

Article



Adsorption Transformation of Heat: The Applicability in Various Climatic Zones of the Russian Federation

Alexandra Grekova^{1,2,*}, Larisa Gordeeva^{1,2}, Alessio Sapienza³ and Yuri Aristov^{1,2}

- ¹ Boreskov Institute of Catalysis, Ac. Lavrentiev av. 5, Novosibirsk 630090, Russia; gordeeva@catalysis.ru (L.G.); aristov@catalysis.ru (Y.A.)
- ² Faculty of Natural Science, Novosibirsk State University, Pirogova str. 2, Novosibirsk 630090, Russia
- ³ Institute for Advanced Energy Technologies "Nicola Giordano", Via Salita S. Lucia sopra Contesse 5, 98126 Messina, Italy; alessio.sapienza@itae.cnr.it
- * Correspondence: grekova@catalysis.ru; Tel.: +7-(383)-326-9454

Received: 8 November 2018; Accepted: 24 December 2018; Published: 3 January 2019



Abstract: Adsorption heat transformation (AHT) is energy and environment saving technology that allows the effective utilization of renewable and waste heat with low-temperature potential. For the enhancement of AHT efficiency, properties of the working pair "adsorbent–adsorbate" have to be intelligently adapted to the operating conditions of the specific AHT cycle. In this work, the applicability of ATH technology in the Russian Federation (RF) was analyzed. For various geographic zones of the RF, the proper AHT application (cooling, heating, heat amplification, or storage) was selected depending on the zone climatic conditions. Data on the adsorption equilibrium for more than 40 "adsorbent–adsorbate" pairs collected from the literature were analyzed to select the most suitable pairs for the particular application/zone. Recommendations on AHT applications and the proper working pairs for the considered RF climatic zones are made.

Keywords: adsorption heat transformation; working pairs; water; methanol; adsorption potential

1. Introduction

Because of the danger posed by the ever-worsening environmental situation on the planet (global warming, depletion of fossil fuels, etc.), initiatives need to be taken to alleviate the current ambiance. The key to solving this problem is to work out the following scientific and technical goals: (1) the decrease in energy consumption through energy efficiency measures including reducing the share of waste heat (thermal waste from industry, transport, etc.) dissipated to the environment; and (2) the use of alternative energy sources (solar energy, geothermal, waste heat, etc.). These thermal energy sources are characterized by a significantly lower temperature potential than that achieved by burning fossil fuels, which opens up broad prospects for the use of adsorption heat transformation (AHT) systems [1]. AHT is an environmentally friendly technology, which allows the utilization of waste or renewable heat and reduction in the consumption of fossil fuels. Contrary to conventional compression heat pumps and chillers, AHT is characterized by low consumption of electricity, production of which is currently dominated by coal and is expected to remain so. Consequently, the broader dissemination of AHT technology will promote the reduction of indirect emissions of greenhouse gases [2,3]. Moreover, this technology is non-freon because benign liquids, such as water and alcohols, are used as working fluids. Significant progress has been achieved in AHT over the past decades [4,5].

AHT is based on reversible exothermal adsorption and endothermal desorption processes and can be used for various applications, namely cooling, heating, heat storage and amplification, and their combinations. It is well known that the adsorbent that is optimal for AHT must exchange a large

amount of adsorbate under the conditions of the cycle under consideration [6]. A high affinity of the adsorbent to the adsorbate is favorable for obtaining a high adsorption capacity. However, such a strong interaction leads to high desorption temperatures (>200–300 °C), as in the case of zeolites. On the other hand, the low affinity of the adsorbent to the adsorbate favors desorption, but it cannot efficiently convert heat during the sorption phase. Temperature lift in this case will be low. Thus, the optimal adsorbent should provide a moderate affinity for the sorbate, which depends on the boundary conditions of the cycle. In other words, the efficiency of the specific AHT cycle depends mainly on the agreement between the operating conditions of an AHT cycle are determined by the boundary temperatures of evaporator, condenser, and external heat source. They, in turn, depend on the climatic conditions of the region in which the AHT cycle is realized, the application (cooling, heating, heat storage, or amplification), and heat source used for the adsorbent regeneration. Therefore, for effective AHT cycle realization, a working pair "adsorbent–adsorbate" should be intelligently selected in accordance with the mentioned boundary conditions of the cycle [6].

There is a fairly large amount of research summarizing data on the adsorption equilibrium of existing working pairs for AHT [7–11]. Taking into account the importance of harmonization between the operating conditions of the AHT cycle and the properties of the employed working pair, the performance of an AHT cycle is usually evaluated considering the specific climatic conditions of the region where it is realized [12–14]. For example, the authors of [15] investigated adsorption cooling for storage of vaccines in the Sahara climate. The work [16] considered the organization of the cycle of sorption cooling in Tokyo's climatic conditions. The authors of [17] discussed sorption cooling and the production of warm water in the conditions of the city Dhaka. Thus, detailed analysis of the applicability of various working pairs for specific AHT applications and climatic conditions will promote the advancement of this energy and environment saving technology.

As the Russian Federation (RF) is one of the top CO_2 emitters, such an analysis performed for the RF is of primary importance. In this work, for the first time, the feasibility analysis of AHT technology under the climatic conditions of the RF is carried out. First, the climatic conditions of selected RF regions are analyzed and the proper AHT applications are defined for each zone. Then, specific requirements to properties of the adsorbent optimal for the selected zones and applications are considered in terms of the Polanyi–Dubinin adsorption potential, corresponding to the adsorption and desorption stages of the analyzed cycle. Finally, the most promising working pairs are selected for the specific application/zone. This selection is based on an analysis of literature data on the adsorption equilibrium of numerous common and innovative adsorbents with water and methanol vapors. These adsorbates are considered as working fluids because of their promise for AHT [6]. Water can be utilized for AHT applications at above-zero temperature, e.g., air conditioning and warm water production in the summer time. For seasonal heat storage and amplification of temperature potential, methanol should be used because of its low freezing temperature and high operating vapor pressure.

2. Methodology of the Analysis

A common AHT cycle consists of two isobars and two isosteres in the Clausius-Clapeyron coordinates $\ln(P)$ vs. (-1/T) (Figure 1a). The temperatures of evaporator *T*ev, condenser *T*con, adsorption *T*ads, and regeneration *T*reg completely define this four temperature (4T) cycle. The efficiency of the adsorbent use in a particular AHT cycle is higher if the amount of adsorbate exchanged under the conditions of the cycle is larger [6]. To estimate the mass of adsorbate that the adsorbent will exchange in a specific cycle the following route is suggested: (1) measurement of adsorption isobar at the pressure *P*ev, and determination of the equilibrium adsorbate uptake *w*max at the temperature *T*ads, (2) measurement of the isobar at the pressure *P*con and determination of the equilibrium adsorbate uptake *w*min at the temperature *T*des as well as the amount of exchanged adsorbed $\Delta w = w \max - w \min$. This difference has to be maximized.

Such measurements are time and labor consuming. On the other hand, for the same working pairs, the adsorption equilibrium data has already been reported in the literature, however, they were measured at temperatures and pressures different from those in the cycle studied. In this case, the equilibrium uptakes can be evaluated from the universal adsorption curve "the adsorption capacity w—the adsorption potential ΔF " plotted on the basis of the already available experimental data. The Polanyi adsorption potential $\Delta F = -RT \ln[P/P_o(T)]$, where P_o is the saturated vapor pressure at temperature T, was introduced in 1914, considering the adsorption process similar to the compression of adsorbate vapor in a certain field of adsorption forces near the adsorbent surface [18]. Later, it was shown that the adsorption potential ΔF can be used as a universal measure of the adsorbent affinity to the adsorptive [19]. It was found in [20] that for many adsorbents, both micro- and mesoporous, there is a one-to-one correspondence between the equilibrium uptake w and the ΔF -value $w = f(\Delta F)$ (Figure 1b).





Figure 1. The *P*-*T* diagram of four temperature (4T) absorption heat transformation (AHT) cycle (**a**), and the universal adsorption curve plotted from experimental isobars of methanol sorption on the composite sorbent LiBr/MWCNT [21] measured at different pressures $P_1 = 72.8$ (•), $P_2 = 127.5$ (•), $P_3 = 217.6$ (•) mbar (**b**).

The weak adsorption isostere (line 3–4 on Figure 1a) corresponds to the adsorption potential ΔF_1 at the end of desorption stage (point 3) and to the minimal uptake $wmin = w (\Delta F_1)$. The rich isostere (line 1–2) corresponds to the end of adsorption stage (point 1) and to the maximal uptake $wmax = w (\Delta F_2)$, where

$$\Delta F_1 = -RT \operatorname{regln}[P(T \operatorname{con})/P(T \operatorname{reg})], \tag{1}$$

$$\Delta F_2 = -RTadsln[P(Tev)/P(Tads)].$$
(2)

Therefore, the requirements for the adsorbent optimal for the specific AHT cycle can be formulated in terms of the boundary adsorption potentials ΔF_1 and ΔF_2 : the adsorbent should exchange as much adsorbate as possible in the ΔF -interval between ΔF_1 and ΔF_2 . The boundary potentials are defined by the operating temperature *Treg*, *T*con, *T*ads, and *Tev*. These temperatures, in turn, depend on the climate of the place where the AHT unit is used, regeneration temperature, and temperature of the required useful heat/cold.

In adsorption technologies, both traditional (activated carbons, zeolites, silica gels) and innovative materials (aluminophosphates, metal organic frameworks, composites "salt in a porous matrix"—CSPM) are used as sorbents. Pure (AIPO) and substituted aluminophosphates (MeAPO) are zeolite-like microporous structures [22,23]. These systems are characterized by moderate hydrophilicity due to the electrically neutral network [24]. Metal organic frameworks (MOFs) are porous crystalline solids characterized by extra-large surface area and porosity due to the structure

formed by metal-oxygen units bonded through organic linkers [25]. Composite sorbents consist of a porous matrix impregnated with an inorganic salt. These sorbents are characterized by high sorption capacity of water and alcohols up to 1 g/g and low regeneration temperature [26]. The equilibrium data on water and methanol adsorption on more than 40 common and innovative "adsorbent–adsorbate" pairs are collected from the literature. Among the analyzed adsorbents are silica gels [27–29], zeolites [27], carbons [30,31], AlPOs [32], SAPOs [32,33], MOFs [34–37], and composites "salt inside porous matrix" (CSPMs) [21,38–41]. Working pairs which are the most promising for each RF climatic zone are selected according to the criteria formulated above.

3. Results and Discussion

3.1. Analysis of the AHT Cycles Demanded in the RF and Appropriate Working Pairs

Seven settlements from different climatic zones of the RF are chosen for further detailed analysis (Figure 2), namely, Astrakhan (I zone), Moscow (II zone, western part of the RF), Vladivostok (II zone, eastern part of the RF), Omsk (III zone), Arkhangelsk (IV zone, northern part of the RF), Yakutsk (IV zone, eastern part of the RF), and Oymyakon (special zone). Using the METEONORM database [42], the following climatic indices are collected for each month of the year and for each settlement selected, namely, the average day and night temperatures as well as the average monthly temperature (Figure 3). These data are used for further analysis of the relevant AHT applications for each climatic zone. The climate in the RF is quite cold, therefore, the most demanded AHT applications are heating, seasonal heat storage, and amplification of the ambient heat [38,43]. The heating applications can be realized during winter time only if a free heat source with a temperature of 2–20 °C is available to drive the evaporation process, which can be underground water, waste heat, non-freezing natural water basins, etc. Another opportunity is the use of highly effective solar collectors, which can provide heat at 10–20 °C even under cold climatic conditions.



Figure 2. Climatic zones of the Russian Federation (RF) [44] selected for the present analysis.



Figure 3. Average day (a) and night (b) temperatures for the climatic RF regions selected.

w, g/g

0,1 0,0

5

∆F. kJ/mol

3.2. Refrigeration/Air Conditioning

Since the average daily temperature in the summer time for the analyzed regions (except Astrakhan) does not exceed 25 °C, the air conditioning application is demanded only for zone I, located in the South of Russia. For all other regions, adsorption refrigeration is considered for food/drugs storage. The boundary adsorption potentials ΔF_1 and ΔF_2 are calculated (Table 1) according to Equations (1) and (2). For each location, the condenser/adsorber temperature, $T \operatorname{con} = T \operatorname{ads}$, is assumed to be equal to the maximum day temperature $T \operatorname{d.max}$ of the hottest month of a year (July). The useful effect is produced in the evaporator, and the evaporator temperature Tev equals the temperature $T \operatorname{uh}$ of the required cold, namely, 3 °C for refrigeration and 10 °C for air-conditioning. The operating conditions of the refrigeration cycle are presented in Figure 4 as the colored areas confined between the boundary potentials ΔF_1 and ΔF_2 for the climatic zones analyzed with water as refrigerant.

	City	Treg °C	ΔF, kJ/mol		Adsorbont	$\Delta w. g/g$		
	City	1106, C	ΔF_2	ΔF_1	Ausorbent	<i>Lw, 6</i> 6		
		Air conditioning					—	
	Astrakhan	85	4.0	6.9	LiCl/MWCNT	0.6	_	
			Refrig	eration			_	
	Astrakhan	85	5.2	6.9	LiCl/vermiculite LiCl/MWCNT	0.3 0.4	_	
	Omsk	75	4.8	5.9	LiCl/vermiculite ALPO—18	0.5 0.2		
	Yakutsk	65	4.5	4.8	CAU10	0.2		
	Moscow	65	4.2	5.0	CAU10	0.3		
	Oimyakon	65	4.2	4.8	CAU10	0.3		
	Vladivostok	60	3.9	4.7	MIL125NH2	0.3		
	Arkhangelsk	60	3.8	5.1	MIL125NH2	0.3	_	
0,9 0,8 0,7 0,6 0,5 0,4 0,3 0,2	Oimyakon Yakutsk Astrakhan	LiCl/ver LiCl/MV ALPO1 CAU10 MIL125	vcnt 8 NH2	0,9 0,8 0,7 0,6 0,5 ≤ 0,4 0,3 0,2	Moscow		iCl/ver iCl/MWCNT LPO18 :AU10 iIL125NH2	b)

Table 1. The boundary conditions of cooling cycles analyzed and the amount of water exchanged under the discussed conditions for the adsorbents optimal for each zone.

Figure 4. The operating ranges of the adsorption potential (colored areas) which correspond to the refrigeration cycle ($Tev = 3 \ ^{\circ}C$, Tcon = Tads = Td.max) for the climatic zones analyzed and the universal curves of water adsorption on the adsorbents, optimal for each zone (Table 1). The refrigerant is water vapor.

0,0

5

∆F. kJ/mol

The most promising adsorbents for the refrigeration cycle are LiCl/MWCNT, LiCl/vermiculite, and MIL-125-NH₂ for Astrakhan, Omsk, and Archangelsk regions, respectively (Table 1, Figure 4). The sorbent CAU10 is the best for Moscow and Yakutsk.

3.3. Heating

We consider the adsorptive heating cycle for the domestic production of warm water with the temperature $Tuh = 45 \,^{\circ}C$ suitable for dishwashing, cooking, and showering during the warm season (May–September). This is relevant for countryside summer houses, which are very popular in Russia. At heating mode, *T*ev equals the daily temperature *T*d.av averaged over each month. The useful heat is produced in a condenser during regeneration and in an adsorber during adsorption stage. The condenser and adsorption temperatures equal the temperature of the useful heat required to the consumer (*T*con = *T*ads = *T*uh). The boundary adsorption potentials ΔF_1 and ΔF_2 are calculated for water as the working fluid by Equations (1) and (2) for Treg varying from 75 to 90 °C (Table 2). Composites—LiCl/Verm and LiCl/MWCNT, MOFs—MIL-125-NH₂ and CAU-10, and FAM-Z01 appear to be the most promising for the heating mode, with the amount of cycled water Δw varying from 0.1 to 0.9 g/g for different locations and months (Table 2). For Vladivostok, water heating up to the temperature Tuh = 45 °C is realistic from May to October, but for other zones, only during the summer months (Table 2). The minimum regeneration temperature Treg depends on the conditions during adsorption stage and the ΔF_2 -value. For example, in Oimyakon (zone IV), with low ambient temperature (*Tev*), an adsorbent with quite strong affinity is required ($\Delta F_2 = 4.2-4.8 \text{ kJ/mol}$ (Table 2)) to get useful heat at Tuh = 45 °C. A temperature of 75 °C is not enough to drive the cycle, even in summer (Figure 5), because the calculated potential during the adsorption stage is higher than the potential during desorption stage ($\Delta F_2 > \Delta F_1$). This means that regeneration of any studied adsorbent under such conditions is impossible.

City	Treg, °C	ΔF_2 , kJ/mol	ΔF_1 , kJ/mol	Δw , g/g		Period
	90	2.5–3.8	6.2	LiCl/Ver	0.6–0.9	May-Sept
				LiCl/MWCNT	0.3–0.5	
Astrakhan	85		4.8	MIL125NH2	0.3–0.4	
-	75	2.5–2.9	4.1	FAMZ01	0.2	Jun–Aug
				LiCl/Ver	0.1–0.3	
	90	3.7–5.0	6.2	LiCl/Ver	0.5–0.6	May-Sept
Moscow	80	3.7-4.0	4.8	CAU10	0.3	- Jun-Aug
				MIL125NH2	0.2–0.4	
Vladivostok	90	3.5–5.4	6.2	LiCl/Ver	0.4–0.6	May-Oct
Omsk	90	3.4–5.0	6.2	LiCl/Ver	0.4–0.6	May–Sept
Chisk	80	3.4–4.0	4.8	MIL125NH2	0.2–0.4	Jun–Aug
Arkhangelsk	90	4.1–4.7	6.2	LiCl/Ver	0.4–0.6	Jun–Aug
	90	- 3.5-4.1	6.2	LiCl/Ver	0.6	
Yakutsk	80		4.8	CAU10	0.3	Jun–Aug
	00			MIL125NH2	0.2–0.4	
Oimyakon	90	4.2–4.8	6.2	LiCl/Ver	0.5–0.6	Jun–Aug

Table 2. The boundary conditions of the heating cycles, the promising adsorbents, and the amount of exchanged water.



Figure 5. Boundary conditions for the adsorptive heating cycles (Tcon = Tads = Tuh = 45 °C) considered and the universal curves of water adsorption on the adsorbents, promising for Oimyakon (Table 2). Vertical lines—boundary potentials of the cycle (black—sorption stage, blue—desorption stage). 1—LiCl/vermiculite, 2—LiCl/ MWCNT, 3—CAU10, 4—Ca(NO₃)₂/silica, 5—ALPO18, 6—MIL125NH2.

3.4. Heat Storage

We consider seasonal heat storage when the heat absorbed in summer is used for heating during the cold period. For the RF, providing heating throughout the whole winter using only heat stored in the summer seems not to be realistic due to the cold climate and huge demand for heating. However, the heat storage cycle can be utilized for heating detached or semi-detached houses during a moderately cold autumn and spring, which could lead to the reduction of fossil fuel consumption. At the heat release stage during autumn and spring time, the evaporator is at the ambient temperature, and *Tev* equals the average night temperature *T*n.av. The condenser is at the ambient temperature in summer, when the heat is stored, and *T*con is the average day temperature *T*d.av during July. The useful heat is produced in an adsorber during the adsorption stage, and the adsorption temperature *T*ads equals the temperature of useful heat *T*uh supplied to a consumer. We consider *T*uh = 35 °C, which can be used for floor heating systems. The regeneration temperature is fixed at 90 °C. The adsorption potentials ΔF_1 and ΔF_2 are calculated using Equations (1) and (2) with methanol as the working fluid and presented in Table 3. For each location, the optimal adsorbent is proposed based on the amount of methanol cycled (Table 3, Figure 6).

Table 3. The boundary adsorption potentials, the promising adsorbents, and the specific mass of methanol exchanged for the tested heat storage cycle (Treg = 90 $^{\circ}$ C).

City	ΔF_2 , kJ/mol	ΔF_1 , kJ/mol	Adsorbent	Δw , g/g	Heating Period
Astrakhan	3.8	8.0	LiCl/MWCNT	0.9	Apr, May, Sept, Oct
Moscow	4.3	9.1	LiCl/SiO ₂	0.6	Apr, May, Sept, Oct
Vladivostok	4.6	9.0	UiO67	0.4	Apr, May, Sept, Oct
Omsk	4.9	8.9	MaxSorbIII	0.3	Apr, May, Sept, Oct
Oimyakon	5.1	9.7	LiBr/SiO ₂	0.4	May, Sept
Oimyakon	8.1	9.7	LiBr/SiO ₂	0.1	Apr, Oct
Arkhangelsk	5.3	9.6	LiBr/SiO ₂	0.3	Apr, May, Sept, Oct
Yakutsk	6.6	8.9	LiBr/SiO ₂ , MaxSorbIII	0.1	Apr, May, Sept, Oct



Figure 6. Boundary conditions (vertical lines) for the adsorption heat storage cycles (*T*ev = *T*n.av, *T*con = *T*d.av, *T*uh = 35 °C, *T*reg = 90 °C) tested and the universal adsorption curves for: 1—LiBr/SiO₂, 2—MaxSorbIII, 3—UiO67, 4—LiCl/SiO₂, 5—LiCl/MWCNT. The refrigerant is methanol.

If groundwater or domestic waste water at $10 \,^{\circ}$ C can be used as the heat source for evaporation during the cold period, the heat can be produced during winter as well, and the best material for all locations is the LiCl/MWCNT composite.

3.5. Heat Amplification Cycle "Heat from Cold" (HeCol)

In the heat amplification cycle "Heat from Cold" (HeCol), recently suggested for upgrading the temperature of the environment heat in cold countries [43], two natural heat reservoirs, namely, the ambient air at low temperature $T_{\rm L}$ and non-freezing water basins (or underground water) at middle temperature $T_{\rm M}$, are used as the heat sink and heat source, respectively, to get a useful heat at higher temperature $T_{\rm H}$ suitable for heating (Figure 7) [43].



Figure 7. P-T diagram of the isothermal "Heat from Cold" (HeCol) cycle [43].

The initial adsorbent state (point 1 in Figure 7) corresponds to the temperature T_M and the pressure of the adsorbate vapor $P_L = P_0(T_L)$, where $P_0(T_L)$ is the adsorbate saturation pressure at temperature T_L . Under these conditions, the equilibrium adsorbate content $wmin = w(T_M, P_L)$ is low due to the low adsorbate pressure P_L . Then, the adsorbent is heated up to temperature T_H (stage 1–2) at constant uptake wmin. At point 2, the adsorber is connected to an evaporator maintained at T_M which generates the constant pressure $P_M = P_0(T_M)$ of adsorbate. This pressure jump causes the vapor adsorption that leads to an increase in the equilibrium uptake to $wmax = w(T_H, P_M)$ (point 3 in Figure 7).

The evaporation heat Qev is absorbed in the evaporator at T_M and the useful adsorption heat Qads is released at constant temperature T_H (isotherm 2–3) in the adsorber and supplied to the heating circuit of a consumer. Then, the adsorber is disconnected from the evaporator and cooled down to temperature T_M (isostere 3–4) at constant uptake *w*max. At point 4, the adsorber is connected to the condenser maintained at temperature T_L and pressure P_L . The pressure drop results in the adsorbate desorption to restore the initial uptake *w*min = $w(T_M, P_L)$ (point 1). The heat Qdes needed for adsobate desorption is supplied to the adsorbent from the water basin at temperature T_M (isotherm 4–1). The desorbed vapor is collected in the condenser releasing the heat Qcon to the ambient, and the cycle is closed. The work is required to pump the liquid adsorbate from the low pressure level in the condenser to the high pressure level in the evaporator. This work is small as compared to the latent heat in the cycle [45].

This process can be realized in regions with a cold climate, where the difference $(T_{\rm M} - T_{\rm L}) = 30-50$ °C. Therefore, the analysis is carried out for Yakutsk (IV climatic zone) and Oimyakon (Special zone, Figure 1). We assume that $T_{\rm L}$ equals the average temperature *T*av during winter months. For Yakutsk $T_{\rm L} = T$ av varies from -28.9 °C (November) to -40.7 °C (January); for Oimyakon from -32.3 °C (March) to -47.1 °C (January). The reservoir at $T_{\rm M} = 3$ °C (non-freezing water under ice) or 10 °C (ground water) is used as a heat source for evaporation and desorption, and $T_{\rm H}$ of useful heat varies from 30 to 50 °C (Table 4). The boundary adsorption potentials ΔF_1 and ΔF_2 (Table 4, Figure 8) are determined as

$$\Delta F_2 = -RT_H \ln[P(T_M)/P(T_H)], \qquad (3)$$

$$\Delta F_1 = -RT_M \ln[P(T_L)/P(T_M)]. \tag{4}$$

<i>T</i> _M , °C	$T_{\rm H}, {}^{\circ}{\rm C}$	ΔF_2 , kJ/mol	ΔF_1 , kJ/mol	Adsorbent	Δw , g/g	Period		
Yakutsk								
3	30	3.8	5.0-7.2	LiCl/MWCNT	0.97	Nov–Feb		
	35	4.5	5.0-7.2	LiCl/SiO ₂	0.38	Nov–Feb		
	40	5.1	6.4–7.2	MaxSorbIII	0.14	Dec–Feb		
10	30	2.7	4.8-8.4	LiCl/MWCNT	1.37	Nov-March		
	40	4.0	4.8-8.4	LiCl/MWCNT, LiCl/SiO ₂	0.67 0.70	Nov–March		
	50	5.4	7.4-8.4	MaxSorbIII	0.19	Dec–Feb		
Oimyakon								
	30	3.8	6.7–9.0	LiCl/MWCNT	0.97	Nov-March		
3	35	4.5	6.7–9.0	LiCl/SiO ₂	0.38	Nov-March		
	40	5.1	8.4–9.0	MaxSorbIII	0.14	Dec–Feb		
	30	2.7	7.9–10.2	LiCl/MWCNT	1.37	Nov-March		
10	40	4.0	7.9–10.2	LiCl/MWCNT, LiCl/SiO ₂	0.67 0.70	Nov–March		
	50	5.4	9.6–10.2	LiBr/SiO ₂	0.26	Dec–Feb		

Table 4. The boundary conditions, the promising adsorbents, and the mass of exchanged methanol for the HeCol cycle tested.



Figure 8. The boundary conditions of the HeCol cycle for Yakutsk and the universal adsorption curves for: 1—LiCl/MWCNT, 2—MaxSorbIII, 3—LiBr/SiO₂, 4—LiCl/SiO₂. The refrigerant is methanol.

For cycles with the useful heat temperature $T_{\rm H} = 30$ °C, the composite sorbent LiCl/MWCNT appears to be the most promising. LiCl/SiO₂ and MaxSorbIII allow the useful heat at $T_{\rm H} = 35$ °C to be produced. While the LiBr/SiO₂ composite with the highest affinity to methanol vapor can be employed for HeCol cycles with the highest useful heat temperature $T_{\rm H} = 50$ °C (Table 4).

4. Conclusions

The paper addresses the preliminary feasibility analysis of AHT technology under the climatic conditions of the RF. For each of the seven RF climatic zones selected for the analysis, the most demanded AHT applications, among cooling, heating, heat storage, or amplification, are identified by the analysis of the climatic conditions. For a wide range of conventional and innovative adsorbents (activated carbons, silica gels, MeAPOs, MOFs, composites "salt in porous matrix", etc.), the literature data on their adsorption equilibrium with water and methanol vapors are collected and analyzed. Based on these data, the promising working pairs for the demanded applications for each climatic RF zone are selected. Thus, the analysis carried out demonstrates that AHT technology might have good potential for the RF. The most demanded applications are heating, heat storage, and cooling for food/drug storage. The promising working pairs are selected for each application and each climatic zone. We believe that the obtained results will promote the dissemination of energy and environmentally saving AHT technology in the Russian Federation.

Author Contributions: Analysis and validation, project administration and writing—original draft preparation, A.G., software and resources, A.S., methodology, L.G., discussing methodology and results, writing—review and editing, Y.A.

Funding: This research was funded by the Russian Science Foundation (project Nº 17-79-10103).

Conflicts of Interest: The authors declare no conflicts of interest.

References

- 1. Aristov, Y.I. Novel materials for adsorptive heat pumping and storage: Screening and nanotailoring of sorption properties. *J. Chem. Eng. Jpn.* **2007**, *40*, 1242–1251. [CrossRef]
- 2. Meunier, F. Adsorptive cooling: A clean technology. Clean. Prod. Proc. 2001, 3, 8–20. [CrossRef]
- 3. Deng, J.; Wang, R.Z.; Han, G.Y. A review of thermally activated cooling technologies for combined cooling, heating and power systems. *Prog. Energy Combust. Sci.* **2011**, *37*, 172–203. [CrossRef]
- 4. Wang, R.; Wang, L.; Wu, J. Adsorption Refrigeration Technology: Theory and Application; John Wiley & Sons: Singapore, 2014.
- Advances in Adsorption Technologies; Saha, B.; Ng, K.S. (Eds.) Nova Science Publishers: New York, NY, USA, 2010; ISBN 978-1-60876-833-2.

- 6. Aristov, Y.I. Concept of adsorbent optimal for adsorptive cooling/heating. *Appl. Therm. Eng.* **2014**, 72, 166–175. [CrossRef]
- Henninger, S.K.; Ernst, S.-J.; Gordeeva, L.; Bendix, P.; Fröhlich, D.; Grekova, A.; Bonaccorsi, L.; Aristov, Y.; Jaenchen, J. New materials for adsorption heat transformation and storage. *Renew. Energy* 2017, 110, 59–68. [CrossRef]
- Gordeeva, L.G.; Aristov, Y.I. Adsorptive heat storage and amplification: New cycles and adsorbents. *Energy* 2019, 167, 440–453. [CrossRef]
- Shmroukh, A.N.; Ali, A.H.H.; Ookawara, S. Adsorption working pairs for adsorption cooling chillers: A review based on adsorption capacity and environmental impact. *Renew. Sustain. Energy Rev.* 2015, 50, 445–456. [CrossRef]
- Scapino, L.; Zondag, H.A.; Bael, J.V.; Diriken, J.; Rindt, C.C.M. Sorption heat storage for long-term low-temperature applications: A review on the advancements at material and prototype scale. *Appl. Energy* 2017, 190, 920–948. [CrossRef]
- 11. Askalany, A.A.; Salem, M.; Ismael, I.M.; Ali, A.H.H.; Morsy, M.G.; Saha, B.B. An overview on adsorption pairs for cooling. *Renew. Sustain. Energy Rev.* **2013**, *19*, 565–572. [CrossRef]
- 12. Alahmer, A.; Wang, X.; Al-Rbaihat, R.; Alam, K.C.A.; Saha, B.B. Performance evaluation of a solar adsorption chiller under different climatic conditions. *Appl. Energy* **2016**, *175*, 293–304. [CrossRef]
- Trapani, F.; Polyzoidis, A.; Loebbecke, S.; Piscopo, C.G. On the general water harvesting capability of metal-organic frameworks under well-defined climatic conditions. *Microporous Mesoporous Mater.* 2016, 230, 20–24. [CrossRef]
- 14. Habib, K.; Saha, B.B.; Chakraborty, A.; TaekOh, S.; Koyama, S. Study on solar driven combined adsorption refrigeration cycles in tropical climate. *Appl. Therm. Eng.* **2013**, *50*, 1582–1589. [CrossRef]
- Allouhi, A.; Kousksou, T.; Jamil, A.; Agrouaz, Y.; Bouhal, T.; Saidur, R.; Benbassou, A. Performance evaluation of solar adsorption cooling systems for vaccine preservation in Sub-Saharan Africa. *Appl. Energy* 2016, 170, 232–241. [CrossRef]
- 16. Alam, K.C.A.; Saha, B.B.; Akisawa, A. Adsorption cooling driven by solar collector: A case study for Tokyo solar data. *Appl. Therm. Eng.* **2013**, *50*, 1603–1609. [CrossRef]
- 17. Rouf, R.A.; Alam, K.C.A.; Khan, M.A.H. Solar Adsorption Cooling and Hot Water Supply for Climatic Condition of Dhaka. *Procedia Eng.* **2015**, *105*, 705–712. [CrossRef]
- 18. Polanyi, M. Theories of the adsorption of gas. Trans. Faraday Soc. 1932, 28, 16.
- 19. Dubinin, M.M. Theory of physical adsorption of gases and vapour and adsorption properties of adsorbents of various natures and porous structures. *Bull. Div. Chem. Soc.* **1960**, *9*, 1072–1078. [CrossRef]
- 20. Aristov, Y.I.; Sharonov, V.E.; Tokarev, M.M. Universal relation between the boundary temperatures of a basic cycle of sorption heat machines. *Chem. Eng. Sci.* 2008, *63*, 2907–2912. [CrossRef]
- 21. Grekova, A.; Gordeeva, L.; Aristov, Y. Composite sorbents "Li/Ca halogenides inside Multi-wall Carbon Nano-tubes" for Thermal Energy Storage. *Sol. Energy Mater. Sol. Cells* **2016**, *155*, 176–183. [CrossRef]
- 22. Wilson, S.T.; Lok, B.M.; Messina, C.A.; Cannan, T.R.; Flanigen, E.M. Aluminophosphate molecular sieves: A new class of microporous crystalline inorganic solids. *J. Am. Chem. Soc.* **1982**, *104*, 1146–1147. [CrossRef]
- 23. Martens, J.A.; Jacobs, P. Crystalline microporous phosphates: A family of versatile catalysts and adsorbents, in advanced zeolite science and application. *Stud. Surf. Sci. Catal.* **1994**, *85*, 653–685. [CrossRef]
- 24. Ng, E.P.; Mintova, S. Nanoporous materials with enhanced hydrophilicity and high water sorption capacity. *Microporous Mesoporous Mater.* **2008**, *114*, 1–26. [CrossRef]
- 25. Kitagawa, S.; Kitaura, R.; Noro, S. Functional porous coordination polymers. *Angew. Chem. Int. Ed.* **2004**, *43*, 2334–2375. [CrossRef] [PubMed]
- 26. Gordeeva, L.G.; Aristov, Y.I. Composites "salt inside porous matrix" for adsorption heat transformation: A current state of the art and new trends". *Int. J. Low Carb. Tech.* **2012**, *7*, 288–302. [CrossRef]
- 27. Henninger, S.K.; Jeremias, F.; Kummer, H.; Schlossig, P.; Henning, H.-M. Novel sorption materials for solar heating and cooling. *Energy Procedia* 2012, *30*, 279–288. [CrossRef]
- 28. Aristov, Y.I.; Tokarev, M.M.; Freni, A.; Glaznev, I.S.; Restuccia, G. Kinetics of water adsorption on silica Fuji Davison RD. *Microporous Mesoporous Mater.* **2006**, *96*, 65–71. [CrossRef]
- 29. Thua, K.; Chakrabortyc, A.; Sahad, B.B.; Ng, K.C. Thermo-physical properties of silica gel for adsorption desalination cycle. *Appl. Therm. Eng.* **2013**, *50*, 1596–1602. [CrossRef]

- 30. El-Sharkawy, I.I.; Hassan, M.; Saha, B.B.; Koyama, S.; Nasr, M.M. Study on adsorption of methanol onto carbon based adsorbents. *Int. J. Refrig.* **2009**, *32*, 1579–1586. [CrossRef]
- 31. Henninger, S.K.; Schicktanz, M.; HuEgenell, P.P.C.; Sievers, H.; Henning, H.-M. Evaluation of methanol adsorption on activated carbons for thermally driven chillers part I: Thermophysical characterization. *Int. J. Refrig.* **2012**, *35*, 543–553. [CrossRef]
- 32. Brancato, V.; Frazzica, A. Characterisation and comparative analysis of zeotype water dsorbents for heat transformation applications. *Sol. Energy Mater. Sol. Cells* **2018**, *15*, 91–102. [CrossRef]
- 33. Kohler, T.; Hinze, M.; Miller, K.; Schwieger, W. Temperature independent description of water adsorption on zeotypes showing a type V adsorption isotherm. *Energy* **2017**, *135*, 227–236. [CrossRef]
- 34. Kim, S.-N.; Kim, J.; Kim, H.-Y.; Cho, H.-Y.; Ahn, W.-S. Adsorption/catalytic properties of MIL-125 and NH2-MIL-125. *Catal. Today* 2013, 204, 85–93. [CrossRef]
- 35. Jasuja, H.; Huang, Y.; Walton, K.S. Adjusting the Stability of Metal–Organic Frameworks under Humid Conditions by Ligand Functionalization. *Langmuir* **2012**, *28*, 16874–16880. [CrossRef] [PubMed]
- 36. Akiyama, G.; Matsuda, R.; Sato, H.; Hori, A.; Takata, M.; Kitagawa, S. Effect of functional groups in MIL-101 on water sorption behavior. *Microporous Mesoporous Mater.* **2012**, *157*, 89–93. [CrossRef]
- Küsgens, P.; Rose, M.; Senkovska, I.; Fröde, H.; Henschel, A.; Siegle, S.; Kaskel, S. Characterization of metal-organic frameworks by water adsorption. *Microporous Mesoporous Mater.* 2009, 120, 325–330. [CrossRef]
- Grekova, A.D.; Gordeeva, L.G.; Aristov, Y.I. Composite "LiCl/vermiculite" as advanced water sorbent for thermal energy storage. *Appl. Therm. Eng.* 2017, 124, 1401–1408. [CrossRef]
- Gordeeva, L.G.; Freni, A.; Krieger, T.A.; Restuccia, G.; Aristov, Y.I. Composites "lithium halides in silica gel pores": Methanol sorption equilibrium. *Microporous Mesoporous Mater.* 2008, 112, 264–271. [CrossRef]
- 40. Simonova, I.A.; Freni, A.; Restuccia, G.; Aristov, Y.I. Water sorption on composite "silica modified by calcium nitrate". *Microporous Mater.* **2009**, *122*, 223–228. [CrossRef]
- 41. Yuan, Y.; Zhang, H.; Yang, F.; Zhang, N.; Cao, X. Inorganic composite sorbents for water vapor sorption: A research progress. *Renew. Sustain. Energy Rev.* **2016**, *54*, 761–776. [CrossRef]
- 42. Meteonorm. Available online: http://www.meteonorm.com/ (accessed on 20 December 2018).
- 43. Aristov, Y.I. Adsorptive transformation of ambient heat: A new cycle. *Appl. Therm. Eng.* **2017**, *124*, 521–524. [CrossRef]
- 44. The Map Climatic zones of the Russian Federation. Available online: http://meteoinfo.ru/climate (accessed on 20 December 2018).
- 45. Aristov, Y.I. A new adsorptive cycle "HeCol" for upgrading ambient heat: The current state of the art. *Int. J. Refrig.* **2018**. submitted. [CrossRef]



© 2019 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/).