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1   Introduction

Hydrogen production in reaction of alkali metal borohydride with water is actively studied to develop hydrogen generators for fuel cells. Sodium borohydride $NaBH_4$ is the most promising one from the point of view of mass content of hydrogen storage and safety (non-flammable and solution is non-toxic). The aqueous solutions of $NaBH_4$ may be used for high purity hydrogen generation (99.99%). The reaction of hydrolysis

$$NaBH_4 + 2\,H_2O = 4\,H_2 + NaBO_2 - 212\ kJ/mole$$
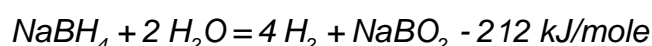
is accompanied by heat release calculated by components enthalpies [1]:

$$H_{NaBH_4} = -191.84\ kJ/mole,\ \ H_{NaBO_2} = -975.71,\ \ H_{H_2O(liquid)} = -285.83\ kJ/mole.$$

To develop hydrogen generator using $NaBH_4$ hydrolysis some decisions have to be accepted to determine basic features of the design.

2   Type and Working Volume of Reactor (single-pass or circulating)

The choice of either single-pass or circulation type reactor is one of the principal ones. Prima facie, single-pass system is more simple, $NaBH_4$ solution is supplied to reactor, and the yields are H_2 and a solution of sodium metaborate $NaBO_2$. Controlling solution flow rate, the production capacity of generator can be changed. In the car we are used to the fact that an increase in the fuel supply immediately leads to an increase in engine power. The catalytic hydrolysis of $NaBH_4$ is rather a quick process, but its rate is much less than the combustion one. This means that either the gradual change of generator efficiency must be accepted, or the receiver of sufficient volume must be set after the reactor in hydrogen line to match the rapid changes in the productivity desired by user with a slower response of reactor. The more the hydrogen mass in the receiver is, the weaker the limitations on reactor performance are. Inclusion of receiver into the working scheme is the first argument in favor of the circulation scheme.

Maximum capacity of the generator W_{max} (in moles of hydrogen) determines the ratio between water flow Q_{max} (in liters) and molality concentration $\mathcal{M}_{NaBH4}$ of working solution:

$$4 Q_{max} \mathcal{M}_{NaBH_4} = W_{max} \, .$$

At maximum generator productivity the contact time of solution with catalyst will be the smallest and expressed in terms of volume V_{cat} of the catalytic unit of the reactor:

$$\tau_{min} = V_{cat} / Q_{max} = 4 V_{cat} \mathcal{M}_{NaBH_4} / W_{max} \, .$$

This expression is equally applicable to single-pass reactor and circulating scheme; there is difference in flow through catalytic unit. In the first case fresh working solution is at inlet, and $NaBO_2$ solution has to be at outlet for single pass. The front part of catalytic unit is working with a concentrated solution, the output - with the lean one. In circulating scheme solution repeatedly passes through the catalytic unit, the velocity of solution flow and mass transfer processes are more intensive and the entire catalyst is working under approximately the same conditions. In light of these considerations the following benefits circulation schemes can be expected: thermal regime of catalyst is more uniform, it gets easier to control the ultimate hydrolysis rate, as a result, the less efficient catalyst can be used and / or the size of catalytic unit can be decreased. Circulating regime presumes cyclic repetition of three stages: filling the reactor with fresh working solution, the circulation of solution through catalytic unit and draining of $NaBO_2$ solution after the completion of hydrolysis.

Let's estimate the volume of catalytic unit required for the generator with H_2 production $W_{max} = 180$ mole/hr ≈ 4 Nm^3/hr and working solution with $\mathcal{M}_{NaBH4} = 5$ mole/l. Then $Q_{max} = 0.15$ l/min, i.e. required volume of catalytic unit has to be equal to 0.15 liters to ensure contact time of solution with catalyst about one minute. Time required for complete solution hydrolysis depends on catalyst activity, the total surface of catalytic centers, the working temperature and the efficiency of mass transfer processes.

## 3   Thermal Regime of Reactor and Catalyst Efficiency

Quite a lot of publications [2-7] are devoted to the study of the fine powder catalysts efficiency. Such catalysts are designed for disposable fuel cells, while they are not applicable to hydrogen generators. Discussed catalytic unit can be implemented as a filling of pellets, or a certain frame (a set of grids, highly porous ceramics) whose surface is covered with a catalyst. When filtering the solution through such structure the hydrolysis processes are controlled by the heterogeneous mechanism on the catalyst surface, and homogeneous one in working solution. Comparing catalyst efficiency it is considered that the more efficient catalyst provides higher hydrolysis rate at the same temperature and identical area of catalytic surface. At low hydrolysis rates (low temperature) the properties of catalytic material become important. At high temperatures the mass-exchange processes play the main role; they are controlled by the structure of porous medium and filtration velocity. Intensive hydrogen release and evaporation (boiling) of water further complicate the running processes. One should take into consideration that at high temperatures the homogeneous hydrolysis is also highly accelerated. It might be possible that when the processes of mass

transfer running in catalytic unit are rationally organized, the simple catalysts could be used instead of highly efficient ones. We have tested three kinds of granular catalysts, which are traditionally used in the processes of partial oxidation of hydrocarbons. The characteristics of these catalysts are collected in table 1 below.

Table 1:   The characteristics of the used catalysts.

Catalyst	Content	Carrier	Form	Dimensions
Pd	1%	Al_2O_3	cylinder	$\varnothing$ 3.2 mm, h=3.7 mm
Pt	0.5%	Al_2O_3	cylinder	$\varnothing$ 3.2 mm, h=3.6 mm
Rh	0.1%	Al_2O_3	ball	$\varnothing$ 5 mm

The comparison of these catalysts shown in Figure 1 was conducted at room temperature. It has merely technical sense, because at the same bulk amount of grains the catalyst content, shape and mean size of the grains are not identical. The process of hydrolysis is highly accelerated by temperature rise, while intensive evaporation of water affects limiting values of working temperature. According to [8] the actual range of operating temperatures will be 120-140°C. Though we could not conduct these experiments at this temperature range, the experimental results for the "slowest" catalyst (Rh) of three ones obtained at three temperatures, presented in Figure 2, can be used for qualitative assessment of hydrolysis acceleration rate. Based on these data the value of resident time equal to 1 minute accepted above would be sufficient to complete hydrolysis, when operating temperature is about 120°C. There is no sense in using the operating temperature higher than the required one, because it increases the amount of water vapor in outlet gas flow. In any case, the design of generator should contain cooling device for vapor condensation and water recycling. Uncontrolled water loss will result in increase of metaborate concentration and risk of its deposition on catalyst and tubes. Another problem caused by temperature increase might be generation of toxic gas diborane, whose formation is probable in conditions of high temperature hydrolysis at significant scarcity of water.
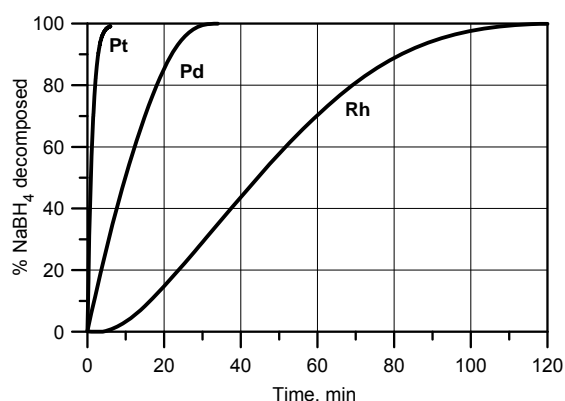
Figure 1:   The rate of catalytic hydrolysis of NaBH$_4$ solution at 25°C.
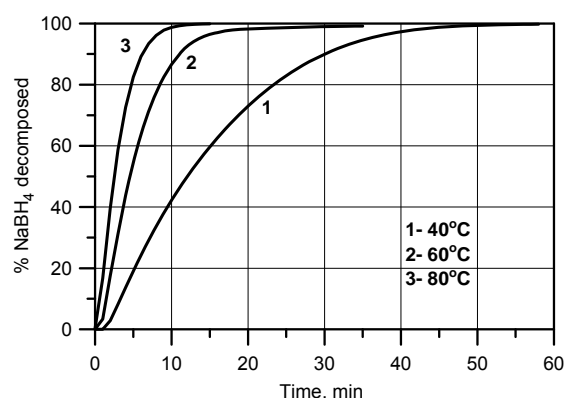
Figure 2:   Effect of temperature on the rate of catalytic hydrolysis of NaBH$_4$ solution.

4   Concentration of Working Solution

The concentration of working solution should not be below the certain minimum $\mathcal{M}_{NaBH4,min}$, which maintains the working temperature T_{work}. This value can be estimated by condition of thermal balance:

$$\mathcal{M}_{NaBH_4}^{min} H_{Hyd} = (1+\varepsilon) c_{H_2O} \left(T_{work} - T_{in} \right)$$

where H_{Hyd} is the heat of hydrolysis per one mole of NaBH$_4$, $c_{H2O} \approx 4.2$ kJ/kg – specific heat of water, T_{in} is the temperature of solution at reactor inlet and ε is parameter determining the portion of thermal losses. If ε = 0.5 and $T_{work} - T_{in}$ = 100, $\mathcal{M}_{NaBH4,min} \approx 3$ mole/l. The upper molality concentration limit $\mathcal{M}_{NaBH4,max}$ is determined by solubility of generated NaBO$_2$. In order to avoid the deposition of solid metaborate from solution in catalytic unit and in tubes connecting the reactor and collection vessel, outlet concentration of NaBO$_2$ has to be lower than the solubility limit at temperature T_{out}. For example, if T_{out} = 80 °C the limiting value is $\mathcal{M}_{NaBH4,max\_80} \approx 12.3$ mole/l [9], and calculated value

$$\mathcal{M}_{NaBH_4}^{max} \text{ is } \frac{55.5 \mathcal{M}_{NaBO_2}^{max\_80}}{55.5 + 2 \mathcal{M}_{NaBO_2}^{max\_80}} \approx 8.5 \text{ mole/l.}$$

Within the range $\mathcal{M}_{NaBH4,min} - \mathcal{M}_{NaBH4,max}$ there is freedom of choice to meet additional optimality conditions, for example, minimum amount of water used, or absence of NaBO$_2$ condensation at a given temperature, etc.

5   Start-up and Shut-down of Generator

The problem of generator start-up can be solved by incorporating heater in the path of solution supply to catalytic unit. This solution is applicable to both types of reactors; it looks quite simple and, what is the most important, controllable. In this case the estimated value of start-up is about few minutes. In case of very effective catalyst the problem of cold start could be solved by catalyst self-heating. At usage of single-pass scheme the task is somewhat simpler than in circulating case, when preheating of catalyst and all elements is required to ensure the circulation of solution. Moreover the implementation of self-heating regime requires the usage of the most effective catalyst and working solution with concentration close to the maximum value. Nevertheless, even in such case at low temperatures (say about 0°C) start-up may fail. In circulating scheme the process of self-heating is additionally hampered by necessity to heat the catalyst and all elements ensuring the circulation of solution. Currently, the forced preheating at process start-up looks more preferable, but usage of efficient catalysts can significantly decreases the threshold of start temperature. At generator shut-down it is necessary to complete the solution hydrolysis in catalytic unit and to release (or even wash) it from NaBO$_2$ solution. In the circulation scheme, such operations are the parts of the natural cycle, for single-pass reactor it is an additional element of design.

6   Preparation and Storage of Working Solution

The problem of working solution preparation has two ways: preparation in advance and storage until usage, or dosing preparation just before hydrolysis. In first case the ready made "fuel" is loaded into the generator, while in "fuel tank" hydrolysis process runs without catalyst. This feature caused the problem of stabilization and storage of borohydride solutions, which is complicated with temperature growing. The increase of solution pH by adding alkali inhibits the hydrolysis. Experimental results of stabilization obtained at 25 и 40 °C are illustrated in Figure 3.
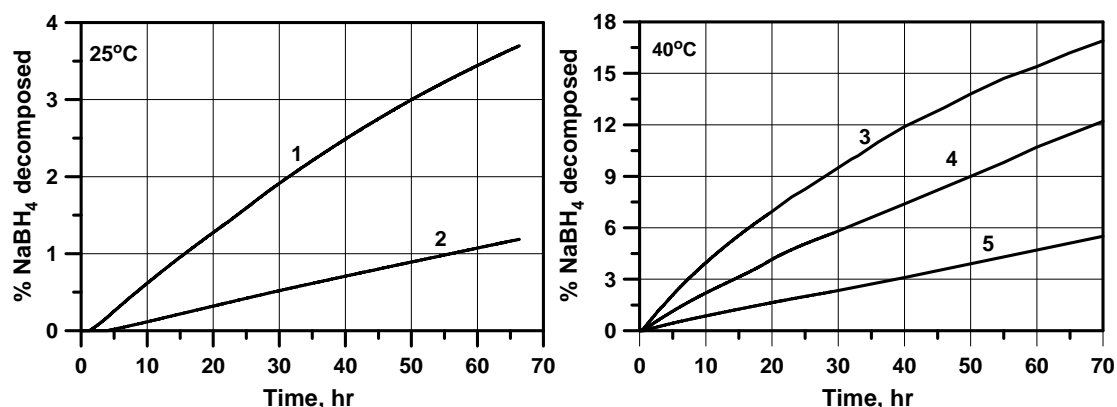
Figure 3:   Effect of NaOH on hydrolysis rate for molar composition of solution
$NaBH_4/ H_2O$ = 1/9. C_{NaOH} = 1 wt. % (1), 2 wt. % (2), 3 wt. % (3), 4 wt. % (4), 5 wt. % (5).

Too high concentration of NaOH is required (> 3 wt. %) to maintain low rates of hydrolysis at temperature above 40 °C.

Excluding the usage of preliminary prepared working solutions can solve stability problem, but requires additional unit to prepare small portions of solution with generator running. Dosing hygroscopic powder $NaBH_4$ raises some technical difficulties, but they do not seem insurmountable. Immediate preparation of the solution just before hydrolysis is easier combined with circulating scheme of generator, where the dissolution of $NaBH_4$ may complete in circulation loop, where the temperature is high.

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