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Characterization of Stearic Acid and Paraffin Incorporated with Aluminium as Filer for the Development of Phase Change Material Composite in Thermal Energy Storage

S Z Abidin[1,3*], S A A Ghani[1], UO Osarieme[2, 4], S S Jamari[2]

[1]Department of Chemical Engineering, College of Engineering, Universiti Malaysia Pahang, Lebuhraya Tun Razak, 26300 Gambang, Kuantan, Pahang, Malaysia.
[2]Faculty of Chemical and Process Engineering Technology, College of Engineering Technology, Universiti Malaysia Pahang, Lebuhraya Tun Razak, 26300 Gambang, Kuantan, Pahang, Malaysia.
[3]Centre of Excellence of Advanced Research in Fluid Flow (CARIFF), Universiti Malaysia Pahang, Lebuhraya Tun Razak, 26300 Gambang, Kuantan, Pahang, Malaysia
[4]Department of Chemical Engineering, University of Benin, PMB 1154, Benin City Edo State, Nigeria

*Corresponding author: sumaiya@ump.edu.my

Abstract. With the increasing energy demand, shortage of energy has drawn attention towards the utilization of non-renewable energy sources. The development of thermal energy storage (TES) to fulfil the energy demand that has increased progressively over time is of great interest. TES systems are widely employed industrially especially for phase change materials (PCM) used in many fields with several applications. This study aims to synthesize, characterize and study the physicochemical and thermal properties of stearic acid and paraffin incorporated with aluminium as filler for the development of PCM composite. The PCM composites were prepared using 80wt% for the Al/SA and 80wt% Al/paraffin, respectively. The PCM composites were characterized using thermal gravimetric analysis, differential scanning calorimetry and scanning electron microscopy. Results showed good compatibility in physicochemical properties between stearic acid (SA), paraffin and aluminium (Al), respectively. It was observed that the thermal stability studied using thermal gravimetric analysis revealed slightly better stability exhibited by the paraffin PCM composite. This was as a result of the steeper slope exhibited by the stearic acid TGA curve as against that of the paraffin curve. Also, density analysis has resulted in an increment for both composite materials whereas; aluminium incorporated in paraffin composite has shown higher increment of density as compared with stearic acid composite. Therefore, PCM composite made from paraffin will be more effective as a TES material when used industrially as compared to the stearic acid PCM composite.

1. Introduction
Besides the high usage of fossil fuels coupled with the rise in cost of renewable energy, demand for energy has been on the increase very recently [1]. This has resulted to energy crisis and rising demand from time to time [2]. Furthermore, generation of aluminium waste has also increased yearly and has become a significant burden to landfill. From 1960 to 2015 the amount of aluminium in landfill increased from 340 tons to 3610 tons and since aluminium waste is non-biodegradable, landfill disposal is not a suitable option anymore [3]. Many countries offer a solution to reduce, reuse and recycle the aluminium waste since recycling 1 ton of aluminium waste can save up to 10 cubic yards of the landfill

yards [4]. It has therefore become more valuable to find a solution to reduce the amount of waste aluminium by reusing the aluminium waste.

The industrialization growth era, demand and growth of energy supply in many applications have resulted in supply difficulties, thereby decreasing non-renewable energy resources and environmental problems [5]. In Malaysia, about 82.1% usage of fossil fuels is recorded followed by hydro power which is about 14.0% [6]. In order to meet the energy requirement and solve energy challenges ranging from environmental pollution to high cost, thermal energy storage (TES) systems; devices that can protect the environment from pollution and minimize depletion of fossil fuels can be applied [7], [8].

TES is an emerging method for saving energy via sensible heat storage, latent heat storage and chemical reaction energy storage [7], [9]. TES can be classified into two major storages; the sensible heat and latent heat energy storage. The latent heat thermal energy storage (LHTES) is mainly used industrial application [10], [11], [12]. One way to store these heats is via the application of the PCM. PCM's are commonly used for energy supply, demand and space as a result of their high energy storage density and its ability to absorb and liberate large quantity of energy with the least change in temperature [13]. Compared to other PCMs, the Solid-liquid PCM has been better studied and researched upon amongst material used in latent heat storage due because of its high capacity to store latent heat storage [14]. Latent heat of PCM stores energy approximately 5 - 10 times that of the sensible heat storage [11], [13].

PCM can be categorized into 3 types of components which are organic, inorganic and eutectic mixture [15]. Eutectic mixture is a mixture of more than one component either from inorganic-inorganic, organic-organic or organic-inorganic materials forming a mixture of crystals during crystallization [9], [13]. Organic PCMs are widely used in many applications because of their thermal and physicochemical properties [16]. For the organic PCMs, they are classified as paraffin and non-paraffin. Fatty acids; which are categorized as non-paraffin PCM has received the most attention from researchers since it was proven to be effective as PCM in building applications such as air-conditioning system and solar heating water systems [17]. PCM wallboards which are being applied in building applications is the passive system that can improve the comfort of the indoor environment [11]. For instance, an application of PCM is the free cooling system which enables it store coolness outdoor at night and release it during the day [13].

There are many previous studies that used fatty acids as PCM in their research study [18], [19], [20]. This is because fatty acids and their eutectics have many advantages in terms of their enthalpy phase change, chemical and thermal stability and wide range of melting temperature [9], [21], [22]. Yuan et al. [17] used eutectic mixture that consisted capric-palmitic-stearic acid as PCMs, since eutectic mixtures can enhance the properties of PCM by lowering the melting point with a certain ratio and also the eutectics fatty acids was incorporated with activated carbon to enhance the PCM's thermal conductivity (TC). In order to prevent leakage in the PCM composite, Lin et al. [14] chose palmitic acid as PCM for thermal energy storage and polyvinyl butyral as supporting material while being incorporated into graphite to enhance the TC. The result greatly improved the thermal properties and desirable TC.

Drawback of the organic PCM is its low TC; hence, initiatives are taken to incorporate organic PCM with fillers that can improve its TC. There are many types of fillers that can be incorporated into the PCM to improve the thermal properties into favourable thermal conductivities and excellent heat conduction properties. These fillers include carbon nanotubes, carbon fiber, graphite, expanded perlite and activated carbon. High TC is required to make the PCM absorb and release heat faster during the melting and solidification. In a specific application, low TC means the storage absorb and heat release rate are slower throughout the PCM hence, giving disadvantages to certain application [23]. Many researchers have incorporated PCMs with materials that are highly conductive which can improve its thermal conductivities. Dinker et al. [24] enhanced the TC of stearic acid by adding expanded graphite because expanded graphite can increase the rate of heat transfer, have rapid thermal charging and discharging rate and better thermal efficiency. Atinafu et. al.[25] studied the binary eutectic mixture between myristic-stearic acid and mesoporous-N-doped carbon as addictive to improve TC and give solid support to form-stable PCM. Li et. al. [1] studied stearic acid to form shape-stabilized PCM by encapsulating it with titanium dioxide which also have good TC. The significant finding from this

research study is that it resulted to all PCM having improved thermal conductivities when incorporated with good thermal conductivities materials.

There are few studies that have incorporated waste as fillers in organic PCM. Acurio et al. [10] used spent diatomite from palm bleaching process to enhance TC of organic PCM. In their study, commercial stearic acid was applied as support material and incorporated inside the PCM, hence allowing the spent diatomite to enhance TC of PCM and also give a good supporting material from the palm fiber. Yang et. al. [26] studied waste saw-dust as support for polyethylene glycol (PEG). In the study, expanded graphite was also used as TC addictive which resulted in improvement in the TC and good structural support for PCM. Zhang et. al. [27] utilized blast furnace slag that were incorporated with inorganic PCM which includes $NaNO_3$, Al and Na_2SO_4 to produce high temperature composite phase change material. The result showed that $NaNO_3$ was good for TC and also showed good chemical and physical compatibility with the blast furnace slag during the incorporation, since blast furnace slag was a good supporting material. Barreneche et al. [28] used electric arc furnace dust (EAFD) from residue of recycled steel process to form new shape-stabilized PCM composite which enhanced the thermal inertia for storing thermal energy. Also, the use of EAFD as fillers enhanced the insulation properties to the materials.

Therefore, this study compares the thermal and physicochemical properties of the synthesized PCM composite with 80wt% Aluminium (Al) on stearic acid (SA) and 80wt% Aluminium (Al) on paraffin. The Al/SA and Al/paraffin were characterized to obtain their morphological/microstructure and thermal properties.

2. Materials and methods

2.1. Materials
Stearic acid (SA; analytical grade, 97%), purchased from Merck Millipore Co. Ltd. was used as one of the phase change material. In addition, 99 % purity paraffin wax, purchased from Sigma-Aldrich Corporation was employed as the second PCM. Aluminium can, obtained from Kg. Sg. Ikan landfill, Kuala Terengganu were oven dried for 6 h at 100 °C and incorporated into the stearic acid and paraffin wax as fillers, respectively, to improve the TC.

2.2. Pre-treatment and preparation SA/Al
Stearic acid (SA; analytical grade, 97%), purchased from Merck Millipore Co. Ltd. was used as one of the phase change material. In addition, 99% purity paraffin wax, purchased from Sigma-Aldrich Corporation was employed as the second PCM. Aluminium can, obtained from Kg. Sg. Ikan landfill, Kuala Terengganu were oven dried for 6h at 100 °C and incorporated into the stearic acid and paraffin wax as fillers, respectively, to improve the TC.

2.3. Characterization analysis
2.3.1. Scanning Electron Microscopy (SEM). SEM analysis was used to study the microstructural structure of the composite samples. Also, the morphology of the as-prepared composite PCMs was analysed using SEM instrument (SEM Hitachi Se4700). A voltage of 10kV with working distance from 9mm to 10mm was used to obtain clear images of Al/SA. Samples were coated with gold coating before being analysed at $3000 \times$ magnification.

2.3.2. Differential Scanning Calorimeter (DSC). DSC analysis was employed to evaluate the sample's enthalpy and phase change temperature. The PCM composite were measured using a DSC TA Instrument Q1000. The analysis was carried out at temperature ramping of 10°C min^{-1} in a temperature range from -50°C to 250°C. Testing was done using temperature ramping of 10°C min^{-1} (from 25 - 250°C) and cooled until -10°C.

2.3.3. Thermal Gravimetric analysis (TGA). TGA analysis was used to measure the amount/rate of weight change and thermal stability of the samples. TGA for the PCM composites was carried out on a TA Instruments Q500 thermal gravimetric analyser in an N_2 environment. Mass of samples of about 5mg was placed on the TGA pan/boat with a 10°C min^{-1} heating rate until temperature of 900°C was achieved.

2.3.4 Gas Pyconometer (GP). GP analysis gave the accurate composite material densities. Using Micromeritics AccuPyc II 1340, the samples' densities were calculated after N_2 gas was introduced into the sample chamber until the pressure of 20psig was achieved.

3. Result and discussions

3.1. Scanning Electron Microscopy (SEM)
In order to obtain the waste composite PCM morphology, the textural analysis was conducted on 80wt% Al/PCM (PCM; SA and paraffin). The morphology of the various samples is represented in Fig. 1. It can be seen in Fig. 1a that the 80wt% Al/SA sample has highly porous rough surfaces with shiny appearance, which is likely to enhance its TC. Previous studies have shown that porous PCM filler is desirable to enhance surface area contact and increase access of PCM while heating and cooling takes place. For the Al/paraffin composite represented in Fig. 1b, a smooth surface was observed due to the wax-like nature of the composite. Furthermore, the SEM analysis for both samples showed that the aluminum fillers were properly dispersed into the SA and paraffin PCM, respectively which enhances the potentials for better contact surface and TC which are key thermal properties in thermal energy storage industrial applications [30].
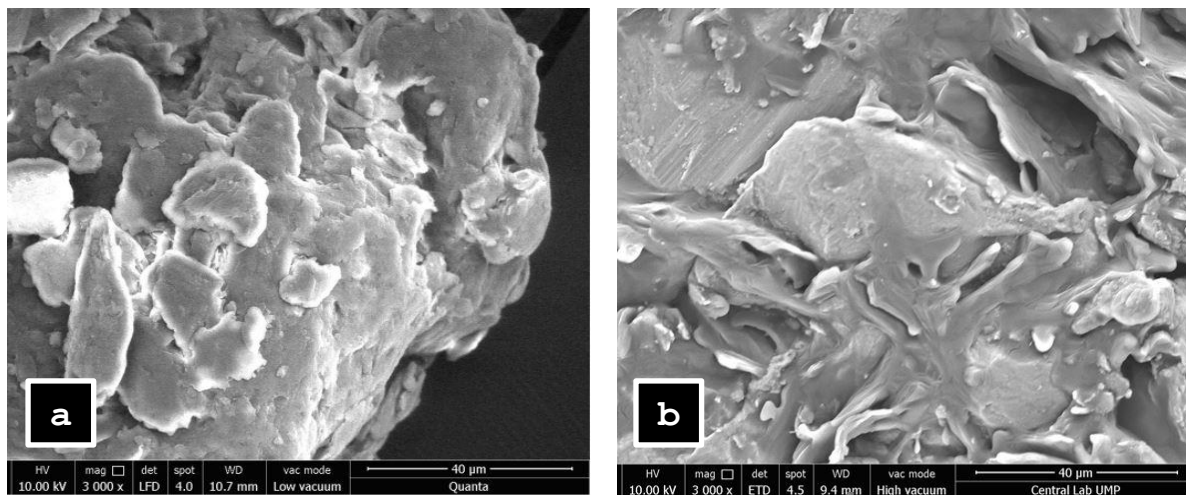

Fig. 1 Surface morphology comparison at 3000 × magnification of a) 80wt% Al/SA, b) 80wt% Al/paraffin.

3.2. Thermal properties of SA and paraffin PCM composite incorporated with 80wt% Al using Differential scanning calorimeter (DSC)
The thermal properties of 80wt% Al/SA and 80wt% Al/paraffin were measured in terms of latent heat occurring during melting and freezing (ΔH_m) and (ΔH_c). The onset melting and freezing temperature (T_m) and (T_c) which occurs during heating and cooling with a 10 °C min-1 heating rate is tabulated in Table 1. The composite sample containing stearic acid has slightly higher latent heat during melting (56.77 Jg^{-1}) than the composite sample containing paraffins (53.05 Jg^{-1}). For the latent heat during freezing, the values were approximately similar for both PCM composite with the Al/SA having value of 30.31 Jg^{-1} and Al/paraffin having values of 30.63 Jg^{-1}. In the real sense, fillers in PCM composite only slightly helps to sustain the amount of heat in the PCM as the actual absorption of heat and subsequent release is actually carried out by the PCM composite itself. However, in this study, due to the high amount of fillers (80wt% Al), the mass percentage of the PCM is reduced; hence the efficiency of impregnation is also reduced. Yuan et al. [17] in their study also stated that the PCM is responsible for the absorption and release of thermal energy, while the fillers acts as additives which assist in preventing leakages during installation processes of PCM. This means that as the amount of PCM in sample increases, the capacity to store latent heat also increases. Hence, PCM materials with high fillers loading (above 60wt% Al) are likely to have high stability, they are however not suitable for thermal energy applications because of their low capacity to store latent heat.

Table 1. Thermal properties of SA and paraffin PCM composite incorporated with 80wt% Al

No.	Sample	Onset Temperature	Latent heat during heating	Onset Temperature	Latent heat during cooling
		T_m (°C)	ΔH_m(J/g)	T_c (°C)	ΔH_c(J/g)
1.	80wt% Al/SA	56.77	30.87	51.07	30.31
2.	80wt% Al/paraffin	53.05	28.85	55.53	30.63

3.3. Thermal stability of the SA and paraffin PCM composite incorporated with 80wt% Al Thermo Gravimetric analyses (TGA)

Previous studies [31–34] have all reported that thermal stability is vital in determining the effective performance of formulated PCM composites. Fig. 2 represents the TGA profile of 80 wt% Al PCM composites (SA and paraffin), respectively. From the profile, similar weight loss is observed when both samples are heated from 0 to 900 °C. A total weight loss of about 15 % is observed between approximately 220 – 320 °C before the weight stabilizes. Furthermore, it can be seen that the effect of heating the different PCM composite material (in this case; paraffin and stearic acid) was quite similar in terms of the amount of weight loss of the PCM composites. Moreover, Li et al. [32] previously reported that fillers (aluminum) loading is more related to the stability of the composites and have much more significant effect. However, for the sample containing stearic acid, the slope of degradation is slightly steeper than that of the sample containing paraffin, indicative of a slightly better stability exhibited by the paraffin sample as compared to the stearic acid sample.
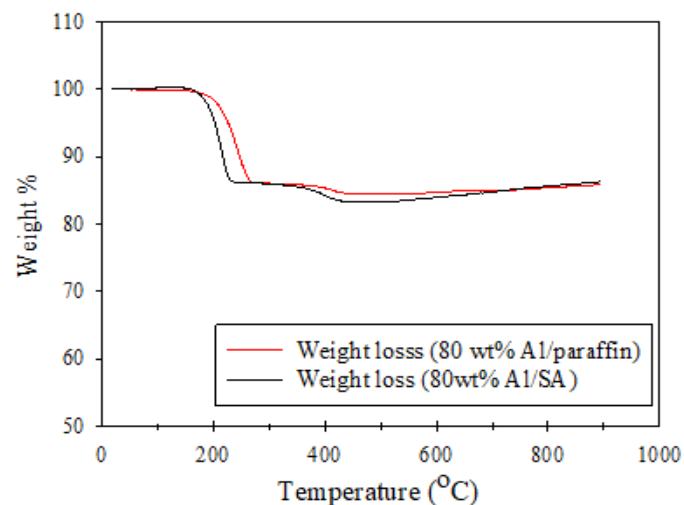
Fig. 2. TGA profile of 80wt% Al/ paraffin and 80wt% Al/SA

3.4. Density measurement of SA and paraffin PCM composite incorporated with 80wt% Al using gas pycnometer analysis

According to Ortega et al. [35] density measurement is one of the thermo-physical properties which measures the potential heat of a storage material as a result of the heat flow of the process. When molecules collide, energy is produced due to heat flow. Therefore, when there is an increase in the collision of materials, a corresponding increase in energy and heat flow is observed. Hence, in Table 2, the density of paraffin, stearic acid and formulated composite material are listed. Referring to Table 2, the density of composite materials is higher when compared with single PCM. Adding waste aluminium into the paraffin and stearic acid increases the density with about 91.94 % for 80wt % Al/paraffin and 89.79 % for 80wt % Al/SA. However, the 80wt % Al incorporated into stearic acid has shown higher density than the 80wt % Al incorporated into paraffin. Although, both formulated composite materials

have the required properties to be good heat storage materials and have great potential towards the TES system.

Table 2. Thermal properties of SA and paraffin PCM composite incorporated with 80 wt% Al

No.	Sample	Average density (g/cm^3)	Increment$= \dfrac{\text{Composite material} - \text{Pure PCM}}{\text{Pure PCM}} \times 100$
1.	Paraffin	0.9132 ± 0.0004	
2.	80 wt% Al/paraffin	1.7528 ± 0.0010	91.94%
3.	Stearic acid	1.0338 ± 0.0001	
4.	80wt% Al/SA	1.9621 ± 0.0014	89.79%

Conclusions

In this study, aluminium was incorporated into two different PCM composite materials; paraffin and stearic acid, to ascertain the morphological, thermal stability and property variation of the PCM composites which are utilized for TES processes. The result revealed that the use of aluminium incorporated into stearic acid and paraffin showed good compatibility in terms of their chemical and physical properties. For the thermal properties, 80 wt% AL/SA had slightly higher latent heat during heating (30.87 Jg-1 at onset temperature of 56.77 °C) than the 80 wt% Al/paraffin (28.85 Jg-1 at onset temperature of 53.05 °C). In addition, slightly better thermal stability was exhibited by the paraffin PCM composite as a result of the steeper slope (weight loss) which was observed in the stearic acid PCM composite. Also, the density analysis revealed that the addition of aluminium into stearic acid and paraffin has improved the thermo-physical properties which translate to enhanced heat and energy storage potentials.

References
[1]   Li C, He G, Yan H, Yu H, Song Y 2018 *Energy Procedia* **152** 390–394
[2]   Wang F, Lin W, Ling Z, Fang X 2019 *Sol. Energy Mater. Sol. Cells* **191** 218–234
[3]   United States Environmental Protection Agency (EPA) 2018 Retrieved from Facts and Figures about Materials, Waste and Recycling - EPA: https://www.epa.gov/facts-and-figures-about-materials-waste-and- recy, Dec 17, 2018
[4]   The Aluminium Association. 2018 Retrieved from The Aluminium Association: https://www.aluminum.org/industries/production/recycling, Dec 18 2018
[5]   Memon S A, Lo T Y, Cui H 2013 *Energy Build.* **66** 405–414
[6]   Energy Consumption in Malaysia 2015. Retrieved from Worlddata.info: https://www.worlddata.info/asia/malaysia/energy-consumption.php, June 2015
[7]   Li M, Mu B 2019 *Appl. Energy* **242** 695–715
[8]   Liang J, Zhimeng L, Ye Y, Yanjun W, Jingxin Y, Changlin Z 2018 *Energy Build.* **171** 88–99
[9]   Zhang X, Huang Z, Yin Z, Zhang W, Huang Y, Liu Y, Fang M, Wu X, Min X 2017 *Energy Build.* **154** 46–54
[10] Acurio K, Chico-Proano A, Martínez-Gómez J, Ávila C F, Ávila Á., Orozco M 2018 *Constr. Build. Mater.* **192** 633–642
[11] Yuan Y, Zhang N, Tao W, Cao X, He Y 2014 *Renew. Sustain. Energy Rev.* **29** 482–498
[12] Caliano M, Bianco N, Graditi G, Mongibello L 2019 *Appl. Energy.* **256** 113-121
[13] Kalnæs S E, Jelle B.P 2015 *Energy Build.* **94** 150–176
[14] Lin Y, Zhu C, Alva G, Fang G 2018 *Appl. Energy* **228** 1801–1809
[15] Gulfam R, Zhang P, Meng Z 2019 *Appl. Energy.* **238** 582–611
[16] Sharma R K, Ganesan P, Tyagi V V, Metselaar H S C, Sandaran S C 2015 *Energy Convers. Manag.* **95** 193–228
[17] Yuan Y, Li T, Zhang N, Cao X, Yang X 2016 *J. Therm. Anal. Calorim.* **124** 881–888
[18] Bashiri Rezaie A, Montazer M 2020 *Appl. Energy.* **262** 114501.

[19]   Jin J, Liu L, Liu R, Wei H, Qian G, Zheng J, Xie W, Lin F, Xie J 2019 *Constr. Build. Mater.* **226** 616–624

[20]   Yang L, Cao X, Zhang N, Xiang B, Zhang Z, Qian B 2019 *Sustain. Cities Soc.* **46** 101380

[21]   Song X, Cai Y, Wang W, Sun X, Wu Y, Wei Q, Hu Y 2019 *Sol. Energy Mater. Sol. Cells.* **191** 306–315

[22]   Murthy R B V, Gumtapure V 2019 *J. Energy Storage* **25** 100870

[23]   Boussaba L, Makhlouf S, Foufa A, Lefebvre G, Royon L 2019 *J. Build. Eng.* **21** 222–229

[24]   Dinker A, Agarwal M 2008 *Certif. Int. J. Eng. Sci. Innov. Technol.* **9001** 2319–5967

[25]   Atinafu D G, Dong W, Huang X, Gao H, Wang G 2018 *Appl. Energy.* **211** 1203–1215

[26]   Yang H, Wang Y, Liu Z, Liang D, Liu F, Zhang W, Di X, Wang C, Ho S H, Chen W H 2017 *Bioresour. Bioprocess.* **4** 52-64.

[27]   Zhang Y, Liu J, Su Z, Liu B, Lu M, Li G, Anderson C, Jiang T 2018 *Constr. Build. Mater.* **177** 184–191

[28]   Barreneche C, Navarro M E, Niubó M, Cabeza L F, Fernández A I 2014 *Energy Build.* **68** 1–6

[29]   Zhang H, Baeyens J, Cáceres G, Degrève J, Lv Y 2016 *Prog. Energy Combust. Sci.* **53** 1–40

[30]   Wu S, Li T X, Yan T, Dai Y J, Wang R Z 2016 *Int. J. Heat Mass Transf.* **102** 733–744

[31]   Magendran S S, Khan F S A, Mubarak N M, Vaka M, Walvekar R, Khalid M, Abdullah E C, Nizamuddin S, Karri R R 2019 *Nano-Structures & Nano-Objects* **20** 100399

[32]   Li C, Wang M, Xie B, Ma H, Chen J 2020 *Renew. Energy.* **147** 265–274

[33]   Li C, Li Q, Cong L, Li Y, Liu X, Xuan Y, Ding Y 2019 *Sol. Energy Mater. Sol. Cells.* **196** 25–35

[34]   Zhang N, Yuan Y, Yuan Y, Li T, Cao X 2014 *Energy Build.* **82** 505–511

[35]   Ortega I, Faik A, Gil A, Rodríguez-aseguinolaza J, Aguanno B D 2015 *Energy Procedia.* **69** 968–977