Finite Volume Analysis of Thermal Energy Storage in a Thermochemical Material

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Abstract

This paper focus on finite volume analysis of thermal energy storage in a thermochemical material (TCM). The storage of energy becomes important as the production of renewable energy increases. The performance of thermal energy storage material is depends on many factors like energy storage density, available energy for storage, nature of the TCM etc. A generalised computer code is developed in FORTRAN and the process of thermal energy storage and the influence of various factors like input heat flux, porosity, relative humidity etc. are analysed. The effect of these factors in the thermochemical energy storage process are discussed and an optimum condition to maximise the performance has been obtained using Thaguchi method.

Keywords: Energy storage, Thermochemical material, Thermochemical reaction, Thermal energy storage

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1. Introduction

Developing efficient and inexpensive energy storage devices is as important as developing new sources of energy. The thermal energy storage (TES) can be defined as the temporary storage of thermal energy at high or low temperatures. The TES is not a new concept, and at has been used for centuries. Energy storage can reduce the time or rate mismatch between energy supply and energy demand, and it plays an important role in energy conservation.One of the important characteristics of a storage system is the length of time during which energy can be kept stored with acceptable losses. If solar energy is converted into a fuel such as hydrogen, there will be no such a time limit. Storage in the form of thermal energy may last for very short times because of losses by radiation,convection and conduction. Another important characteristic of a storage system is its volumetric energy capacity, or the amount of energy stored per unit volume. The smaller the volume, the better is the storage system. Therefore, a good system should have a long storage time and a small volume per unit of stored energy. There are three types of thermal energy storage(TES), they are, Sensible

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TES, Latent TES and Thermochemical TES. Among these three types of thermal energy storage methods the Thermochemical energy storage is the best method to store the energy because of its high energy density, longer period of storage, minimum losses, compact in size, easy transportability, and low material cost [3]. In this method, the energy storage is done by reversible chemical reaction, the chemicals are not consumed, merely acting as energy carriers in this cyclic process. Thermochemical TES has the potential of efficient long-term energy storage and efficient long-distance energy transport because both are possible at near-ambient temperatures.

The range of possible applications for the purpose of heat storage using thermochemi- cal reactions is very wide. Starting from temperatures of around 70^oC (salt-hydrates and solutions), to typical dissociation processes of hydroxides at around 350^oC, ammonia dis- sociation at 700^oC [1], and for metal oxides the temperature range is about 1200^oC, which used in concentrated solar power plants.[2]. The selection of a TCM for a certain appli- cation depends on the regeneration temperature levels needed, desired temperature levels of usage, technical requirements like energy demand, power, number of load cycles during lifetime, technical infrastructure and costs of the storage materials. Salt solutions, salt hy- drates, ammonia, hydroxides, carbonates and metals are promising candidates for future thermochemical storage applications. The numbers for energy density are theoretical values for pure materials under ideal reaction conditions. The factors affecting the choice of ther- mochemical material are Cost, Cycling behavior (reversibility and degradation over large numbers of cycles), Availability, Toxicity and safety, Corrosiveness, Energy storage density and Reaction temperature [3]

Many researchers are working in this area around the world to increase the efficiency and to develop new reactor concepts [4]. Different Thermochemical material (TCM) combi- nations have been studied for both low and high temperature heat storage [5][6][7][8]. The parameters which influencing the energy storage and release such as new materials (with higher storage density), humidification process, effective utilization of waste heat or solar energy are studied by various authors [9][10] and the issues in implementing the energy storage and release process are being taken care of the researchers worldwide now. One of the important aspect of thermochemical energy storage is the possibility of the use of solar energy to charge the (store the energy) TCM [11]. Many researchers are working on this in short term and long term or seasonal storage applications and found higher storage density, minimum or no loss of energy etc. [7]. Some experimental works in this field shows the suitability of the thermochemical TES in Refrigeration and air conditioning [12]. Different thermochemical reactor concepts have been discussed in various papers. Both open and closed type reactors are studied various factors affecting the thermal power output has been identified [13]. Analytical studies say that the geometrical configuration of the reactor may have an influence on the performance of the reactor and an optimization is needed in this [14]. The mathematical model developed by G Balasubrahmanyan et al. [15] will help to identify the proper salt material for a given set of working conditions. Another work shows the strong non-linear relationship between the process efficiency and dimensionless parame- ters like modified Damkohler number, dimensionless thermochemical heat capacity and the rate of water vapour supplied [16]. The experimental study conducted by Benoit Mitchel et al. [17] confirms the prediction of optimization of both energy density and permeability of the reactive bed from a mathematical model. Simulation softwares like COMSOL, TRN- SYS etc. also used for the numerical investigation of regeneration strategies for different thermochemical reactors [11]. The results obtained from the simulation has been verified by comparing with experimental investigation. In this paper, a mathematical model for characterizing the thermochemical energy storage process is discussed. The factors affecting the thermochemical energy storage for a thermochemical material is also analysed.

2. Methodology

2.1. Range of modeling scales for a complete solid sorption heat storage system

Physical processes like hydration/dehydration and heat and vapor transport take place at different length scales ranging from molecular scale up to the reactor scale. When designing a heat storage system, integration of the reactor into the complete system also plays an important role.

2.1.1. Molecular level modelling

Atomistic simulations are used to study heat transfer and chemical reaction both on nano and micro scale. On nano scale, molecular dynamics models are employed. With these , the dynamics of the chemical reactions on molecular levels are calculated, either using the parameters that are determined in the models or that are derived from micro scale experiments. Effect of impurities and crystal structure on the chemical parameters and thus the thermal energy storage potential of compact storage materials can be studied in this range of modeling.

2.1.2. Reactor level modelling

Numerical schemes solving all time and length scales of physical processes in mass, mo- mentum and energy transfer can be applied on the reactor level by assuming a continuum model. But various properties or empirical correlations that are required to solve these transport equations are obtained from molecular level of modelling.

2.1.3. System level modelling

A system consists of numerous components. So modeling in system level require approx- imate model for the physical processes on the reactor level and the a final integration of all these models.

In this work the reactor level modelling is used because we are concentrating the effects of various parameters in the reactor level.

2.2. Mathematical model for charging (Storage of energy)

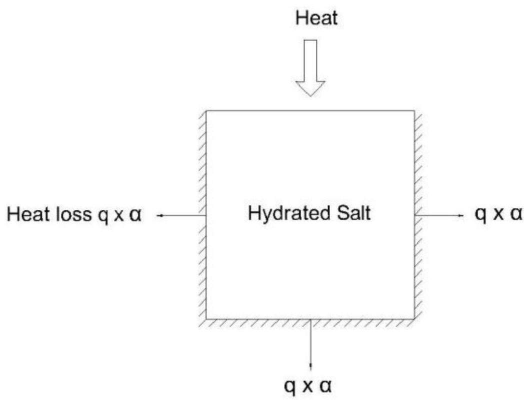

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Figure 1: simulated model

The figure shows the simulated domain. A square box filled with $MgSO_47H_2O$ (Magnesium sulphate hepta hydrate) and the domain is assumed to be porous. A constant heat flux is given to the box at one of its sides and all other sides are insulated. A small amount of input heat flux is assumed to be lost through the other three sides which is denoted as αq. Energy, mass and chemical species are conserved during the dehydration of the salt. The temperatures of hydrated salt anhydrous salt and water vapour are assumed to be same throughout (local thermodynamic equilibrium). The convective thermal and mass transport due to movement of water vapour is negligible.

2.3. Governing equations

2.3.1. Conservation of mass

$$M_h \frac{\partial N_h}{\partial t} + M_s \frac{\partial N_s}{\partial t} + M_g \frac{\partial N_g}{\partial t} = 0 \tag{1}$$

Where, M_h is the molar mass of the hydrated salt; M_s is the molar mass of the anhydrous salt; M_g is the molar mass of the water vapour; and N_h, N_s, N_g are the respective concentrations. Since the system is closed, there is no mass exchange with its surroundings. Thus, an increase or decrease in concentration of magnesium sulphate heptahydrate results in a decrease or increase in the concentrations of the pure magnesium sulphate and water vapor. Hence, the above equation satisfies the conservation of mass

2.3.2. Decomposition rate of Magnesium sulphate heptahydrate

The chemical changes occurred in the domain is governed by the Arrhenius equation. the disassociation of $MgSO_47H_2O$ into $MgSO_4$ and water vapor (H_2O) is a first order chemical reaction, the rate r for which can be described in an Arrhenius form as;

$$\frac{\partial N_h}{\partial t} = -r N_h \tag{2}$$

The dehydration of 'n' moles of $MgSO_4 7H_2O$ produces 'n' moles of $MgSO_4$ and '7n' moles of H_2O, the rates of change of the concentrations of the hydrate and its anhydrous counterpart are identical,

$$\frac{\partial N_s}{\partial t} = -\frac{\partial N_h}{\partial t} \qquad (3)$$

2.3.3. Conservation of energy

The hydrated salt gradually getting hot upto its dehydration temperature (T_r) when it reaches this temperature it start releasing the water vapour from the hydrate and become anhydrous salt. The chemical energy required to convert the salt hydrate into its anhydrous form depends upon the reaction rate r and the enthalpy of dehydration (ΔH) of the hydrate.

$$\frac{\partial}{\partial t}[(M_h N_h C_h + M_s N_s C_s + M_g N_g C_g)] = \nabla(K\nabla T) + rM_h N_h \Delta H \qquad (4)$$

Where $r = A\exp(-\frac{E}{RT})$, Thermal conductivity $K = \beta_h K_h + \beta_s K_s + \beta_g K_g$, β is the mass fraction.

The governing equations are then transformed into nondimensional form and the significant non-dimensional numbers for the model D_m, which describes the speed of the thermo- chemical energy transfer occurs in comparison to heat conduction through the material, χ the magnitude of the dehydration enthalpy relative to the total heat capacity of the mate- rial, and q that compares the external input flux to that diffusing through the material are identified.

. To validate the code developed, as in the case of work done by G Balasubrahmanyam [15], a 0.1m X0.1m square box is considered and the heat flux 1000W/m is supplied at its top surface. The walls are assumed to be partially insulated by allowing a fraction of heat supplied (αq) to flow out of the system. For a perfectly insulated system the value of α is 0. The material properties of $MgSO_4 7H_2O$ and $MgSO_4$ are also taken from the same work.

2.3.4. Boundary and Initial conditions

The system initially contains only hydrated salt with 10% porosity and no anhydrous salt and vater vapour.

$K\nabla T.n = -q$ at the top surface,

$K\nabla T.n = -\alpha q$ on other three surfaces. where n is the normal vector.

$T = T_i$ T_i and T_r are the initial and reaction temperatures.

2.3.5. Numerical schemes

For the descretisation of concentration of hydrated salt, water vapour and dry salt finite difference method is adopted. This is because we assume there is no spatial variation for concentrations of hydrated salt, anhydrous salt and water vapour, and it is a function of time only. Conservation of energy equation is discretised using finite volume method. This method is better than finite difference method because in finite difference method we are approximating the governing equation itself using Taylor series expansion and there will be some truncation error. But in finite volume method we are selecting a control volume and assuming a suitable profile for the dependent variable (here temperature) and integrate the differential equation over the control volume. We usually assume a linear variation of temperature over the control volume.[18]

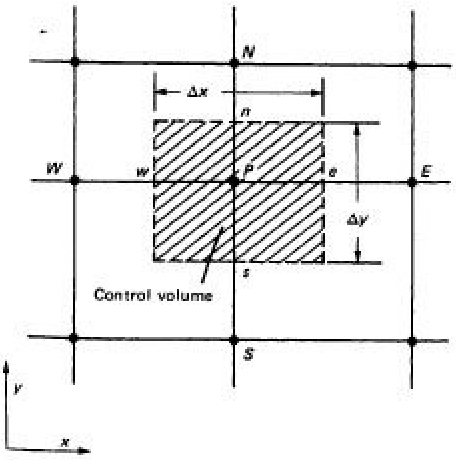

Figure 2: Finite volume method

The nondimensionalised form of energy equation is

$$[\eta_h + \eta_s + \eta_g]\frac{\partial T}{\partial t} = K\nabla^2 T + D_m N_h \chi exp(-\frac{E}{T}) \qquad (5)$$

Unsteady term = diffusion (conduction term) + heat source term
Considering a 2D problem and P is any inner node point. The right node of P is E, the left node is W, top node is N and bottom node is S as shown in figure. A control volume is taken with length Δx and width Δy such that the node P lies inside the control volume. Small letters, w, n and s represents the right, left, top and bottom interfaces of the control volume.
Integrating the differential equation over the control volume with respect to time.

$$(\eta_h + \eta_s + \eta_g)\int_s^n \int_w^e \int_t^{t+dt} \frac{\partial T}{\partial t} dtdxdy = \int_s^n \int_w^e \int_t^{t+dt} [\frac{\partial}{\partial x}(K\frac{\partial T}{\partial x}) + \frac{\partial}{\partial y}(K\frac{\partial T}{\partial y}) + S]dtdxdy \qquad (6)$$

where S is the source term.

Assuming linear profile for temperature
at ’e’ $K(\frac{\partial T}{\partial x}) = K\frac{T_E - T_P}{\Delta x}$
at ’w’ $K(\frac{\partial T}{\partial x}) = K\frac{T_P - T_W}{\Delta x}$
at ’n’ $K(\frac{\partial T}{\partial y}) = K\frac{T_N - T_P}{\Delta y}$
at ’s’ $K(\frac{\partial T}{\partial y}) = K\frac{T_P - T_S}{\Delta y}$
Then the energy equation becomes;

$$(\eta_h+\eta_s+\eta_g)\Delta x\Delta y(T_P - T_P^0) = \int_t^{t+dt}\left[\left(K\frac{T_E - T_P}{\Delta x}\right) - \left(K\frac{T_P - T_W}{\Delta x}\right)\right] + \left[K\frac{T_N - T_P}{\Delta y} - K\frac{T_P - T_S}{\Delta y}\right]dt + S\Delta x\Delta y \tag{7}$$

T_P and T_P^0 are the values of temperatures at time ’t’ and $t + dt$ respectively. While integrating the equation we use explicit scheme ie; We are assuming that the old value of temperature prevails at the entire time step except at $t + \Delta t$. Therefore

$$\int_t^{t+dt} T_P\,dt = T_P^0\Delta t \tag{8}$$

2.3.6. Source term linearisation

The source term $S = S_c + S_pT_p$

Where $S_c = D_m\eta_h\chi\exp\frac{-E}{T_P^0}(1+\frac{E}{T_P^0})$ and

$$S_P = \frac{-D_m\eta_h\chi E\exp\frac{-E}{T_P^0}}{(T_P^0)^2}$$

Since the source term is in a non linear form (contains an exponential term) we need to make it linear so that our final discretized equation or algebraic equation is more compatible [**?**] The final descretised form of energy equation is

$$a_P T_P = a_E T_E^0 + a_W T_W^0 + a_N T_N^0 + a_S T_S^0 + b \tag{9}$$

For boundary nodes the control volume will be half of the control volume specified and for corner nodes it will be one fourth. The coding is done using FORTRAN. The properties of thermochemical material is selected [15]. The initial and boundary conditions are specified as same as the work of G Balasubrahmanian [15]. Then three concentrations are solved sequentially and using these concentrations temperature at each grid points are solved. A number of simulations are conducted with varying numbers of control volumes in the domain to suitably define an appropriate grid and ensure grid independency of the simulation results.

2.4. Optimisation of parameters

A full factorial design is one in which all possible combinations of the various factors at different levels are studied. While factorial experimentation is very useful and is based on strong statistical foundations, it becomes unmanageable when there is large number of factors at large number of different levels. To address the issue, the statisticians have devel- oped Fractional Factorial designs. The experimental design proposed by Taguchi involves using orthogonal arrays to organize the parameters affecting the process and the levels at which they should be varied is used. Thaguchi method is used for designing the experiments in this work. These designs can be used by engineers/scientists without acquiring advanced statistical knowledge. The main advantage of theses designs lies in their simplicity, easy adaptability to more complex experiments involving number of factors with different num- ber of levels.

The various factors affecting the performance of the system are heat flux, porosity, heat loss through the boundaries and dehydration temperature of the salt. Inorder to maximise the performance of the process these factors have to be optimised. A 3 level 4 factor standard orthogonal array is used for the optimisation.

3. Results and Discussion

3.1. Charging process

The governing equations are numerically solved to obtain the temperature variations at different locations in the domain. The temperature of the upper most region is gradually increased upto the reaction temperature, then there will be a sudden change occurs and the temperature reaches a higher value. After this the increase in temperature is linear The FVM code is validated by comparing the results obtained from the work of G Balasubrah- manian [15], with their conditions. figure 4 and 5 shows the comparison of FDM and FVM

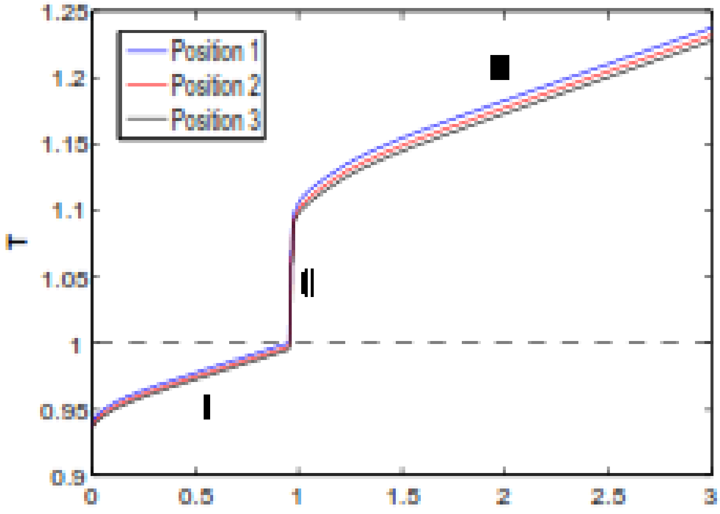

Figure 3: Temperature profile using FDM [15]

The comparison of results obtained in finite volume method with that of finite dierence method shows the same trend. So we can conclude that the code written in FORTRAN is validated and can be treated as a generalised code for analysis of performance in thermo- chemical energy storage of any material.

3.2. Optimization of charging process

In thaguchi methods we used a 3 level 4 factor standard orthogonal array is used for the optimisation of parameters. The four factors and levels are in table 1

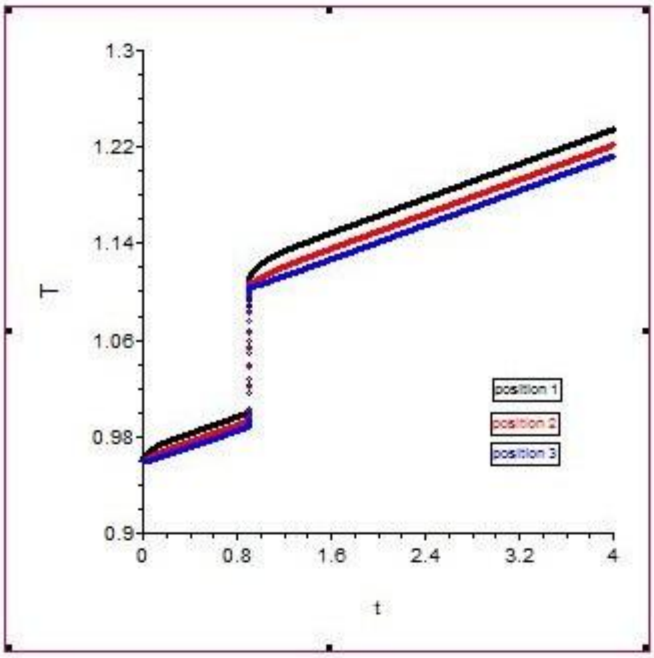

Figure 4: Temperature profile using FVM

Level	Input heat flux (W/m)	Heat loss fraction	Porosity	Relative Humidity
1	1500	0	10	80
2	1000	0.05	15	75
3	500	0.10	20	70

Table 1

The result from the Thaguchi method are shown in figure 6-9. The values are taken from the mid-position of the control volume.

Figure 5 shows the effect of input heat flux in the charging process. If input heat flux increases the charging taking place well before. This is because the increase in heat flux rise the temperature of the TCM rapidly and attains the reaction temperature early. The effect of heat loss is also very important. In figure 6 it is clear that when heat loss increases the time required to initiate the charging process increases. So we have to ensure that the heat loss from the reactor surface is minimum. The effect of porosity in charging of a TCM shows a variation (figure 7), first the reaction time increases and then it dips. If we consider the porosity, the pore size and particle diameter are another important factors which affect the reaction time. In this study we have not taken these factors, this could be the reason for the abnormality in the effect of porosity. Another important factor is the relative humidity of the supplied air. In charging process the effect of relative humidity is shown in figure 8. If the relative humidity is high more time is taken to initiate the reaction.

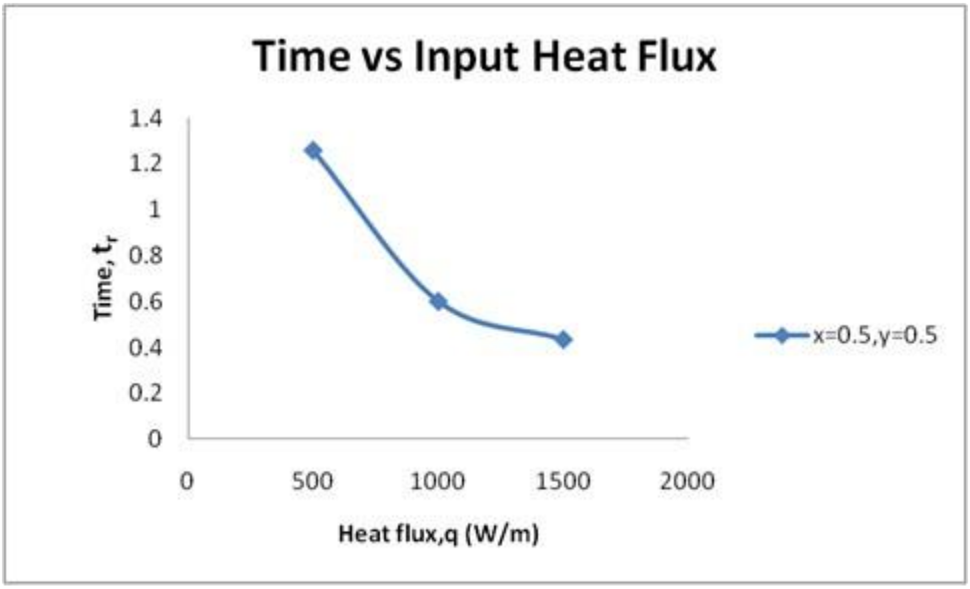

Figure 5: Time Vs Input heat flux

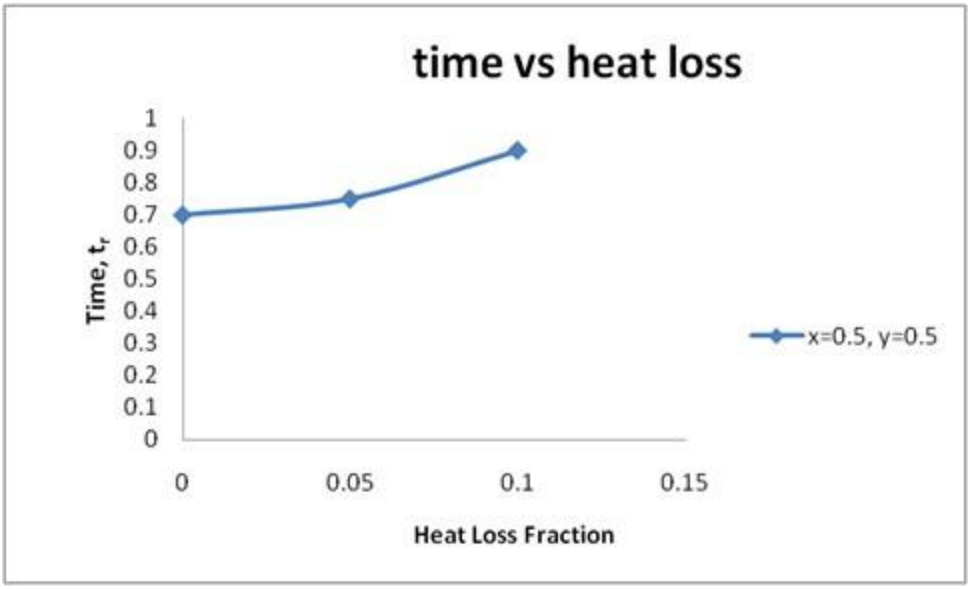

Figure 6: Time Vs Heat loss

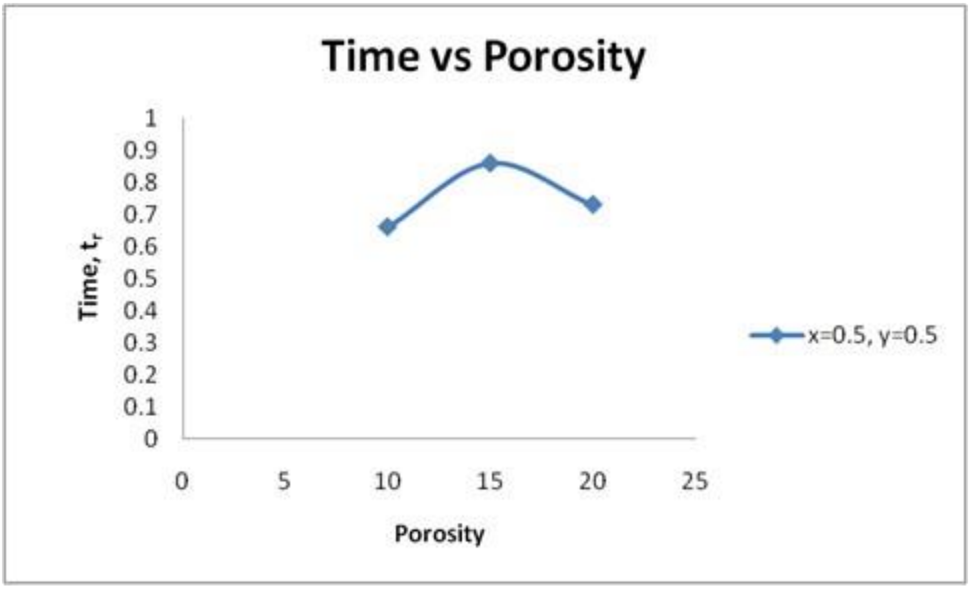

Figure 7: Time Vs Porosity

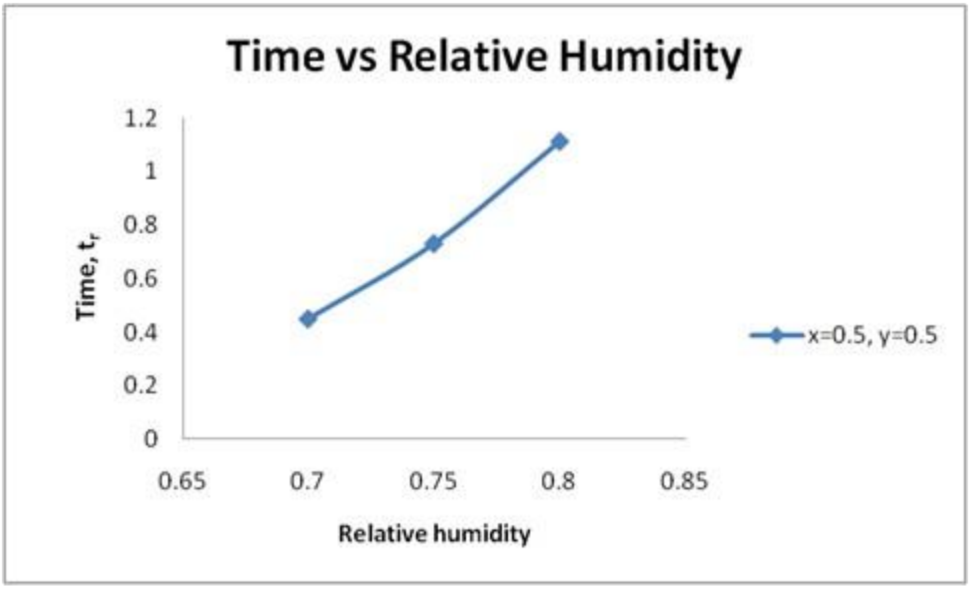

Figure 8: Time Vs Relative humidity

The increased humid salt require large amount of energy to start the evaporation process. So for a fixed input heat flux the time taken to start the thermochemical reaction will be more.

4. Conclusion

The Mathematical modelling of the thermochemical reaction is done using finite vol- ume method. The code is validated by comparing the results obtained in the same con- ditions of a work done previously. Thus this code can be used to analyse the thermo- chemical energy storage and release of any material. The results obtained by assuming indian conditions raises some challenges including the optimisation of material porosity and input heat flux for minimum time to start the thermochemical reaction. The tem- perature gradient increases sharply when the thermochemical reaction is initiated due to the effect of the enthalpy of dehydration during thermochemical energy conversion. While water vapor is released during the thermochemical desorption reaction, the energy sup- plied to the hydrate is more gradually stored in the anhydrous salt. The time required to initiate the reaction depends nonlinearly on the input heat flux, and increases with heat losses from the system boundaries.The process performance can be improved by ap- plying high input heat flux and using thermochemical material with high thermal con- ductivities. The effect of porosity shows an abnormal trend and this is because of the effect of pore size and particle diameter. So more studies are required in this field to get a clear understanding of the thermochemical process under different porous conditions.

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