


WATER-PARAFFIN DISPERSION SYSTEMS: MANUFACTURING AND APPLICATION

Alla Yovchenko

Cherkasy State Technological University, Department of Energy Technologies
460 Shevchenko Boulevard, 18006 Cherkasy, Ukraine

 <https://orcid.org/0000-0002-7069-1092>


Sergii Bepalko*

Cherkasy State Technological University, Department of Energy Technologies
460 Shevchenko Boulevard, 18006 Cherkasy, Ukraine, s.bepalko@chdtu.edu.ua

 <https://orcid.org/0000-0002-7542-5498>

Oksana Tryhub

Cherkasy State Technological University, Department of Automobiles and Technology of their Operation
460 Shevchenko Boulevard, 18006 Cherkasy, Ukraine

 <https://orcid.org/0000-0001-7312-6921>

Sviatoslav Poliakov

Cherkasy State Technological University, Department of Energy Technologies
460 Shevchenko Boulevard, 18006 Cherkasy, Ukraine

Guy Baret

Nexthorizon Sasu
12 rue de la Martellière, 38500 Voiron, France

Alberto Munoz Miranda

University of Rostock, R&D in Renewable Energy
Erich-Schlesinger Str. 20, 18059 Rostock, Germany

Abstract

The paper presents the study results of the stability and heat storage capacity of paraffin-in-water phase change suspensions (PCSs) obtained by the homogenization of paraffin and water in the developed rotary hydrodynamic homogenizer. The optimal concentration of components for obtaining stable paraffin-in-water suspensions is found. It is shown that the stable PCSs in the form of pastes, gels, and liquids can be obtained depending on the concentration of water, paraffin, and the surface-active agent (SAA) as well as its type.

In addition, the scheme of the solar heating system with the heat storage tank where the PCS functions both as the heat transfer fluid and the heat storage media is presented. It is shown that the use of PCS in the domestic solar heating system allowed the heat storage capacity of the storage tank to be increased by 25% as a result of the high fusion heat of paraffin and the high value of the water specific heat capacity. The estimation of the saving rate from applying fluid PCS as a heat storage medium is also presented and discussed.

Keywords

heat storage; phase change material; phase change suspension; surface-active agent; enthalpy; solar heating system

Abbreviations

PCM	phase change material
PCS	phase change suspension
SAA	surface-active agent
HLB	hydrophilic-lipophilic balance
LED	light emitted diode
GnP	graphene nano-platelets

Nomenclature

Δh_w	enthalpy change of water, kJ/kg
Δh_{PCM_s}	enthalpy change of PCM when heated from the initial temperature to the melting point, kJ/kg
Δh_{PCM}	latent heat of PCM, kJ/kg
Δh_{PCM_l}	enthalpy change of PCM when heated from the melting point to the final temperature, kJ/kg
$\Delta h_{SAA1}, \Delta h_{SAA2}$	enthalpy change of the Tween hydrophilic surfactants and the Span hydrophobic surfactants respectively, kJ/kg
$X_{PCM}, X_w, X_{SAA1}, X_{SAA2}$	mass concentration of PCM, water, hydrophilic surfactants Tween, hydrophobic surfactants Span, respectively, %
c_p^w	isobaric specific heat of water, kJ/kg·K
$c_p^{PCM_s}$	isobaric specific heat of the PCM in a solid state, kJ/kg·K
$c_p^{PCM_l}$	isobaric specific heat of the PCM in a liquid state, kJ/kg·K
c_p^{SAA1}	isobaric specific heat of Span surfactants, kJ/kg·K
c_p^{SAA2}	isobaric specific heat of Tween surfactants, kJ/kg·K
t_1, t_2	initial and final temperatures respectively, °C
t_{pt}	phase-transition temperature of PCM, °C
Δt	difference between the initial and the final temperatures, °C.

Introduction

Mixtures of water and PCM are one of the most promising heat-storage materials for use in heating, ventilation, and air-conditioning systems. The mixtures are called phase change suspensions (PCSs) because they can change their aggregate state at operating temperatures.

Most often, paraffin consisting mainly of straight- or branched-chain hydrocarbons C_nH_{2n+2} is used as PCM [1]. The crystallization of the hydrocarbon chains releases a large amount of latent heat. For example, octacosane $C_{28}H_{58}$ when melted at +61.3 °C may store about 224.3 kJ/kg of heat. In contrast to paraffin, about 4.2 kJ of heat is required to change the temperature of 1 kg of water by 1 °C. That is to say, that a storage tank filled with paraffin heated from +61.3 °C to +63.3 °C (2 degrees only) stores as much heat as a storage tank filled with water and heated from +26 °C to +80 °C.

The melting point of PCM defines the field of the potential PCS applications. For example, tetradecane-based PCS ($C_{14}H_{30}$) with a crystallization temperature of around 8 °C is suitable for use in air-conditioning systems [1]. Hexadecane-based PCS ($C_{16}H_{34}$) with a crystallization temperature of about 20 °C is used for increasing the heat storage capacity of building materials [2, 3]. Octacosane ($C_{28}H_{58}$) with a melting point at 61.3 °C is an appropriate material for the storage of thermal energy in the domestic solar heating and hot water supply systems [4, 5].

The main tasks of the recent R&D efforts in this field were as follows:

- Estimation of the optimal weight concentration of PCM, SAA, and nanoparticles for decreasing the subcooling effect, increasing PCS heat storage capacity and heat conductivity as well as the study of the properties of the obtained PCS [4-14],
- Development of the systems for practical PCS applications [8, 15, 16],
- Determination of optimal configuration of the heat exchangers for the heat transfer enhancement [10, 17-25],
- Study of the heat transfer processes in PCS at natural and forced convections [17-23, 24-27].

Reddy K. et al. [6], studied various heat transfer methods to improve the performance of the heat storage tank in the solar heating system. It was shown that the main reason, which limits the use of PCSs, is their time instability. It was concluded that the application of PCSs, which can undergo many melting-crystallization cycles without affecting the thermophysical properties, is necessary.

The methodology for determining the thermal characteristics of the solar heating system depending on the solar radiation intensity and the operating temperature of the PCM was proposed by P. Feliński [7]. According to that study, the heat storage capacity of a tank filled with PCMs is higher by 20.5% compared to the conventional heat storage tank filled with water. It was concluded that the performance of the solar heating system can be improved by applying PCMs with different melting points and operating temperatures. Nevertheless, further research is still needed to overcome some drawbacks relevant to PCMs.

Mohamed E. Zayed et al. [8] described various schemes of thermal energy storage systems. In the study, different ways useful for the improvement of the heat transfer in PCM, heat storage efficiency, and thermodynamic optimization have been evaluated.

In recent years, PCSs are considered not only as a heat storage material but simultaneously as a heat transfer fluid in the solar heating systems. In the research work by Chen J. and Zhang P. [9], the conditions under which PCS is still a fluid medium, and whether it can be conveyed by a regular pump were considered. According to the obtained data, PCS is a fluid with a maximum PCM concentration of up to 30 % displaying Newtonian fluid properties. The thermophysical characteristics of PCSs at such PCM concentrations were defined. It was shown that the most common problems of using PCM in the heat storage systems are subcooling, low thermal conductivity, and low heat transfer rate, which lead to an increase in the time of charging and discharging of the heat storage reservoir as well as productivity reduction.

The application of PCS as a heat storage substance has the following advantages:

- the PCS components are not toxic as well as neither flammable nor explosive in the working temperature ranges,
- possibility to be reused or recycled,
- can easily be separated from other materials,
- chemical inertness to the structural materials of a storage reservoir,
- small change in the specific volume during melting-crystallization,
- enhanced heat storage capacity because of the high fusion heat of paraffin and the high specific heat capacity of water,
- less volume and size of the reservoir needed to store the same heat amount compared to water,
- less heat losses due to the isothermality of the heat storage with PCS,
- possibility to convey PCS using a regular pump,
- in some cases, the possibility to substitute conventional heat transfer fluids for PCS undergoing the phase change,
- availability in large quantities and cost effectiveness.

Despite the above-mentioned advantages, PCS also has some drawbacks:

- relatively less stability of PCS (up to 300 proven melting-crystallization cycles at the highest temperature of about 80 °C),
- subcooling effect, i.e. state of the substance when the PCM remains a fluid medium at temperatures well below its crystallization point,
- low heat transfer rate leading to longer charging and discharging, which results in less productivity,
- necessity to apply special facilities for homogenization of water and PCM,
- necessity to add SAA to make PCSs more stable.

In the research [10-14], the use of nanoparticles of various materials with high thermal conductivity, e.g. metal oxides, metal nitrides, silicon oxide, graphite, graphene, and etc. was proposed to reduce the subcooling phenomenon. The influence of the size, type, and a number of nanoparticles on the PCS thermal conductivity and reduction of the subcooling phenomenon was also studied.

Z. Khan and Z. Ahmad Khan [10] experimentally and numerically studied the thermal conductivity and dynamic viscosity of PCS as well as the heat transfer rate, temperature distribution, velocity of the phase change, and the heat storage capacity of the system depending on the size and concentration of the nanoparticles such as aluminum oxide (Al₂O₃), aluminum nitride (AlN), graphite (Gt) and graphene nano-platelets (GnP). According to the research results obtained, all additives affect the overall heat storage capacity of the latent heat storage system and increase the dynamic viscosity of PCSs, which in turn affect natural convection. On the other hand, the effective thermal conductivity of paraffin is significantly enhanced with the additives.

Fangxian Wang et al. [11], investigated influence of graphite nanoparticles added to the fluidic PCSs on the heat transfer. It was shown that PCSs based on the 20% of PCM and 0.1 % of the graphite additive have a 20% higher heat conductivity compared to PCSs without additives. In the temperature range from 18°C to 80 °C, heat storage efficiency is 86%, which shows that PCSs have great potential for applications as the advanced heat transfer fluid in the low temperature systems with direct absorption solar collectors.

In other research work, Fangxian Wang et al. [12] studied thermal properties of PCSs in the range of the PCM and graphite mass fractions from 15 to 25 wt.% and 0.04-0.1 wt.% respectively. According to the research, results obtained PCSs based on 20 wt.% of C₂₈H₅₈ paraffin and 0.07 wt.% of graphite exhibits better performance. At such concentration of the components, the overall heat storage capacity of PCSs is 1.64 times higher compared to distilled water.

Zhang et al. [13], applied hydrophobic SiO₂ nanoparticles as a nucleating agent to reduce the supercooling effect.

It was shown that the increase in the SiO₂ concentration up to 3 wt.% reduces supercooling. Nevertheless, further increase in the SiO₂ concentration up to 5 wt.%, along with the further supercooling reduction, leads to a decrease in the heat storage capacity by 20%. That is why the optimal concentration of the additive nanoparticles was found to be 3 wt.%.

Fangxian Wang et al. [14, 15], comprehensively studied PCSs with regard to their production process, thermal properties, rheological behavior, heat transfer process as well as PCS applications in the solar heating systems.

Inaba et al. [17], studied heat transfer at the natural convection in a rectangular vessel filled with PCS containing PCMs in the range of concentrations between 5-30%. The results show that the PCM concentration has a negligible effect on the Nusselt number when the PCM is in a solid state. However, during the phase change at low Rayleigh numbers and with increase in the PCM concentration, the Nusselt number rises. It is also shown that viscosity decreases the natural convection at the PCM concentration of more than 10%.

Morimoto and Kumano [18], experimentally and numerically studied the laminar forced convection in a cylindrical pipe. It was shown that the developed mathematical model agrees with the experimental results excepting PCSs based on 10% of PCM.

According to the research works [18-23], the heat transfer characteristics are enhanced at the laminar forced convection in the phase change of PCSs. It was also revealed that the Nusselt number increases with the rise in the PCM concentration, Reynolds numbers [21] and with applying a coiled double-tube heat exchanger [19, 20]. It was also found that the pressure drop due to the viscous friction grows with the increase in the PCM concentration [23].

The analysis of the turbulent forced convection revealed that its properties are similar to those at the laminar forced convection [24-27].

The issue of obtaining stable suspensions and the forces acting in the homogeneous paraffin-water mixture was considered by Sanfeld et al. [28]. As a result, a concept of the suspension stability based on the droplet deformation theory was presented.

Recently, various methods for studying the kinetic stability of PCSs have been developed. Subjecting PCSs to melting and crystallization cycles is one of them. Here, the occurring partial coalescence mechanism leads to the destruction of PCS micro volumes, and as a result, a layer of water is liberated. In this case, the PCS stability is determined by the thickness of the water layer formed as well as the time of PCS separation into two phases: the upper phase with a lower density, and the bottom phase with a higher density.

At the same time, the stability of the PCSs depends significantly on the type of the surface-active agent (SAA). Oil-soluble SAAs, characterized by a hydrophilic-lipophilic balance (HLB) lower than 10, are used to prepare so-called water-in-paraffin suspensions. On the other hand, water-soluble SAAs with an HLB higher than 10 are used to produce paraffin-in-water suspensions.

Span Surfactants are oil-soluble and have an HLB range from 1.8 to 4.7. For instance, Span-60 is a sorbitan monostearate with HLB 4.7, Span-80 is a sorbitan monooleate with an HLB of 4.3. In contrast to Span, Tween surfactants are well soluble in water and organic solvents, easy to mix with hydrocarbons and fats. Tween-60 and Tween-80 are polyethylene glycol sorbitan monooleate having an HLB of 14.9 and an HLB of 15.0 respectively.

Golemanov et al. [29] studied the influence of the carbon chain length in the surfactant molecules on the suspension stability. As a result, the dependence of the carbon chain length on the critical osmotic pressure P_{OSM}^{CR} was determined. It was shown that the use of surfactants with long carbon chains (16 or 18 carbon atoms) provides more stable suspensions with a lower degree of hypothermia due to the formation of more compact and ordered adsorption layers [29, 30]. According to the study, surfactant Tween-60 is the most suitable for producing stable PCSs.

Different types of homogenizers to produce PCSs have been developed so far. They are colloid mills, mechanical mills, Manton-Gaulin homogenizing valves, rotary emulsifiers, ultrasonic dispensers, and others. The dispersion rate, stability of the suspensions obtained, and productivity of the colloid mill depend on the gap width, the rotating speed of the rotor, and the time of mixing. The optimal gap width ranges from 0.05 to 0.1 mm. However, it was found [31] that the small gaps significantly reduce the productivity of the colloid mill. The operating principle of the homogenizing valve is based on pumping the fluid mixture through a calibrated hole at a high pressure of about 20 MPa. When passing the valve, the significant pressure drop induces cavitation, which, in turn, efficiently shatters and mixes the paraffin globules with water.

In the rotary emulsifiers, the liquid flows through the nozzles or slits under pressure. Such homogenizers have some advantages compared to the homogenizing valves. They are simpler, less metal consuming, and there is no

rapid wearing of parts. One of the drawbacks is the significant foaming of the product during mixing. The ultrasonic dispersers are increasingly popular for mixing purposes. Their operation is based on the use of oscillations in the ultrasonic wavelength range.

Mechanical mills for the production of suspensions require significantly less energy than colloid mills or homogenizers with similar production rates. However, the suspension obtained in mechanical mills has a poor dispersion rate than obtained in other apparatuses. On the other hand, the mechanical mills consume two times less energy than colloid mills, and 4-6 times less than the ultrasonic dispersers [32].

Analysis of the technologies for the production of PCSs shows that all of them have disadvantages, such as low dispersion efficiency, low productivity, complex construction, and high-energy consumption.

Rotary hydrodynamic homogenizers are the most efficient and multi-functional among a variety of apparatuses for the homogenization of multicomponent heterogeneous liquids. In this type of homogenizer, the fluids flow through the inter-cylinder gap (annulus), where the main process of homogenization takes place. The homogenization process is influenced by the regime of the fluid flow in the inter-cylinder gap. Two dimensionless numbers characterize the fluid motion in the annulus, especially the Reynolds number of axial flow, and the Taylor number. According to [33], depending on the Reynold and Taylor numbers one of the four flow modes is possible: laminar, laminar with Taylor vortices, turbulent, and turbulent with Taylor vortices. The most efficient PCS production occurs in the turbulent regime with the Taylor vortices. In this case, there are significant shear stresses, which, in turn, are responsible for the efficient mixing of paraffin with water and stable PCS formation. However, our literature review revealed that in most cases the laboratory homogenizers such as ULTRA-TURRAX T25 were used for PCS production. That is why the aim of our R&D efforts was to develop the rotor-type hydrodynamic homogenizer with the similar technical characteristics and will be able to produce PCS in large scale.

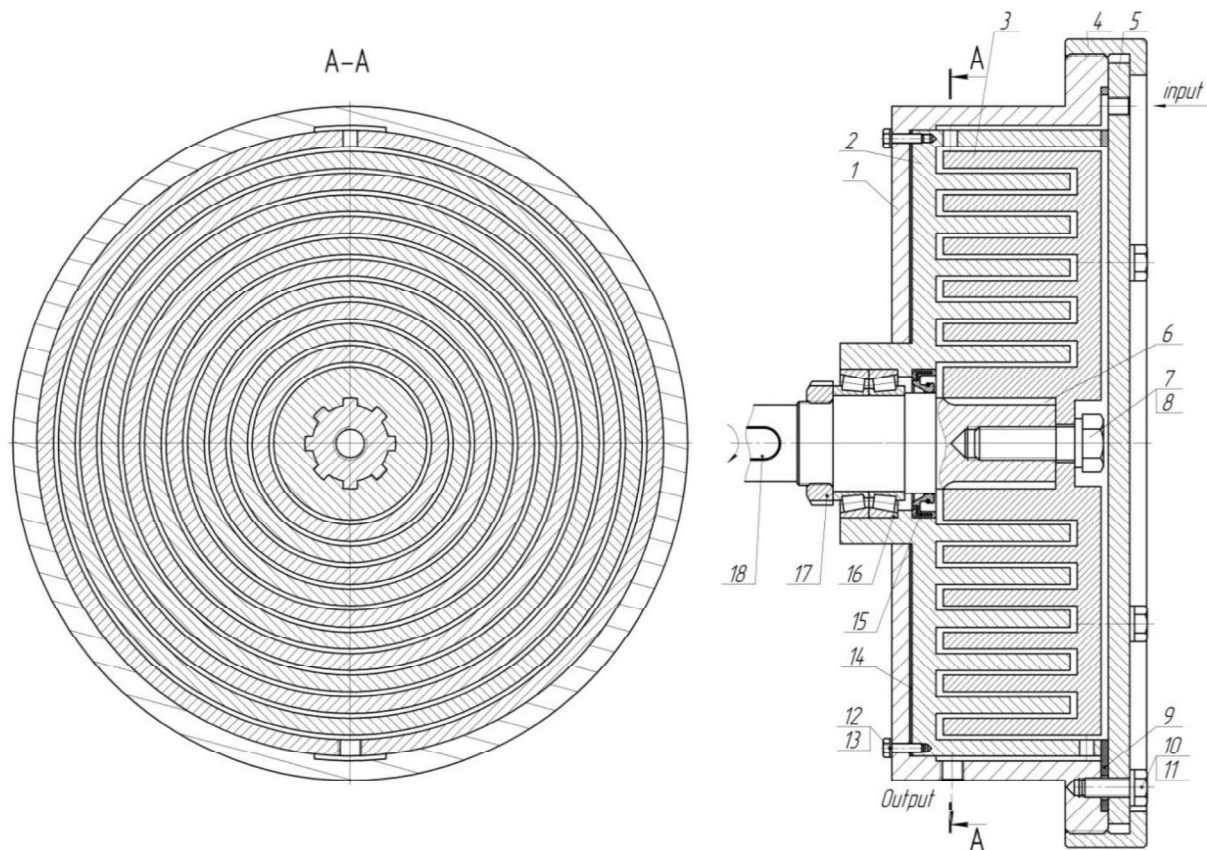
The objectives of this research were as follows:

- to check the performance of the developed rotary hydrodynamic homogenizer;
- to determine the optimal component concentrations, especially distilled water, paraffin, and surfactant, for obtaining stable paraffin-in-water mixtures;
- to determine the heat storage capacity of the PCSs obtained.

Materials and Methods

Description of the experimental setup

Paraffin and water mixing was carried out using the experimental facility (Fig. 1) equipped with a rotary hydrodynamic homogenizer, which is illustrated in Fig. 2. Non-ionic surfactants, especially Tween and Span having hydrophilic and hydrophobic properties respectively, were added to the mixture, which allowed paraffin to form stable internal media, while water continuous outer fluid.



1 – housing; 2 – stator; 3 – rotor; 4 – nut; 5 – cap; 6 – splined shaft; 7, 10, 12 – bolts; 8, 11, 13 – washers; 9, 14 – gaskets; 15 – seal; 16 – bearing; 17 – nut; 18 – keyway

Fig. 2. Hydrodynamic homogenizer

In a mixing, a significant portion of mechanical energy disappears and results in the dissipative liquid heating. Therefore, utilizing the dissipative heat by providing such an internal heat exchange between two circuits is necessary. In this case, the heat flux through the stator surface (2) is used for the preheating of the working fluid. The developed homogenizer may produce up to 1 m³ of PCS per hour.

Method for obtaining suspensions

First, the distilled water heated in the tank (7) up to a temperature level of 61-62 °C was mixed with the Tween hydrophilic surfactant using a propeller blade mixer. At the same time, paraffin, especially octacosanC₂₈H₅₈, heated to the melting point was mixed with the Span hydrophobic surfactant also using a propeller blade mixer. The pump NXL (4) was applied to circulate water-Tween surfactant mixture through the hydraulic system pipeline. The fluid flow rate was controlled by the valve (10), thereby changing the pressure in the system. After filling the hydraulic system with a liquid medium, an electric DC motor (16) started to transmit torque to the rotor of the homogenizer (13). The rotation speed n of the homogenizer was adjusted in the range from 0 to 3000 rpm. After that, the valve (21) was closed.

The water jet ejector (24) was applied for pre-mixing the mixtures of "molten paraffin-surfactant Span" and the mixture " Tween distilled water-surfactant ". After opening the valves (22) and (23), the mixture of " Span molten paraffin-surfactant " was sucked in the mixture of " Tween distilled water-surfactant " by the water jet ejector. This mixing method allowed a more simple and even distribution of the mixture of the "molten paraffin-surfactant Span" in a mixture of the " Tween distilled water-surfactant ", which in turn enhances the main homogenization process in the hydrodynamic homogenizer.

After cooling to room temperature, the paraffin globules crystallized. The obtained homogeneous suspension was in the form of a liquid, gel, or paste, depending on the paraffin concentration. Since PCSs contains water, paraffin, and surfactant, the thermophysical properties of the PCSs are influenced by the properties of these three main components as well as their concentrations [5]. When PCSs are in the liquid form, water provides them with fluidity, while the paraffin microparticles remain in a solid state. As a result, PCSs can be conveyed by

a regular pump. On the other hand, in the case of pastes, PCSs are in the form of a solid plastic mass that cannot be transported by a pump but can take any shape and fill in any cavities.

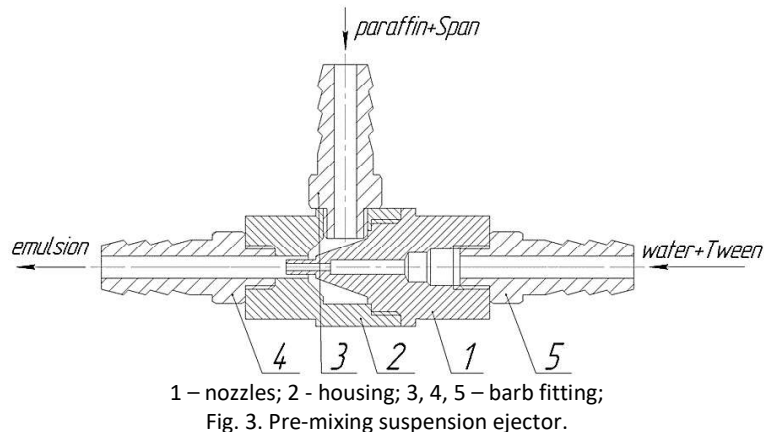


Fig. 3. Pre-mixing suspension ejector.

The procedure used to prepare a PCS is shown in Fig. 4.

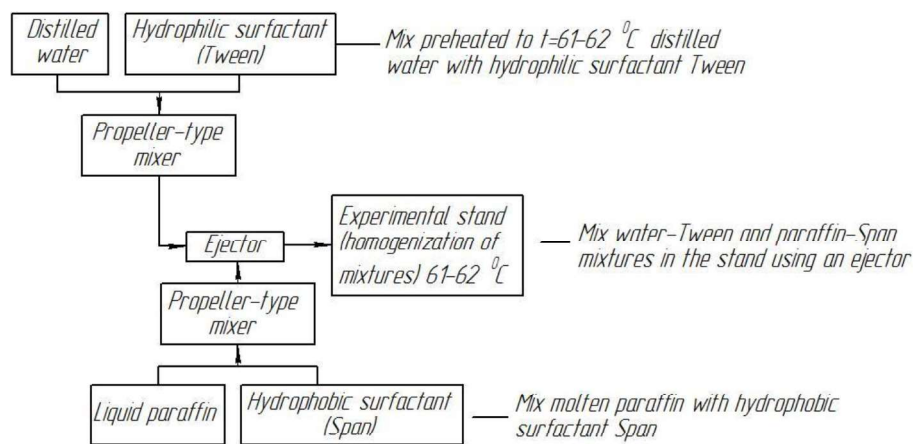


Fig. 4. The flow chart of the homogenization process used to get PCS.

Method for determining the heat storage capacity

The total heat storage capacity of the PCS consists of not only the heat storage capacity of paraffin but also the heat storage capacity of water and surfactants. Thus, in the temperature range from t_1 to t_2 , the enthalpy change of the PCS Δh_{PCS} can be estimated using the expression as follows:

$$\Delta h_{PCS} = \Delta h_w + \Delta h_{PCMs} + \Delta h_{PCM} + \Delta h_{PCMI} + \Delta h_{SAA1} + \Delta h_{SAA2} = X_w \cdot c_p^w \cdot (t_2 - t_1) + X_{PCM} \cdot c_p^{PCMs} \cdot (t_{pt} - t_1) + X_{PCM} \cdot \Delta h_{PCM} + X_{PCM} \cdot c_p^{PCMI} \cdot (t_2 - t_{pt}) + X_{SAA1} \cdot c_p^{SAA1} \cdot (t_2 - t_1) + X_{SAA2} \cdot c_p^{SAA2} \cdot (t_2 - t_1), \quad (1)$$

where Δh_w is the enthalpy change of water in the temperature range from t_1 to t_2 , kJ/kg; Δh_{PCMs} is the enthalpy change of the PCM when heated from the initial temperature to the melting point [34], kJ/kg; Δh_{PCM} is the fusion heat of the PCM [34], kJ/kg; Δh_{PCMI} is the enthalpy change of the PCM when heated from the melting point to the heating temperature [34], kJ/kg; Δh_{SAA1} is the enthalpy change of Tween hydrophilic surfactants in the temperature range from t_1 to t_2 [35], kJ/kg; Δh_{SAA2} is the enthalpy change of Span hydrophobic surfactants in the temperature range from t_1 to t_2 [36], kJ/kg; X_{PCM} , X_w , X_{SAA1} , X_{SAA2} is the mass concentration of PCM, water, Tween hydrophilic surfactants, Span hydrophobic surfactants, respectively, %; c_p^w is the isobaric specific heat of water, kJ/kg·°C; c_p^{PCMs} is the isobaric specific heat of the PCM in a solid state, kJ/kg·°C; c_p^{PCMI} is the isobaric specific heat of the PCM in the liquid state, kJ/kg·°C; c_p^{SAA1} is the isobaric specific heat of Span surfactants, kJ/kg·°C [35], [36]; c_p^{SAA2} is the isobaric specific heat of Tween surfactants, kJ/kg·°C [35-37]; t_1 , t_2 are initial and final temperatures respectively, °C; t_{pt} is the phase-transition temperature of the PCM, °C; Δt is the difference between the initial

and the final temperatures, °C.

Therefore, Eq. (1) is the correlation between the heat storage capacity of the PCS and temperature as well as the concentration of the different components.

Measuring instrument description and uncertainty analysis

• Measuring instrument description

Description of the tools used to measure temperature and mass of the components is presented in Table 1.

Table 1. The measuring instruments and their characteristics

Parameter	Measuring instruments	
	Reference and provider	Main characteristics
Initial and final temperature of PCS (t_1, t_2)	Platinum temperature resistors HEL-705 (Honeywell)	Range: -200÷260 °C Accuracy: $\Delta t = \pm 0.8\%$
Scales, (m)	Kenwood DS 400	Range: 0÷8 kg Accuracy: $\Delta m = \pm 0.25\%$

• Uncertainty analysis

The uncertainty analysis of the measured and calculated parameters was carried out based on the error propagation theory as described by Lee T.-W. [38]. Table 2 contains the total uncertainties of the measured parameters.

Table 2. Uncertainty estimation of the measured parameters

Parameter	Total uncertainty
Initial temperature (t_1)	$\Delta t_1 = \pm 0.12$ °C at 15 °C
Final temperature (t_2)	$\Delta t_2 = \pm 0.5$ °C at 62 °C
Scales, (m)	$\Delta m = \pm 0.25$ %

Table 3. Uncertainty of the thermophysical properties of the components.

Parameter	Main characteristics
Specific enthalpy of PCM (Δh_{PCM})	Accuracy: $\Delta h_{PCM} = \pm 1.8$ kJ/kg
Specific heat of water (c_p^w)	Accuracy: $\Delta c_p^w = \pm 2$ kJ/(kg · °C)
Specific heat of PCM in solid state (c_p^{PCMs})	Accuracy: $\Delta c_p^{PCMs} = \pm 1.7$ kJ/(kg · °C)
Specific heat of PCM in liquid state (c_p^{PCMI})	Accuracy: $\Delta c_p^{PCMI} = \pm 1.92$ kJ/(kg · °C)
Specific heat of surfactants Span (c_p^{SAA1})	Accuracy: $\Delta c_p^{SAA1} = \pm 0.02$ kJ/(kg · °C)
Specific heat of surfactants Tween (c_p^{SAA2})	Accuracy: $\Delta c_p^{SAA2} = \pm 0.005$ kJ/(kg · °C)

The uncertainty of the PCS enthalpy change Δh_{PCS}^{unc} can be estimated as follows:

$$\Delta h_{PCS}^{unc} = [(\Delta h_w^{unc})^2 + (\Delta h_{PCMs}^{unc})^2 + (\Delta h_{PCMI}^{unc})^2 + (\Delta h_{SAA1}^{unc})^2 + (\Delta h_{SAA2}^{unc})^2]^{0.5} \quad (2)$$

$$\Delta h_w^{unc} = [(\partial h_w^{unc} / \partial X_w \cdot \Delta X_w)^2 + (\partial h_w^{unc} / \partial c_p^w \cdot \Delta c_p^w)^2 + (\partial h_w^{unc} / \partial t \cdot \Delta t_1)^2]^{0.5}, \Delta t_1 = (\Delta t_2^2 + \Delta t_1^2)^{0.5}$$

$$\Delta h_{PCMs}^{unc} = [(\partial h_{PCMs}^{unc} / \partial X_{PCM} \cdot \Delta X_{PCM})^2 + (\partial h_{PCMs}^{unc} / \partial c_p^{PCMs} \cdot \Delta c_p^{PCMs})^2 + (\partial h_{PCMs}^{unc} / \partial t_{pt} \cdot \Delta t_{pt})^2]^{0.5}, \Delta t_{pt} = (\Delta t_{pt}^2 + \Delta t_1^2)^{0.5}$$

$$\Delta h_{PCMI}^{unc} = [(\partial h_{PCMI}^{unc} / \partial X_{PCMI} \cdot \Delta X_{PCMI})^2 + (\partial h_{PCMI}^{unc} / \partial c_p^{PCMI} \cdot \Delta c_p^{PCMI})^2]^{0.5}$$

$$\Delta h_{SAA1}^{unc} = [(\partial h_{SAA1}^{unc} / \partial X_{SAA1} \cdot \Delta X_{SAA1})^2 + (\partial h_{SAA1}^{unc} / \partial c_p^{SAA1} \cdot \Delta c_p^{SAA1})^2 + (\partial h_{SAA1}^{unc} / \partial t_2 \cdot \Delta t_2)^2]^{0.5}$$

$$\Delta h_{SAA2}^{unc} = [(\partial h_{SAA2}^{unc} / \partial X_{SAA2} \cdot \Delta X_{SAA2})^2 + (\partial h_{SAA2}^{unc} / \partial c_p^{SAA2} \cdot \Delta c_p^{SAA2})^2 + (\partial h_{SAA2}^{unc} / \partial t_2 \cdot \Delta t_2)^2]^{0.5}$$

Table 4 presents the total uncertainties of the calculated parameters.

Table 4. Uncertainty estimation of the calculated parameters

Parameter	Total uncertainty
Uncertainty of water enthalpy change	$\Delta h_w^{unc} = \pm 2.88$ kJ/kg
Uncertainty of the enthalpy change of the PCM when heated from the initial temperature to the melting point	$\Delta h_{PCM_s}^{unc} = \pm 0.95$ kJ/kg
Uncertainty of the enthalpy change (specific heat) of the PCM	$\Delta h_{PCM}^{unc} = \pm 2.13$ kJ/kg
Uncertainty of the enthalpy change of the PCM when heated from the melting point to the heating temperature	$\Delta h_{PCM}^{unc} = \pm 0.42$ kJ/kg
Uncertainty of the enthalpy change of Tween hydrophilic surfactants	$\Delta h_{SAA1}^{unc} = \pm 1.42$ kJ/kg
Uncertainty of the enthalpy change of Span hydrophobic surfactants	$\Delta h_{SAA2}^{unc} = \pm 0.28$ kJ/kg
Total uncertainty of the PCS enthalpy change	$\Delta h_{PCS}^{unc} = \pm 4$ kJ/kg

Thus, the total uncertainty of the PCS enthalpy change (heat storage capacity) is ± 1.6 %.

Results and discussion

Pastes, gels, or liquids with predetermined properties valuable for enhancing the performance of the heat storage system can be obtained by varying the concentration of the main components in homogenization. Those properties include: the total PCS heat storage capacity, viscosity, density, and thermal conductivity.

For practical use, PCSs must be stable during the long-term period. According to the literature analysis, in our experimental study the Tween 60, Tween 80, Span 60, and Span 80 surfactants were selected for the purpose to obtain stable paraffin-in-water suspensions.

To obtain stable PCSs, the use of surfactants with hydrophilic and hydrophobic properties simultaneously is necessary. Using only one surfactant, e.g. Tween 60, made PCS unstable regardless of the PCM and distilled water concentrations (Table 5, no. 2-5, no. 11-14, no. 22-24). The ability of surfactants to stabilize paraffin-in-water suspensions for a long time is determined by a hydrophilic functional group, such as Tween 60, and a moderately developed hydrophobic part of the diphilic molecule – Span 80 (Table 5). For the first group, the hydrocarbon part of the surfactant molecule is placed in a paraffin globule and hydrophilic in water. In such a way, it protects the dispersed phase particles from coalescence and, accordingly, prevents the subsequent increase in the size of the globules. The most stable suspensions were formed by applying the surfactants with an HLB higher than 12. Increasing surfactant concentration and reducing surface tension affects the suspension stability, droplet size, and viscosity. Thus, the maximum surfactant concentration should not exceed 10 %. If the SAA concentration is higher, excess surfactant goes into the aqueous phase, which leads to an increase in the viscosity of the PCS. In this case, the PCS becomes foamy (Table 5, no. 10, no. 21), which adversely affects the stability of the suspension. The most stable PCSs were obtained at 5 % of the surfactant concentration.

Thus, the performed experiment showed that:

- (1) The required PCM concentration must be greater than 45 % to obtain stable homogeneous mixtures in the form of pastes, 30-45 % to obtain stable gel-like homogeneous mixtures, and no more than 30% to obtain stable liquid homogeneous mixtures;
- (2) The maximum PCM concentration must be 25 % for PCS to be a Newtonian fluid.

Table 5. Results of the experimental study

No.	Paraffin, %	Water, %	SAA, %				PCS stability
			Tween 60	Tween 80	Span 60	Span 80	
PASTES							
1	50	40	-	5	5	-	+
2	45	45	10	-	-	-	-
3	45	45	-	10	-	-	-
4	45	45	-	-	10	-	-
5	45	45	-	-	-	10	-
6	45	45	5	-	5	-	+
7	45	45	5	-	-	5	++
8	45	45	-	5	5	-	+
9	45	45	-	5	-	5	+
10	40	40	-	10	10	-	+
GELS							
11	35.0	60.0	5	-	-	-	-
12	35.0	60.0	-	5	-	-	-
13	35.0	60.0	-	-	5	-	-
14	35.0	60.0	-	-	-	5	-
15	30.0	60.0	-	10	-	-	+
16	30.0	60.0	-	-	10	-	-
17	30.0	60.0	-	5	-	5	+
18	30.0	60.0	-	5	5	-	+
19	30.0	60.0	5	-	-	5	++
20	30.0	60.0	5	-	5	-	+
21	25.0	55.0	-	10	10	-	+
LIQUID PCSs							
22	25.0	70.0	5	-	-	-	-
23	25.0	70.0	-	5	-	-	-
24	25.0	70.0	-	-	5	-	-
25	25.0	70.0	2.5	-	-	2.5	++
26	20.0	75.0	2.5	-	2.5	-	+
27	20.0	75.0	-	2.5	2.5	-	+
28	20.0	75.0	2.5	-	-	2.5	++
29	20.0	75.0	-	2.5	-	2.5	+
30	15.0	80.0	2.5	-	-	2.5	++
31	15.0	80.0	2.5	-	2.5	-	+
32	15.0	80.0	-	2.5	2.5	-	+
33	15.0	80.0	-	2.5	-	2.5	+

«-» - PCS is not stable, «+» - PCS is stable, «++» - the most stable PCSs.

The PCSs stability was checked by the height of the water layer formed after five PCS melting-crystallization cycles. Thus, the PCSs were subjected to the five melting-crystallization cycles, and then tested which of the PCSs formed had the highest water layer, indicating the unstable PCS by itself (Table 5). In pasty suspensions, a water layer formed after ten days of observation at the bottom of the test tube. In gel-like PCSs, this happened after five days of observation. Later, this process proceeded more slowly and the suspension became stable, which was observed for 6 months.

PCSs can be considered stable when there is no increase in the droplet size, or no phase separation, and PCS retains the heat storage capacity in the planned operating conditions during the storage period. The most stable PCSs were obtained by adding Tween 60 and Span 80 surfactants simultaneously. Subsequently, PCSs based on Tween 60 and Span 80 surfactants were selected for the mathematical calculation of heat storage capacity. The photos of the samples obtained are shown in Fig. 5.



a) pasty PCS (45 % paraffin, 45 % water, 10 % SAA (Tween 60:Span 80, 1:1));
 b) gel-like PCS (25 % paraffin, 65 % water and 10 % SAA (Tween 60:Span 80, 1:1));
 c) liquid PCS (25 % paraffin, 70 % water and 5 % SAA (Tween 60:Span 80, 1:1))

Fig. 5. Photos of PCSs “paraffin in water” after 6 months of storage.

The experimental results obtained with regard to the PCS stability correlate well with the results presented in other research papers, especially [9, 11]. In other words, the stable PCSs obtained did not change their stability during the first 300 melting-crystallization cycles.

According to the data obtained, the PCS enthalpy change was calculated in MathCad 15 as a function of the PCM concentration, and the temperature difference between the final and initial states. The graphical representation of the received results is presented in Fig. 6.

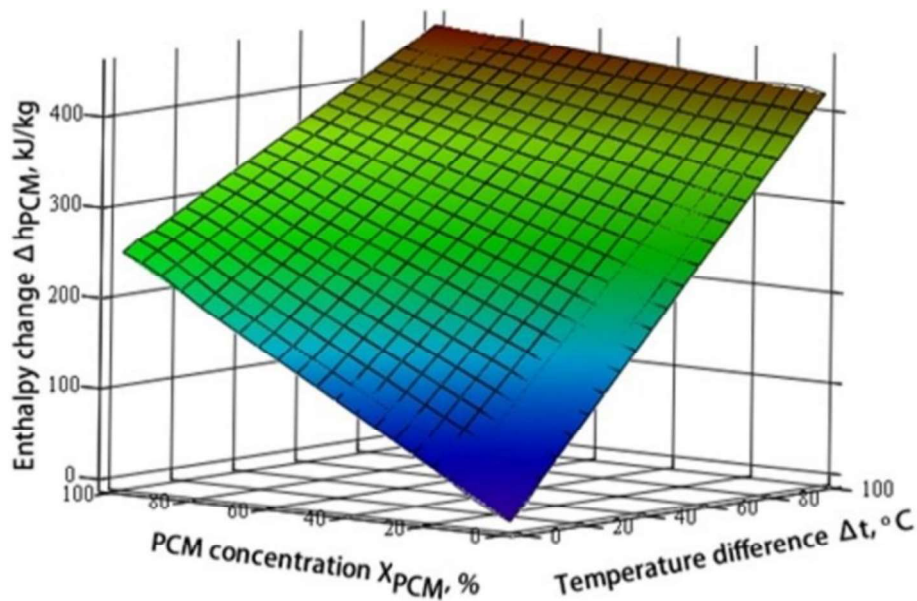


Fig. 6. 3D curve surface of the PCS heat storage capacity as a function of the PCM concentration, and the temperature difference between final and initial states

A regression equation with the regression coefficients was determined using the least-squares method. As can be seen, the regression equation obtained is described by a second-order polynomial function, which is given below:

$$\Delta h = -0.022 \cdot \Delta t \cdot X_{PCM} + 4.196 \cdot \Delta t + 2.5 \cdot X_{PCM} \quad (3)$$

According to this equation, the heat storage capacity of water as a storage media is just 168 kJ/kg at 38 °C temperature difference, whereas the PCS as a heat storage media has a heat storage capacity of about 208.3 kJ/kg at the same temperature difference. That is to say that the heat storage capacity of the PCS is higher by 24 % than that for water (see Fig. 7).

As the temperature difference in the storage tank increases, the difference between the heat storage capacity of water and the PCS decreases. However, most often the temperature difference in the storage tank is in the range of 60 °C.

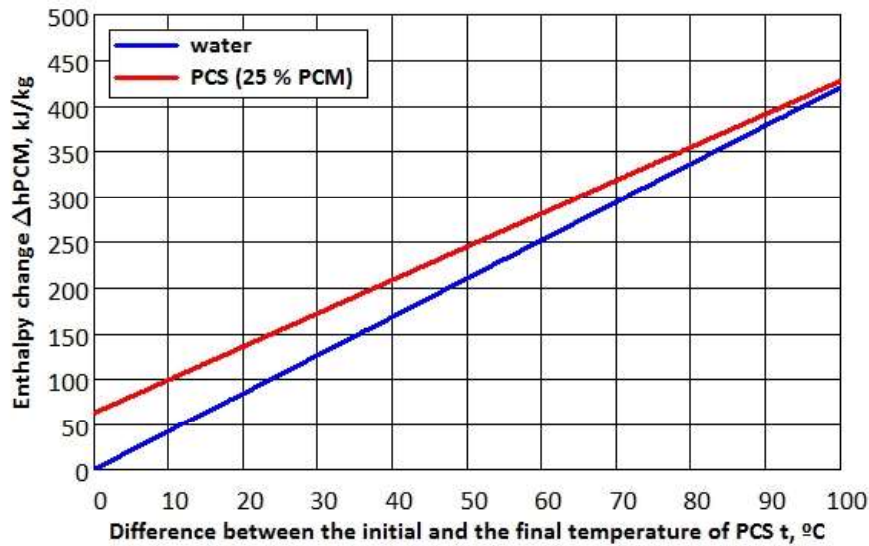


Fig. 7. Heat storage capacity Δh for water and PCS as a function of the temperature difference Δt .

An embodiment of a solar heat system with PCS used as a heat transfer fluid

PCSs show great potential in solar heating systems as new heat storage media as well as a heat transfer fluid. The scheme of a solar heating system where PCSs are applied as a heat transfer fluid is presented in Fig. 8.

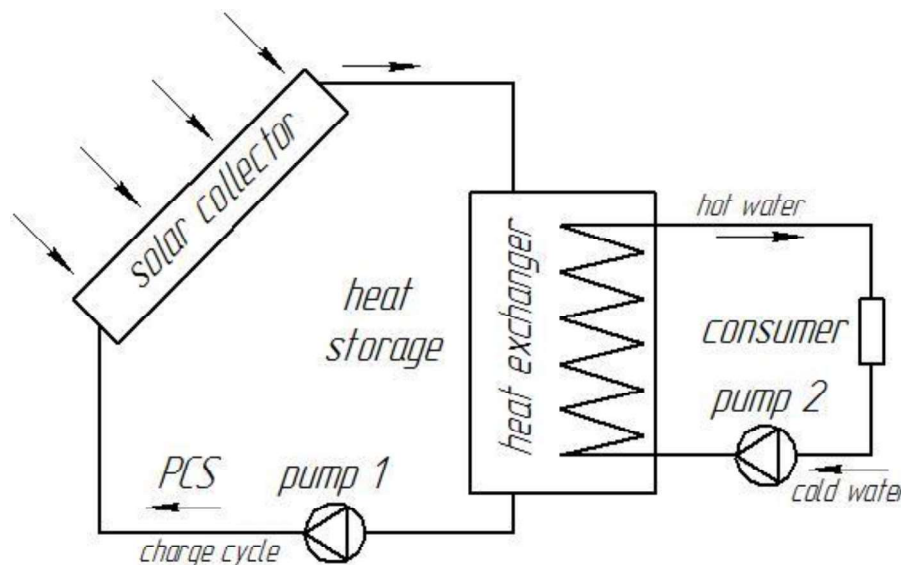


Fig. 8. Scheme of a solar heat system with PCS applied as a heat transfer fluid

In the system, the PCS is conveyed by a pump to the flat-plate collector, where it absorbs solar heat in the daytime heating up on its way to a storage reservoir. In the storage container, a coiled heat exchanger transfers the heat stored to the consumer. The system has improved heat storage capacity due to the use of the latent heat of paraffin and the high specific heat capacity of water. Thus, by applying PCSs it is possible to increase the total heat storage capacity by 24% compared to water.

PCSs with a high heat storage capacity and low energy consumption for pumping have great potential as a new heat storage media and heat transfer fluid for solar heating systems.

The estimation of the saving rate from applying PCSs as a heat storage medium compared to water in the solar heating system is presented in Table 6.

Table 6. Estimation of the saving rate

Parameters	PCS	Water
Operating period	300 melting-crystallization cycles	300 days
Initial temperature, °C	20	
Final temperature, °C	45	
Mass of the heat storage medium, kg	300	
Amount of the heat stored in one charging, kJ	46,200	31,500
Surplus of the heat stored for one charging (compared to water as a storage medium), kJ	14,700	0
Cost of the heat, Euro/GJ**	20	
Saving rate per one charging-discharging cycle, Euro/cycle	0.294	0
Saving rate per operating period, Euro	88.20	0
Cost of the PCS components, Euro***	80.26	-
Overall saving rate per first operating period, Euro	7.94	0
Overall saving rate per second operating period, Euro	88.2	0

* The saving rate was estimated regardless of the cost of homogenization process

** Cost of the thermal energy was taken from [39]

*** Data for cost of the PCS components were extracted from [40-43]

From Table 6 it can be seen that the overall saving rate per first operating period is only EUR 7.94 . Nevertheless, at the end of the first operating period (300 melting-crystallization cycles), the PCS components can be homogenized again for the purpose to be reused as the heat storage medium in next operating period lasted 300 melting-crystallization cycles as well. In this case, the overall saving rate per second operating period will constitute EUR 88.2 because the PCS components are reused.

Impact

One of the ways to decrease human impact on the environment is the use of renewable energy sources. Solar heat is likely to become the ultimate heat source in the future. However, the intermittency challenge of the solar heat generated by solar collectors must be overcome. Heat storage is one of the solutions for this intermittency challenge. That is why an increase in the efficiency and the heat storage capacity of the store is a vital problem. Currently, the most widely used systems are those where the heat storage media and the heat transfer fluid is water. Nevertheless, as shown in this study PCSs display higher heat storage capacity than water.

If PCSs are used as heat-storage media, the storage system will have the following advantages over the traditional system:

- improved heat storage capacity due to the simultaneous use of the fusion heat of paraffin and high specific heat of water;
- small thermal losses due to the isothermal accumulation process;
- the ability to transport PCSs formed by a pump;
- in some cases, it is possible to substitute for a conventional heat transfer fluid with PCSs.

This study will help to choose a correct surfactant for obtaining a stable PCS in the form of liquid, gel, or paste. The proposed PCS will help to improve the energy efficiency of the heat store as well as to increase the share of solar heat utilization. In turn, this will reduce greenhouse gas (CO₂) emissions into the environment, which is a global challenge. Thus, the study has a great impact not only from a technical but also environmental point of view.

The impact of this research will be not only on science but also on the economy because energy companies are interested in increasing the capacity of the heat storage systems operating in tandem with the solar heating systems. This will allow for the share of the solar heat utilized to increase and will result in the reduction of CO₂ emission. The study has shown that the use of PCSs as a heat transfer fluid in solar heating systems increases the heat storage capacity by 24%. This has a significant economic and environmental effect compared to traditional heat stores filled with water.

Conclusions

Based on the results obtained here, the following conclusions can be drawn:

1. The rotor-type hydrodynamic homogenizer has been developed with the productivity rate of about 1 m³ of PCS, which is suitable for commercial application. The corresponding patent application for the homogenizer has been filed.
2. The optimal concentrations of the components, especially distilled water, paraffin, and surfactants, to obtain stable paraffin-in-water mixtures were determined. The required concentration of PCMs to obtain stable pasty mixtures should be greater than 45%, for gel-like 30-45%, for fluid not more than 30%. The most stable suspensions were formed when using a surfactant with a hydrophilic-lipophilic balance of at least 12. The maximum surfactant concentration should not exceed 5%. At higher concentrations, PCSs becomes foamy.
3. The capacity of the heat storage system increased by 24% when PCSs are applied as a heat storage medium compared to the conventional heat store based on water at the temperature difference of 25 °C.
4. PCSs have great potential as new heat transfer fluid and heat storage medium in solar heating systems. Estimation of the economics of the PCS application in the solar heating system has shown that in the first operating period the overall saving rate is only EUR 7.94 , while in each further it constitutes EUR 88.2. This fact shows that use of PCS is attractive from the economic point of view.

Conflict of interest

There are no conflicts to declare.

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