LIFE CYCLE ASSESSMENT OF HIGH TEMPERATURE SORPTION OF CO_2 BY CARBONATE LOOP

Kristína Zakuciová.[a,b]***, Vladimír Kočí.***[a]

[a]*University of Chemistry and Technology Prague, Technická 5, Praha 6*
[b]*Research Centre Rez, Husinec-Řež*
e-mail: zakuciok@vscht.cz

One of the long-term objectives of the environmental policy is to decrease the emissions of different kinds of industries. Research concerning CO_2 capture and storage (CCS) technologies takes place worldwide for many years, but the demand of current energy output has not yet been achieved by economically and technically manageable technology. The most common method of CCS technology is the capture of CO_2 from the flue gas after the combustion of fuel the so-called "post combustion" technology. An alternative method of post combustion technology is the high temperature sorption of CO_2 by carbonate loop. Life Cycle Assessment (LCA) of the carbonate loop contributes to the holistic view in terms of environmental burdens and benefits.

Keywords : Life Cycle Assessment, Carbonate loop.

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1. Introduction

The main goal of the environmental policy since 90's is to decrease the amount of greenhouse gases (GHGs) from different industrial sources. Agenda 20-20-20 EU set up the reduction of emissions by 20 percent in comparison to the emissions level in 1990's. This agenda is also achieving to increase the utilization of renewable sources in 20 percent, and an increase of the energetic efficiency in 20 percent. Another important objective is the achievement of a low carbon economy. The goal of this kind of economy is to integrate technologies with minimum GHGs production into all industrial sectors. In the frame of SET Plan (Strategy Energy Technology Plan), seven roadmaps were proposed to establish the goals of low carbon economy. One of these plans is to achieve competitiveness of Carbon Capture and Storage (CCS) technologies [1]. Life cycle Assessment (LCA) is a suitable tool to assess such technologies. LCA studies are proposed in connection with a functional unit that describes the function of the whole system or technology. The functional unit for CCS can be the amount (in kilograms) of CO_2 captured. Although, the systems previously assessed were usually static without any dynamic changes in the amounts of semi-products. However, CCS systems belong to dynamic systems category, which require modelling in sequential cycles where products complement each other. Other interesting view is the weight of different environmental impact categories. The suitable method for this comparison in LCA is normalization. Normalization is defined by specifying equivalencies (e.g. per capita consumption in Europe). The equivalent value can represent an uncertain factor, which can be quantified based on a normal distribution with a standard deviation.

2. Methodology

Three capture and storage technologies are commonly known in current global energy research:

1. Post-combustion – the CO_2 is separated from the flue gas following the combustion
2. Pre-combustion – the CO_2 is separated from the flue gas following the gasification process
3. Oxyfuel –the fuel is burnt in oxygen rather than air and the combustion products are mainly CO_2 and water

Carbonate loop is uses the chemical sorption of CO_2 on a suitable sorbent by production of carbonates. Chemical sorption operates in two subsequent processes:

1. Carbonation – takes place in the carbonate reactor with production of $CaCO_3$
2. Calcination – takes place in the calcinator with production of CO_2

Both reactions are described as follows:

$$CaO\ (s) + CO_2\ (g) \longrightarrow CaCO_3\ (s)$$
$$CaCO_3(s) \longrightarrow CaO\ (s) + CO_2\ (g)$$

2.1. LCA methodology

Life Cycle assessment (LCA) is a strong tool to analyze the environmental aspects and impacts of production processes, such as energy production. The international standards ISO 14040 and 14044 define the LCA method as a cradle-to-grave analysis. Generally its objective is to preform comparisons of technological processes focusing on their environmental performances. It is essential to include all the phases of the product lifetime and a holistic understanding of the process and the environmental impacts associated with it [3].

LCA can be divided into four blocks: Goal and scope definition, inventory analysis, impact assessment and interpretation (Fig. 1).

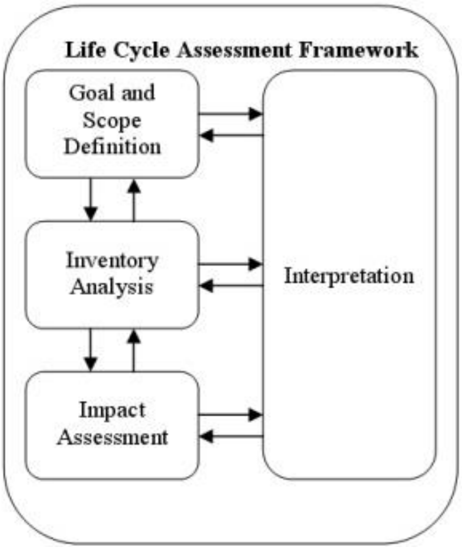

Fig. 1 Life Cycle Assessment framework [3]

2.1.1 Goal and scope definition

The definition of goal and scope must be present in the LCA study as the first component. The crucial concepts of the study are described in the framework of the standard. The goal and scope shall be consistent with the intended application of the assessment. The scope includes the system boundaries and detail level of the LCA will depend on the subject of study. The depth of the study will be determined by the goal of the LCA.

2.1.2 Inventory Analysis

Live Cycle Inventory analysis (LCI) is the second phase of an LCA. In this phase the data is collected and the construction of the model settled in the goal and scope definition is started. LCI is an inventory of input-output data, and the calculations of the resource used and emissions released within the process studied are performed in relation to a functional unit set beforehand [10]. Obtained data are usually concerning infrastructure and operation. Green House Gas emissions are calculated using IPCC 2007 method, and further environmental burdens are calculated using ReCiPe method.

2.1.3 Impact assessment

Life cycle impact assessment (LCIA) correlates a wide number of potential impacts with resource extraction and waste/emissions of the inventory. The results offer additional information to the LCI results and lighten the understanding of the environmental significance the system studied. All the results will be in relation to the functional unit and in terms if impact categories such as global warming potential, acidification potential, land use, resource use, etc [4].

2.1.4 Interpretation

Life cycle interpretation occurs in every stage of the LCA and often includes sensitivity analysis. During interpretation the results of the LCI or LCIA are summarized and discussed in accordance to the goal and scope definition [4].

2.2. Life Cycle Assessment model of Carbonate Loop

LCA is commonly used for assessing and comparing technologies or systems which have the same function (e.g. carbon capture). Therefore, the functional unit is described as amount of CO_2 (in kilograms) captured by the technology. Two approaches were selected to build up the model of carbonate loop:

1. Stoichiometric (ideal) model
2. Model with operational data (realistic model)

The first approach, is described in this paper, and is representing the ideal model determined by chemical reactions for carbon capture with 90 percent efficiency of CO_2 removal from flue gas. It is based on the stoichiometric data and stoichiometric balance of chemical reactions. One of the main requirements for the LCA is the set up the system boundaries. In the case of the carbonate loop, the boundaries include the process of carbonation and calcination, which are connected and repeated in 10 cycles. The modeling of dynamic system, as carbonate loop represents, requires division of the whole system into three plans:

1. Input plan – with all the input materials and energy
2. Intermediate plan– includes carbonation and calcination, where the values of data are the same in the following eight cycles
3. Output plan – includes output data as a waste heat and waste products and closes up the whole system.

2.3. Calculations

These three plans are then connected through the reference flows. To make the whole stoichiometric LCA model logically balanced, there are some chemical assumptions accepted for every single plan. These assumptions are based on chemical balances which could be computed from stoichiometric simple reactions of calcination and carbonation. The basic computations resulting in required data are listed below (Eq. 1- 7). All other data were taken from literature. The summary of the input physical properties are listed in a table below [5].

$$m\,(CO_2\,cap) = RF\,.\,m\,(CO_2\,fg) \tag{1}$$
$$Q_c= [(T3\text{-}T2)\,.\,m\,CaO.\,Cp\,CaO\,].\,10^{-6} \tag{2}$$
$$Q_d = \Delta H_{298}\,(CaCO_3).\,m_i\,(CaCO_3) \tag{3}$$
$$m\,(CaO\ per\ 1mol) = M_{\,CaO} / M_{\,CaCO3}\,.\,m_i\,(CaCO_3) \tag{4}$$
$$Q_h = [(T2\text{-}T1).\,Cp\,CaCO_3.\,m_i\,(CaCO_3)\,]\,.\,10^{-6} \tag{5}$$
$$m\,(CO_2\,fg)=(M\,CO_2/\ M\,CaCO_3).\,m_i\,(CaCO_3) \tag{6}$$
$$m_W\,(CaCO_3)= (1\text{-}RF).\,m_i\,(CaCO_3) \tag{7}$$

RF – recycling factor; recycling factor is 90 percent for $CaCO_3$
$m_i\,(CaCO_3)$ – input amount of calcium carbonate in kg
$m\,(CO_2\,cap)$ – amount of CO_2 captured in kg

m (CO_2 fg) – amount of CO_2 from flue gas in kg per 1 mol
m_W ($CaCO_3$) – amount of waste from calcium carbonate in kg
m (CaO per 1 mol) – amount of CaO in kg per 1 mol
Q_d – heat required for calcium carbonate decomposition in MJ
Q_c – heat required for carbonation process in MJ
Q_h – heat in MJ required for heating up calcium carbonate from 8°C to 650°C
ΔH_{298} ($CaCO_3$) – reactive enthalpy required for calcium carbonate decomposition by standard conditions in MJ/mol (values from literature source [5]).
Cp $CaCO_3$ – specific heat of $CaCO_3$ in J/K
Cp CaO- specific heat of CaO in J/K
ΔH_c – calcination enthalpy in MJ/mol (values from literature source [6])
T1 – outside temperature (around 8°C)
T2 – temperature of calcination (650°C)
T3- temperature of carbonation (950°C)
M (CO_2) – molar mass of CO_2 (44.01 g/mol)
M (CaO) – molar mass of CaO (56.0774 g/mol)
M ($CaCO_3$) – molar mass of $CaCO_3$ (100.0869 g/mol)

Tab. 1 Physical properties of input plan [5,6].

Physical properties	Values
Cp CaO	763 J/kg/K
Cp $CaCO_3$	818 J/kg/K
m (CO_2 cap)	0.0396 kg
m (CO_2 fg)	0.044kg /mol
m (CaO per 1 mol)	0.056kg/mol
Q_c	0.0128 MJ
Q_d	0.176 MJ
Q_h	0.05 MJ
m_W ($CaCO_3$)	0.01 kg
ΔH_c	2. 73 MJ
ΔH ($CaCO_3$)	1. 76 MJ
m_i ($CaCO_3$)	0.1 kg
T1	8°C
T2	650°C
T3	950°C

The Intermediate cycle has the same values of physical properties, but the amount of calcium carbonate is 0,01 kg. This value represents 10 percent of the input amount of calcium carbonate. Subsequently, the energy for heating of 0,01kg $CaCO_3$ will be different – 0, 05 MJ. The output plan shows the total amount of waste as 100 percent of the input fresh calcium carbonate (0,1kg).

Primarily, carbonate loop should decrease the amount of CO_2 in flue gases. However, normalization function is performed in life cycle assessment (LCA) studies in order to better understanding the relative significance of all impact categories. Normalization references are the characterized results of a reference system, typically a national or regional economy. Normalization is widely practiced in LCA-based decision support and policy analysis (e.g., LCA cases in municipal solid waste treatment technologies, renewable energy technologies, and environmentally preferable purchasing programs, etc [2]. The normalization process was made for the whole carbonate loop technology in order to see the influences of the loop in all the impact categories. This function represents the weight of other impact categories rather than only global warming potential (GWP), which can significantly influence the environmental footprint of the whole technology.

3. Results and discussion

The stoichiometric model is based on chemical balances to demonstrate the actual environmental effectiveness of the loop. Therefore, it is suitable to balance the model to the assumption of capturing 1kg CO_2 from flue gases. We divided the impact categories into two groups of GWP and other impact categories. This division was made due to focus on primary CO_2 reduction. Therefore, it is easier to calculate the environmental benefit. On the other hand, normalization can show environmental costs in other impact categories.

3.1 Global Warming Potential (GWP)

The capture of 1kg CO_2 is showing the environmental benefit in the whole life cycle within the system boundaries in 66 percent. The main contributor that increases the output for GWP is the thermal energy utilization for reactive heat and heating up the calcium carbonate in the process of calcination. The production of thermal energy in the Czech Republic is mainly sourced from lignite, which results in high emissions of GHG. On the other hand, the thermal heat that is released from the high exothermic reaction of carbonation could be used for production of the electric energy. 33 percent of the waste thermal energy can be transferred into electric energy which is contributing to the environmental benefit in GWP category which results to 66 percent of effectiveness in the whole life cycle of the carbonate loop. If we would assume no further utilization of the waste heat, the effectiveness of the loop will decrease to 54 percent. The other option which could theoretically decrease the environmental burden is to use the waste heat as a source of thermal energy for utilization in power plant. In this case, there will be less energy losses occurred and effectiveness of the whole system will increase.

3.2 Other Impact Categories

As it was mentioned above, normalization function can demonstrate the different weight of the different impact categories rather than GWP. The normalization factors express the total impact occurring in a reference region for a certain impact category (e.g. climate change, eutrophication, etc.) within a reference year. [7]. Among the all impact categories, abiotic fossil depletion has the highest output values. Results after normalization are shown up in the following graph.

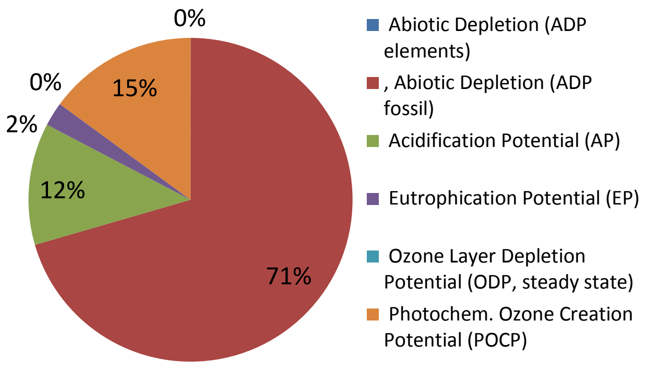

Fig. 2 Environmental cost of carbonate loop in different impact categories after normalization

The graph shows negative environmental impacts among different impact categories. Among all categories abiotic fossils depletion takes the highest part (71%) among all other categories. This result is connected with utilization of thermal energy as an input process for the carbonate loop system. Thermal energy in the Czech energy mix is mainly produced from lignite (41.3 %). Therefore, the contribution to environmental burden is increasing. The dataset of production of heat from lignite includes technology mix and covers all relevant process steps and technologies along the supply chain. The lignite supply includes the whole supply chain of the energy carrier from the exploration, production, processing, and transport of the fuels to the heat plants. On the other hand, carbonate loop technology is increasing the efficiency by saving of negative impact in GWP category of 0,24 kg CO_2 eqv. in the whole life cycle of the carbonate loop. If we summarize all negative and positive impacts, the total efficiency of the carbonate loop in all environmental impact categories refers to 66%.

LCA results can offer different options for improvement of the environmental profile of the system. One of the options which can be considered, is the choice of heat source for calcination process. The improvement could be done by replacing lignite, as the source of thermal energy, by natural gas. The second suggestion is offering the effective utilization of the waste heat. It can cause less energetic losses, if there won´t be any transformation of thermal energy of steam to the electric energy. Heat can be directly used for the systems own heating without transformation and could increase the efficiency up to 90%. Finally, the uncertainty of physical parameters of chemical sorption can also influence the impact categories. For instance, specific heat values in this model are taken from available literature source [5,6]. But the precise experimental values are uncertain in the range of the temperature of carbonation and calcination for $CaCO_3$ and CaO. Specific heats are influenced by the temperature and the transition of temperatures from 8°C – 650°C-950°C is relatively in a high range. The specification of the specific heat values are connected with gathering the data from actual operation of the loop which will be held in the further research.

4. Conclusion

LCA is a conceptual tool for modeling systems that are not yet in operation. LCA can predict the potential environmental impacts in various impact categories. The main benefit of the carbonate loop technology is the reduction of CO_2 present in flue gases. Potential efficiency of technology is counting with 90 % of CO_2 captured. Following the LCA way of thinking it is fundamental to include the environmental impacts of the whole life cycle including all energy and material inputs. LCA evaluation results in the efficiency decrease to 66%. The main reason is the utilization of thermal energy sourced from lignite, which is increasing values in a category of abiotic fossils depletion. Another factor that can reduce the efficiency of the loop to 54% is the non-use of the waste heat produced from the strong exothermic reaction of carbonation. The improvements that could be possibly implemented are following:

- Replacing lignite by natural gas as a source of heat.
- Direct utilization of waste-heat to the systems heating necessities (no transformation to electric energy).
- Precise determination of the heat capacities to ensure accurate model balance and results (representative of the practical process).

Carbon capture technology seems to be a promising technology for the actual CO_2 capture but it is necessary to look at the technology as a whole system with all up and down streams. It will be sufficient to assess carbonate loop in connection with the power plant. Then, the comparison of the systems with and without carbon capture could show the efficiency of the technology in an extended range. Another interesting study which will be further done is to compare different types of sorption for carbon capture technology as amine-based sorption vs active-carbon sorption of CO_2. These studies can contribute significantly to understand and completely evaluate innovative systems that primarily help to decrease the overall environmental costs. It is a matter of data relevance and sensitivity analysis to perform the whole study in a correct and precise way, which will be done in a further research.

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