

HEAT RECOVERY WITH CHEMICAL HEAT PUMP

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Chemical heat pumps (CHP) use reversible exothermal and endothermal chemical reactions to increase the temperature of working fluids. In comparison to the “classical” vapour compression chemical heat pumps, CHP enables us to achieve significantly higher temperatures of a heated medium which is crucial for the potential application, e.g. for production of superheated steam. Despite the advantages presented, currently, there are no installations using CHP for lowgrade waste heat recovery available on the market. The scaling up of industrial processes is still one of the greatest challenges of process engineering. The aim of the theoretical and experimental concept study presented here was to evaluate a method of reclaiming energy from low temperature waste streams and converting it into a saturated steam of temperature from 120 to 150 °C, which can be useful in industry. A chemical heat pump concept, based on the dilution and concentration of phosphoric acid, was used to test the method in the laboratory scale. The heat of dilution and energy needed for water evaporation from the acid solution were experimentally measured. The cycle of successive processes of dilution and concentration has been experimentally confirmed. A theoretical model of the chemical heat pump was tested and coefficient of performance measured.

Keywords: Energy recovery, chemical heat pump, solutions of phosphoric acid

1. INTRODUCTION

In many cases a large fraction of energy applied for processes is wasted with low temperature streams leaving the process (Ogura et al., 2005). Drying alone is a unit operation which can account for up to 15% of total energy used in the industry (Chua et al., 2001). Any energy recovery system in the industry can reduce significantly process energy consumption. Drying assisted with heat pumps, exploiting consecutive compression, condensation, expansion and evaporation of working fluid, is an object of research since the 1980s. Applications of heat pump technology, offer energy saving potential along with temperature control. Installation equipped with heat pumps ensures economical process. In recent years chemical heat pumps have gained more interest by offering higher temperatures and possibility to store energy within chemical substances. Furthermore, on the market some materials appeared, resistant to rough conditions, which created new possibilities in assembling such installation.

Chemical heat pumps (CHPs) use reversible exothermal and endothermal chemical reactions to transfer energy, increasing the temperature of working fluids, and sometimes to store energy by chemical substances (Kawasaki et al., 1999). Selection of these chemical substances is important to absorb and release heat energy (Kato et al., 1996). Numerous chemical substances can be applied in CHP to create

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a cycle of chemical reactions. The following substances have been proposed as working fluids: water systems: hydroxide/oxide, salt hydrate/salt or salt hydrate, ammonia systems: ammoniate/ammoniate or salt, amine complex with salt, sulphur dioxide systems: sulphite/oxide, phryosulphate, carbon dioxide systems: carbonate/oxide, barium oxide/barium carbonate, hydrogen systems: hydride or metal, hydrogenation/dehydrogenation (Wongsuwan et al., 2001).

In comparison to “classical” vapour compression chemical heat pumps, CHP enables us to achieve significantly higher temperatures of the heated medium, which is crucial for the potential application, e.g. for production of saturated steam, usually applied as a heating medium, in majority of industrial processes. Despite the advantages presented, currently, there are no installations using CHP for low-grade waste heat recovery available on the market.

CHP absorbs energy via endothermic, and releases energy via exothermic processes, in the form of chemical reactions. CHP systems utilise a reversible chemical reaction to change the temperature level of the thermal energy, which is stored by chemical substances (Kawasaki et al., 1999). These chemical substances are important in absorbing and releasing heat energy (Kato et al., 1996). Various chemical substances can be used in CHP, for chemical reactions, for example, water system (hydroxide/oxide, salt hydrate/salt or salt hydrate), ammonia system (ammoniate/ammoniate or salt, amine complex with salt), sulphur dioxide system (sulphite/oxide, phryosulphate), carbon dioxide system (carbonate/oxide, barium oxide/barium carbonate), hydrogen system (hydride or metal, hydrogenation/dehydrogenation), etc. have been proposed as a working medium (Wongsuwan et al., 2001).

One of the promising chemical systems for CHP is water solution of phosphoric acid, where waste heat from a low temperature level is accumulated in endothermic and released in exothermic dilution of phosphoric acid (Ducheyne et al., 2007). The results of dilution heat laboratory measurement will be presented.

The distant future aim of the project is to apply CHP system to saturated steam production needed for unit operation using abundant waste heat available from a cooling electricity generator.

2. THE CHP CONCEPT

The basic configuration of CHP is shown in Fig. 1. In general CHP consists of a generator, a reactor, a condenser and an evaporator. Waste heat, in most cases at the same temperature, is provided to the generator Q_G and the evaporator Q_E while upgraded heat is delivered by reactor Q_R . Part of the heat at low temperature is removed from the condenser Q_C . Usually to increase efficiency of the CHP cycle internal heat exchanger, transferring heat between solutions, is added (Horuz and Bener, 2010).

In the concept presenting CHP, a two component working fluid is used. Primary fluid absorbs secondary fluid, producing upgraded heat, while waste heat is consumed in endothermic evaporation of secondary fluid. In the study, a solution of phosphoric acid will be the primary fluid and water is the secondary fluid.

The solution leaving the generator at high concentration, will be referred to as strong solution, while the solution returning from the reactor to the generator, at lower concentration of phosphoric acid, will be referred to as weak solution.

The CHP presented in Fig. 1a operates in the cycle depicted in Fig. 1b. The weak solution 1 enters the generator where part of the secondary fluid is evaporated and a strong solution 2 is produced. A strong solution is returned to the reactor, while vapour 3 is removed from the solution and is condensed, pumped and heated. Water, or water vapour, enters the reactor where it is mixed with a strong solution 2'. The heat of dilution increases the temperature of cooling water. A weak solution is returned to the generator. The CHP

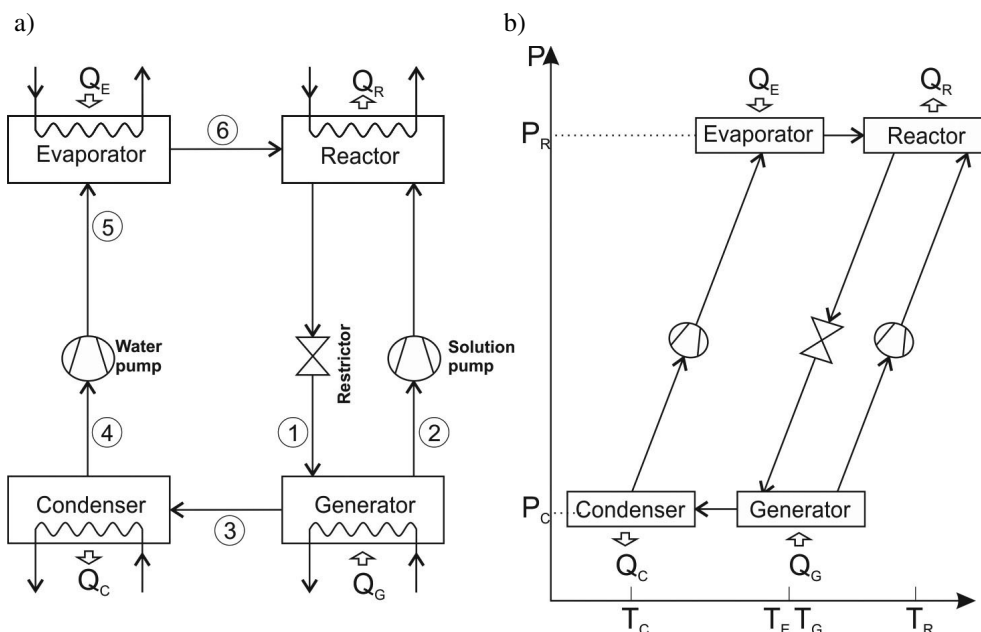


Fig. 1. Chemical heat pump: a) CHP schematic, b) CHP the pressure vs. temperature diagram

operates at two pressure levels, the lower, which is saturation pressure at the condenser temperature, and upper level, which is saturation pressure at the evaporator temperature. As seen in Fig. 1b, there are three temperature levels of CHP: a generator, a condenser and a reactor. In most cases the evaporator and generator use the same heat source so their operational temperatures are the same.

The performance of CHP can be increased with a heat exchanger transferring energy from a weak solution to a strong one or modifying the path of the stream, providing the waste heat. Each industrial application is different, and the CHP system should be well fitted to the real needs. To do so, an exact process model, based on validated experimental data of heat consumption and production, should be developed.

3. MATERIALS AND METHODS

3.1. Materials

85% by weight of phosphoric acid was purchased from Sigma–Aldrich and used without further purification. Demineralised water was used in all dilution experiments.

3.2. Apparatus and calculation of results

Measurements of the heat of dilution were conducted using a diathermic reaction calorimeter (Fig. 2) equipped with PTFE measuring Cell (1) with a capacity of: 50 cm³ and an automatic injection system (8). Temperature was measured using a thermocouple type K (5) of diameter of 0.5 mm. The control and acquisition of data from the measurement system was carried out using the LabView software.

Heat of dilution of phosphoric acid was calculated using the following heat balance:

$$\Delta H_{dil} = r_u \cdot \Delta T_{cor1} \quad (1)$$

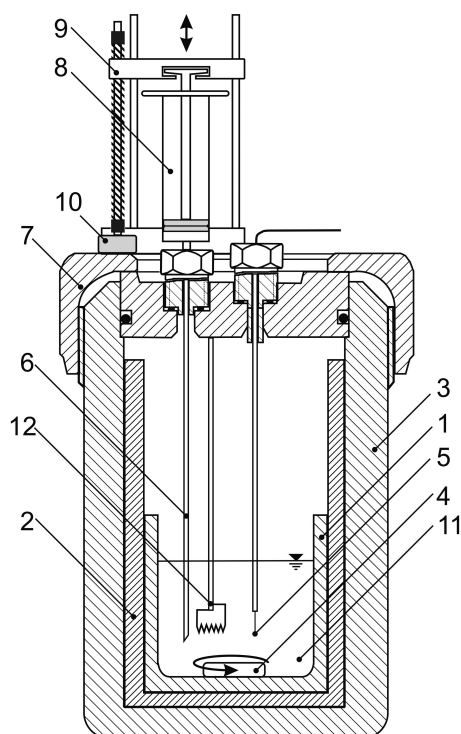


Fig. 2. Scheme of the calorimeter; 1 – PTFE measuring cell, 2 – insulation inserts, 3 – bomb calorimeter, 4 – magnetic stirrer, 5 – thermocouple, 6 – stainless steel chamber, 7 – cover, 8 – syringe, 9 – autosampler controlled by a microprocessor, 10 – stepping motor for autosampler drive, 11 – reaction mixture, 12 – heating coil

Heat capacity of the system was determined by measuring Joule heat provided to the system by heating coil.

$$r_u = \frac{U \cdot i \cdot t}{\Delta T_{cor2}} \quad (2)$$

3.3. Methodology

A sample of acid was placed in a PTFE measuring cell of the reaction calorimeter. Deionised water was injected with autosampler, and the injection time was 0.2 sec. The mass of the water used for the dilution of acid was determined by the difference of the weight of the syringe with water before and after the measurement, with a weighing accuracy of $\Delta m = \pm 0.0001$ g. Temperature measurement with a sampling rate of 0.01/sec lasted 10 minutes. Then, for the obtained reaction mixture, the thermal capacity of the system was measured using a heating coil. The electrical parameters of the process for all measurements were set at $U = 5$ V and $i = 1.2$ A, the heating time of the system was 15 sec. The obtained dependences $T = f(t)$ were used to determine the values: ΔT_{cor1} , ΔT_{cor2} by graphical method. After taking into account the accuracy of the mass measurement and the characteristics of the instruments used, the method error was determined to be $\pm 3\%$.

4. RESULTS AND DISCUSSION

The heat of dilution has been determined over the molar concentration range from 57.8 to 11.8 m (85%:53% by weight) at ambient pressure. The heat of dilution between molality of initial m_1 and final m_2 molality is given in Table 1.

Table 1. Experimental data for phosphoric acid heat of dilution measurement

Run	m_1 [mol/kg]	m_2 [mol/kg]	ΔT_{cor1} [K]	$n_{H_2O}/n_{H_3PO_4}$	ΔH_{dil} [kJ/mol]
1	57.827	29.916	12.206	1.855	3.842
	29.916	20.852	5.505	2.662	2.659
	20.852	15.734	2.848	3.528	1.840
	15.734	12.875	1.071	4.311	1.448
2	57.827	28.458	12.823	1.951	3.795
	29.916	19.053	4.889	2.913	2.230
	20.852	13.894	2.249	3.995	1.409
	15.734	11.182	0.931	4.964	1.281
3	57.827	30.627	12.359	1.812	4.101
	30.627	20.087	5.603	2.763	2.303
	20.087	14.990	2.392	3.703	1.675
	14.990	11.826	1.055	4.694	1.320
4	57.827	18.455	16.204	3.008	2.262
5	57.827	36.657	9.925	1.514	5.379
6	57.827	36.076	10.100	1.539	5.225

The plot of the heat of dilution, versus the molar ratio of solvent and solute, is given in Fig. 3. The heat of dilution of aqueous phosphoric acid solutions, presented in Fig. 3, shows a large non-linear behaviour for molar ratio of less than 3. For a molar ratio of water to phosphoric acid close to 5, the dilution heat is only 1.28 kJ/mol. However, when the molar ratio approaches 1.5, the dilution heat rapidly increases and reaches 5.38 kJ/mol.

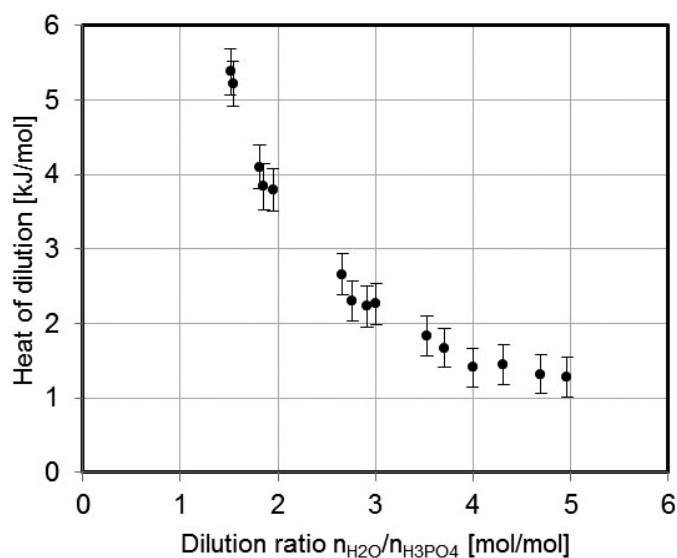


Fig. 3. Phosphoric acid heat of dilution vs water/acid molar ratio

The non-linear dependence of the dilution heat on the molar ratio of water to phosphoric acid (V) indicates that for any chemical use of the pump in industry, there is a limit of the molar ratio below which the benefits of using the pump rapidly disappear.

The results also show that the heat of dilution of phosphoric acid (V) is almost independent of temperature and depends only on the acid concentration and degree of dilution. Our results agree with the values of dilution heat very well, which were also obtained by other authors for low concentration phosphoric acid (Millero et al., 1978; Wakefield et al., 1972).

The complete model of a chemical heat pump requires data on the saturated vapour pressure and the heat of evaporation of phosphoric acid. The experimental measurement of the saturated vapour pressure and the heat of evaporation of phosphoric acid will be a continuation of the presented work.

5. CONCLUSIONS

- Heat pump technology can improve heat efficiency for many processes. Low temperature systems are intensively studied and already implemented in the industry. Chemical heat pumps offer a prospect to generate heat flux at elevated temperatures.
- Heat of dilution for phosphoric acid with high concentration, was experimentally measured at isobaric conditions. Thermal effect of dilution strongly depends on acid concentration.
- A simple calorimetric system enables the measurement of heat generated during the dilution of phosphoric acid with water.
- The results obtained are in good agreement with the dilution heat values measured by other authors for low concentration phosphoric acid.
- Laboratory experiments proved that phosphoric acid and water can be used as an efficient working system in CHP. Heat from dilution is important for energy recovery in heat pump reactors. It enables to produce technologically useful heat flux from a waste heat source.
- The highest amount of heat is released during dilution of the highly concentrated acid (above 80%). The chemical heat pump should be designed to work with as concentrated acid as possible.
- Increased temperature and concentrated acid create a highly corrosive environment, it will be necessary to carefully select construction materials for process equipment.

SYMBOLS

i	electric current passing through the heating coil, A
Q	heat flux, W
ΔH_{dil}	heat generated during dilution of phosphoric acid, J/mol
r_u	heat capacity, J/K
t	heating time, s
ΔT_{cor1}	rectified temperature increase determined by graphical method for the process of acid dilution, K
ΔT_{cor2}	rectified temperature increase determined by graphical method for the electric heating process of the system, K

Subscripts

R	reactor
E	evaporator

C	condenser
G	generator
cor1	temperature increase of acid dilution
cor2	temperature increase of electric heating

The authors wish to acknowledge the support of the Chemat Sp. z o.o. and the National Centre for Research and Development (POIR.01.01.01-00-0809/17-00) for this study.

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Received 19 March 2019

Received in revised form 22 April 2019

Accepted 23 April 2019