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Chemisorption cooling and electric power cogeneration system driven by low grade heat

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A B S T R A C T

A novel integration of chemisorption refrigeration cycle and a scroll expander was investigated for the cogeneration of cooling and electric power. The first lab prototype machine has been built, and the two main components were tested both independently and cooperatively for comparison before and after the integration therefore leading to better knowledge of the interaction between them. Two sets of adsorption cycles utilizing the adsorbent compound of calcium chloride and activated carbon worked out-of-phase for the output continuity, and mass recovery was applied to further elevate the performance. In the cogeneration test, the cooling temperature reached 5.4°C as minimum, while the generated electric power achieved the maximum value of 490 W. The valuable experience and the inspiration on system optimization has been reaped and discussed through this exploration.

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1. Introduction

As the rapid development of technologies and the modernisation of society and human life, heating, cooling, transport and industrial processes will need to increasingly be electrified, and that implies electricity demand in UK is likely to increase by between 30% and 100% by 2050, revealed by recent Department of Energy & Climate Change analysis [1]. Meanwhile, with respect to the environmental concerns UK places high hope on meeting the indicative target of creating a decarbonized power sector which requires an emission intensity cut down to a range of from 50 to 100 gCO₂/kWh from current level around 500 gCO₂/kWh, and that makes it radically essential to enhance the energy utilization efficiency by for example realizing enormous potential of recoverable but wasted heat from UK industries which is estimated to be between 10 TWh and 40 TWh per annum [2], or the penetration of renewable energy to cope with the growing energy demand and the accelerated scarcity of resources. UK’s ambition has been formalised to deliver 15% of the energy demand from renewables by 2020 and to increase the amount of electricity generated by renewables from current 11% to around 30% by that time.

A combined electric power and refrigeration system based on absorption technology driven by low or medium grade heat (like waste heat, solar thermal or geothermal heat) attracts attention, due to the improved energy utilisation efficiency and CO₂ emission reduction [3–9]. The gist of the absorption cogeneration adopts the binary mixture of ammonia and water as the working fluid, and has the rich-ammonia solution from the rectifier expanding through a turbine and then exiting the turbine at a low temperature. Thus the cooling effect is extracted from the sensible heat which is unfortunately limited. In the work by Vijayaraghavan et al. [7], low grade heat source from 87 °C to 207 °C were applied to an absorption-based cogeneration system to assure low temperature exhausted vapour from the turbine and the total thermal efficiency of this theoretical analysis was from 0.05 to 0.12. Later, Liu and Zhang’s work [8] employed separated cooling and power subcycles with heat source around 450 °C to improve the cogeneration capacity. Their design utilized a splitting/absorption unit to maintain the desired ammonia concentrations in different processes and a throttle valve to ensure the sub-cooling state of the working fluid before evaporation. All those additional equipment arrangements further highlighted the system complexity, though the refrigeration...
efficiency and the electricity output efficiency were improved up to 0.06 and to 0.21, respectively.

Adsortion is alternatively appealing refrigeration technology capable of recovering low grade thermal energy. In the desorption process of adsorption cycle, the working fluid vapour is released at high temperature and high pressure, which is capable of driving a turbine/expander to generate mechanical energy or electricity if a generator is attached; in the adsorption process, the cooling effect is produced via evaporation of the working fluid. The significant features of adsorption compared to absorption are: the less complex construction i.e. eliminating auxiliary devises such as a liquid pump, the rectifiers or separators for refrigerator, therefore leading to reinforcement of system reliability and compactness [10–12]; the potentially higher refrigeration efficiency in cogeneration scenario due to the fact that electricity generation and cooling generation are relatively separated in different half cycle [13]. Although the tempting advantages embodied in the adsorption, the concerns with respect to its distinctive characteristics would be: (1) unlike stable and continuous output from absorption, the varying evolutionary profile of chemisorption would affect the stability of electric power generation if integrated with an expansion process; (2) vice versa, the expansion process would compromise the adsorption cycle performance. To discover the mystery, an Ad-Cogen (adsorption cogeneration) prototype system has been designed, manufactured and experimentally investigated in this work for the viability demonstration and influential parameters identification. The system comprised with two adsorption units to overcome the intrinsic intermittence, which employed the compound of CaCl2 and activated carbon as adsorbent with ammonia as the working fluid (termed as ‘refrigerant’ in the following sections), and one oil-free scroll expander, which is recognized as the preferable choice to convert low grade heat to electricity especially for small scale power generation [14–17]. The interaction between these two main components has been analysed through the comparison between the individual and incorporated performance. Potential approaches are discussed to guide the further optimization work on Ad-Cogen.

2. Cogeneration principle and theoretical analysis

The synergy operation of two adsorption units realizes continuous cogeneration. Each adsorption unit was composed of one adsorbent bed, one condenser and one evaporator as shown in Fig. 1. A boiler and a water vessel were designated to generate heat source steam and to store heat-sink water, respectively. On one side, the desorbed refrigerant entered the expander to convert thermal energy to mechanical energy while on the other side the adsorption extracted vaporized refrigerant from evaporator to yield cooling effect.

The cogeneration principle is described as follows:

(1) Electric power generation. As shown in Fig. 1(a), Ads 1 (adsorbent bed 1) is heated by hot steam that comes from the boiler through valve V1 and then return to the boiler via V3. Because of heat input the thermodynamic state of the salt complex in Ads 1 deviates from the equilibrium, and that releases high temperature and high pressure refrigerant vapour heading towards the expander through one-way valve and valve V5, resulting in work output which could generate electric power if a generator mounted. The exhausted refrigerant flows through V6 and the Con 1 (condenser 1), and ends up in the Evp 1 (evaporator 1).

(2) Cooling power generation. The internally circulated heat-sink water remains at certain temperature and dissipates heat through a plate heat exchanger that is connected with an external cooling tower. In order to simplify the water pipeline and to compact the whole system, the internal heat-sink water maintains a constant circulating route, flowing through Con 2, Con 1 and Ads 2 (or Ads 1 depending on cycles) sequentially before finally return to the water vessel. Once the Ads 2 is being cooled down, it starts to adsorb the refrigerant from the Evp 2 where the refrigerator experiences evaporation while it captures vaporization heat from surroundings. That is how the cooling effect is produced.

(3) Synchronized performance and alternate operation. As depicted in above (1) and (2), Ads 1 is undertaking decomposition while Ads 2 is simultaneously carrying out synthesis process. Afterwards, the performance of these two adsorbent beds swap, i.e. switch three-way valve V1, V2 and V3, close V5, V6, V10 and open V7, V8, V9 valves as shown in Fig. 1(b), Ads 1 would be disconnected from expander and absorb refrigerant from Evp 1 to generate cooling while Ads 2 would be integrated with expander and undertake desorption to supply electric power generation with refrigerant.

(4) Repeat above three steps to achieve continuous cogeneration. A mass recovery process, where adsorbent uses a pressure equalization technique, is introduced at the switch interval to enhance the cyclic refrigerator quantity and boost the performance. In other words, at the end of a half cycle when Ads 1 is desorbing refrigerant vapour and becoming less saturated but its pressure is higher from the external heating, while Ads 2 is adsorbing vapour and approaching saturated state but its pressure is lower due to the external cooling, the mass recovery could be triggered by opening the valve connecting Ads 1 and Ads 2 for a short time period (45 s in this work). Therefore the pressures in two beds become equalized, and the sudden pressure swing results into that: Ads 1 experiences a further desorption and simultaneously the Ads 2 undergoes an extended adsorption, leading to the increment in the cyclic transferred amount of refrigerant. This approach has been proven effective in many works [18–20].

Fig. 2 illustrates an ideal working principle in Claperon diagram as CaCl2 being the reactive adsorbent. A to B in Fig. 2 represents the heating process of the adsorbent. The temperature and pressure of the adsorbent escalate along the equilibrium line without any reaction happening until the adsorbent pressure (point B or B') is higher than the saturated pressure of the refrigerator ammonia corresponding to the heat sink temperature (point D), then the pressure difference propels the decomposition and the refrigerator transfers. The process B to C symbolises an isentropic expansion process. For the purpose of improving output power, as B' point displayed in
Fig. 2, the heating temperature could be adjusted higher to achieve distinct increment (comparing $B_0$ to $B_1$). The process of $B$ to $C$ is followed by a refrigerant condensation, from $C$ to $D$ to $E$. Afterwards, once the adsorbent receives sufficient cooling and the pressure of it drops below that of saturated refrigerant at the required low temperature, $E$ to $A$ process occurs as it indicates the synthesis of the salt complex at the meantime the refrigerant evaporation, and its finishing then marks the closure of a complete cycle.

3. Experiment set-up and process

3.1. Experimental set-up

Fig. 3 are the photos of Ad-Cogen prototype system. Four shell-and-tube type vessels were used as two adsorbent beds, each contained two connected vessels and each vessel wrapped 6 finned pipes. There were 17.5 kg CaCl$_2$ impregnated in activated carbon.
with a mass ratio of 4:1 to form the compound adsorbent which was squeezed into the fi n gaps of the fi nned pipes, while the heat exchange fluid fiowed through the fi nned pipes and the refrigerant vapour occupied the rest space inside the shell. Activated carbon can effectively enhance the mass transfer and adsorption effec-
tiveness due to its porous construction and additional physical adsorption capacity [21–23]. The condensers were also shell-and-tube type, with the heat-sink water in tubes and the refrigerant vapour in the shell. The evaporators were installed with electric heaters, by which the electricity energy consumed for heating liquid refrigerant to remain at required low temperature level was registered. Based on the thermal balance theory, this electricity could be reckoned equal to the useful cooling capacity. Such a design enhanced system compactness and eliminated some possible distractions. The system was charged with around 28 kg ammonia, which was determined by the stoichiometric amount corresponding to CaCl2 amount plus the extra amount that was estimated for half-full evaporator to avoid dry-heat of the heater.

An oil-free scroll expander (E15H22N4.25, designed and produced by Air Squared Company ©), with nominal output of 1 kW attached with an AC generator (Voltmaster ©, AB30L (WEIPU)) via magnetic coupling was employed in this work, which had an expansion ratio of 3.5:1 and displacement of 12 cc/rev. The magnetic coupling eliminated any refrigerant leakage path. A few light bulbs with a total nominal power around 800 W were the load bank.

Pressure sensors (full scale from 0 to 2.5 MPa with tolerance of ±0.1%) were placed at the inlet and outlet of the expander and in the adsorbent beds as well as the evaporators. Pt 100 thermal resistance temperature sensors were used with 0.5% accuracy. A vortex flow metre with tolerance of ±1% was mounted along the straight pipeline before the expander. A power metre (Qingzhi ©, ZW2613, 0.5% accuracy) was registering the real-time output in terms of voltage, current and power. A Pocket Tachometer HHT12 from OMEGA © was used for expander rotation speed measurement with an accuracy of 0.01%, the rest of experimental data were monitored and logged by a DataTaker © DT85. Based on all the accuracies of measurement sensors and power metre, the calculated errors of cooling power, COP (coefficient of performance) and cooling capacity are respectively at 0.5%, 1% and 1.6%.

3.2. Experimental methodology

In order to obtain better knowledge of the system performance for in-depth analysis and of optimization strategies, individual test on each main component was carried out before the cogeneration performance experiment. The refrigeration performance of the adsorption unit has been investigated under different heating temperature, different cycle duration and with or without mass recovery process. The scroll expander was also independently tested with nitrogen gas under different inlet pressure from 4 to 11 bar while the inlet temperature controlled from 28 °C to 30 °C. The exhausted nitrogen was released to atmosphere directly, therefore the expander was running with a pressure difference (ΔPexp) in the range of 3–10 bar.

After the individual tests, the cogeneration system shown in Fig. 3 was tested. The heat source temperature in the boiler was in the range of 120 °C–130 °C, which gave an inlet pressure of the expander up to 12–14 bar (allowing some temperature drop through heat exchanger due to the heat transfer losses). The condensation was maintained at around the ambient temperature from 27 °C to 35 °C (tests in summer time, temperature was wobbling periodically as recurring operation), and the corresponding ammonia saturated pressure was 10.0–13.5 bar.

4. Results and discussions

4.1. Adsorption refrigeration

Fig. 4(a) shows the temperature in condensers/evaporators when two sets of the adsorbent beds were decomposing and synthesizing respectively in alternation during refrigeration test, and Fig. 4(b) are for the corresponding pressure. Comparative analysis between the tests with and without mass recovery was based on two and half stabilised consecutive cycles. The adsorption ability was strengthened by the more suffi cient desorption benefiting from mass recovery, therefore, more cooling power and the higher COP was achieved, which was about 53% and 43% increment respectively compared with non-mass recovery cycles, as shown in Table 1. The bonus of the more fulfilled desorption and adsorption

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Fig. 2. Claperon diagram of CaCl2–NH3 adsorption cogeneration process.

Fig. 3. Photos of the adsorption cogeneration prototype.
processes was the broader span of the temperature and pressure variation, in the other words, potential favourable environment of the larger pressure difference for power generation. The maximum pressure in desorption process of mass recovery cycles was from 2 to 4 bar more than that without mass recovery.

Analysing Figs. 4 and 5 for the performance comparison under different cycle times, the bump as highlighted in Fig. 5(a) appearing in every cycle curve, distinguishes the quick reaction period from the inefficient part throughout the long time process (26 min). The efficient cooling process commonly happened in the first 12–15 min, therefore, the 13 min cycle time would be sensible choice for the presented prototype as being also proven by the data in Table 1. Although the cooling capacity of the 26-min cycles, 430 kJ per kg of CaCl₂ on average was 53% higher than that of 13-min cycles (284 kJ/kg), the cooling power and the coefficient of performance (COP) of the 13-min cycles were 32% and 43% respectively higher than those of the 26-min cycles. The higher cooling power and the higher COP, which indicate the working efficiency and the energy utilisation efficiency, sometimes would be more desired. The poor COP of the latter one can be ascribed to the rewardless heat input during the extra 13-min desorption process, the pressure plateau at the maximum value at the end of each cycle in Fig. 5(b) also hints the very slow vapour regeneration and the majority of energy consumption during that period was presumably wasted for sensible heat instead of the reaction enthalpy.

4.2. Power generation

Nitrogen gas supply for the expander was from nitrogen cylinder, the supplying pressure of the cylinder was adjusted by a pressure regulator and the temperature remained almost constant

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Refrigeration performance of adsorption unit with and without mass recovery, at 13 min or 26 min cycles.</th>
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</thead>
<tbody>
<tr>
<td>Cycle time (min)</td>
<td>Average heating temperature (°C)</td>
</tr>
<tr>
<td>MR</td>
<td>13</td>
</tr>
<tr>
<td>Non-MR</td>
<td>13</td>
</tr>
<tr>
<td>MR</td>
<td>26</td>
</tr>
</tbody>
</table>

Fig. 4. Comparison of the adsorption refrigeration cycles with and without mass recovery when the heat source at 125 °C, heat sink at 27 °C and cycle time of 13 min. (a) evaporation temperature; (b) system pressure.
around 28–30 °C. As the heat convection on the outside surface of the expander could be neglected in this work so that it could be approximately treated as an isentropic expansion, Fig. 6 depicts the performance of the scroll expander at steady state as well as the rotation speed of the scroll under different inlet pressure. The electricity power generation increased approximately linearly from 21 W to 530 W with corresponding rotation speed of from 1650 to 3300 rpm. At the meantime, the temperature of the exhausted gas was around from 10 °C to –17 °C as increasing the inlet gas pressure from 4 to 11 bar.

As can be seen from Fig. 7, the gas could competently afford flat stable supply when the expander inlet pressure was lower (around 4 bar), however, the supply gas pressure became wavy as the required inlet pressure was increasing, naturally leading to un-steady power output as shown in Fig. 7(b). Relatively, higher inlet pressure elevated the rotating speed, thus the expander would tend to extract more working gas into the orbiting chambers, therefore the larger flow rate would be further required for the plateau of power generation. Otherwise both the increasing rotation speed of the expander and the limited supplying gas from nitrogen cylinder contributed to the fluctuating profile at high inlet pressure region in Fig. 7. This also implies how influential the adequate flow rate is towards the stable power output. Predictively, one could consciously think of the dramatically varying desorption rate associated with chemical kinetics potentially exaggerating the fluctuation of the output.

4.3. Cogeneration

As aforementioned, the used heat source in the cogeneration was 120–130 °C, however the released ammonia gas from the decomposition bed was measured at the pressure of 12–14 bar and the temperature of 85–95 °C because of heat transfer temperature difference. Under such condition, it was found that the output electricity power in cogeneration mode as the function of the pressure difference (ΔPex) coincidently almost shared the same linear fitting lines with the tests using nitrogen (4–11 bar, 28–30 °C), and they also had close values with the same ΔPex as shown in Fig. 8. It suggests that the power generation by cogeneration mode is potentially comparable to the traditional mere power generation, let alone that the system could be driven by low grade thermal energy to achieve refrigeration and electricity generation simultaneously.

As cogeneration test, the decomposition reaction was found severely hindered by the existence of expander, because ΔP_ad-con which should have fully focused on the driving force of the decomposition was partially consumed by the expander. The smaller ΔP_ad-con was, the slower desorption rate became, and that suggests the consequently smaller flow rate for the expansion, resulting in unstable rotating movement of the expander or it could be even worse that the expander stopped running. In order to obtain as much power output as possible with current situation, the method that had been tried in this experiment was holding on the flow for a while with the valve V5 shown in Fig. 1(or V7, depending on which one undertakes desorption process) closed and then releasing it. That made the flow rate behaving like pulses as shown in Fig. 9 which depicts one power generation cycle on each set of adsorption group. That rendered the expander several segmental power generations as each one lasted for a very short time. The maximum power output was nearly 490 W and the overall average value was 120 W. Since a consecutive generation failed, the total generated electricity amount was quite small. Simultaneously, the refrigeration was also yielded with the minimum temperature down to 5.4 °C in evaporator, and the time length of cooling generation below 15 °C was 3 min. Although manipulating the valves as
aforementioned was not an ideal approach to conduct tests, at least it was worth trying to explore the potential of the cogeneration and other information might be useful for next step of improvement with this first prototype machine which was inevitably flawed. One of the crucial factors to build up an Ad-Cogen prototype was the selection of a small scale expander, which was supposed to match with the magnitude of adsorption chiller for proper and stable operation. However, most of off-the-shelf expander products were neither small enough to couple with predesigned adsorption unit in this work with the given flow rate, nor oil-free to avoid the contamination of the refrigerant ammonia. On the other hand, the size of the adsorption unit was limited by the laboratory scale and the possible complexity. Therefore one system flaw existing from the very beginning was the capability mismatch between the adsorption unit and the scroll expander which was not customised for this test specification. In addition, this expander, the smallest type available during the selection period, has the maximum inlet pressure limited to 13.8 bar, whereas the normal decomposition pressure is at least as high as 20 bar. That was the reason why the heat source in this adsorption test was controlled lower to prevent desorption pressure from exceeding the expander limits, and that compromised the decomposition effectiveness and caused the collateral losses of power generation.

One of the conflicted facts in Ad-Cogen was between the peaked curve profile of desorption rate and the stable input requirement by the steady power generation. As shown in Fig. 7 especially in the high pressure region, the pressure in the central chamber of the expander became wavy when the flow rate was not adequate. Moreover, such a feature would be gradually exaggerated by decreasing the flow rate from that point. The worse scenario is that the refrigerant was supplied by dynamic chemisorption and after the very first one powerful flush at high pressure and relatively high flow rate due to the most efficient reaction at the beginning, there would be a pause waiting for the desorbed refrigerant being accumulated till adequate amount, afterwards the next wave-up power generation could be expected. Moreover, according to our former simulation study [13], the mutual constraint between up-stream decomposition and downstream expansion and the mismatch between them were also playing the important roles causing the non-stable power generation. Because of the similar thermodynamic requirement between desorption and expansion, i.e. both need high pressure at the upstream while low pressure at the downstream, these two would contradict each other if being...
4.4. Potential improved performance

To resolve the root cause of poor performance with the existing design and contradictory natures between components there needs (1) an expander which can withstand higher inlet pressure (should be comparable to the decomposition pressure) and that would allow the heat source being upgraded to, for example, 125 °C (Fig. 2), for this instance, the energy and exergy efficiency with 125 °C heat source are theoretically 0.46 and 0.25 respectively, which are 4.5% and 90% higher than that of using 100 °C heat source; (2) lower temperature heat-sink water to guarantee the lower saturated pressure of the ammonia in the downstream condenser so that there would be a sufficient \( \Delta P_{\text{ex}} \) for example with the given decomposition pressure around 13.8 bar, around 7.5 bar of \( \Delta P_{\text{ex}} \) for 350 W electric power output ideally needs the condensation temperature at 10 °C, and 5.4 bar of \( \Delta P_{\text{ex}} \) for 250 W output needs condensation at 20 °C; (3) implement mass recovery not just at the switch period but also at the time whenever during the process the backpressure of the expander is not low enough, however, it would compromise some cooling product. Off-set operation of mass recovery for two or multi-sets adsorption units could be elaborately arranged to achieve improvement; (4) electricity storage device like batteries or supercapacitors could be considered to store the unstable output from Ad-Cogen, but regenerate electricity later on for stable end use.

A new design shown in Fig. 10 is a potential solution to mitigate the mutual constraint of decomposition in reaction bed and expansion in expander and lead to a fairly stable operation of both components. A secondary condenser is added to the system, which can be installed between adsorbent bed and expander. As illustrated in Fig. 10 the heat exchange fluid running through secondary condenser can be the downstream heat-sink water from primary one. The condensation temperature in the secondary one should be higher than that of the primary one, then the pressure in the secondary condenser will be higher than that in the primary one, which supplies a pressure difference to drive the expander. Meanwhile, the pressure in the secondary condenser must be not too high to pose an obstacle for the decomposition, otherwise there is a risk of no pressure difference between the adsorbent bed and the secondary condenser to drive the decomposition reaction. The key point is just so long as to maintain the temperature of the secondary condenser, the working fluid within it would remain at a certain saturated and stable state. Therefore, the existence of this condenser divides the pressure difference between adsorbent bed and primary condenser into two parts, one stable \( \Delta P_1 \) for decomposition and the other stable \( \Delta P_2 \) for expansion. By installing this condenser, not only the direct connection of adsorbent bed and expander is avoided, but also a buffer area is created to alleviate the mismatch of decomposition rate and the inlet flow rate required by the expander. Then the decomposition and expansion can be considered as two independent processes as long as the pressure (temperature) in the secondary condenser was maintained at desired value. Though the maximum power output would be relatively lower than the original design, the operation of the entire system is expected to be stable and continuous. Theoretically, such a design can make the cogeneration simply equals to the sum effect of combination of decomposition and expansion, and that allows the system performance more foreseeable according to preliminary design.
5. Conclusions

A lab-scale chemisorption cogeneration prototype system was designed, manufactured and experimentally investigated. The prototype system consists of a chemisorption system with two sets of adsorption cycles working out-of-phase for cooling generation and a scroll expander for power generation. As this concept is as novel as it has been the first prototype machine, the viability of adsorption cogeneration has been experimentally investigated. This practical test has collected valuable information and knowledge for further development and optimisation of this technology which would promisingly address the energy scarcity and environmental issues globally confronted.

The major challenges were the capacity mismatch between the two main components, the mutual constrain between the desorption process and expansion process and the contradiction between the desorption rate varying with a peaked curve profile and the stable inlet requirement by power generation. For the direction of developing next generation of adsorption cogeneration system, a couple of optimization methods have been proposed and discussed based on the current design: ample preparation for better match between the adsorption unit and the expander; more sophisticated program and operation of mass recovery; integration with batteries or supercapacitor for unstable electricity output storage and later-on electricity regeneration of stable end use; introducing a secondary condenser between the adsorbent bed and the expander to mitigate the mismatch between them.

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