FACULTY OF SuSt a in abi l i t y

I n s t I t u t e FOR En v i r o n mEn t a l c hemist r y

Ph.D. Research Proposal:

THERMOCHEMICAL HEAT STORAGE FOR HOUSEHOLDS: THERMAL TRANSFERS AND CHEMICAL REACTION

by:

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SUMMARY

Abstract:

Energy storage is very important for improving the efficiency of renewable energy systems and their large-scale utilization. In the past decade, sorption and thermochemical heat storage have generated a lot of interest, especially for households applications. Sorption and thermochemical heat storage systems for energy storage use a reversible physicochemical phenomenon: AB + Heat $\rightleftharpoons$ A + B (Eq. 1). Heat need to compound AB, thus dissociated into compounds A and B, will be provided by Combined Heat and Power (CHP), which are designed for decentralized electricity and heat generation without transmission losses by a central generator. This innovation, which will lead us on household applications with daily fluctuations, involved chemical reactions and thermal management understanding to set an efficient storage system. In that way, the investigation is needed amongst other in thermal decomposition (heat and mass), species diffusion processes and reactor reactions dependence in temperature and pressure. We intend to develop laboratory test reactors and finally a prototype. Dynamic simulations based on a build-up model will be used to analyze some characteristics (the pressure, the temperature, the mass, the mass fraction, the power, the efficiency, the storage capacity etc. of the storage system) to optimize the system functioning.

I. Introduction:

In a global rise of economy, Germany, to boost its technology drives to promote climate change protection, new energy technologies and energy efficiency. In his new integrated energy and climate program, CHP, also known as cogeneration, tops the list of key elements. CHP which uses 90% of the input energy to produce both electricity and heat may significantly reduce the peak demand (peak shaving) of electricity [1]. In the other hand, the thermal energy (heat or cooling) produced by CHP can be easily stored and later delivered to meet demand. (*See figure 1 in Appendix*)

Germany is one of the most industrialized countries in Europe, and over 50% of the country's energy used in winter for heating of households water, cars and facilities could be provided through micro-CHP [2]. In addition, the government’s decision to disconnect nuclear plants (represents 25% of energy production) from the German grid to preserve the environment and the fact that about 80% of gas consumption is imported from Norway and Russia will seriously decrease domestic energy production due to the depletion of reserves[3].

To face this situation, it is important to find a way to store heat (generated by electricity production, gas plants) that is supposed to be lost to a high extent. This way of renewable energy could replace/save the fossil fuels in several years. So the development of heat storage device in combination to CHP to compensate electricity fluctuations would be a solution to this problem. This implies new insights through thermochemical (solid-gas) reactions.

II. State of the research:

Reversible chemical reactions, which could be useful for thermochemical heat storage, have been studied since the 1930's and first use appeared in the early 1990's [4]. Besides this form of thermal energy storage, there is sensible and latent heat storage which is most studied technologies and are at an advanced stage of development [5]. In sensible heat storage, thermal energy is store by raising the temperature of a material and the storage density is equal to the product of the specific heat of this material by the temperature change. Hot water storage and underground thermal energy storage are two main applications.

Latent heat is the quantity of heat absorbed or released by a material, while changing its phase at a constant temperature; this material is called Phase Change Material (PCM). Studies using various types of PCMs show that latent heat storage can store 5-14 times more heat than sensible heat materials [6], which are regardless cheaper. However, these two forms of storage required insulation and large volume (or quantity) for a high storage density, and at the same time occurring heat losses.

Our interest in thermochemical issue is the high storage capacity, long term storage of both reactants and products, very lower of heat loss. Assuming the classification of chemical reaction systems [6], the substance dehydration/hydration which normally operates with batch process, involves solid-gas or solid-liquid reaction depending on the phase of working substance.

2.1. Chemical reactions in the reactor

The basis thermochemical transformer is the mono-variant reversible solid-gas chemical reaction which takes place in a fixed bed chemical reactor coupled with a condenser and an evaporator. The process is not suitable for continuous production as it is based on two successive phases: synthesis (exothermal in direction 1) and decomposition (endothermal in direction 2) according to thermodynamic conditions. It is typically presented as follows:

$$A\cdot mB + heat \underset{2\leftarrow}{\overset{1\rightarrow}{\rightleftarrows}} A\cdot(m-n)B + nB \qquad \text{(Eq. 2)}$$

Where A is the reactive solid (sometimes with additive to increase some properties), B is the reactive gas and the heat of chemical reaction. Thermochemical material used in the present work will come from experimental results of Rammelberg [8] on different thermochemical materials ($MgCl_2{\cdot}6H_2O$, $MgSO_4{\cdot}7H_2O$, $MgCl_2{\cdot}6NH_3$, $Ca(OH)_2$, $CaCl_2{\cdot}2CH_3OH$), which implement the heat amount at least 100kJ/mol and operating with low-temperatures range (below 100 °C) provided by CHP (available at any moment, not only in summer). In accordance with laboratory experiments, we will try to figure out numerically, reaction equilibrium through pressure in the reactor and material size effect (during dehydration and hydration). That is on the way of finding parameters which influences system's performance, but mostly parameters that influenced heat transfer.

2.2. Thermal management

In a chosen reactor (two phase, three phase, plate, fixed or fluidized bed, etc.) for thermochemical storage system, the reactants must be heated to reaction temperature first. When this temperature is reached, heat is transferred while the endothermic or exothermic is taking place assuming that the temperature and pressure are in range where the reaction is not limited by kinetics. This implies to choose closed or open system. An evaluation of material, like zeolite (reversible but low storage density) for heat pump in open system [9] shows the big advantage of this system. In closed system, the reactants have to be store [10]. In case of solid, the storage temperature may be the same as during reaction whereas gaseous products have to be cooled down and pressurized. Let noticed that during the dehydration and hydration of the thermochemical material, thermal transfers occur: heat transfer, mass transfer, fluid flow, reaction rate.

For the mass transfer, we have to define the gas flow type according to the calorimetric experimental results and to determine gas mass flux. In previous work in gas-solid reaction LU [7] used a Knudsen type flow. Consequently, the solid mass rate will be studied by size growth evolution and inform us on the degradation of the thermochemical material.

The synthesis-decomposition reaction cycle is accompanied by convective and radiative heat transfer between the gas and the surface of solid particles, and by conduction heat transfer within the TCM, which can include reactant and/or product. The three forms (conduction, convection and radiation) will be taking into account for the study of transfer mechanisms. The heat transfer between solid and gas is defined by the heat transfer coefficient and the material size (diameter, if we assume that TCM is a particle). There is also heat transfer between thermochemical material (TCM) and heat exchanger that would be investigate in order to establish thermal management of the system.

2.3. Models

To carry out thermal transfers and chemical reaction for thermochemical heat storage device through a chosen reactor, a detailed dynamic model has to be set. This model should consider the transient characteristics of the system, inherent in the operating conditions of the process that will change day-round. Numerous models have been hitherto developed, but few could account for the specifications of dehydration/hydration of gas-solid media with kinetic reaction. These models concern either the grain of elementary reactant or fixed bed of reactants [11]. There are many types of models, i.e. shrinking core models, grain-pellet models, volume reaction model, cracking core models, random pore model. The most use today is the grain-pellet model which compared to previous models take account the dependence on pressure of the diffusivity.

Based on energy and mass balance equations, chemical reaction equation and the properties of the TCM (like $MgCl_2 \cdot 6H_2O$), the model will take first into account all system components and the following mechanisms: physical properties of the grain as function of local pressures and temperatures, mass transfer coefficient at the surface of the grain, heat and mass transfers in the solid complex generally characterized by conduction-diffusion equations [12] and chemical kinetics of the grain as function of local pressures and temperatures.

2.4. Investigation Methods

Our studies are characterized by an online and offline library research, in which a finite element method (FEM) will be used to discretize model equations. For the microscopic level study, we will adopt the future microscopic calorimetric study of Rammelberg and identify chemical kinetics equations. And for coupling heat and mass transfer with chemical reaction, modeling will be carried out with a computational multiphysics program COMSOL.

III. Methodology:

3.1. Theoretical studies of thermochemical reaction system

The chemical reaction system is a set of components including reaction tanks that are either skid-mounted or supplied with a catwalk frame and are completely piped and wired. Reactant or product has to pump or flow into tanks, so the concentration tank has to be taking into account. Some system consists of a fixed bed solid-gas reactor coupled with condenser-evaporator which is under constant pressure [15]. Also theoretical study of different TCM ($MgCl_2 \cdot 6H_2O$, $MgSO_4 \cdot 7H_2O$, $MgCl_2 \cdot 6NH_3$, $Ca(OH)_2$, $CaCl_2 \cdot 2CH_3OH$) to figure out storage density, coefficient of performance (COP) and thermodynamic characteristics according the behavior of system during charge and discharge; and to meet criteria of efficiency [17]. Finally an overview of inorganic and organic reaction system will be introduced relating advantage and inconvenient.

3.2. Optimization of lab-scale prototype by dynamic analysis and dynamic simulations

To make the present study come true, i.e. real, a prototype has to be designed. This requires the optimization of overall system, particularly the amount of TCM per volume, heat exchanging and process performance. This implies dynamic simulation (system evolution, effects of the operating conditions, etc.). The simplified dynamic models have been used to simulate thermal comfort (heating) in electrical vehicles and storage by solid-gas system for person wearing insulated garment [19]. Our application lead to a house heating connected to a Combined Heat and Power (CHP) (*See figure 3 in Appendix*). By the inverse method, which consists to make some measurements on a family house (in and out temperature, wall temperature, house dimension, heat needs, etc.) and use it to dynamic simulation, we will figure out dynamic evolution (daily) of the system.

IV. Theoretical and conceptual framework :

The Leuphana University of Lüneburg has five faculties, including the Faculty of Sustainability. The Institute for Environmental Chemistry is part of it and is equipped with laboratories for sustainable chemistry, environmental chemistry and sustainable energy. The present work will be in majority in this institute, and the results obtained will allow us:

- ✓ Economically, the activation of a sustainable modernizing and developing impulse for the convergence of local enterprises to manufacture the prototype at big-scale and create new jobs in the region.
- ✓ Scientifically, this thesis developed in this report may also insights and solutions for the storage of renewable energies, to increase the local power of research including offers concerning education and continuing education.

- ✓ On the environmental side this work will contribute to save fossils fuels, fight against CO_2 emissions and bring people to use more renewable energies.

V. Research plan (provisory):

TASK	2012-2013												2013-2014												2014-2015											
Months	M	J	J	A	S	N	D	J	F	M	A	M	M	J	J	A	S	N	D	J	F	M	A	M	M	J	J	A	S	N	D	J	F	M	A	M
Literature Review	*	*	*	*																																
Analysis and writing of data from the literature			*	*	*	*	*	*	*																											
Model development									*	*	*	*	*	*	*	*	*	*	*	*	*															
Numerical simulations									*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*												
Experimentations									*	*	*	*	*	*	*	*	*	*	*	*	*	*														
Analysis and interpretation of simulation results									*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*												
Writing paper for publication								*	*	*	*	*	*			*	*	*	*	*					*	*	*									
Evaluation report on the progress of work									*					*							*				*											
Writing final report															*	*	*	*	*	*	*	*	*	*	*	*	*	*	*							
Administrative procedure																											*	*	*	*	*	*	*	*	*	
Thesis Defense																																				*

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VII. Appendix :

Figure 1: *Alternative approaches of CHP [1]*

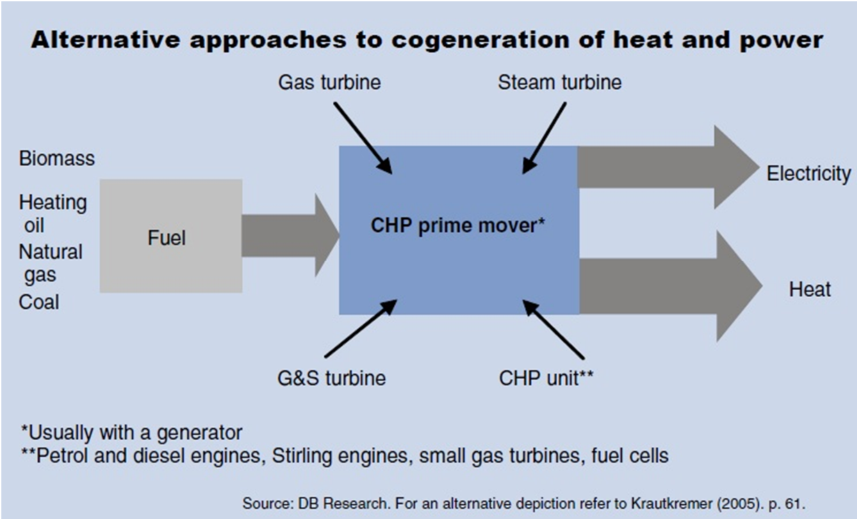

Figure 2: *General principle of thermochemical heat storage [adapted from Sebastian Ross Master Thesis].*

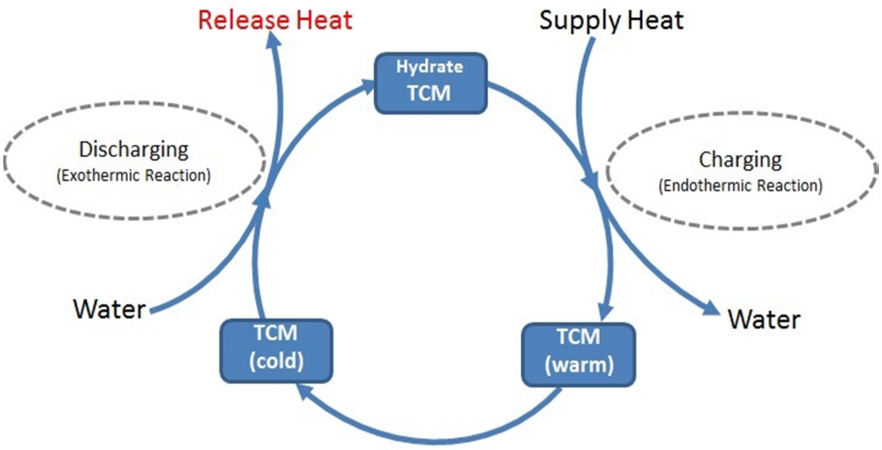

Figure 3: *The general Aim Thermochemical Heat Storage System*