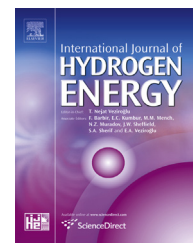




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# Modeling of cooling system for hydrogen storage process with sodium alanate and catalyzed by titanium chloride

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## ABSTRACT

One of the greatest problems to implement the use of hydrogen in automotive or stationary systems is the control in the temperature to regulate the storage capacity and the absorption and desorption process of material used to store the hydrogen. Metal organic compounds have generated a significant interest due to a high proportion of hydrogen in their structure, by this reason most of the researches are focused on the development of storage systems based on these compounds, but the regulation of temperature and mass transfer are yet a drawback to increase the efficiency of these systems. In this paper, we study the feasibility of a cooling system for a hydrogen storage system using Sodium alanate catalyzed by Titanium chloride as the hydrogen storage material in a cylindrical vessel with a suitable distribution of feed and cooling systems. A temperature of 170 °C was chosen for hydrogen input according to the storage properties of the selected storage medium looking for the increase of store capacity in terms of high density of hydrogen accumulation to obtain an adequate storage system to be implemented in automotive applications. One of the main characteristics to determine the efficiency of cooling systems is the quantity of time necessary to decrease the temperature to a normal range. In this case was obtained an effective time of 1100 s for a structure composed by a central and external system of coolant pipes, using the ethylene glycol properties as coolant to unify the use of the same coolant for hydrogen storage and engine cooling.

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## Introduction

An increasing interest in alternative fuels produced by a constant diminishing in petroleum reserves generates the investigation of different renewable resources to supply the demand in order to avoid the increase in fuel price and to decrease the production of air pollutants [1].

In this way a liquid fuel composed by a mixture of fatty acids methyl esters called Biodiesel is one of the best alternatives to replace diesel obtained from petroleum [2]. It has gained a great acceptance and market share in the United States and Europe due to engines do not need modifications to work. However investigation in other alternatives to it is increasing due to the need to decrease the pollutants produced in combustion and found new sources much cleaner

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without byproducts in production process as in the case of biodiesel with glycerol generation [3].

Hydrogen is one of the best alternatives to replace polluting fuels due to it has a high calorific value and it has a lot of pathways to be obtained, producing only water as byproduct of its combustion [4]. The main alternative to use hydrogen as a combustible is in the automotive industry. In this case a vehicle operating with hydrogen has a yield of 161 km by kilogram of hydrogen [5].

The main problem in this case to incorporate hydrogen to automotive systems is the change of a liquid fuel for a gaseous fuel and the major drawback to achieve it is the hydrogen storage [6]. There are four methods for hydrogen storage according to its storage state which are compressed hydrogen in the case of gaseous state, liquid hydrogen and metal hydrides and adsorbent packed bed in the case of solid state [4].

The use of liquid and compressed hydrogen has been declined in practical applications due to the need for maintain extreme conditions of temperature and pressure to preserve the safe state of storage. Much more in the case of hydrogen, some leaks may occur through the vessel wall due to the small size of its atoms [7].

By this reason the hydrogen storage in solid compounds is a good choice to facilitate its transport due to by this way the cost and operative conditions are reduced while the process safety increases [8]. In this manner the effectiveness in the hydrogen economy depends large of the development and the incorporation of materials with a high hydrogen storage efficiency and reversibility to obtain hydrogen in gaseous state from solid compound without high energy requirements [9].

According to solid compounds used to hydrogen storage, metal hydrides, metal organic frameworks (MOF) and graphitic sorption nanomaterials have been largely studied due to their properties to hold back a high quantity of hydrogen [10]. The main problem to carry out the implementation of these types of storage materials is that some of them have a reversible desorption constraint, in this case metal hydrides possess a very strong metal-H binding and by this reason a high temperature is necessary to produce the hydrogen desorption [9,11] while a low temperature is necessary in the case of physical adsorption of hydrogen in porous materials to maintain the hydrogen stored [12].

Metal hydrides are highly investigated nowadays due to their high storage capacity produces a high density of hydrogen on the storage vessel reducing the size and weight of itself [13]. This is particularly important due to these characteristics reduce the consumption of energy to mobilize the automotive vehicle increasing the transport capacity and decreasing the additional mass unused which conform the structure to retain the hydrogen [14].

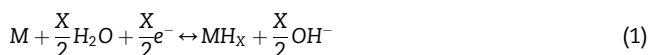
The storage with metal hydrides is a highly exothermic process, and a thermic control is needed to maintain the control of the system seeking to reduce the time of storage recharging which involves a high heat ratio [15]. By this reason the selection of an appropriate cooling system is necessary in addition to the selection of an adequate metal hydride to store the hydrogen due to these operative conditions determine the ability of the system to comply with adsorption and desorption ratio [16]. In the same way a detailed analysis of

temperature distribution is important to ensure a uniform content of hydrogen along of the bed [17].

## Metal hydride selection

Metal hydrides are binary compounds constituted by hydrogen and a metallic element. In terms of hydrogen storage the composition of hydride is very important due to it determine the mass storage capacity and the storage conditions [13]. Those characteristics are due to metal hydrides have a higher hydrogen-storage density than another compounds as in the case of  $MgH_2$  with a density of 6.5 atoms/cm<sup>3</sup> and 7.6wt% of hydrogen or  $LiAlH_4$  which contains 10.6 wt% hydrogen, compared gaseous and liquid hydrogen (0.99 atoms/cm<sup>3</sup> and 4.2 atoms/cm<sup>3</sup> respectively) [18].

The process of hydriding of a metal is possible by two ways, there are electrochemical splitting of water and direct chemisorption, expressed respectively by the chemical equations shown below (equations (1) and (2)):



In this case metal in the structure is represented by “M”, and it shows the possibility of one of these atoms to be added to different quantities of hydrogen atoms. Metal atoms usually form two kinds of hydrides according to the hydrogen saturation in the molecule, there are the  $\alpha$ -phase and the  $\beta$ -phase at which hydride is formed completely [19].

Within these compounds, the anhydrides of sodium, lithium, boron and beryllium are much more used due to its storage capacity and operative conditions such as temperature and pressure [20]. By the same reason alanates, amides, imides and borohydrides are interesting complex hydrides because of its high content of hydrogen and low weight.

In this way, alanates and borates are especially interesting for the capacity to absorb a large number of hydrogen atoms per metal atom. For example the hydrogen content for  $LiBH_4$  reaches the value of 18 wt% [19], according to the storage conditions implemented.

However borates are actually one of the compounds with the high hydrogen storage capacity, the main problem in its implementation in regular systems is the high temperature needed to hydrogenation and dehydrogenation process (350 °C and 450 °C respectively) compared to sodium alanates which have a range between 100 and 200 °C in these properties and 2,5 to 5 wt% of  $H_2$  storage capacity according to the catalyst used [21]. By this reason the interest in the study of alanates is higher due to the energy used to charge and discharge the storage tank is an important topic about the reduction of energy cost of these systems.

Although its theoretical capacity is 5.6 wt%, practical storage capacity of sodium alanate is smaller as previously mentioned due to some reasons such as the limited refueling time for real systems (much more in the case of automotive vehicles, where it is necessary fast recharges), the characteristics of additives used to enhance the absorption and

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