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Concept of heat recovery in drying with chemical heat pump

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Abstract

Drying is one of the most energy intensive unit operations. It easily accounts for up to 15% of all industrial energy consumption. In the most drying processes heat is required to evaporate moisture which is later removed with a flow of air. The hot, humid air leaving the dryer is often considered as a waste stream, and a large fraction of energy is lost. 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 to useful in industry saturated steam of temperature from 120 to 150 °C. Chemical heat pump concept based on the dilution and concentration of phosphoric acid was used to test the method in the laboratory. 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. Theoretical model of the chemical heat pump was tested and coefficient of performance measured. Energy balance of the drying system and efficiency increase of the dryer supported with chemical heat pump were calculated.

Keywords: *Efficiency of drying; energy recovery; chemical heat pump*

1. Introduction

Drying is very intensive unit operation which, on the global scale, can accounts for up to 15% of all energy used in the industry [1](Chua et al. 2001). In many cases a large fraction of energy applied for drying is wasted with low temperature streams leaving the process [2](Ogura et al. 2005). Any energy recovery system in the drying can reduce significantly process energy consumption. Applications of heat pump technology offers energy saving potential along with temperature and humidity control. Drying assisted with heat pumps exploiting consecutive compression, condensation, expansion and evaporation of working fluid, is an object of research since eighties of last century. Dryers with heat pumps ensure economical process and at the same time product's quality especially agriculture and food products. In the recent years chemical heat pumps have gained more interest as offering higher temperatures and possibility to store energy in chemical substances.

Chemical heat pumps (CHP) are using reversible exothermal and endothermal chemical reactions to transfer energy, increase the temperature of working fluids and sometimes to store energy by chemical substances [3](Kawasaki et al. 1999). Selection of these chemical substances is important to absorb and release heat energy [4](Kato et al. 1996). Numerous chemical substances can be used in CHP to create 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, sulfur dioxide systems: sulphite/oxide, phyrosulphate, carbon dioxide systems: carbonate/oxide, barium oxide/barium carbonate, hydrogen systems: hydride or metal, hydrogenation/ dehydrogenation [5](Wongsuwan et al. 2001).

Unlike the "classical" vapor compression heat pumps CHP enable to achieve significantly higher temperatures of 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 presented advantages, currently, there are no installations using CHP for low-grade waste heat recovery available on the market.

CHP absorbs energy via endothermic and release energy via exothermic in the form of chemical. CHP systems utilize the reversible chemical reaction to change the temperature level of the thermal energy, which stored by chemical substances [3](Kawasaki et al. 1999). These chemical substances are important in absorb and release heat energy [4](Kato et al. 1996). Various chemical substance can be use in CHP for chemical reaction, for examples, water system (hydroxide/oxide, salt hydrate/salt or salt hydrate), ammonia system (ammoniate/ammoniate or salt, amine complex with salt), sulfur dioxide system (sulphite/oxide, phyrosulphate), carbon dioxide system (carbonate/oxide, barium oxide/barium carbonate), hydrogen system (hydride or metal, hydrogenation/ dehydrogenation), etc. has been proposed as working medium [5](Wongsuwan et al. 2001).

One of promising chemical systems for CHP is water solution of phosphoric acid where waste heat of low temperature level is accumulated in endothermic and released in exothermic dilution of phosphoric acid [6](Ducheyne 2017). The results of dilution heat laboratory measurement will be presented.

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

2. CHP concept

The basic configuration of CHP is shown on Fig.1. In general CHP consists of a generator, a reactor, 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 CHP cycle internal heat exchanger transferring heat between solutions is added [7](Horuz and Kurt 2010).

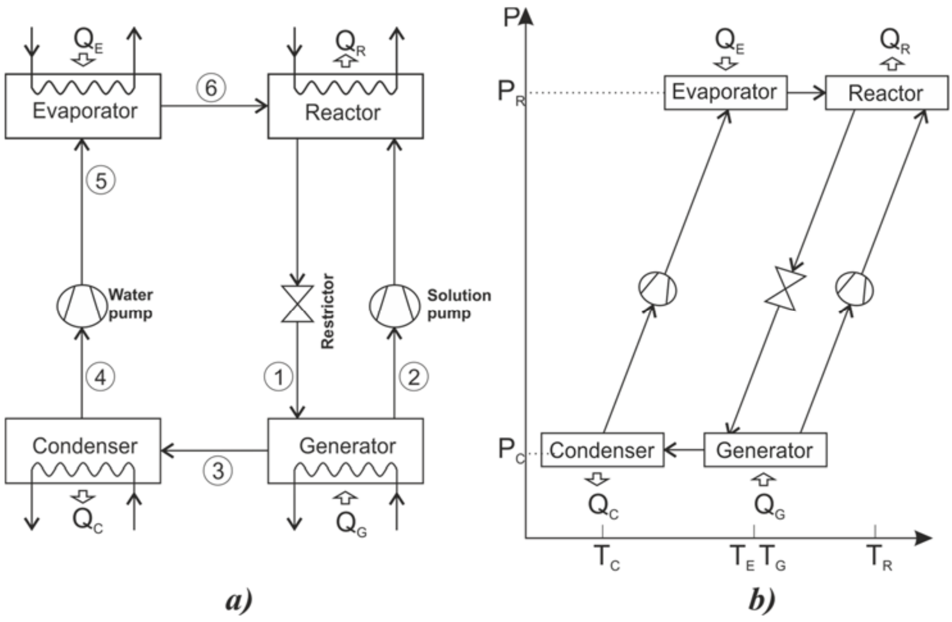

Fig. 1 Chemical heat pump: a) CHP schematic, b) CHP the pressure vs. temperature diagram.

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

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

The CHP presented in Fig 1a operate with the cycle depicted in Fig. 1b The weak solution 1 is entering the generator where part of the secondary fluid is evaporated and strong solution 2 is produced. Strong solution is returned to the reactor, while vapour 3 removed from solution is condensed, pumped and heated. Water or water vapour enters the reactor where it is mixed with strong solution 2'. The heat of dilution increase the temperature of cooling water. Weak solution is returned to the generator. The CHP operate at two pressure levels, lower which is saturation pressure at the condenser temperature and upper level which is saturation pressure at the evaporator temperature. As Fig. 1b present there are three temperature levels of CHP: a generator, a condenser and reactor. In most cases the evaporator and generator are using the same heat source so their operation temperatures are the same.

The performance of CHP can be increased with heat exchanger transferring energy from weak solution to strong solution, or modifying path of the stream providing waste heat. Every industrial application is different and 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

The 85% by weight phosphoric acid was purchased from Sigma-Aldrich and used without further purification. Demineralized 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 cm^3 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 sofware.

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

$$\Delta H_{dil} = r_u \cdot \Delta T_{cor1} \tag{1}$$

Where: ΔH_{dil} - heat generated during dilution of phosphoric acid, J; r_u - heat capacity of the system ; ΔT_{cor1} - rectified temperature increase determined by graphical method for the process of acid dilution.

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

$$r_u = \frac{U \cdot i \cdot t}{\Delta T_{cor2}} \tag{2}$$

Where: U - potential difference applied to the heating coil, V; i - electric current passing through the heating coil, A; t – heating time, sec; ΔT_{cor2} - rectified temperature increase determined by graphical method for the electric heating process of the system.

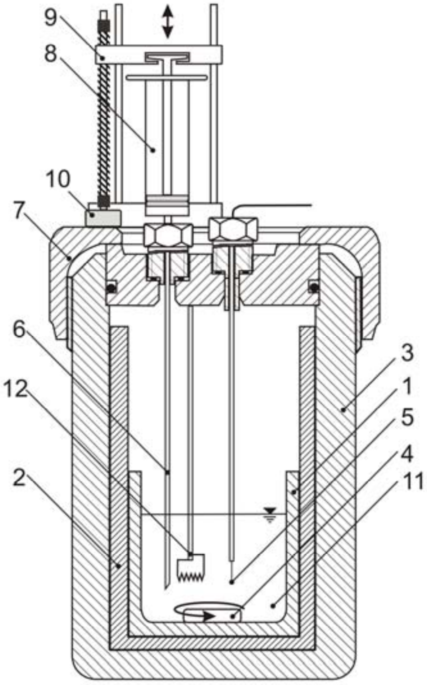

Fig.2 Scheme of the calorimeter

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

3.3. Methodology

A sample of acid was placed in a PTFE measuring cell of the reaction calorimeter. Deionized water was injected with autosampler, and the injection time was 0.2 sec. The mass of the water used for the dilution of the acid was determined by the difference of the weight of the syringe with water before and after the measurement, with a weighing accuracy of $\Delta m = \pm 0.0001g$. 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 $U = 5V$ 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 ± 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 are given in the 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_{H2O}/n_{H3PO4}** -	**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

Plot of heat of dilution versus molar ratio of solvent and solute is given in Fig. 3. The heat of dilution of aqueous phosphoric acid solutions, presented in Fig3, show a large curvature for molar ratio less than 3.

Our results are in a good agreement with the values of dilution heat obtained by other workers for low concentration phosphoric acid. [8, 9](Wakefield 1972, Millero 1978).

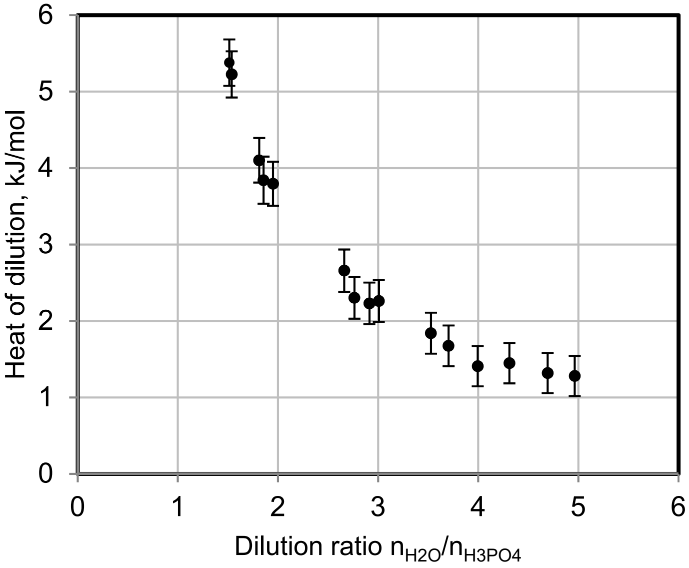

Fig.3 Phosphoric acid heat of dilution vs water /acid molar ratio.

5. Conclusions

Heat pump technology can improve heat efficiency of many drying processes. Low temperature systems are intensively studied and already implemented in the industry. Chemical heat pumps offers prospect to generate heat flux at elevated temperature.

Heat of dilution for phosphoric acid of high concentration was experimentally measured at isobaric conditions. Thermal effect of dilution strongly depends on acid concentration.

Laboratory experiments proved that phosphoric acid and water can be used as a efficient working system in CHP. Heat of dilution important for energy recovery in heat pump reactor, enable to produce technologicaly useful heat flux from waste heat source.

6. Nomenclature

Q	heat flux, J	W
ΔH_{dil}	heat of dilution	J mol^{-1}
r_u	heat capacity	J K^{-1}
ΔT	temperature increase	K
U	potential difference	V
i	electric current	A

Subscripts

R	reactor
E	evaporator
C	condenser
G	generator
cor1	temperature increase of acid dilution
cor2	temperature increase for the electric heating

7. Acknowledgements

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