CHEMICAL HEAT PUMP USING CARBON FABRICS AS BINDING AND CONDUCTING MATERIALS

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Abstract

A chemical heat pump (thermochemical transformer) based on a reversible solid sorption will be attractive if the process can store high energy density and if heating or cooling power is high enough. For that, the reactor must contain a large quantity of reactive mixture and the kinetics of the gas-solid reaction will be sufficiently fast.

Mass and thermal transfer must be high, which implies good porosity and high thermal conductivity of the reactor material. In the case of ammonia-salt reaction, the uses of a salt-binder mixture (carbon, exfoliated graphite, graphite intercalation compounds and intercalated or impregnated carbon fibers) enhanced the energy and power performances of the system. Another solution was found in our laboratory in order to more easily fill up the reactor of the heat pump: the use of impregnated carbon fabrics.

Several carbon textiles from different kinds of fiber precursors and treatments (high treatment temperature, surface activation…) were tested. Their gas permeability and thermal conductivity were determined.

After impregnation with a metal chloride as nickel, manganese or magnesium chlorides, the materials were tested in a laboratory heat-pump. Ammonia sorption kinetics, reaction advancement, cycle reversibility and other thermo-physical properties were measured. The method based on the modeling of the reactor was used to determine the thermal conductivity of the impregnated textiles. The performances of the chemical heat pump are globally enhanced.

KEYWORDS:

Chemical heat-pump; Carbon textile; Carbon fibers; Impregnation; Metal chloride; Ammonia; Thermal conductivity

INTRODUCTION

A chemical heat pump based on intermittent cycles is a heat-driven system which is constituted of a reactor connected to a heat exchanger working as a condenser or evaporator when there is a need for heating or cooling. The volatile fluid is contained in the evaporator in which takes place the physical reaction:

$$L_{(liq.)} \rightarrow G_{(gas)} \qquad \Delta H_{vap.} > 0 \qquad (1)$$

This endothermic reaction produces cold. Ammonia is largely used because it exhibited outstanding properties as a working fluid:

$$NH_{3\,(liq.)} \rightarrow NH_{3\,(gas)} \qquad (2)$$

Moreover, ammonia is a non-CFC refrigerant and does not contribute to the depletion of the atmosphere ozone layer
In absorption-evaporation phase, the reactor operates as absorber in which a solid material reacts with the gas to produce an exothermic reaction:

$$S_{(sol.)} + n\,G_{(gas)} \rightarrow S\,G_{n\,(sol.)} \qquad \Delta H_{react.} < 0 \qquad (3)$$

Practically, this chemical reaction is equilibrated, and for example, in the case of transition metal chloride MCl_2 (S) and ammonia (G), the following reaction is observed:

$$M(NH_3)_2\,Cl_{2\,(sol.)} + 4\,NH_{3\,(gas)} \rightarrow M(NH_3)_6\,Cl_{2\,(sol.)} \qquad (4)$$

The enthalpy of reaction $\Delta H_{react.}$ produced in (4) is about 50 kJ/NH_3 mol. for heating, whereas about 21 kJ/NH_3 mol. for cooling is produced by the reaction (2) into the evaporator.

Heat and mass transfer characteristics are particularly important towards the chemical reaction kinetics into the reactor [1, 2]. The poor thermal conductivity of the solid salt (about 0.1 W/m.K.) and the very high expansion factor of the salt S during its reaction with the gas G, are two important coefficients being able to reduce the heat-pump performances. Heat has to be evacuated outside during the chemical reaction of absorption, and ammonia diffusion has not to be slackened to reach the solid. Conversely, in desorption-condensation phase, the reactor operates as regenerator in an endothermic reaction.

The use of additives to the salt has two functions:
- the increase of the thermal conduction of the reactant and of the heat exchange coefficient at the interface between reactant and wall,
- the maintenance of a high porosity of the medium during the solid-gas reaction.

The addition to the salt of carbon powders [3], graphite compounds [4], expanded graphite [5], activated carbons [6], carbon fibers [7], carbon fabrics [8]… have enhanced the performances of the chemical heat-pump…

It is particularly convenient to use carbon fabrics because they possess the following main qualities:
- 2D high thermal conduction (if the precursor fibers have good thermal conductivity),
- gas permeability into the inter-fibers space,
- no discontinuities of the thermal conductivity between the reactor core and the heat exchanger wall.

EXPERIMENTAL and RESULTS

Carbon textiles. Several kinds of 2D woven carbon fibers have been used: ex-polyacrylonitrile (PAN) carbon fibers textiles, ex-rayon carbon textiles, activated carbon textiles (table I). Effective thermal conductivity is a function of the specimen orientation due to the preferred alignment of the fibers. It has not been already determined for all the samples. Several techniques can be used to measure or to calculate the thermal conductivity λ (parallel to the textile plan) of the textiles:
- The flash method: this method consists in generating a thermal impulse on one side of a sample, and in measuring the temperature evolution on the opposite side of the sample [9]. Unfortunately, it gives too low values (about 0.08 W/m.K. for C1600), non-accurate due to the high thermal contact resistance with the wall inside the measuring device.
- The estimation procedure based on a theoretical parallel model:

$$\lambda = \varepsilon\lambda_{gas} + (1-\varepsilon)\lambda_{fibers} \text{ (with } \varepsilon \text{ the porosity)}$$

  It necessitates the knowledge of the effective thermal conductivity of the individual fiber, but it is relatively simply to calculate with parallel fibers. In the case of a textile, the calculation is more dependant of the spatial orientation of each element of the textile structure [10],
- The estimation based on the reactor modeling: it has been satisfactory for a reactor using a medium made up of pitch-based carbon fibers. In this case, thermal conductivity of 15 W/m.K. has been achieved [11].

Gas permeability of carbon textile was measured by means of a laboratory permporometer using nitrogen as gas flowing. The permeability of C1200 carbon textile calculated with the Darcy formula

varies from 1 to 10 10^{-12} m^2 as a function of the bulk density. Its value is slightly weaker than carbon fibers one for the same density. Tortuousness of the textile can explain this difference.

Table I Some characteristics of carbon fabrics

Carbon fabrics	Precursors	Company name	Reference	g/m^2
ex-rayon carbon fibers textile	Rayon textile	Messier-Bugatti (Carbone Industrie), F	C1200 C1600 C2200	290 280 270
ex-rayon carbon fibers textile	Rayon textile	Le Carbone Lorraine, F	TGM 389	120
ex-PAN carbon fibers textile	Azko AG (High tenacity carbon fibers, λ = 17 W/mK)	R&G, D	Carbon fabric 93 Carbon fabric UD140	93 140
Activated carbon fibers textile (1500 m^2/g)	ex-rayon carbon fibers textile	Actitex, F	VS15	170

Salts. Different metal halogenides ($MnCl_2$, $NiCl_2$ or $MgCl_2$) were placed into the reactor. A new process was used to impregnate the carbon fabrics with the salt: the procedure of the textile impregnation consisted to dip the textile into a mixture of the salt dissolved in a 50-50% water-alcohol solution. The addition of 1% of 2-hydro-ethyl-cellulose to this solution was necessary to increase the solution viscosity in order to allow the drying of the impregnated textile without leakage of the salt solution. After drying at 80°C, a regular film of salt was obtained on the two opposite faces of the textile. Thus, the filling of the reactor with these impregnated textile layers is facilitated and becomes more homogeneous.

Gas permeability of the impregnated (C1200) fabrics was determined parallel to the textile plan. For a bulk density of about 300 kg/m^3 (as used in the reactor of the heat-pump), the permeability varies from 3 to 4 10^{-12} m^2 also slightly weaker than the impregnated carbon fibers permeability.

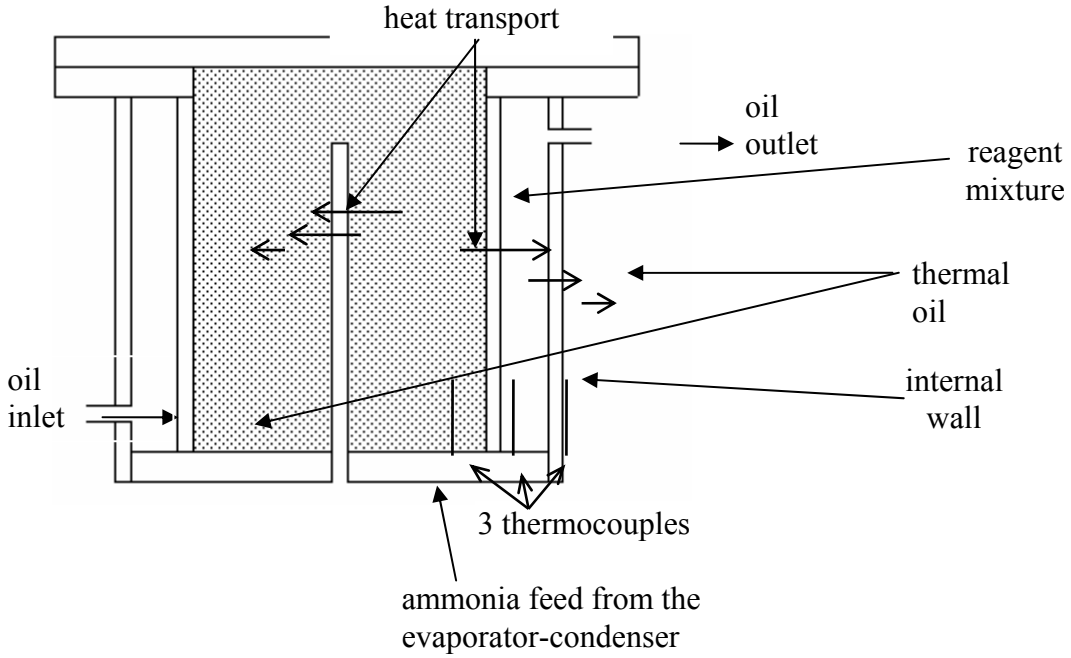


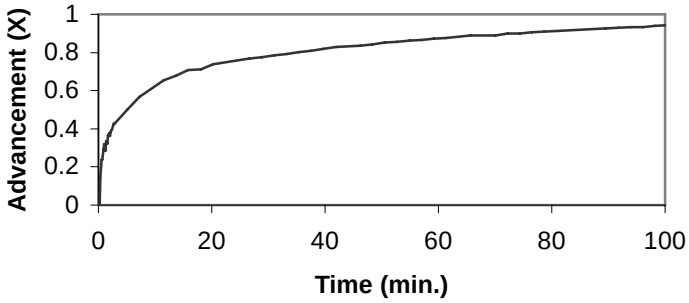
Fig. 1:Shema of the reactor of the laboratory pilot plant

Laboratory pilot. The laboratory heat-pump has been described [12]. Figure 1 shows the reactor used in this system. Arrows indicate the direction of the heat transfer during the heat production of the cycle. The system was completely monitored by a computer which records ammonia pressure, float displacement of the liquid ammonia and temperatures. Reaction advancement X and power P are directly calculated. The heat exchange coefficient between the reagent bed and the reactor wall (h_w) can be calculated according to the classical equation [13]:

$$\frac{1}{h} = \frac{1}{h_w} + \frac{e}{\lambda_w} + \frac{1}{h_f}$$

in which e is the wall thickness, h_f the heat exchange coefficient between the wall and the fluid, λ_w the thermal conductivity of the wall and h the whole heat exchange (h is determined with $h = P / S(T_b - T_f)$ with the temperatures difference between the solid bed b and the fluid f, and S the exchange area). In the case of pitch carbon fibers, h_w = 137 W/m^2.K., and in the case of carbon textiles, h_w ranges from 70 to about 110 W/m^2.K.
Figures from 2 to 5 show typical curves of ammonia absorption respectively by nickel chloride impregnated in a rayon carbon textile, by magnesium chloride impregnated in a PAN carbon textile, by manganese chloride impregnated in a rayon carbon textile and by manganese chloride impregnated in an activated carbon textile. These experiments have been made in a 200 mL reactor with respectively 28 g of $NiCl_2$, 15 g of $MgCl_2$, 54 g of $MnCl_2$ or 74 g of $MnCl_2$ impregnated on 40-50 layers of textiles (30-40% of the total mass), with a global porosity of 60-80%. The ammonia pressure was maintained at 5-6 bars. We observe a very high rate of absorption, which also determines a high power during the first minutes of the reaction. The advancement corresponding to the molar ratio for example in the case of the reaction (4) [ammonia molecules]/[4 x metal chloride molecules] was close to 90% of the theoretical value, and practically independent of the cycles number.

Fig. 2 Advancement evolution of the reaction of ammonia on $NiCl_2$/C2200 ex-rayon carbon textile (3rd cycle)



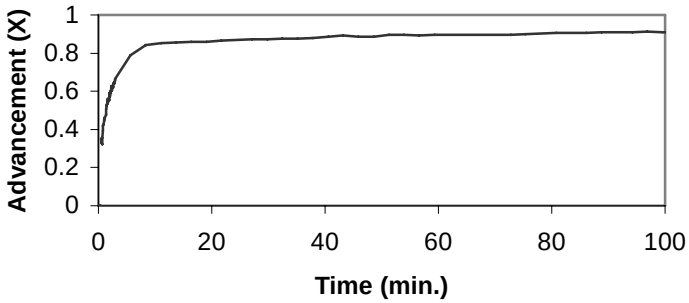


Fig. 3 Advancement evolution of the reaction of ammonia on $MgCl_2$/R&G 93 ex-PAN carbon textile (5th cycle)

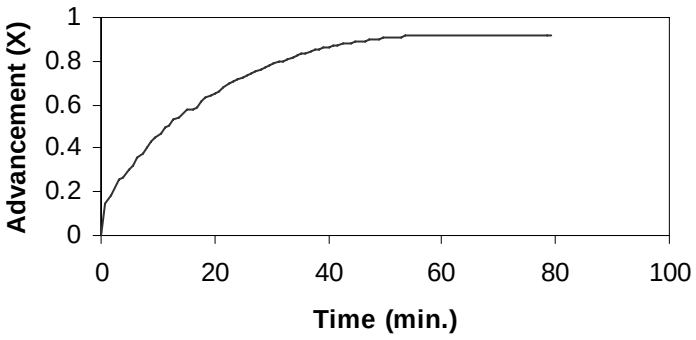


Fig. 4 Advancement evolution of the reaction of ammonia on $MnCl_2$/TGM389 ex-rayon carbon textile (6^{th} cycle)

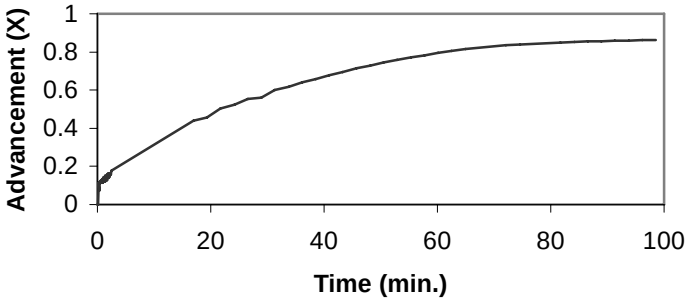


Fig. 5 Advancement evolution of the reaction of ammonia on $MnCl_2$/VS15 activated carbon textile (2^{nd} cycle)

An example of the power evolution is shown on the figures 6 and 7. A calculation based on a 40 minutes of working of the heat-pump leads to a power of about 250 W/kg of the reactive mass. The considered reactive mass is the sum of all the reactants masses : metal chloride + ammonia + carbon textile. Note that the utilization of very high thermal conductivity carbon fibers can lead to highest power: for example [7], the use of pitch-based carbon fibers (λ = 150 to 600 W/m.K.) permits to obtain a total reaction in less than 10 minutes and can give more than 1100 W/kg of the total mass of reactants. Figure 2 shows an experiment in which the total reaction is practically achieved in 10 minutes. The calculated power based on 10 minutes of working is 830 W/kg of the total mass.

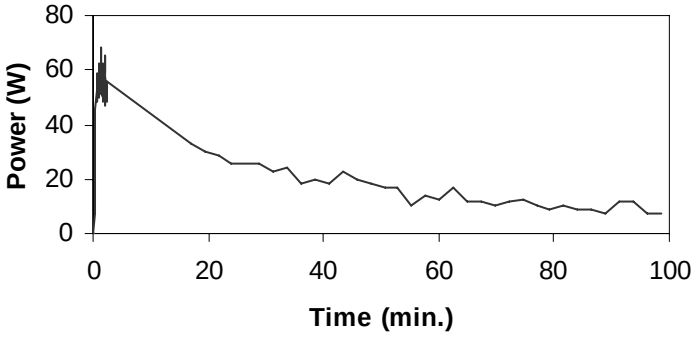


Fig. 6 Example of power evolution during the reaction of ammonia on $MnCl_2$/TGM389 ex-rayon carbon textile (reactor of 200 mL, 6^{th} cycle)

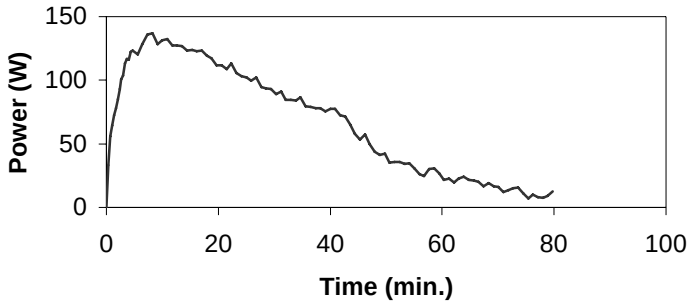


Fig. 7 Example of power evolution during the reaction of ammonia on $NiCl_2$/C1600 ex-rayon carbon textile (reactor of 450 mL, 3rd cycle)

CONCLUSION

Thermochemical transformers (chemical heat-pumps) are particularly attractive for smaller applications not only for heating purposes but also for air conditioning, ice production, refrigeration… They could be driven by heat from different origins such as electricity, wood or gas combustion, solar energy as well as waste heat, and they can run during the absorption phase without need of mechanical work. Ammonia or eventually water are not pollutant gasses. However, high power are necessary for some applications. This can be obtained with high heat and mass transfer inside the chemical reactor. Owing to their good thermal conductivities and permeabilities, carbon textiles impregnated with salt improve the characteristics of the heat-pump in particular power and efficiency. Nevertheless, the utilization of carbon textile made of high thermal conductivity fibers (for example pitch-based carbon fibers) will enhance still more the power capacity.

Acknowledgments

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