

Current Status and Perspectives of Thermomolecular Engine Developments

V.A. Eroshenko*¹, A. Popyk²

National Technical University of Ukraine "KPI", Department of Energy Saving and Energy Management,
 Laboratory of Thermomolecular Energetics, Peremogu pr. 37, Kiev, Ukraine.
 E-mail: ¹eroshenko@kpi.ua, ²art_popyk@ukr.net

Abstract

A fundamentally new concept of a heat engine on the basis of heterogeneous working body, consisting of liquid and lyophobic towards it capillary-porous matrix was proposed in the middle 1980's. The unusualness of the new thermodynamic cycle and engine is that the interface of condensed heterogeneous lyophobic systems (HWB), "liquid- rigid solid capillary-porous matrix", the carrier of free surface energy, serves as a working body (in a thermodynamic sense) instead of traditional gas/steam. In this paper the main advantages, challenges and prospects for use of HWB as the working fluid for external combustion engine are discussed.

Keywords: Heat engine; lyophobic; surface tension; colloids.

1. Introduction

Depletion of natural resources, environmental pollution, and price increases for oil products leads to activation of various research programs devoted to the study of both traditional and non-traditional heat engines.

Lately there has been a revival of interest in external combustion engines (Stirling cycle, combined Eriksson-Brayton cycle, Schoell cycle, etc.) [1-3]. External combustion engines have many advantages. Perhaps the main advantage is the ability to work from any source of heat: geothermal, radiant light and heat from the sun, excess heat emitted by industry, different types of fuel, nuclear and chemical reactors, etc.

The main disadvantages of external combustion engines are: complexity of design, high weight due to presence of heat exchangers, and low thermal efficiency. Use of modern materials and technologies, methods of calculation and design techniques may allow the characteristics of these engines to closer approach those of modern internal combustion engines (for example, Otto and Diesel).

This article is focused on an unusual external combustion engine developed in Ukraine.

2. Working Bodies: Volume or Surface? Eroshenko Cycle.

A fundamentally new concept of a heat engine [4,5] on the basis of a heterogeneous working body (HWB), consisting of liquid and lyophobic towards it capillary-porous matrix was proposed in the middle 1980's. The unusualness of the new thermodynamic cycle and engine is that the interface of condensed heterogeneous lyophobic body (HWB), "liquid- rigid solid capillary-porous matrix", the carrier of free surface energy, serves as a working body (in thermodynamic sense) instead of traditional gas/steam. It was first proposed to use the potential energy of intermolecular interaction instead of kinetic energy of the random motion of gas (vapor) molecules in a wide range of thermal machines.

Table 1. Volumetric energy density of different working bodies.

Working body	Energy density, E_V (MJ/m ³)
Fuel mixture "air - gasoline"	3,636
Fuel mixture "air - diesel"	3,604
Fuel mixture "air - hydrogen"	3,030
Fuel mixture: "air - ethanol"	3,067
Water, $V=1$ m ³ (its potential energy at fall from a height of 100 m)	0,001
Water as a bimolecular film ($\delta = 7\text{\AA}$, $V=1$ m ³ , $m = 1000$ kg)	208
Compressed air (adiabatic compression, without losses, $V=1$ m ³ , $P = 200$ bar)	50
HWB "silicalite-2 - water" with total volume of 1m ³ and matrix porosity 0,12 m ³ /m ³ (initial data taken from [17])	15,8

The above mentioned HWB based on a capillary-porous matrix with extremely high surface area (from 200 to 1000 m²/g of matrix) and wide variety of liquids (from water to low-temperature metal alloys and eutectics) have a significant energy density (see Table 1).

The change in volume of condensed HWB is due to input and output of fluid from a pore space of the matrix, which is accompanied by development and reduction of the interphase surface Ω . Due to phobicity of the system (contact angle $\theta \gg 90^\circ$) it is necessary to overcome a certain barrier (Laplace capillary pressure) in order to introduce the liquid into the pore space (to develop the interfacial surface). As the capillary pressure P (in Washburn form [6]) is proportional to the surface tension of the liquid σ

$$P = \frac{2\sigma \cos\theta}{r} \quad (1)$$

(Here and below we use the modulus of $\cos\theta$),

and for simple liquids the last mentioned decreases almost linearly with the temperature increase

$$\sigma = \sigma_0 \left(1 - \frac{T}{T_{CR}}\right) \quad (2)$$

(where: σ_0 -hypothetical value of the surface tension at $T = 0$; T - current temperature value; T_{CR} - critical temperature value of the liquid at which $\sigma = 0$), so high temperature values facilitate forced intrusion of liquid in pores (decreasing of HWB volume). When the temperature is going down, the volume is going up (operating cycle) due to spontaneous extrusion of liquid from the pores of solid matrix. Further, this unusual phenomenon will be discussed in more detail. This is one of the main features of a new working body: temperature decreasing leads to volume increasing.

Let us consider the basic cycle of a thermomolecular engine [7,8] for a system “single pore – single volume of liquid” (heat capacity is constant, thermal expansion is absent). PV and TS graphs of the cycle are shown in Figure 1. Figure 2 shows the cycle schematic.

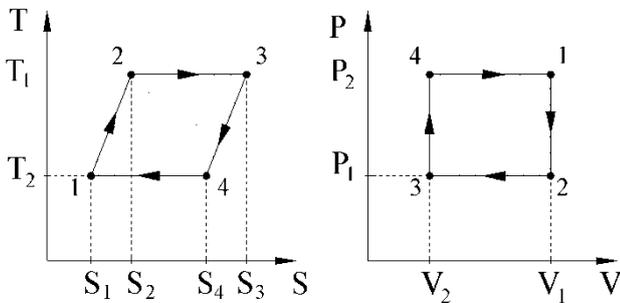


Figure 1. T-S and P-V diagrams of the thermomolecular engine cycle.

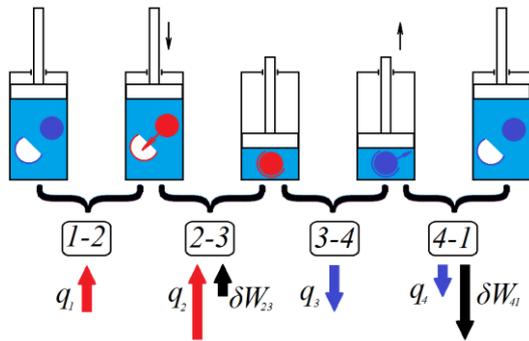


Figure 2. Basic four-step cycle of the thermomolecular engine.

In the initial state (point 1) the working fluid at minimum temperature T_2 and maximum volume V_1 is characterized by a maximum pressure P_2 . The liquid remains outside the pores of the lyophobic solid matrix (interphase surface $\Omega = \Omega_{min} \rightarrow 0$). During the process of isochoric heating (1-2) heat q_1 is supplied to working body:

$$q_1 = c_V (T_1 - T_2), \quad (3)$$

where: c_V - total heat capacity of a heterogeneous working body.

Temperature increases from T_2 to T_1 . Interfacial contact area remains unchanged: $\Omega_{12} = \Omega_{MIN} = \text{const}$. In this case

in an enclosed volume $V_1 = \text{const}$ and pressure is reduced to P_1 (the Laplace pressure is reduced due to the fall of the value of the surface tension to σ_1):

$$P_L = \frac{2\sigma_1 \cos \theta}{r}, \quad (4)$$

For the isobaric-isothermal process (2-3) of interface surface development Ω up to the value of $\Omega_{23} = \Omega_{MAX}$, the system is supplied with a large amount of heat q_2 and small amount of mechanical work δW_{23} [9,10].

$$q_2 = \dot{\Omega}_1 \cdot \frac{d\sigma}{dT} \cos \theta \Omega_{MAX}, \quad (5)$$

where $d\sigma/dT$ – temperature coefficient of surface tension of the liquid (the value is negative, here and below we use the absolute value of this quantity);

$$\delta W_{23} = P_1 (V_2 - V_1) = -P_1 \Delta V_{23} = \sigma_1 \cos \theta \Omega_{MAX} \quad (6)$$

In an isochoric process (3-4) the heat is taken away from the thermodynamic system ($q_3 = -q_1$), and the temperature decreases from T_1 to T_2 .

$$q_3 = -c_V (T_1 - T_2) \quad (7)$$

At the same time in an enclosed space $V_2 = \text{const}$ ($\Omega_{34} = \Omega_{MAX} = \text{const}$) pressure increases to a maximum level

$$P_2 = \frac{2\sigma_2 \cos \theta}{r} \quad (8)$$

because $\sigma_1 < \sigma_2$, according to (2).

In an isobaric-isothermal process (4-1) a spontaneous expulsion of fluid from the pore space at maximum constant pressure P_2 (power stroke) takes place. The interphase surface decreases to $\Omega_{41} = \Omega_{MIN}$. The system performs the work δW_{41} against external forces and returns to its initial state:

$$\delta W_{41} = -P_2 \Delta V_{41} = -\sigma_2 \cos \theta \Omega_{MAX} \quad (9)$$

where $\Delta V_{41} = V_1 - V_2$.

At the same time a small amount of heat q_4 is taken away (heat of an isobaric-isothermal reduction of the surface):

$$q_4 = -\dot{\Omega}_2 \frac{d\sigma}{dT} \cos \theta \Omega_{MAX} \quad (10)$$

Useful work in the cycle:

$$\begin{aligned} \delta W &= \delta W_{41} - \delta W_{23} = (P_2 - P_1) \Delta V = \\ &= (\dot{\Omega}_1 - \dot{\Omega}_2) \frac{d\sigma}{dT} \cos \theta (\Omega_{MAX} - \Omega_{MIN}) \end{aligned} \quad (11)$$

Unusual properties and characteristics of HWB [7, 11, 12] have attracted attention of leading research centers. Over the past 20 years a lot of papers have been published about theoretical, experimental and design aspects of various devices based on HWB (see Fig. 3 and Table 2).

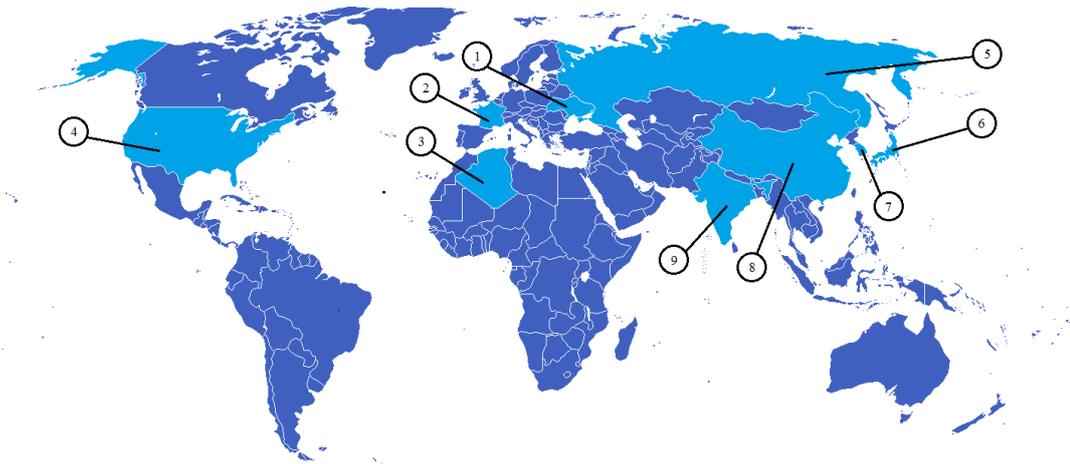


Figure 3. Countries involved in research of HWB and development of HWB-based devices.

Table 2. Explanations to Figure 3.

№	Country	Organization	Field of research	Ref.
1	Ukraine	Laboratory of thermomolecular energy	Theoretical and experimental studies; damper, shock absorber, accumulator, thermal key, heat engine	[7, 11-16]
2	France	Institute of Materials in Mulhouse; University of Nancy; SNECMA.	Theoretical and experimental studies; damper; aviation devices	[17-20]
3	Algeria	University of Jijel	Theoretical studies	[21]
4	USA	Massachusetts Institute of Technology; University of San-Diego; Columbia University.	Theoretical and experimental studies; damper, shock absorber, fuel cell, actuator	[22-29]
5	Russian Federation	Leypunsky Physics and Power Engineering Institute; National Research Nuclear University "Moscow Engineering Physics Institute"	Theoretical and experimental studies; damper, shock absorber, hydraulic compensator	[30-33]
6	Japan	Fukuoka Institute of Technology; Kobe University; Oiles Corp; Toyota.	Theoretical and experimental studies; damper	[34-37]
7	South Korea	Pusan National University; Samsung Heavy Industry; S&T Daewoo	Theoretical and experimental studies	[38, 39]
8	China	Peking University	Theoretical and experimental studies	[40]
9	India	Vels University	Theoretical and experimental studies;	[41]

2. Thermodynamic Compactness and Thermal Efficiency of the Thermomolecular Engine. The Basic Requirements to HWB.

A new criterion of thermodynamic perfection of heat engines – "thermodynamic compactness of cycle" was introduced in 1987 [13]. Thermodynamic compactness is defined as the ratio of useful work in the cycle to the change of the generalized coordinate ΔY (for example, volume, length of the spring, surface, etc.) and to temperature difference between heater T_1 and cooler T_2 in a cycle:

$$l = \frac{\delta W}{\Delta Y \cdot \Delta T} \quad (12)$$

The formula shows that for $\Delta Y = \Delta V$ dimension of thermodynamic compactness is (J/m^3K) . Thus, the thermodynamic compactness (hereinafter - TC) shows the ability to conversion of the energy per volume unit of a

working body in the cycle, referred to 1 degree of working temperature difference.

For example, TC for Otto-Baux de Roche cycle is described by the expression [13]:

$$l_{OTTO} = \frac{R}{\mu \cdot v_{MAX}} \cdot \frac{(\lambda - 1)(\varepsilon^{\chi-1} - 1)}{(\chi - 1)(\lambda \varepsilon^{\chi-1} - 1)(1 - 1/\varepsilon)}, \quad (13)$$

where R is the universal gas constant; μ is the molar mass of the substance of a working body; v_{MAX} is the maximum value of the specific volume of working body in the thermodynamic cycle; $\chi = c_p/c_v$ is the adiabatic index; $\lambda = P_3/P_2$ is the pressure ratio in the isochoric process of heat supply; and $\varepsilon = V_1/V_2$ is the compression ratio in the adiabatic process;

For Diesel cycle TC is determined as [13]:

$$l_{DIESEL} = \frac{R}{\mu v_{MAX}} \cdot \frac{1}{\chi - 1} \cdot \frac{\chi \varepsilon^{\chi-1} (\pi - 1) - (\pi^\chi - 1)}{(\pi \varepsilon^{\chi-1} - 1)(1 - 1/\varepsilon)}, \quad (14)$$

where $\pi = V_3/V_1$ is the degree of expansion in the isobaric process of heat supply. For different cycles of heat engines TC value varies in the range of 100-550 (J/m³·K) [13]. Optimization of "gas" cycles by TC value is a complex multiparameter problem, because some of the variables are determined by the nature of working body, the other part is by modes of engine operation.

TC of thermomolecular engine, in accordance to (11) and (12) will be determined as:

$$l_{\Omega} = \frac{\delta W}{\Delta Y \cdot \Delta T} = \frac{\Delta \dot{\Omega} \frac{d\sigma}{dT} \cos \theta \Delta \Omega}{k r \Delta \Omega \Delta \dot{\Omega}} = \frac{d\sigma}{dT} \cdot \frac{\cos \theta}{k r}, \quad (15)$$

where $\Delta Y = \Delta V = V_1 - V_2 = k r \Delta \Omega$ is the volume change of HWB during the cycle.

Eqn (15) is much easier than Eqns (13) and (14). TC of the thermomolecular engine depends only on the parameters of HWB ($d\sigma/dT$, $\cos\theta$, r) and exceeds analog values for "gas" engines by 2-3 orders [13,16]. This is quite logical for condensed system working without explosions in a working chamber and phase transitions "liquid-vapor".

Thermal efficiency of the cycle η_E is determined by the expression:

$$\eta_E = \frac{\eta_k}{1 + r \cdot \eta_k \cdot \frac{k \cdot c_V}{\frac{d\sigma}{dT} \cos \theta}}, \quad (16)$$

where η_k is the Carnot cycle efficiency: $\eta_k = 1 - T_2/T_1$; r is the radius of the pores (for different materials, from a few to a few thousand angstroms); k -form factor of the pores ($k = 0,33 \dots 0,5$); c_V is the total volumetric heat capacity of HWB.

Present in the denominator of the Eqn (16), η_k indicates another feature of the cycle such as high Carnot efficiency at low-temperature heat sources running (see Fig. 4e).

In order to estimate the effect of various parameters of HWB on the carnotization level, a cycle for real system "distilled water - silicalite-2" was calculated. Table 3-1 shows the main parameters of HWB in the indicated temperature range, and Table 3-2 shows the cycle

characteristics (Data of Table 3-2 were obtained by substituting the values from Table 3-1 in Eqns (15) and (16)). The influence of HWB parameters on the carnotization level of cycle is shown in Fig. 4(a-f).

Analysis of dependences, shown in Figure 4 (a-f), allows formulating the basic requirements of HWB to achieve maximum carnotization level of the cycle:

- + high level of lyophobicity of porous matrix (value of the contact angle starting from 110° and higher);
- + small pore radius of the matrix (a few angstroms);
- + high value of the temperature derivative $d\sigma/dT$ (strongly marked dependence of surface tension on the temperature);
- + low heat capacity of HWB components.

Experiments made with different HWB allow to add additional (maintenance and constructional) requirements:

- + Operational stability of HWB (no matrix degradation - mechanical breaking of porous particles and damage of the hydrophobizing surface coating).

+ Maximum system pressure should not exceed 700 bar (according to [42]).

+ Minimum (preferably - zero) hysteresis level (the difference between the intrusion pressure (P_{int}) and the extrusion pressure (P_{ext}) is shown as a loop on PV -isotherm of compression-expansion [12,19]. Large hysteresis reduces the efficiency of the engine and complicates its construction (in this document the influence of hysteresis is not considered).

Conversely, in order to create high effective dampers and shock absorbers, it is necessary to maximize the amount of hysteresis (see Figure 5) [12, 15, 28, 37].

3. Different Approaches on HWB Development.

Synthesis of a new HWB meeting specified requirements is a complex task involving various branches of science (surface chemistry, colloid chemistry, chemical thermodynamics) and technology (synthesis of porous materials with specific pore geometry and topology of the pore space; lyophobicising of matrices that is a covering of porous inner surface by low-energy materials with controlled coating thickness; getting suspensions and colloids). There are two approaches to HWB development: theoretical and technological.

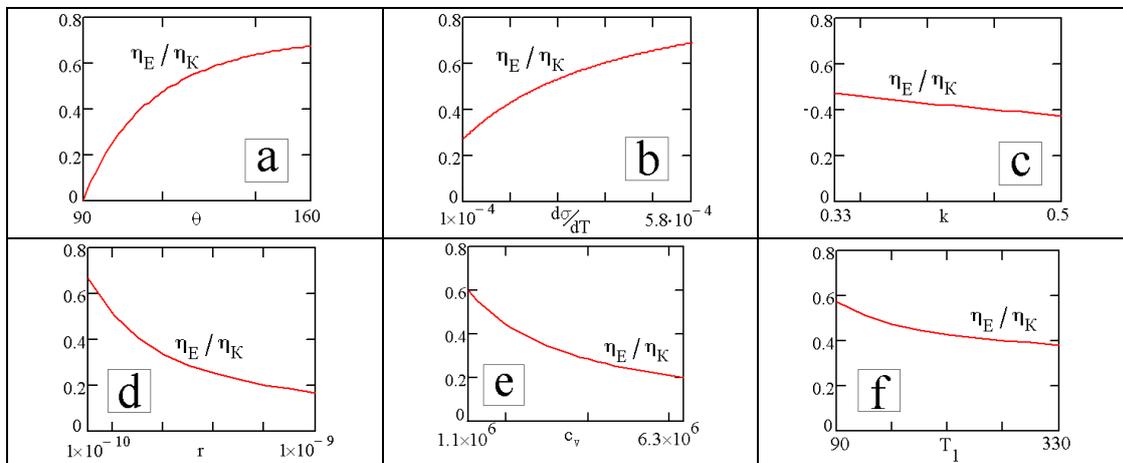


Figure 4. Carnotization level of the cycle, depending on: a) the value of the contact angle ($\theta = 90 \dots 160^\circ$); b) the value of $d\sigma/dT$ ($d\sigma/dT = 9,7 \cdot 10^{-5} \dots 5,9 \cdot 10^{-5} \text{ N/(m}\cdot\text{K)}$); c) the value of the shape factor of pores k ($k = 0,33 \dots 0,5$); d) pore radius r ($r = 1 \dots 10 \text{ \AA}$); e) the total heat capacity of HWB ($c_V = 1,1 \dots 6,3 \cdot 10^6 \text{ J/(kg}\cdot\text{K)}$); f) temperature of the hot source, T_1 ($T_1 = 363 \dots 603 \text{ K}$).

Table 3-1. Main computational parameters of HWB "distilled water - silicalite-2."

Parameter	Value
Temperature of heater, T_1 [K]	473
Temperature of cooler, T_2 [K]	293
Surface tension of water at T_1 , σ_1 [N/m]	$35.51 \cdot 10^{-3}$
Surface tension of water at T_2 , σ_2 [N/m]	$72.88 \cdot 10^{-3}$
Temperature derivative $d\sigma/dT$, [N/(m · K)]	$1.97 \cdot 10^{-4}$
Heat capacity of water, c_W [J/(kg · K)]	4200
Density of silicalite-2, ρ [m ³ /kg]	$1.76 \cdot 10^3$
Water contact angle, θ [°]	110
Specific porous volume of the silicalite-2, φ [m ³ /kg]	$0.18 \cdot 10^3$
Pore radius, r [m]	$2.7 \cdot 10^{-10}$
Heat capacity of silicalite, c_S [J/(kg · K)]	821
Total heat capacity of the HWB, c_V [J/(m ³ · K)]	$2.108 \cdot 10^6$

Table 3-2. Characteristics of the cycle on the basis of HWB "distilled water - silicalite-2."

Parameter	Value
Carnot cycle efficiency, η_C	0.393
Eroshenko cycle efficiency, η_E	0.169
Carnotisation level, η_C / η_E	0.43
Thermodynamic compactness, l_Q [J/(m ³ · K)]	$498 \cdot 10^3$

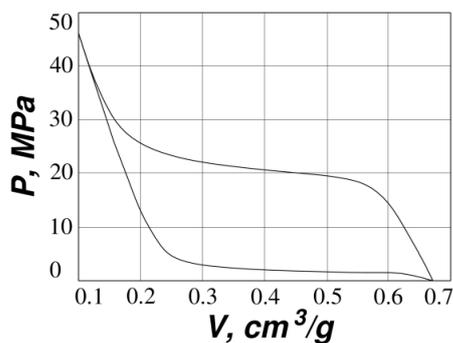


Figure 5. PV-isotherm of HWB "modified silica - distilled water," with a large hysteresis [12].

The theoretical approach implies further development of concepts about the nature of the surface tension of liquids and its dependence on temperature and chemical composition; behavior of the fluid in the lyophobic nanochannels; development of thermodynamic HWB models based on matrices with various pore size distributions [8,43]. The technological approach provides the improvement of existing technologies of HWB synthesis components as well as search and development of new technologies based on the latest achievements of science:

- Improvement of the technology of matrix synthesis and modification.

Presence of crystalline structure defects in the porous matrix, along with the imperfection of the coating application (irregularity, mosaic) on the walls of pores leads to deterioration of HWB parameters. Therefore, it is necessary to use more advanced techniques of synthesis of HWB matrices, their further thermal and (or) hydrothermal treatment, that leads to improvement of HWB operational characteristics [17,44].

- Obtaining of superhydrophobic coatings.

Recently a lot of articles devoted to the development of new superhydrophobic coatings with a contact angle of

150-170 degrees [45-47] have been published. Use of materials or coatings with a large contact angle leads, according to Eqns (15) and (16), to increasing of TC and thermal efficiency of the cycle. The main difficulty of chemical modification of the inner space of the HWB matrix is the small size of pores and channels (in the range of 0.5-50 nm).

- Obtaining coatings with controlled wettability.

There are some techniques to control the contact angle using the different control actions, such as, deformation, light, electric potential, temperature and pH-level [48-50].

The most promising, in our opinion, is an electrically-driven wetting. Using of coatings that can reversibly change its state from superhydrophilic to superhydrophobic under electric potential, like polipirol films [48], will allow to create an electrically-controlled HWB for different devices, which require the quick change in HWB behavior (for example, emergency braking devices).

- Synthesis of HWB with controllable properties based on polyelectrolyte solutions.

One of the most active trends involves use of different salt solutions to create new HWB that are sensitive to temperature. HWB based on electrolyte solutions have a number of features compared to HWB based on distilled water:

+*Anomalous temperature-sensitiveness.* Usually, for water-based HWB temperature increasing leads to decreasing of intrusion pressure, according to Eqns (1) and (2). At the same time, HWB based on salt solutions, shows anomalous temperature dependence: with temperature increase the intrusion pressure first grows ($dP/dT > 0$) and then falls ($dP/dT < 0$). The authors explain that it is due to ion-exchanged effect: when the temperature is rising the negatively charged ions in solution penetrate into pores and interact with positively charged groups on the channel walls (in fact these groups are defects of hydrophobic coating application). Its leads to increasing of hydrophobicity of matrix (contact angle θ). Moreover, $|\cos(\theta)|$ is growing faster, then σ falls up to a certain temperature level. It causes, according to the Eqn (1), an anomalous dependence $P_{int}(T)$ [23,24].

+*Dependence of HWB parameters (P_{int} and the value of hysteresis) on type and concentration of the salt.* For water-based HWB changing of P_{int} and value of hysteresis is realized by changing of porous matrix properties (pore radius and shape, type of hydrophobizing coating and thoroughness of its application). Usage of electrolyte solutions as a liquid phase allows to receive HWB with different values of P_{int} [25, 44, 51] and hysteresis [22] on the basis of the same porous matrix. It is more convenient, because in general case it is easier and faster to receive a new solution than a new matrix.

+*Increasing of HWB sensitivity to control actions.* ($T, \Delta U$). Apart from the anomalous temperature sensitivity described above, HWB based on electrolyte solutions are more sensitive to temperature change in comparison with water-based HWB. Moreover, anomalous temperature sensitivity may disappear for HWB based on salt solutions with cations and anions approximately of the same size, which can easily penetrate into the pores. At the same time, such a HWB has a more significant, compared to the "water" HWB, dependence of $P_{int}(T)$ ($dP/dT < 0$).

There is also more significant dependence of intrusion pressure from applied potential difference $P_{\text{int}}(U)$ [27, 52]. It is necessary to emphasize the reverse effect: the appearance of a potential difference at compression of HWB based on salt solutions [26]. Table 4 shows the composition and characteristics of different HWB, described by various research groups.

4. Conclusions

From the moment of first publications about the use of interface area as working body appeared, a lot of studies, related to theoretical and practical aspects of HWB, were realized: about the nature of the phenomena occurring inside the lyophobic pore space of matrix filled with liquid; about the influence of the characteristics of the liquid and porous matrix on the properties of HWB; about the technology of synthesis and possibilities of application.

While the earlier studies were concerned on fundamental, phenomenological and empirical aspects, recent ones have been focused on the practical use. A lot of models are patented; prototypes and pilot specimens are created and tested. It seems that in the nearest future we can expect the appearance of a number of thermo-mechanical transducers based on HWB to solve a wide range of tasks related to dissipation, energy conversion and storage. It should be noted that intensive works on creating a production piece of an automotive shock absorber based on HWB are conducted in France [12, 53], Ukraine [12, 54] and Japan [34-37].

The development of thermomolecular engine (with an external heat supply) may become an important step in overcoming the energy crisis, as it may provide fuel and structural materials savings, wider use of renewable sources of heat and as a consequence reduction of energetic and transport impact on the environment.

Acknowledgements:

The authors would like to thank Kateryna Dobrova, Ievgeniia Mykheieva and Derek K. Baker for their kind assistances in preparation of the English version of this article.

Nomenclature

c	mass heat capacity	$\text{J K}^{-1}\text{kg}^{-1}$
c_V	volumetric heat capacity	$\text{J K}^{-1}\text{m}^{-3}$
$d\sigma/dT$	temperature derivative	$\text{N m}^{-1}\text{K}^{-1}$
E	volumetric energy density	MJ m^{-3}
H	hysteresis	-
HWB	heterogeneous working body	
k	form factor of the pores	-
l	thermodynamic compactness	$\text{J m}^{-3}\text{K}^{-1}$
m	mass	kg
P	pressure	Pa
q	heat	J
r	pore radius	nm
R	universal gas constant	$\text{J K}^{-1}\text{mol}^{-1}$
T	temperature	K
TC	thermodynamic compactness	
V	volume	m^3
W	work	J
ΔU	difference of potentials	V
Ω	interface surface	m^3

σ	surface tension	N m^{-1}
γ	concentration	-
v	specific volume	kg m^{-1}
ε	compression ratio	-
η	cycle efficiency	-
θ	contact angle	deg
λ	pressure ratio	-
μ	molar mass	mol
π	the degree of expansion	-
ρ	density	kg m^{-3}
φ	specific porous volume	kg m^{-3}
χ	adiabatic index	-

Subscripts

CR	critical
m	mass
max	maximum
min	minimum
int	intrusion
ext	extrusion
V	volume
Ω	interface surface

References

- [1] J. P. Carroll, *US Patent No. 2009/0007562 (A1)*. Moorpark, CA, US, 2009. Retrieved from <http://www.freepatentsonline.com>.
- [2] R. A. Proeschel, *US Patent No. 7028476*. Thousand Oaks, CA, US, 2006. Retrieved from <http://www.freepatentsonline.com>.
- [3] H. Schoell, *US Patent No. 7080512*. Thousand Oaks, CA, US, 2006. Retrieved from <http://www.freepatentsonline.com>.
- [4] V. A. Eroshenko, Unusual Properties of One complex Thermodynamic System (in Russian). *C. R. Acad. Sci. Ukraine, Ser. A, 10, 77-80*, 1990.
- [5] V. A. Eroshenko, Thermomolecular energetics (in Russian). *Industrial Heat Engineering, 14, 22-25*, 1992.
- [6] E.W. Washburn, The Dynamics of Capillary Flow. *The Phys. Review, 17, 273-283*, 1922.
- [7] V. A. Eroshenko, Thermal engine (in Russian). *Soviet-Russian Patent No. 1,434,881*, 1985.
- [8] V.A. Eroshenko, T.L. Yarosh, Synthesis liquids with a high value of the temperature coefficient of surface tension - a promising way to energy and material storage. *Research Bulletin of the NTUU "KPI", 2, 37-50*, 2012.
- [9] T. Reis, P. Woog, *Introduction a la chimie-fisique des surfaces* (vol. 1). Paris, Dunod, 1952.
- [10] V.A. Eroshenko, Non-compressibilité et non-dilatabilité adiabatique d'un système thermodynamique complexe. *Entropie, 196, 17-23*, 1996.
- [11] V. A. Eroshenko, Rotary Eroshenko's thermal engine (in Russian). *Soviet-Russian Patent No. 1,452,262*, 1986.

Table 4. Characteristics of modern HWB.

№	The composition of HWB		HWB parameters							Reference
	Liquid	Matrix	P_{int} , MPa	P_{ext} , MPa	H , (%)	T , °C	ΔU , V	γ , %	r_{pore} , nm	
1		Silica gel KSK(mod. $C_8H_{17}Cl_3Si$)	21	1	95	298	0	0	n/a	[12]
2		Silica gel(mod. alkyl chains)	34	3	34	293	0	0	0.5-20	[36]*
3		Zeolite SSZ-24 (mod. TMAOH ^a)	58	55	5	env.	0	0	73	
4		Zeolite ZSM-22 (mod. 1-butylamine)	186	172	8	env.	0	0	46-57	
5		ZeoliteFerrierite (mod. piridine)	147	142	3	env.	0	0	35-48	[17]
6		Zeolite Silicalite-1 (mod. TPABr ^d)	96	91	5	env.	0	0	51-56	
7	Distilled water	Zeolite Silicalite-2 (mod. DMDEPOH ^e)	63	58	8	env.	0	0	53-54	
8		Silica MTS-1g (mod. n-octyl-dimethylchlorosilane)	59.5	47.8	20	323			1.3	
			59.5	30.8	48	298				
9		Silica MTS-2g ¹⁾	44.4	6.2	86	298	0	0	1.6	[55]
10		Silica MTS-3g ¹⁾	35	2.5	94	273			2	
11		Silica MTS-4g ¹⁾	14.4	- ²⁾	- ²⁾	273			5.4	
12		Silica gel SymmetryPrep C8 ²⁾	19	1	95	278	0	0	4.2	[56]
			17.3	3.1	82	333				
13			17	0	100				0 _v	
14	W.s. ethanol	Silica Fluka 100 C ₈ (mod. silane groups)	7	0	100		0		9.1 _v	7.8 ±
15			5	0	100	env.			16.7 _v	2.4
16			0 ³⁾	- ³⁾	-	268				
17	W.s. KCl	Zeolite CBV-901 HY (mod. SiCl ₄)	6	14	50	313	0	24 _m	&&&	[24]*
18			11	17	29	353			&&&	
19	W.s. sarcosil ⁴⁾		16	0	100	env.		0		
20	W.s. SCH ⁵⁾	Silica Fluka 100 C ₈ (see above)	4	0	100	env.	0	5	7.8 ±	[22]*
21			2	0	100	env.		5	2.4	
22			56	56	≈0	358		0		
23	W.s. NaCl	Zeolite ZSM-5 (no mod.)	82	82	≈0	295	0	0	0.53	[25]
24			112	112	≈0	295		26 _m		
25			9.3					-380		
26			9.5					-200		
27			10.7					-100		
28	W.s. KCl	Silica Davsil (mod. silyl groups)	11,1	n/a	-	env.		0	15	7.4
29			10.8					+100		[52]*
30			9.9					+200		
31			9.6					+300		
32			9.4					+420		
33			125			273				
34			145			283				
35			157			293				
36	W.s. CH ₃ COONa	Zeolite ZSM-5 (no mod.)	186	n/a	-	303	0	58 _m	0.56	[23]*
37			203			313				
38			180			323				
39			160			333				

Terms and abbreviations used in the table:

* The values obtained from PV-diagrams.

n / a - not available.

env. – Environment temperature. Exact value is not specified.

W.s. - Water solution.

Concentration:

24m. - Mass concentration (γ_m);

24v. - Bulk concentration (γ_v);

24 - type is not specified.

1) The method of modification - the same as for the MTS-1g.

2) The method of modification is not specified. Material is hydrophobized by the manufacturer.

3) At temperature of -5° C HWB has hydrophilic properties. Intrusion occurs spontaneously, extrusion doesn't occur.

4) Chemical formula of sarcosil - $CH_3(CH_2)_{10}CON(CH_3)CH_2COONa$.

5) Chemical formula of SCH - $CH_{39}NaO_5 \times H_2O$.

■ Control action that changes HWB properties.

[12] V. A. Eroshenko, A New Paradigm of Mechanical Energy Dissipation. Part 1-2: Theoretical Aspects and practical Solutions. *Journal Proceedings of Mechanical Engineers, Part D: Journal of Automobile Engineering*, 221, 285–312, 2007.

[13] V. A. Eroshenko, Limiting efficiency or maximum thermodynamic compactness of Heat Engines (in Russian). *USSR Academy of Science J., Energy and Transport*, 2, 125–133, 1987.

- [14] V. A. Eroshenko, Hydrocapillary engine with external heat supply (in Russian). *Soviet-Russian Patent No. 1,508,665*, 1987.
- [15] V. A. Eroshenko, *US Patent No. 6615959*. Colombes, FR, 2003. Retrieved from <http://www.freepatentsonline.com>.
- [16] V. A. Eroshenko and V. I. Aistov, Heat Engine Cycles Optimization According to Thermodynamic Compactness (in Russian). *Industrial Heat Engineering*, 12, 60–64, 1990.
- [17] L. Tzanis, M. Trzpit, M. Soulard & J. Patarin., Energetic performances of channel and cage-type zeolites. *J. Phys. Chem. C*, 116, 20389–20395, 2012.
- [18] M.A. Saada, M. Soulard, B. Marler, G. Gies J. Patarin, High-pressure water intrusion investigation of pure silica RUB-41 and S-SOD Zeolite Materials. *J. Phys. Chem.*, 115, 425-430, 2011.
- [19] A. Laouir, L. Luo, D. Tondeur, Thermal machines based on surface energy of wetting: Thermodynamic analysis. *AIChE Journal*, 49, 764–781, 2003.
- [20] E.J. Jadczyk, C. Magret, P. Ollivier, F. Quenardel, *US Patent No 2013/022448 (A1)*. SNECMA, Paris, FR, 2013. Retrieved from <http://www.freepatentsonline.com>.
- [21] A. Laouir, D. Tondeur, Thermodynamic Aspects of Capillary Flows., *African Physical Review*, 1, 24-25, 2007.
- [22] A. Han, Y. Qiao, Pressure-induced infiltration of aqueous solutions of multiple promoters in a nanoporous silica. *J. Am. Chem. Soc.*, 128, 10348-10349, 2006.
- [23] A. Han, Y. Qiao, Thermal effects on infiltration of a solubility-sensitive volume-memory liquid. *Philosophical Magazine Letters.*, 87, 25-31, 2007.
- [24] A. Han, Y. Qiao, A volume-memory liquid. *Applied Physics Letters*, 91, 173123-1 - 173123-3, 2007.
- [25] A. Han, Y. Qiao, Infiltration pressure of a nanoporous liquid spring modified by an electrolyte. *J. Mater. Res.*, 22, 644-648, 2007.
- [26] Y. Qiao, *US Patent No. 2009/0243428 (A1)*. San Diego, CA, US, 2009. Retrieved from <http://www.freepatentsonline.com>.
- [27] Y. Qiao, Z. Kong, *US Patent No. 2010/0225199 (A1)*. Akron, OH, US, 2010. Retrieved from <http://www.freepatentsonline.com>.
- [28] A. Galatsis, *US Patent No. 2006/0246288 (A1)*. Lexington, MA, US, 2006. Retrieved from <http://www.freepatentsonline.com>.
- [29] L. Liu, *Nanofluidics: Fundamentals and Applications in Energy Conversion*. (Dissertation, submitted in partial fulfillment of the requirements for the degree of PhD), Columbia University, USA, 2010. Retrieved from <http://academiccommons.columbia.edu/>.
- [30] V.S. Egorov, A. Portyanoy, A.P. Sorokin, V.G. Malcev & R. M. Voznesenskiy. *RU Patent No. 2138086 (CI)*. Obninsk, Russian Federation, 1999. Abstract retrieved from <http://ru-patent.info>.
- [31] A.G. Portyanoy, E.N. Serdun, A.P. Sorokin & V.G. Malcev, *RU Patent No. 2187742 (CI)*. Obninsk, Russian Federation, 2002. Abstract retrieved from <http://ru-patent.info>.
- [32] G.A. Portyanoy, G.A. Sorokin, *RU Patent No. 2084750 (CI)*. Obninsk, Russian Federation, 1997. Abstract retrieved from <http://ru-patent.info>.
- [33] V.N. Bogomolov, Capillary effects in ultra-thin channels. *J. of Technical Physics*, 62, 152-157, 1992.
- [34] T. Iwatsubo, C. V. Suci, M. Ikenagao & K. Yaguchio, Dynamic characteristics of a new damping element based on surface extension principle in nanopore. *Journal of Sound and Vibration*, 308, 579-590, 2007.
- [35] C.V. Suci, T. Iwatsubo, S. Deki, Investigation of a colloidal damper. *J. Colloid and Interface Sci.*, 259, 62-80, 2003.
- [36] C.V. Suci, K. Yaguchi, Endurance tests on a colloidal damper destined to vehicle suspension. *Exp. Mech.*, 49(3), 383-393, 2009.
- [37] T. Aramizu, *US Patent No. 2010/0072010(A1)*. Kanagawa, JP, 2010. Retrieved from <http://www.freepatentsonline.com>.
- [38] W.J. Song et al., Experimental Study on Mechanical Damping System Using Colloid Suspension, *Key Engineering Materials*, 274-276, 775-780, 2004.
- [39] T.W. Ku et al., Numerical and experimental approach on energy dissipation in nano colloidal damper. *Journal of Mechanical Science and Technology*, 21, 2007.1464-1470, 2007.
- [40] H. Liu and G. Cao, Interaction between Mechanical Wave and Nanoporous Energy Absorption System. *J. Phys. Chem. C*, 117, 4245–4252, 2013.
- [41] N. Gokulakrishnan et al., Intrusion/Extrusion of Water Into Organic Grafted SBA-15 Silica Materials for Energy Storage. *Journal of Nanoscience and Nanotechnology*, 13, 2847-2852, 2013.
- [42] *ISO 2944:1974*. Fluid power systems and components – Nominal pressures, 2000. Retrieved from <http://www.iso.org>.
- [43] V.A. Eroshenko, Y.G. Grosu, Properties of heterogeneous lyophobic systems based on non-uniporous matrices. *Industrial Heat Engineering*, 33, 73-79, 2011.
- [44] Y. Qiao, *Understanding energy adsorption behaviors of nanoporous materials: Final report*. (Accession No. ADA513572), University of California, San Diego, La Jolla, US, 2008. Retrieved from <http://www.science.gov>.
- [45] C.H. Xue, Sh.T. Jia, J. Zhang & J.J. Ma, Large-area fabrication of superhydrophobic surfaces for practical applications: an overview. *Sci. Technol. Adv. Mater.*, 11, 1-15, 2010.
- [46] M. Ma, Y. Mao, M. Gupta, K.K. Gleason & G.C. Rutledge, Superhydrophobic fabrics produced by electrospinning and chemical vapor deposition. *Macromolecules*, 38, 9742–9748, 2005.
- [47] E. Martines, K. Seunarine, H. Morgan, N. Gadegaard, C.D. Wilkinson & M.O. Riehle, Superhydrophobicity and

- superhydrophilicity of regular nanopatterns. *Nano Letters*, 5, 2097-2103, 2005.
- [48] L. Xu, W. Chen, A. Mulchandani & Y. Yan. Reversible conversion of conducting polymer films from superhydrophobic to superhydrophilic. *Angew. Chem. Int. Ed.*, 44, 6009-6012, 2005.
- [49] L. Xu, Z. Chen, A. Mulchandani & Y. Yan, Electrochemical synthesis of perfluorinated ion doped conducting polyaniline films consisting of helical fibers and their reversible switching between superhydrophobicity and superhydrophilicity. *Macromol. Rapid Commun.*, 29, 832-838, 2008.
- [50] F. Xia, L. Feng, S. Wang, T. Sun, W. Song, W. Jiang, & L. Jiang, Dual-responsive surfaces that switch between superhydrophilicity and superhydrophobicity. *Adv. Mater.*, 18, 432-436, 2006.
- [51] X. Kong, F.B. Surani, Y. Qiao, Effects of addition of ethanol on the infiltration pressure of a mesoporous silica. *J. Mater. Res.*, 20, 1042-1045, 2005.
- [52] W. Lu, T. Kim, A. Han, X. Chen & Y. Qiao, Electrowetting effect in a nanoporous silica. *Langmuir*, 25, 9463-9466, 2009.
- [53] V. A. Eroshenko, *European Patent No. 1250539 B1*. Paris, FR, 2002. Retrieved from <http://www.freepatentsonline.com>.
- [54] V. A. Eroshenko, Yu. F. Lazarev, Rheology and dynamics of repulsive clathrates. *J. Applied Mechanics Technical Physics*, 53, 114-131, 2012.
- [55] B. Lefevre, A. Saugey, J.L. Barrat, L. Bocquet, E. Charlaix, P. F. Gobin & G. Vigier, Intrusion and extrusion of water in hydrophobic mesopores. *J. Chem. Phys.* 120, 4927-4938, 2004.
- [56] L. Coiffard, V. Eroshenko, Temperature effect on water intrusion/expulsion on grafted silica gels. *J. Colloid Interface Sci.* 300, 304-309, 2006.