-change solvents, a holistic assessment including health and environmental impact is still missing. Thus, the focus of the current study is analysis of potential problems related to the use of phase-change solvents in carbon capture systems and estimation of the potential impact of such systems. The analysis is done with the help of combined life cycle and safety, environmental and health hazard analysis supplemented by an exposure analysis. Such a combined method allows to perform a holistic assessment of the system to anticipate the potential harm related to the phase-change solvents before proceeding to larger scale implementation of the technology. This type of holistic assessment is presented for the first time in the context of phase-change solvents for CO_2 capture.

2. Method

The method includes analysis of the potential problems associated with the molecular structure of phase-change solvents, quality of the feed flue gas and process design of the system. The analysis evaluates to what extent the problems of the conventional carbon capture systems also appear in the new phase-change system. Such an analysis helps to introduce necessary mitigation equipment and improve the process design. The improved process design is then assessed by life cycle (LCA) and environmental, health and safety hazard assessment (EHS) supplemented by an exposure analysis to evaluate if the improved system can still potentially pose harm to the plant workers and environment and which aspects of the system require particular attention.

The method is applied to the carbon capture system utilizing the phase-change solvent MCA (methylcyclohexylamine). Process design data are based on simulations for the process structure of Figure 1. Flue gases of different quality, coming from a lime plant (Flue gas 1) and natural gas power plant (Flue gas 2), are considered in the analysis. The compositions differ in the content of CO_2, NO_X and SO_X. Flue gas 1 contains 3 times (mol %) more CO_2 and significant amounts of SO_x and NO_x (350 and 400 mg/Nm^3), while Flue gas 2 has no SO_x and only 21 mg/Nm^3 of NO_x. Both gases contain soot.

2.1 Characterization of potential problems and mitigation techniques

MCA is a secondary amine subjected to degradation. Zhang (2013) reports higher MCA loss compared to MEA, when exposed to oxygen and high temperatures, but the exact ratio is unknown due to the dissimilarity in conditions of experiment. The ratio 1.2 - 3 times of MEA rate was used in calculations for oxidative and 2 times - for thermal degradation. The major degradation products are assumed to be cyclohexanone oxime and ammonia (Zhang, 2013). Other unwanted components formed in the amine capture systems, nitrosamines, are known to be soluble in water (Drewes et al., 2006), and the process design with the recycling rich in water flowing back to the absorber might increase the rates of nitrosamines built-up in the system; an additional reclaimer after the absorber may be necessary to prevent the accumulation or, in a more novel design, nitrosamines and other harmful compounds can be treated by UV light and ozone.

The amounts of SO_x and soot in the flue gas significantly affect the amount of aerosols formed in the system (Khakharia et al., 2013), while NO_x influences the nitrosamines levels (Fine, 2015). Flue gas 1 has NO_x and SO_x compounds in high amounts, therefore NO_x and SO_x scrubber is required as additional equipment for the emissions control. The cleaning of the flue gas 2 can be avoided due to low concentrations of these substances. Both flue gases 1 and 2 contain soot and a Brownian Demister Unit (BDU) (or alternative) and water wash are required to minimize the effect of aerosols. The washing equipment and additional cooling also prevents loss of the MCA due to volatility.

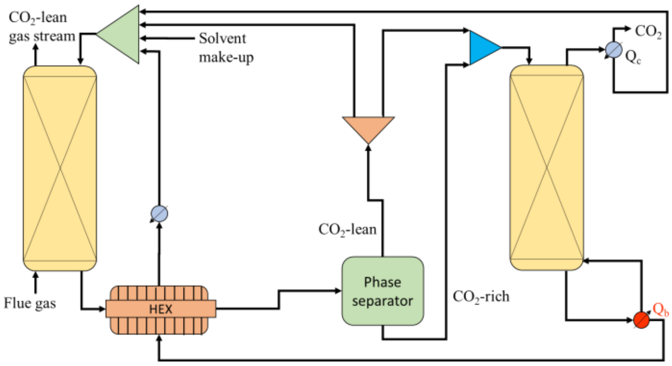

Figure 1: Process structure of CO_2 capture process utilizing phase-change solvent

2.2 LCA

The goal and scope of LCA in this framework is to evaluate the cradle-to-gate impact from capturing 1 t of CO_2 by the MCA solvent-based capture system. Thus, the functional unit of the framework is 1 t of 90 % captured CO_2 from the flue gases with a purity of 98 % (by mole). The system boundary is “cradle-to-gate”, including the impacts from solvent, chemical auxiliaries and energy utilities production, the process emissions from the CO_2 capture system and the solvent reclaimer and waste treatment units for processing purge streams from the capture process. The result of the assessment is given as global warming potential (GWP 100a), cumulative energy demand (CED) and single score value obtained by the ReCiPe-2008 method (ReCiPe (H,A)).

The process inventories (i.e., material and energy consumption and process emissions) are based on the process flowsheets and models created within ROLINCAP project (ROLINCAP, 2019), and impact values for chemical auxiliaries and energy utilities are based on Ecoinvent 3.4 database. Life cycle impact of the solvent manufacturing is predicted by short-cut FineChem models (Wernet et al., 2009) and the impact of the treatment of waste flows is estimated by waste treatment models (Kohler et al., 2007).

2.3 EHS

EHS hazard assessment evaluates immediate to long-term effects on humans and ecosystems that come in contact with the chemical molecules present in the carbon capture system if they are released to work- and natural environment as a result of process accidents, equipment leakages, spills, etc. EHS comprises safety, health and environmental aspects. The Safety (S) aspect gives an indication of the potential accidental risk focusing on immediate damage to humans or the process plant. The Health (H) aspect assesses the potential (long-term) impact to the health of the plant personnel. The Environmental (E) aspect evaluates potential damage to the environment caused by emission of chemicals from the process. To calculate single S, H and E scores, various dangerous property values should be available for the substance under investigation (Table 1). If available, dangerous properties used for EHS are obtained from material safety data sheets (MSDS), otherwise estimated by group contribution methods, data mining methods, and available tools.

As an example, the total S value, is calculated by Eq(1) (Sugiyama et al., 2008):

$$S = \sum_{iS} \frac{max_F[\sum_j m_j^F I_j^{iS}]}{S_{MEA}} \qquad (1)$$

where m_j^F is the mass flow of a specific substance j in stream F of the process system per kg of CO_2 captured under the same conditions as in LCA, I_j^{iS} is the impact index of the substance j for dangerous property i in safety category, and S_{MEA} is used to normalize the S value to the corresponding one of the MEA case (Badr, 2016). H and E are computed in a similar manner.

Besides these hazard indices used for relative comparison purposes, absolute EHS impacts are expressed by the effective dangerous property approach and the respective potential of danger (PoD) metric (Koller et al., 2000). PoD represents the magnitude of EHS effects by a physical unit such as releasable energy content of the system or the volume of air/water required to dilute a dangerous chemical to levels of threshold concentration.

2.4 Exposure analysis

Exposure analysis is performed to determine if spills, leakages and emissions occurring in the system can pose a potential harm to the health of the personnel working at the CO_2 capture plant. Exposure to nitrosamines is evaluated based on the potential equilibrium concentration in the liquid phase and a liquid concentration threshold of 13.7 mM (Badr, 2016) that leads to the air concentration corresponding to the lowest observed-effects concentration. Nitrosamine’ s steady state concentrations are estimated by equations reported by Fine (2015).

Small leakages of the solvent (a drop with an arbitrary radius of 0.25 cm) are assumed to occur at a constant amount and evaporation rate. The concentration of the chemical in the working environment is calculated by Eq(2) (Keil and Nicas, 2003):

$$C(t) = \frac{E_i}{\beta}\left[1 - \exp\left(-\frac{\beta}{V_Z}t\right)\right] \qquad (2)$$

where E_i is a constant emission rate of the solvent estimated by a simplified model (Mitchell Scientific 2007), V_Z is the volume of the zone (Z) that contains the emission source and the individual’s breathing zone, and β is the airflow ratio (m^3/min) ($\beta = 0.5 \times S \times FSA$, where S is wind speed, assumed 1m/s at ground level, and FSA is the free surface area of the zone Z through which air moves).

Table 1: Dangerous properties used for EHS assessment

Dangerous Property	Parameter
	Safety
Mobility	Difference between boiling point of the pure substance and highest process temperature
Fire/ Explosion	Difference between flashpoint of the pure substance and highest process temperature
Acute Toxicity	LD50oral (rat) – the amount of orally ingested chemical that causes death to 50 % of rats (mg/kg body weight)
	Health
Chronic Toxicity	Permissible exposure level (PEL) – US legal exposure limit (mg/m^3) of an employee to a chemical, given as the average exposure concentration over 8 h
	Environment
Water Mediated Effects	Toxicity (LC50/EC50$_{aquatic}$) – concentration (mg/L) of a chemical in water that causes death/effect to 50 % of most sensitive aquatic species
Degradation in the Environment	Persistency (d) - half-life of a chemical in the environment (water)
Air Mediated Effects	Chronic toxicity index
Accumulation	Bioconcentration factor (BCF) - factor expressing accumulation of a chemical in a living organism, calculated as concentration of the chemical in an aquatic organism divided by the concentration in the water

Exponentially decreasing mass emission rate is assumed for a spill. The air concentration (mg/m^3) at time t after the spill is calculated according to Eq(3) (Keil and Nicas, 2003) :

$$C_t = \frac{\alpha M_0}{\alpha V_z - Q}\left[e^{-\left(\frac{Q}{V_z}\right)t} - e^{-\alpha t}\right] \tag{3}$$

where M_0 is mass spilled (mg), Q is ventilation rate (in this case equals β), V_Z is the volume of the zone (Z) containing the emission source and the individual's breathing zone, and α is the emission rate (L/min), ($\alpha = 0.000524\,VP + 0.0108\frac{SA}{Vol}$, where SA/Vol is the spill's surface area to volume ratio (cm^{-1}) and VP is the chemical's vapor pressure (mm Hg)).

3. Results

3.1 LCA

The LCA impact for the MCA system is presented in Figure 2. As expected, preparation of CO_2 for transport, including compressing and pumping of the liquid CO_2 in accordance with CO_2 pipeline transport specifications, and reboiler steam for solvent regeneration are responsible for the greatest share of the impact for both flue gas systems in all three categories (CED, GWP100 and Recipe). Overall impact is higher for the Flue gas 2 as result of higher feed flue gas/t CO_2 captured ratio, in other words because of the feed flue gas being more diluted in CO_2.

Due to the uncertainties with regards to the MCA/MEA degradation ratio and amounts of degradation products in vapor and liquid phase, different scenarios were calculated. It has been found that the degradation ratio, as well as the distribution between volatile and non-volatile components, does not have a significant effect on the results: the difference between the impact of different degradation cases was found to be less than 2 % in all the categories.

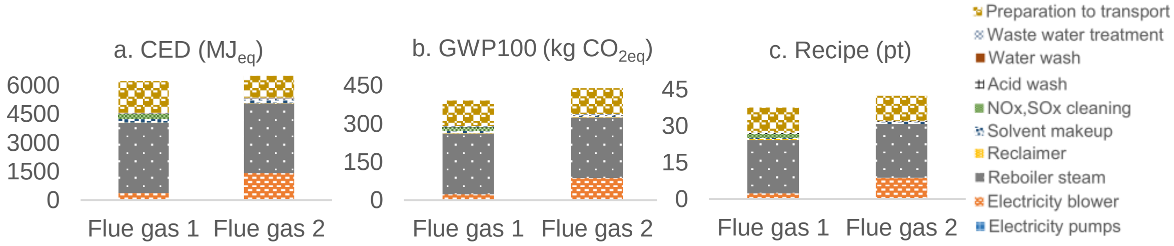

Figure 2: LCA impact and main contributors to the impact per t CO_2 captured

The comparison with the MEA (Badr, 2016) indicates that overall life cycle impact of the MCA system is smaller.

3.2 EHS

The respective results for both cases normalized to MEA (Badr, 2016) are presented in Figure 3. The current evidence suggest that the results are better or similar to those of the MEA. Fire/Explosion is responsible for the greatest impact in the Safety category (Figure 1a) due to the low flash point of MCA. Degradation contributes the most to the Environment category: compounds present in the system (mostly MCA) are persistent, rather than toxic.

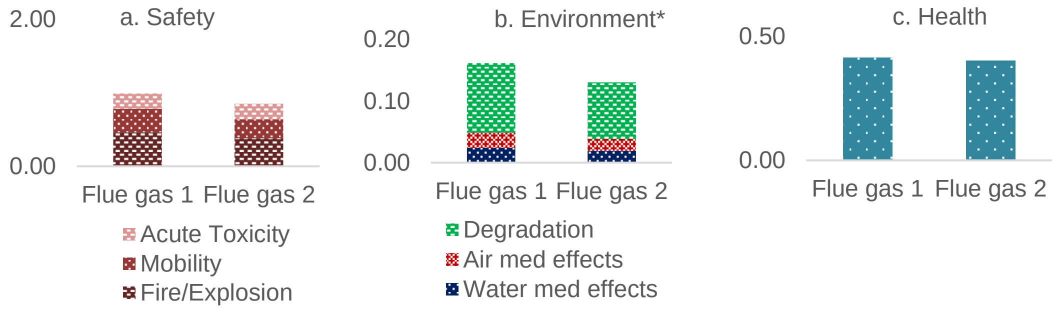

*Figure 3: EHS values for Flue gas 1 and Flue gas 2. * Accumulation value equals to 0, therefore omitted*

Figure 4 shows contribution of substances to the PoD. Nitrosamines are responsible for the high share of the danger in Health categories (Figure 4a, b) and water and air mediated effects (Figure 4c,d) in Environment due to their cancerogenicity to living organisms. The solvent contributes the most to water mediated effects (Figure 4d), probably due to the relatively high acute aquatic toxicity of the molecule and presence in high amounts in the system.

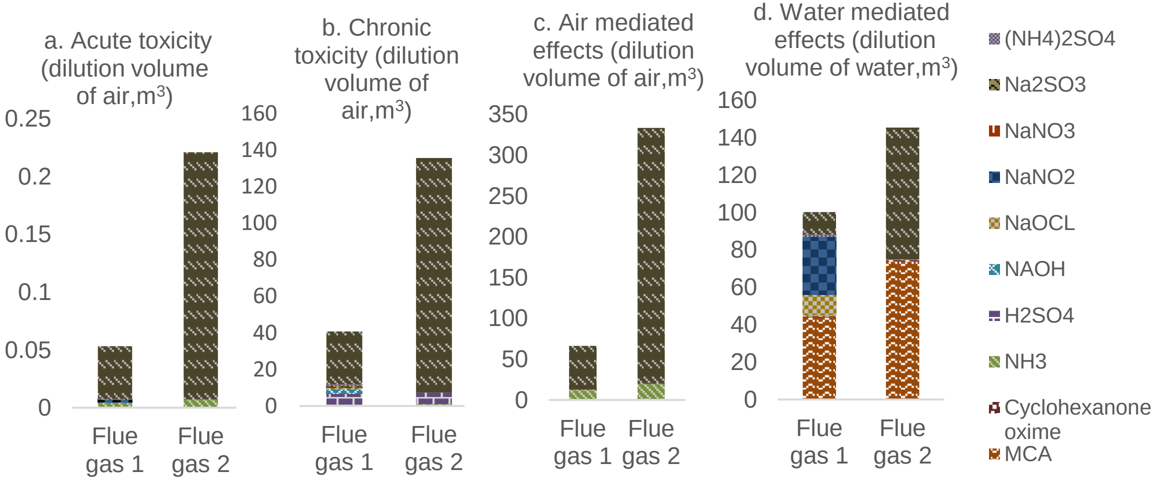

Figure 4. Potential of danger (PoD) per tonne of CO_2 captured (Impact of CO_2, H_2O, O_2 and N_2 molecules is not included as hazardous, absorber inlet flue gas NO_x=10ppm)

3.3 Exposure analysis

Exposure analysis showed that in case of a leakage or a small spill there is no danger for the workers after 15 min of the accident. However, if the spills are large, the concentration should be compared to immediately dangerous to life or health (IDLH) values likely to cause death or irreversible health effects. There are no published IDLH value for MCA, therefore a value for the most structurally similar compound from the IDLH substances list is used as a benchmark. It was found that relatively large solvent spills (radius of the spill is larger than 50 cm) can potentially pose immediate danger to the plant workers.

According to the analysis, nitrosamines can potentially exceed the liquid concentration threshold values if NO_x concentration after the flue gas pre-treatment exceeds 10 ppm in the Flue gas 1 and 5 ppm in the Flue gas 2.

4. Conclusions

It has been found that steam for the reboiler, CO_2 compression for transport and electricity consumption by the flue gas blower are the main contributors to the life cycle impact.

The results of the EHS assessment demonstrate that the largest share of the impact in the safety aspect of the system comes from Fire/Explosion dangerous property due to the presence of chemicals, mostly MCA, with low flash point. The environmental and health problems of the system are correlated with the persistency and toxicity of the chemicals, especially nitrosamines and ammonia as a result of solvent degradation.

According to exposure analysis, leakages and small spills of the solvent were found not to be a danger to the health of the workers, however, larger spills should be prevented.

In sum, the study underscores that capture systems with phase-change solvents might face the problem of accumulation of harmful products, like nitrosamines, due to the design of the process and incoming flue gas quality that favors their accumulation, therefore, additional hazard mitigation measures might be required. However, the overall environmental impact is expected to be smaller than for the conventional systems.

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