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Angeles Rivero Pacho
MEng, MSc, PhD,
Winner Ted Perry Student
Research award

Innovation in carbon- ammonia adsorption heat pump technology: a case study

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Why this topic?

This paper presents a piece of award winning research designed to help achieve low carbon heating in domestic buildings. If you are interested in emerging technologies and the analysis of their potential, this paper will provide valuable insights into a very specific area: carbon-ammonia driven heat pump technologies using adsorption cycles.

It covers topics such as computational modelling, heat transfer studies as well as a critical evaluation of the design, manufacture and testing of a modelled heat pump cycle in order to validate the computational modelling.

The contents will be particularly valuable for anyone looking for inspiration in the areas of heat pump development, adsorption cycle application and heat exchanger manufacturing.

Thermodynamic and heat transfer analysis of a four-bed carbon–ammonia adsorption heat pump

1 Introduction

A heat driven heat pump was chosen to be developed rather than a mechanically driven vapour compression system, as it uses primary energy sources more efficiently and can use energy from renewable sources such as solar collectors or waste heat from other sources.

An adsorption system was used instead of an absorption one, because of their low operational cost and maintenance, higher reliability, simple and continuous operations and no crystallisation, corrosion or chemical disposal issues.

A carbon-ammonia pair was chosen because ammonia is a good refrigerant due to its high latent heat and small and polar molecules which improve its adsorption by the adsorbent. In addition its high operating pressures avoid mass transfer effects in the adsorption generators. Ammonia does not harm the ozone layer and has no global warming potential. Active carbons are relatively inexpensive, have a high density, can adsorb high quantities of ammonia and their activation can be tailored to their application.

The objectives of the project were:

- To carry out the computational modelling of a four-bed heat pump cycle.
- To carry out a heat transfer study of the active carbon available for the heat pump in order to identify the best sorbent sample.
- To design, manufacture and test the modelled heat pump cycle in order to validate the computational modelling.

2 Adsorption cycle

The most basic adsorption refrigeration cycle is shown in Figure 1 where two linked vessels are presented. The vessel on the left hand side acts as the generator, containing the solid adsorbent and adsorbed refrigerant, whilst the vessel on the right hand side acts as a receiver, condenser and evaporator during the cycle, containing refrigerant gas.

In the Stage (a) of the cycle the system is at low pressure and ambient temperature. The adsorbent contains a high concentration of adsorbed refrigerant whilst the right hand vessel contains refrigerant gas. When the vessel on the left is heated, the adsorbed refrigerant gets driven out and the pressure of the system increases. In Stage (b) the pressure of the system is high enough so that the refrigerant gas starts to condense in the right hand vessel whilst rejecting heat. After that the generator is cooled back to the initial low temperature re-adsorbing the refrigerant in the adsorbent material which creates a drop in the pressure of the system. When the pressure drops, the liquid refrigerant boils and produces the cooling effect, absorbing heat. In Stage (c) the system returns back to the initial state and the cycle is completed.

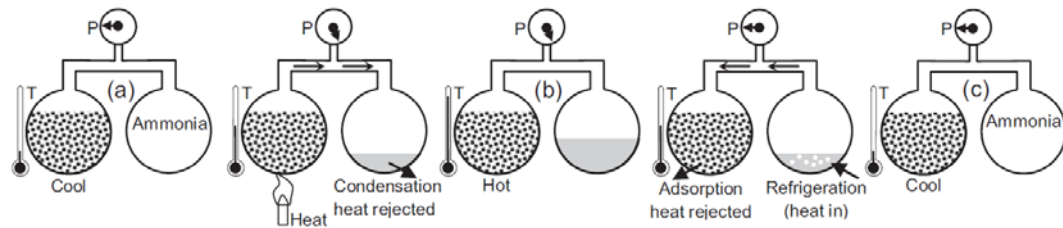


Figure 1 – Simple adsorption cycle schematic [2]

The cycle provides heating / cooling discontinuously for approximately half of the cycle time. If two or more generators are operated out of phase, the heating / cooling could be produced continuously. When continuous heating / cooling is produced the right hand vessel mentioned above is usually split into two separate components: a condenser and evaporator. Each generator of the system is connected to the condenser and to the evaporator via separate automatic check valves. Once the refrigerant is desorbed from the generator, it is condensed in the condenser and it passes through an expansion valve to reduce its pressure. After that the refrigerant evaporates in the evaporator and finally it can be adsorbed in the generator completing a cycle.

The ideal adsorption cycle assumes that the condensation and evaporation occur at constant pressures and that the void volume in the bed is zero so that the pressurisation and depressurisation are isosteric processes.

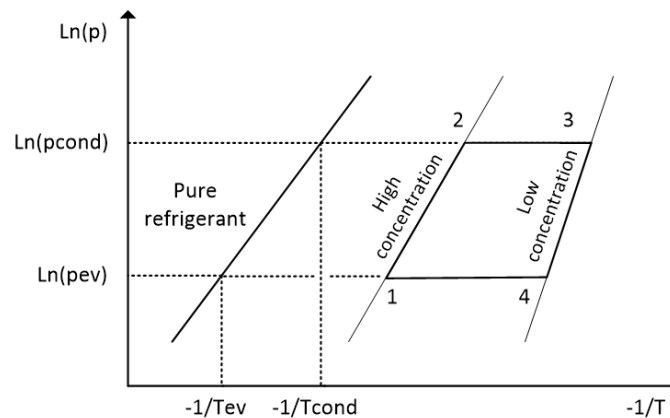


Figure 2 – p-T-x (Clapeyron) diagram for a single adsorption cycle

Figure 2 presents the adsorption cycle, that can be described in four stages:

- Stage 1 → 2 – isosteric pressurisation: The adsorbent in the bed is heated and its pressure rises from evaporating to condensing pressure.
- Stage 2 → 3 – isobaric desorption: The adsorbent continues to be heated and starts desorbing refrigerant at the condensing pressure while the refrigerant condenses in the condenser.
- Stage 3 → 4 – isosteric depressurisation: The adsorbent in the bed is cooled and its pressure decreases from condensing to evaporating pressure.
- Stage 4 → 1 – isobaric adsorption: The adsorbent continues to be cooled and starts adsorbing refrigerant at the evaporating pressure while the refrigerant evaporates in the evaporator.

The COP of the basic adsorption cycle presented above is quite low. In order to increase it, heat regeneration techniques that allow efficient heat transfer from one adsorption generator to another should be used. Multiple bed cycles are a simple but way of achieving heat recovery between the generators, in addition a good heat transfer design in the generators is needed to achieve a good performance.

3 Specifications of the product

The designed heat pump in this project was intended to be used in a domestic environment (space and water heating), replacing a gas condensing boiler, the most widespread product used for domestic space heating in the UK. The domestic market has potential for significant reductions in energy usage and therefore carbon dioxide emissions.

For space heating of a typical family home in the UK, a three bedroom semi-detached house, which is required to be maintained at an internal temperature of 18 °C, the heat pump should supply a heating power of 7 kW [3].

An overview of the system design is shown in Figure 3. The machine was driven by the heat supplied by a gas burner and used pressurised water as heat transfer fluid. The water used in the heating system of the house is passed through the ammonia condenser and then through the cooler (fluid to fluid heat exchanger) where it increases its temperature.

The prototype of the heat pump designed and modelled was an air source heat pump.

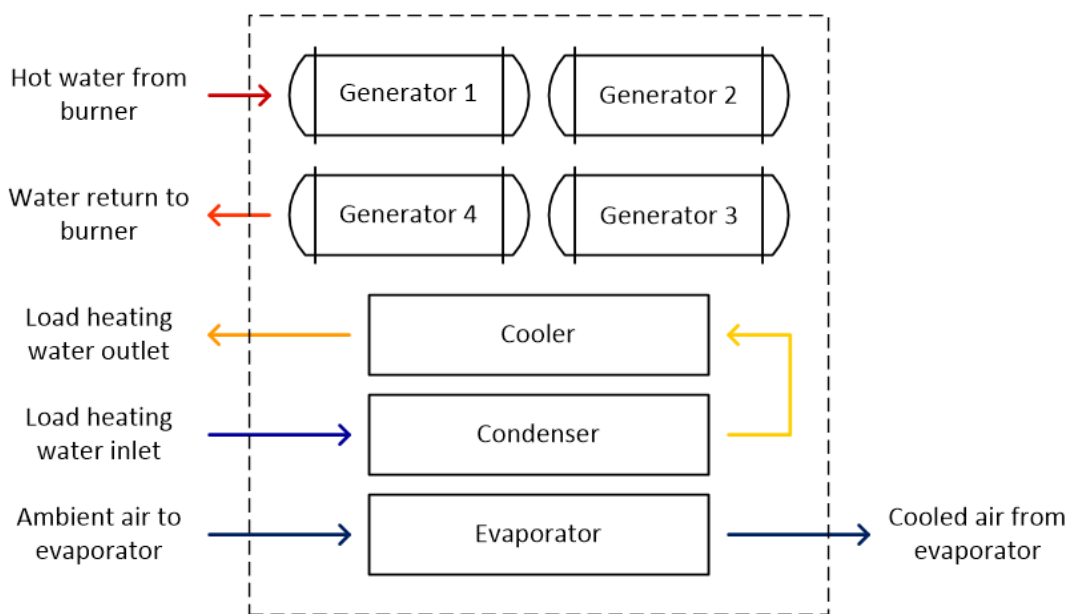


Figure 3 – Heat pump system diagram

4 Generators design

The generators or sorption beds are heat exchangers that transfer heat between the sorption material (active carbon) and the heat transfer fluid (water). The type of heat exchanger used in this project was shell and tube.

The core of generators was made of stainless steel 304 and their tubes had an outer diameter of 1.2 mm and an inner diameter of 0.8 mm. The end plates of the generators had a diameter of 144.5 mm and 1777 tubes that were nickel brazed together creating the core of the generator.



Figure 4 – a) Generator core, b) Generator shell

After the core was filled with the chosen sorption material, it was slid inside the generator shell. The shell had three openings, one of them was used both as an ammonia inlet from the evaporator or outlet to the condenser, the second one had an ammonia relief valve connected, and the third opening had a pressure sensor and the ammonia feed connector fitting connected.

Once the generator is placed in the shell two spiral water distributors are placed at both ends of the core. These water distributors were manufactured by a rapid prototyping machine and were made of a high performance thermoplastic with a glass transition temperature of 186 °C. They were used to distribute the heat transfer fluid (water) evenly among all the generator tubes and create a uniform temperature fluid front.

Finally, two flanges were attached at the ends of the shell completing the generator assembly.

Active carbon specifications

The granular and powder carbon used in the generators were supplied by Chemviron Carbon Ltd., both being type 208C based on coconut shell precursor. The specifications of the different carbon sizes are shown in Table 1.

Size	Max. sieve opening	Min. sieve opening	Bulk density
12 x 30 USS	1.7 mm	600 µm	560 kg/m ³
20 x 40 USS	850 µm	425 µm	527 kg/m ³
30 x 70 USS	600 µm	212 µm	553 kg/m ³
50 x 100 USS	300 µm	150 µm	513 kg/m ³
Powder	180 µm	0 µm	544 kg/m ³

Table 1 - Granular carbon specifications

5 Sorption material thermal properties enhancement

The heat transfer characteristics of different carbon samples of grains and powder suitable for adsorption heat pumping purposes were measured and analysed. The characteristics studied were the intrinsic thermal conductivity of the sorption material in the generators and the wall contact resistance between the tubes of the generators and the sorption material (measured as a contact layer thickness of air).

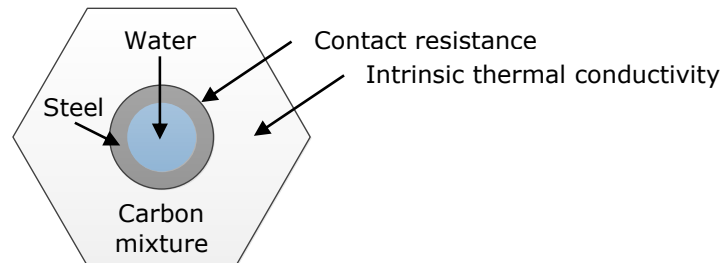


Figure 5 – Heat transfer in a single tube of the generator

The samples studied were the carbon grains mentioned earlier as well as binary mixtures of different ratios of grains and powder. Every grade was measured on its own and then three binary mixtures of 66.7% grains - 33.3% powder, 50.0% grains - 50.0% powder and lastly 33.3% grains - 66.7% powder (by weight) for each carbon grain were measured.

The heat transfer characteristics were measured using two different methods, steady state and transient.

Steady state flat plate measurements

The effective thermal conductivity of the carbon samples was directly measured following the ASTM E1530 – 11 Standard Test Method the Guarded Heat Flow Meter Technique [4], using an Anter Quickline-10TM machine. A 2-inch in diameter carbon sample is placed in between the flat plates of the machine while a heat flux across the sample is generated.

Once a complete set of effective thermal conductivity data for all the samples is obtained it is possible to calculate their intrinsic thermal conductivity. The difference between the effective and the intrinsic thermal conductivities is that the first one neglects the effect of the contact resistance between the sample and the sample holders whilst the latter measures the thermal conductivity within the bulk of the material.

Transient hot tube measurements

The transient hot wire (or in this case, hot tube) technique is well-developed and widely used for measuring the thermal conductivity of fluids and solids. It consists of a tube of a resistive element immersed in the solid sample and the experiment is simply performed by recording the voltage change over the source/sensor element while its temperature is raised by an electrical current. The source element in this case is a stainless steel tube extracted from one of the sorption generators. A computational simulation was developed in order to analyse the results obtained in the transient hot tube experiments.

The relationship between intrinsic thermal conductivity and density obtained with the two techniques is plotted in Figure 6 and the relationship between the contact air layer thickness between the hot tube and the carbon sample and the sample densities obtained by the transient technique is plotted in Figure 7 for the different carbon mixtures.

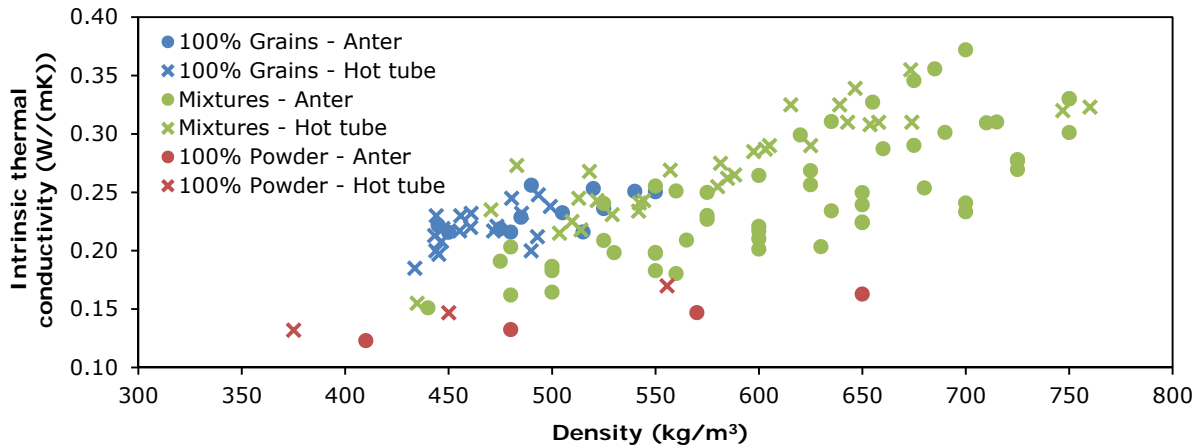


Figure 6 - Intrinsic thermal conductivity of various grain sizes and powder mixtures measured by steady state and transient techniques

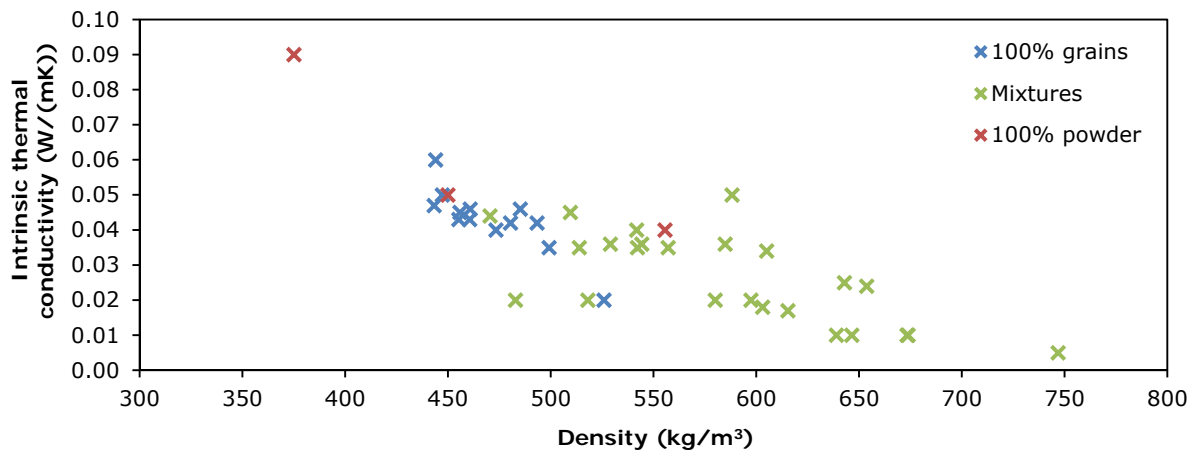


Figure 7 – Contact air layer thickness of various grain sizes and powder mixtures measured by transient technique

The heat transfer characteristics of the best carbon mixtures obtained in the experiments were evaluated for heat pumping purposes with the shell and tube heat exchanger used in this project.

The relationship between the intrinsic carbon thermal conductivity and the ammonia contact layer thickness is plotted in Figure 8 for different combinations of three different carbon thickness layers that surround the generator tubes, 0.25, 0.5 and 0.9 mm, and an U-value of 600 W/(m²K).

The relationship is an approximation of conductive radial heat transfer through a thin layer (modelled as a slab) of carbon plus convective heat transfer modelled as a conductive thin layer of gas (ammonia). In addition to the curves, the best heat transfer performing sample values obtained in the thermal conductivity and thermal contact resistance experiments are shown.

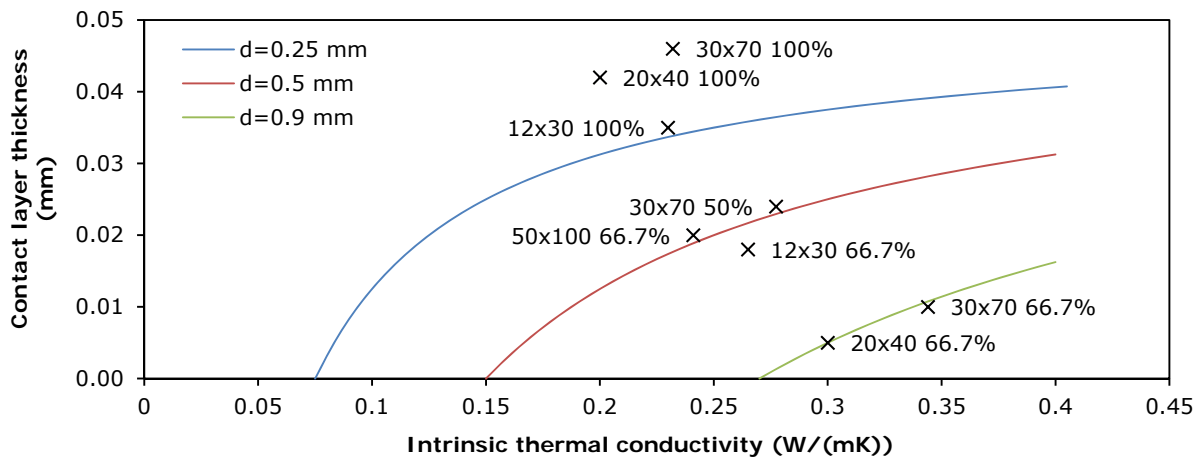


Figure 8 – Relationship between carbon intrinsic thermal conductivity and ammonia contact layer thickness for a generator U-value of 600 W/(m²K) at different surrounding carbon layer thickness and the best performing experimental values obtained

The samples plotted next to the green curve comprise carbon samples of 66.7% of 30x70 and 20x40 grains. They achieve the highest intrinsic thermal conductivities (around 0.325 W/(mK)) and lowest air contact layer thickness (around 0.01 mm) of all the samples tested. According to the calculations these samples could achieve the desired U value with a surrounding carbon layer around the tubes of 0.9 mm that corresponds to the current generator’s geometry.

6 Model programming and simulation results

A computational model using a two-dimensional finite difference grid was written in order to analyse the performance of the four-bed heat pump cycle.

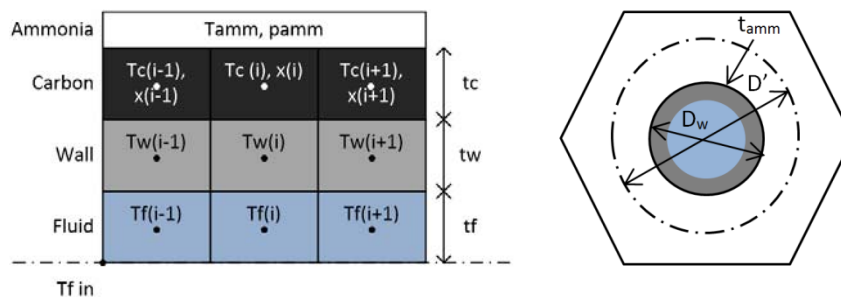


Figure 9 – a) Schematic diagram of the modelled generator, b) Cross section area of a generator’s tube with convective effect of ammonia on the tube

The generator model is a lumped finite difference model in which the heat transfer fluid, the wall and the sorption material are represented by single elements, as shown in Figure 9a. The generator model contains two heat transfer coefficients, one between the fluid and the wall and other between the wall and the carbon grains mixture. In the case of the wall-carbon heat transfer coefficient it is assumed that there exists a wall contact resistance equivalent to the resistance effect of a thin layer of ammonia around the wall, Figure 9b.

In Figure 10a the heating COP is plotted against the specific heating power for the complete set of parameters investigated, varying heating fluid mass flow rates and cycle times whilst keeping the heat driving temperature constant at 170 °C, condensing temperature at 40 °C, evaporating temperature at 0 °C and using a thermal conductivity of 0.3 W/(mK). The performance envelope of the machine, trade-off between COP and power output, under the simulated conditions was also plotted.

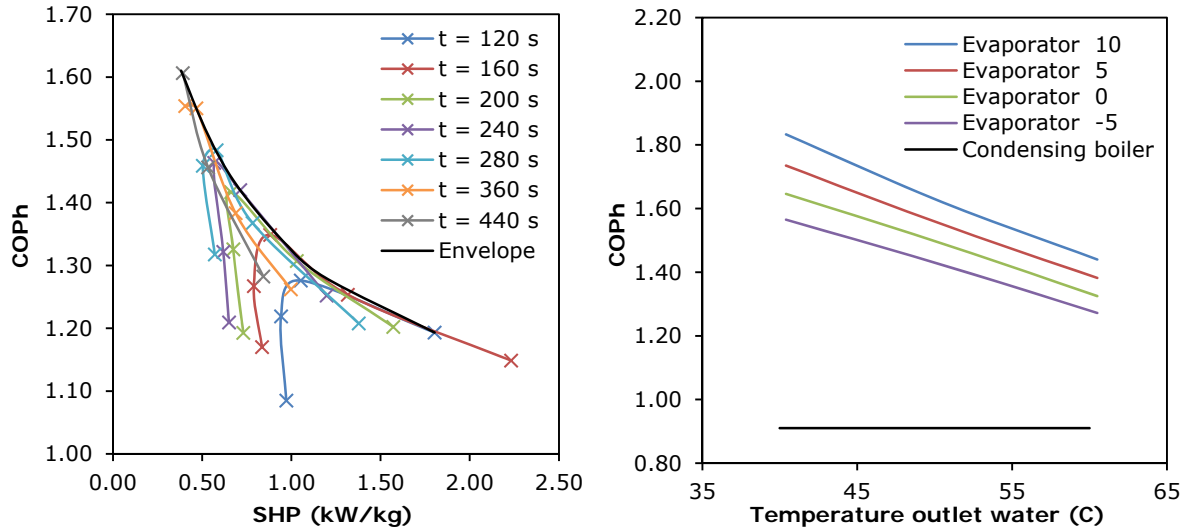


Figure 10 – a) Heat pump operating points and performance envelope (lines of constant cycle time), b) Relationship between the heating COP and the output water temperature for a power output of 7 kW and different evaporating temperatures (comparison a condensing boiler efficiency)

Figure 10b shows the relationship between the heating COP and the output temperature of the water heated by the heat pump at different evaporating temperatures when the power output of the heat pump is 7 kW. Along with the performance of the heat pump, the efficiency of a condensing boiler was also plotted in order to compare them. As it can be seen in the graph, the boiler can produce hot water in the same range as the heat pump but its efficiency remains constant at 91%, much lower than the performance of the heat pump.

7 Construction of prototype system, instrumentation and control

The heat pump prototype was constructed to test the performance of the generators along with the chosen carbon mixture and to validate the computational model developed.

The water schematic and the ammonia pipework of the heat pump are shown in Figure 11a,b.

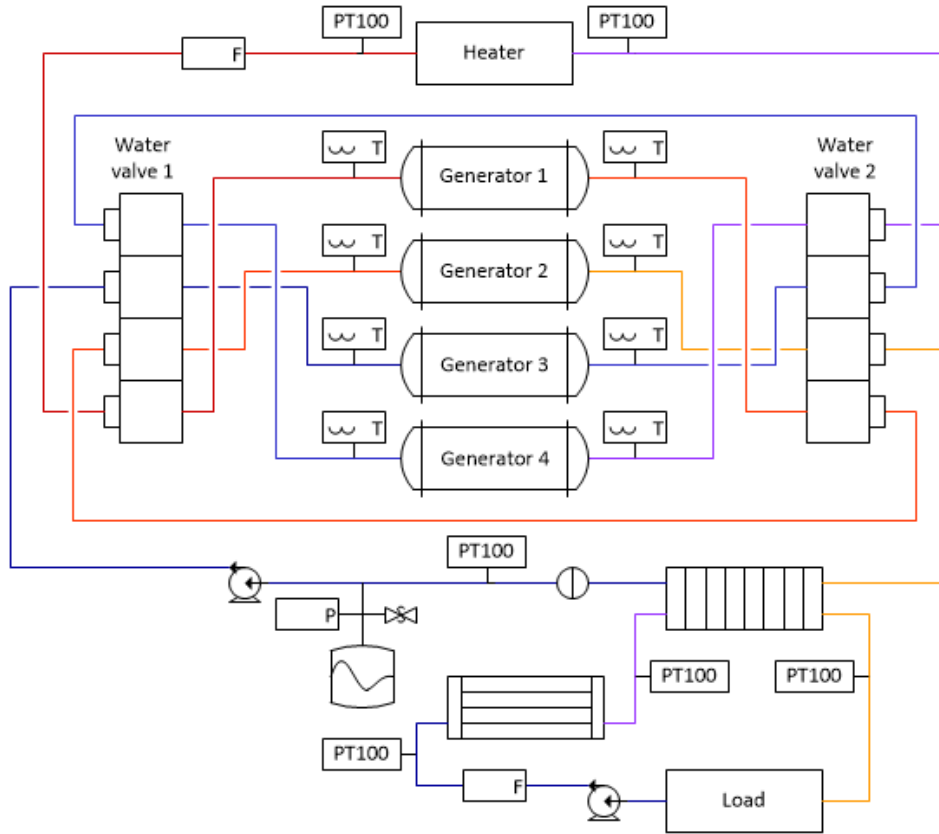


Figure 11a - Water schematic

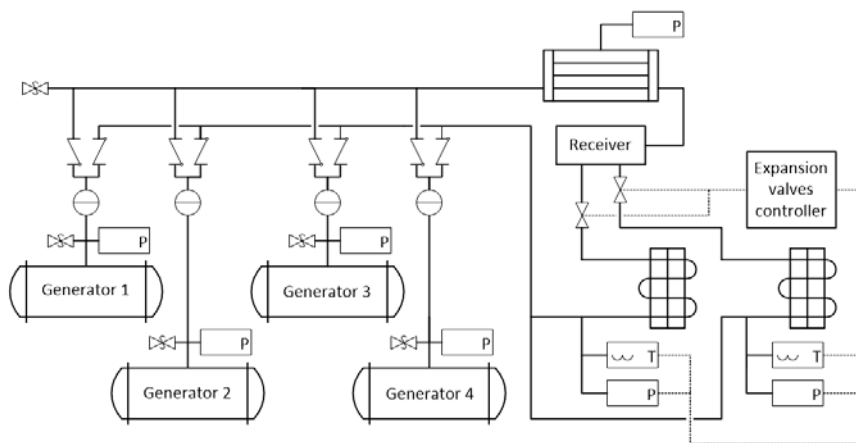


Figure 11b - Ammonia pipework circuits

The components used in the prototype were:

- Generators: as previously described.
- Condenser and cooler: plate heat exchangers.
- Evaporators: fan coils with stainless steel tubes and aluminium fins.
- Receiver: cylindrical stainless steel vessel made by the University of Warwick workshops.
- Expansion valves: electronic controlled especially design for ammonia.
- Check valves: poppet type check valves later modified and exchanged for a ball bearing.
- Gas burner / Heater: even though the heat pump was design to be heat driven by gas, during the testing the hot water was supplied by an electric heater rather than a gas burner since it was more convenient and controllable.
- Water valves: specifically designed and manufactured for this project, were as analogous to four-poles four-way switches.
- Water pumps: two pumps were used in the system. One of them was fitted in the generators water circuit and another one was located in the load circuit.
- Expansion vessel: used to pressurise the water in the machine as it was operated at high temperatures (120 to 170 °C).

The heat pump was tested in an environmental chamber specially designed for the University of Warwick that meets European standards for heat pumping testing. The heat pump was located in one of the rooms and the load (heaters) was located in the other room. In the first room winter environmental conditions were simulated, 0, 5 or 10 °C and humidity of 50% during testing whilst in the second room a house interior was simulated and the temperature was set to 25, 30 or 35 °C to ensure a constant return water temperature to the condenser.

The data acquisition and control of the machine was performed through actuators that switched the water valves and through electronic controls that switched the water pumps.

The main challenge encountered during the experimental tests was the formation of salts inside the system. These salts were formed when the active carbon was in contact with ammonia at high pressure and temperature. The salts could create relatively large, sticky and hard crystals that stack to every component in the refrigerant circuit, jamming check valves and obstructing and completely blocking pipes and hoses.

In order to try to eliminate them, the system was filled and emptied with ammonia 5 times but still some salts were formed that jammed the poppet type check valves making really challenging to test the system for a long time. To avoid this, the poppet of the check valves, that had a tight tolerance with the body and could easily be jammed with a salt crystal, was replaced by a stainless steel precision ball that perfectly sealed with the existing gasket but had less chance of getting jammed by the salts.

8 Experimental results and analysis

Previously to cycle testing, the complete heat pump assembly (except for the evaporators) was insulated with polyethylene foam and glass fibre and a heat loss test was carried out in order to calibrate the machine.

The heat pump was tested at a hot driving temperature of 123 °C, condensing temperature of 30 °C, evaporating temperature of 11.5 °C, mass flow rate of 0.032 kg/s and a cycle time of 400 s. The cycle time indicated in the graph is 404 s due to the fact that every time the stage of the cycle changes the water pump is stopped and the water valves change position. This takes approximately 1 s per cycle stage, 4 s in total in a cycle.

With these conditions the heating COP obtained was 1.31 if taking into account the heat losses (1.18 without heat losses) and the power output was 4.51 kW if taking into account the heat losses (4.30 kW without heat losses). These values were lower than those obtained by the simulation, the heating COP and output power were 1.67 and 4.84 kW respectively.

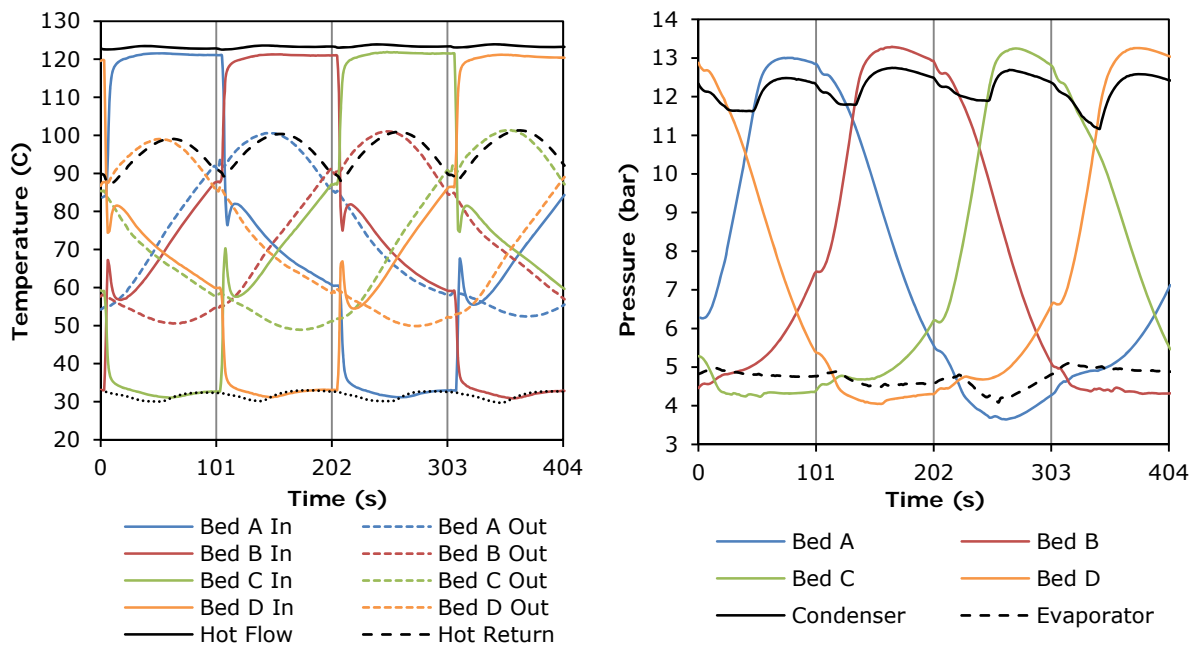


Figure 12– a) Water temperature profiles, b) Beds, evaporators and condenser pressures during a complete cycle (nominal cycle time = 400s, mass flow = 0.032 kg/s)

Figure 12a shows the temperature profiles at the inlet and outlet of each bed as well as the temperature of the water leaving and entering the heater and the cooler outlet temperature. It is possible to see that all the beds perform in a very similar way and that there is symmetry between the heating and cooling stages.

In Figure 12b the pressures of the beds over a cycle are plotted along with the pressure of the condenser and evaporators. It can be observed that there is a slight difference in pressure profile between the beds possibly due to small differences in carbon content, heat transfer in the bed or problems with the sealing of the check valves. The graph shows that with this cycle time and mass flow rate combination only one bed desorbs/adsorbs at a time. The cracking pressure of the condenser/evaporators check valves can be observed in the graph.

Modelling simulation comparison

Figure 13a shows both experimental and simulation profiles of water in and out of Bed A, hot water driving temperature, return temperature of water to the boiler and temperature of the water leaving the cooler.

It can be observed that the temperature of the water entering the bed in the experiment and in the simulation show very similar results, except for phase 4 where the experimental values are lower. This could be due to heat losses to the environment or heat losses between components of the machine.

The temperature profile of the water exiting the bed in the experiment is lower to the one predicted by simulation. This could be due to poor thermal properties of the generators.

The temperature profiles of the water return to the boiler show differences, being higher in the simulation results. This could be due to the poor thermal properties of the generators and heat losses of the machine.

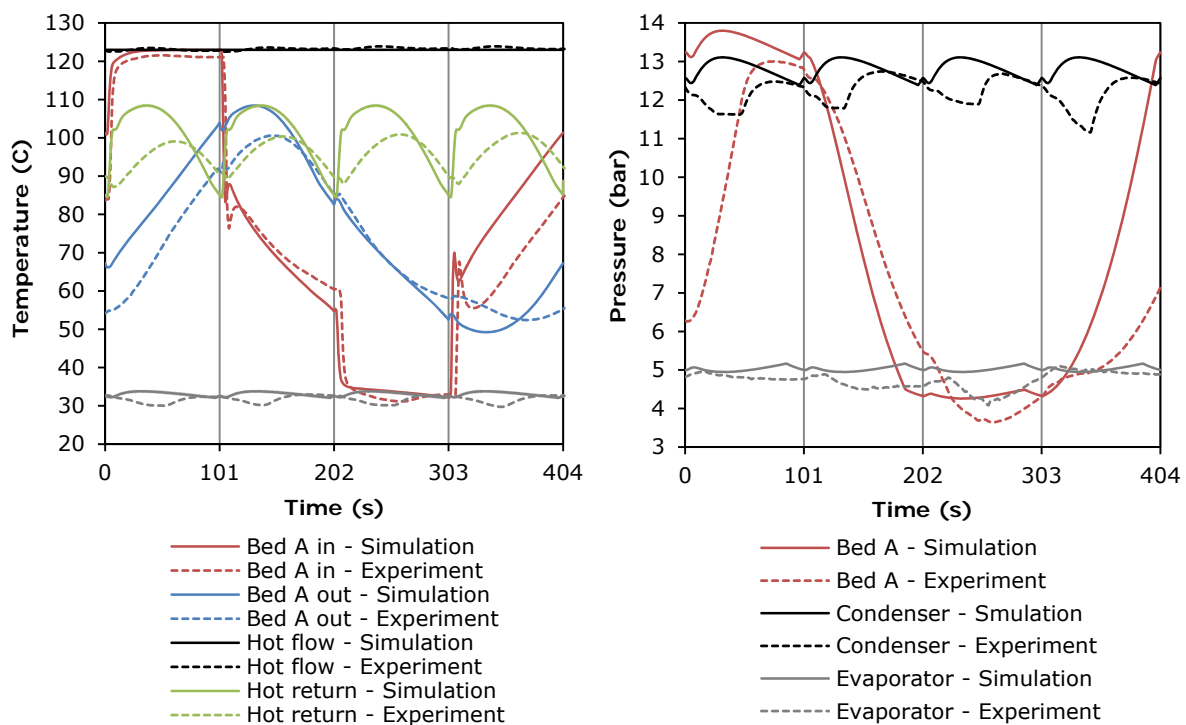


Figure 13 – a) Experimental and simulation comparison of water temperature profiles, b) Experimental and simulation comparison of beds, evaporators and condenser pressures during a complete cycle (nominal cycle time = 400 s, mass flow = 0.032 kg/s)

In Figure 13b it can be observed that the profiles of the experiment and simulation of the bed pressure show important differences. There exists an important delay of pressurisation and depressurisation of the bed and the length of time that the check valves of the bed remain open is much shorter during the experiment. This could be due to poor thermal properties of the generators and poor performance of the check valves.

This Figure also shows differences between the condenser and evaporator pressures. This is due to irregular behaviour of the four beds (A, B, C and D) during the testing as they were influenced by the poor performance of the check valves.

9 Conclusions

The objectives of the project were:

- To carry out the computational modelling of a four-bed heat pump cycle.
- To carry out a heat transfer study of the active carbon available to use in the heat pump in order to identify the best sorbent sample.
- To design, manufacture and test the modelled heat pump cycle in order to validate the computational modelling.

All the project objectives presented above were met:

- The design and manufacturing process of a low thermal mass and high density power sorption shell and tube heat exchanger was presented.
- The performance of the four-bed heat pump cycle was analysed through computational modelling and compared for many different sets of conditions in order to understand its behaviour and the effect these conditions have on the heating COP and heat output power.
- The sorbent material, active carbon, filling technique was presented and developed.
- The measurement of the heat transfer properties of the active carbon were carried out. The intrinsic thermal conductivity of different carbon samples was tested by two methods, steady state flat plate and transient hot tube technique, along with the measurement of their wall contact resistance by the transient hot tube technique.
- Binary mixtures of grains and powder were tested and it was found that they could achieve much higher densities, higher thermal conductivities and lower contact resistances at the same vibration or compression rates than grains on their own.
- The laboratory heat pump system was designed and constructed to test the adsorption generators and cycle. The testing of the machine showed results that were lower than the simulation predictions.
- After the testing, the beds were opened and it was discovered that the installed water distributors were completely distorted and deformed, blocking most of the tubes of the heat exchanger. This was the main reason for the low performance of the machine.

Further work

More work is still needed to be done in order to develop further the system in order to make it marketable. The generators manufacturing technique should be developed in order to being able to mass produce them at a low cost.

The generators spiral water distributors should be remanufactured in a material that does not deteriorate at the heat pump driving water temperature (around 170 °C). A proposed material to use would be aluminium due to its high thermal conductivity, high fusion temperature and easy machinability.

A better positioning of the water valves and the generators could be achieved in order to reduce the dead volumes of water that affect the efficiency of the system.

A carbon pre-treatment should be developed in order to remove the impurities that react with the ammonia creating the ammonia salts presented that were the cause of pipes blockage and check valves jamming.

More research on heat transfer in carbon beds should be carried out in order to find a way to reduce the wall contact resistance in the generators. This would make possible to reduce the size of the adsorption generators and make the system more compact and marketable.



About Angeles Rivero-Pacho

Angeles is currently a Project Manager and Research Fellow, working at the University of Warwick. She achieved her PhD in 2014 and post PhD continues to work on conductivity enhancement in order to move closer to developing a cost-effective domestic gas-fired heat pump.

Angeles was the winner of the IOR's Ted Perry award for this research in 2014. The research was described by one of the judges as "a practical research project with a high potential for commercial exploitation."

About the Ted Perry Award

This Award was set up by the Institute of Refrigeration after the death of Ted Perry, a lifetime worker in the field of refrigeration and a past President of the Institute.

The aim of the Award is to encourage young engineers to investigate the special and diverse skills required in refrigeration with the hope of encouraging them to enter the field professionally.

The Award is open to anyone submitting a piece of work on an engineering topic related to refrigeration and undertaken as part of a degree course or doctorate.

Ted was always a practical man who enjoyed new challenges. Accordingly, the judges look particularly for a demonstration of the understanding of the problems that researchers are addressing in their work, for technical flair and for practical applicability. Work that addresses immediate problems is particularly favoured.

For more information about the award and nominations contact the IOR

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Discussion report for “Innovation in carbon-ammonia adsorption heating pump technology: a case study” by Dr Angeles Rivero-Pacho

Students from the University of Birmingham asked the following questions:

Is this system being aimed at the domestic market and what are the advantages of this system for that market?

Yes, the system is being aimed for the domestic market. The system is design to provide heating for an average UK household (3 bedroom semi-detached house) and can save between 30 and 40% of its gas consumption.

What is the size of the machine?

The prototype machine size is 1 x 0.5 x 1.5 m³. The aim of the machine development is to achieve a very compact final product that, except for the evaporators, has a similar size of a gas boiler.

How will the problem of the salt build up in the system be resolved?

The carbon will need to be pre-treated at high pressure and temperature conditions in order to be cleaned.

What is the maximum temperature that the system can deliver?

The system can deliver hot water at 60 °C at a heating COP of between 1.25 and 1.45 depending on evaporating temperatures. Higher delivery temperatures could be achieved but the heating COP will drop.

Could the system be used to deliver domestic hot water?

It could deliver a small amount of hot water from the storage tank that will be installed with the machine.

What is the ammonia charge?

The ammonia charge in the machine is 1.5 kg.

What is the predicated cost of the system?

The prototype system cost around £10,000. If the machine gets commercialised and mass produced its price could go down to a price range between £5,000 and £2,000 depending on the amount of quantities produced.