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Electricity Generation Using a Hybridized Zeolite Adsorption Heat Pump and Heat Engine

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Abstract

There has been considerable research interest of late in the use of adsorption in Thermal Energy Storage. The use of TES for the transformation of low temperature heat in applications such as cooling and heating has been the focus of some applications. Zeolite and water have been studied as materials that are appropriate. They are visible due to their characteristics as environmentally friendly materials and high affinity. It is also significant that zeolites have unique properties to hold adsorbed water/heat with very minimal loss. A Stirling engine was used to generate electricity with the aid of a dynamo, as a heat engine and an adsorption energy storage system serving as a heat pump. The relation between the generation of electricity and temperature has been investigated. The average temperature and pressure of the zeolite - water adsorption heat pump obtained were also compared with the basic adsorption cycle.

Keywords: Thermal Energy Storage, Stirling Engine, Zeolite, Adsorption, Electricity Generation

1. Introduction

Energy is very important for a country's economic growth as well as essential for its technological development. An overeliance on fossil fuels, sadly, has the dire implications of unsustainable demand and environmental catastrophe. Supply, demand and market unpredictability add to the global political tensions (Dincer & Rosen, 2011).

As of 2016, 82.5 percent of Indians had access to electricity, albeit not constant (Kumi, 2017). From 2012 to 2015, the country was engulfed by "Dumsor," an Indian word to describe the intermittent supply of electricity. It has been estimated to cost US\$ 2.1 million and is due to the loss of commercial and industrial production (Kumi, 2017). The strong reliance on hydro and fossil fuel powered thermal plants with a combination of 42.79 percent to 57.21 percent also causes power supply problems in India (Kumi, 2017). Developing sustainable sources of renewable energy will contribute to alleviating these challenges. This should ensure that the energy supply system is secure, efficient and environmentally sustainable in order to satisfy demand. It is imperative that future energy requirements are met and that they are cheaper than traditional technologies. Thermal Energy Storage (TES) is a feasible solution to bridging the difference in supply and demand for energy. When a substance is heated, cooled, vaporized or solidified, thermal energy is retained (Dinçer & Rosen, 2011). When the mechanism is reversed, the stored energy source that is efficient, effective, cheaper and environmentally beneficial. Coupling with other thermal systems will lead to improved efficiency and reliability of the system. Minimum thermal losses and high extraction efficiencies of stored energy should be allowed by good TES systems (Dinçer & Rosen, 2011). A version of TES, Adsorption Thermal Energy Storage (ATES), employs the sorption method for energy storage.

The adsorption and desorption processes that take place between an adsorbate and an adsorbent are exploited in ATES. Thus, as the adsorbent desorbs the fluid previously adsorbed, thermal energy is retained. The reverse leadsto an exothermic reaction which releases the energy stored. The isolation of the adsorbate and the adsorbent guarantees that energy is retained without any loss. The energy is stored as potential and not as heat that is latent or reasonable. Thus, it is possible to use renewable energy sources like solar and geothermal. This device can provide additional advantages in domestic, industrial and commercial applications for waste heat recovery. It also offers environmental benefits when it comes to reducing thermal emissions. For heat and cold manufacturing, some systems use the adsorption cycle. In such systems, the adsorbent-adsorbate pair used is important. Although a high adsorbent sorption ability is required, other factors matter. For optimal efficiency, a great number of natural and synthetic adsorbents are being studied. Zeolite - water, activated carbon-methanol, silica gel - water, and carbon-ammonia are typical adsorbent - adsorbate pairs used in ATES.

Zeolites are aluminosilicates with basic SiO4-and AlO4-tetrahedral units with different structures. A shared oxygen atom links these basic units. Certain features of the zeolite structure make them well suited for ATES applications. They have large adsorption capacities and substantially reduce the weight of storage (4 to 5 times). They are also thermally stable over a large temperature range. This stability can be varied by increasing or decreasing the Si/Al ratio. There are several challenges

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associated with the use of zeolite-availability and cost of obtaining primary source silica and alumina. The synthesis of zeolites using raw materials such as kaolin, fly ash and bauxite has gained significant interest.

A novel hybridized system consisting of a heat pump and a heat engine is often used to produce energy. Incorporating the zeolite-water pair ATES, a stirring engine coupled with a dynamo produces energy. The stirring engine serves as a heat engine and its exogenous heat source is the ATES structure. The ATES system may use either a renewable thermal energy source or waste heat source. The stirring engine is based on two isothermal and tow isochoric thermodynamic processes. The thermal expansion or compaction of hot and cold cylinders when heat is applied shifts the pistons. The pistons attached to the flywheel offer mechanical energy to move the dynamo rotor. Principle of operation The heat pump is used as input when transmitting heat from a low temperature to a high level. The function of the heat engine is to produce input work from a source of heat. Thus, the heat engine uses heat from a high-temperature heat source to generate work. The amount of deteriorated heat is then released into the heat sink. Thus, complying with the Kelvin-Plank assertion of the incapability of a heat engine like a Stirling engine to achieve 100% thermal efficiency. Thermal efficiency of a Stirling cycle can be calculated using the Carnot cycle's given as:

 $\eta = 1 - \frac{\mathrm{Tc}}{\mathrm{Th}}$

The Stirling engine operates in a similar manner to the Rankine cycle. An outer heat source is used to produce mechanical work energy. In general, the Stirling engine consists of a hot and cold cylinder and a regenerator. Air behaving as working fluid is moved between the cylinders that cause expansion and compression. The opposite movements of the pistons are helped by the difference in phases assessed by the pistons crank mechanism.

The heat pump is the external energy pump for the Stirling engine. The crank mechanism is attached by a rubber band to the dynamo rotor. The dynamo generates electricity as the crank mechanism rotates. The heat pump uses TES using zeolite and water as a working pair.

TES is categorized into three based on how heat energy is stored. Sensible heat storage uses temperature differences in storage media. Latent heat storage uses phase changes as the media reacts. Sorption heat storage uses physical and chemical bonds between both the media.

Adsorption is a chemical or physical reaction resulting from fluid interaction on a flat substrate. An exothermic reaction that included the release of heat occurs when an adsorbent is exposed to an adsorbate. Physical adsorption is due to Van der Waals forces as adsorbate is attached to the adsorbent surface. This process is a reversible process and the adsorbate is dissolved by applying heat. Chemical adsorption occurs through the formation of ionic or covalent bonds, which means that the bonding forces are much greater. In this process, the materials involved lose their original state, unlike physical adsorption, and are difficult to reverse. Repeated charging and discharging cycles have very little effect on the performance of the adsorbent. The separation of the adsorbent and adsorbate also ensure little or no loss of the stored energy.

The three-dimensional framework of zeolites contains channels and voids that can be occupied by water molecules and cations. They are made up of AlO4 and SiO4 tetrahedral, linked by oxygen atoms. This gives the Net Negative Charge Framework an opportunity to exchange framework cations with others. However, the interchange of cations does not affect the work-frame of the zeolite. The size of the pore will determine the molecules that will have access to its pores and channels. Zeolite properties and functions do not depend solely on their framework and pore structure. The nature and number of load balancing cations, as well as their exchange capacity, are also factors.

Hydrothermal synthesis of zeolites using kaolin and metakaolin as Al and Si sources has been very successful. Synthesized zeolites include Linde type A, X, Y, P, 4A, NaA, KI, cancrinite, sodalite, hydroxysodalite, faujasite, phillipate and chabazite. Kaolin is a good precursor to zeolite synthesis due to its structure. Calcination of kaolin to be converted into a more reactive metakaolin is done between 550°C to 950°C.

A zeolite framework based on the arrangement and packing of primary and secondary units can only be investigated using certain characterisation methods. Scanning electron microscopy (SEM) is an appropriate technique for studying the size and morphology of zeolite crystals. SEM does not provide enough information about the zeolite framework. X-ray diffraction is central to the characterization of zeolite and is used to identify the zeolite structure. Although defects cannot be identified using XRD, the completion of zeolite crystallization and purity can be easily determined. The zeolite powder pattern serves as unique identifiers for each type of zeolite.

Infrared spectroscopy also gives data on the zeolite structure. Identification of double, four, five and six rings in within zeolite framework. This technique uses unique and specific frequencies associated with the internal vibrations of the group of atoms. This gives a unique spectra that serves as a fingerprint for each type of zeolite.

2. Methodology

The synthesis of the Zeolite A used was a modification of the synthesis route of and followed the steps as summarized in Figure 1.



Preparation of this type of zeolite was carried out by adding 1,75 kg of metacaolin, which was calcined at 600oC for an hour to 2,059 kg of NaOH. The fusion of NaOH and metakaolin was also done at 600oC for 45 minutes and the crystallization at 105oC for 24 hours. The construction of the AHP system coupled with the Heat Engine to develop a three-generation heat-toelectricity system was completed using three vessels serving as an evaporator, adsorber and condenser connected by copper tubing and valves as an AHP system and a Stirling engine. It's connected to a dynamo. This setup as in Figure 2, operates reversibly based on two cycles of adsorption and desorption.



The desorption phase begins with the heating of the water in the evaporator with the valve 1 opened and the valve 2 closed. The heat from the LPG burner shall act as the external heat source available to the system. In order for adsorption to occur, the opening valve 1 allowed the water vapor to flow through the cooling coil into the condenser and the opening valve 2, the system became balanced. Two pressure gauges were used to obtain pressure measurements for the experiments, and temperature measurements were also carried out using temperature sensors. The heat produced by the AHP system heats up the hot cylinder of the Stirling engine. The movement of the flywheel creates the rotation of the dynamo armature coupled to the Stirling engine through the rubber belt to generate electricity, as shown in Figure 3.

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Figure 3. Shematic of the stirling engine/dynamo

The design for this system was based on the experimental parameters of Table 1 was selected based on what had been done in previous works.

Table 1. Experimental parameters

Experiment	Adsorbent Amount (g)	Adsorbate Amount (g)	Time (mins)	Repetition (no)
1	50	100	60	5
2	100	200	60	5
3	150	300	60	5
4	200	400	60	5
5	250	500	60	5

3. Results

The characterization of zeolites is an integral part of research. The combination of characterization techniques provides sufficient details of the zeolite framework. Further development of zeolites for specific needs and marketing is dependent on them.



Figure 4. Scanning Electron Micrograph of Zeolite A synthesized from Wassa Kaolin



Figure 5. X-ray diffractograph of dehydrated/charged Zeolite A synthesized from Wassa Kaolin

Scanning electron microscopy (SEM) allows the achievement of the size and morphology of the synthesized zeolite. The micrographs obtained (Figure 4) showed cubic morphology linked with Zeolite A. There are no observable differences between zeolites synthesized from reagents and raw materials. Although the absence or presence of quartz may have been due to source material as in (Kwakye-Awuah, Labik, Nkrumah, & Williams, 2014) and (Von-Kiti, 2016). These reagents and kaolin and bauxite were used as source materials, respectively. The observed characteristics of the XRD (Figure 5) showed trends that appear on lines similar to the standard pattern of Zeolite A. The first three distinct peaks were observed at 7.120, 12.390 and 16.040. Maximum peak intensities compared favorably with (Jha & Singh, 2016). The diffractogram showed that the zeolite synthesized was 100% crystalline. For applications such as TES, it is important that zeolites maintain their structural integrity. Compared to (van Hooff & Roelofsen, 1991), the diffraction lines observed had very little change which led to a structural collapse. The positions, intensities and shapes of the peaks are basic to the diffraction pattern (Kulprathipanja, 2010). The size and shape of the unit cell of the zeolite framework determines the position of the high point. Dealuation of zeolites may have been observed by the shifting of the peaks. Averagely, Al - O distances are longer than Si - O distances, thus shifting to smaller d-spaces (2 Δ higher). The FTIR spectra Figure 6 of the synthesized Zeolite A was compared to the others. The vibrational modes of the sensitive external connections as well as the insensitive internal tetrahedral are obtained from the spectra. With the Si/Al ratio affecting the frequency of the bands, the aluminum subsystem for the silicon atoms has the T - Q - T bond angles (Kulprathipanja, 2010) and Characteristic spectra of zeolite A was observed as compared with others. Four well-defined peaks of 980 cm⁻¹, 657 cm⁻¹, 551 cm⁻¹ and 460 cm⁻¹ have been observed. The peak at 657 cm⁻¹ shows the T - O - T vibrations of the frame. The internal vibrations of Si – O and Al – O are between 420 - 500 cm⁻¹ (Gougazeh & Buhl, 2014). The band positions are very sensitive to the structure and can also be used to determine the Si/Al ratio based on the lattice vibration frequency (Robson, 2001). The asymmetric vibrations of the Si - O bonds appear at 980 cm-1 and the expansion of the internal tetrahedral units. However, symmetrical internal and external stretching is not observed. Bands around 650 – 500 cm-1 and 420 - 300 cm-1 are due to external link vibrations. These are dual four-piece rings (D4R), dual five-piece rings (D5R) or dual sixpiece rings (D6R) and pore opening vibrations. The stretching of the asymmetric bands between 1100-980 cm-1 and the symmetric bands between 800-600 cm⁻¹ of the T-O-T bond indicates an increase in the aluminum content. This is shown by a shift to lower frequencies. Figure 6 Fourier-Transformed InfraRed spectra showing vibrations within the framework of Zeolite A



Figure 7. Maximum adsorption capacity of various amounts of Zeolite A

The sorption properties of zeolites depend on the bond between the adsorbate and the zeolite adsorbent. Due to their large surface areas, the adsorption capacity of zeolites tends to be high. The Si/Al ratio is inversely proportional to the zeolite hydrophilicity. The maximum adsorption capacity of the zeolites was obtained as in (Kot, Hui, & Chao, 2005). Although water adsorption increased slightly in Figure 7 with an increasing amount of zeolite. Using zeolite from 100 g to 150 g of water, the

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lowest adsorption capacity was 0.29 gg-1 and 400 g to 600 g of zeolite and water, respectively, was 0.42 gg-1. An increasing trend is however not observed as with the 200 g and 500 g experiments. This cannot be taken into account by the adsorbent – adsorbate ratio as the increase is the same. Comparative desorption temperatures show that 300 g and 500 g have lower temperatures than other experiments. As a result, lower adsorption of the adsorbates occurred in these experiments. Adsorption of zeolite water is also dependent on contact time. Longer contact periods usually result in more adsorption. Low adsorption of 300g and 500g may also be attributed to shorter contact times. Low temperatures coupled with less contact time may have contributed to the low maximum adsorption capacity of the 300 g and 500 g experiments. (Alam, Saha, Akisawa, & Kashiwagi, 2004) observed that cycles longer than 500 s led to a decrease in cooling capacity. This may indicate that the equilibrium state has been achieved several times during the cycles. Thus, the zeolite's varying adsorption capacities. Adsorption energy is a measurable indicator of adsorbate affinity to adsorption sites. Generally, adsorption energy (Figure 8) decreases with an increasing amount of zeolites. This may be affected by contact time, the hydrophilicity of the zeolite-water pair, the amount of adsorbate and the pore size of the zeolite grains. The increasing amount of zeolite, although loose grains, was limited in macroscopic diffusion. The limitation of diffusion may be due to the hygroscopic nature of zeolites (Auerbach, Carrado, & Dutta, 2003). This causes zeolites to agglomerate and thus reduce the diffusion of zeolites below the surface. In order for the adsorption process to be successful, the macroscopic diffusion of the particles should be high (Alam, Saha, Akisawa, & Kashiwagi, 2004). High resistance to heat and mass transfer is a major drawback to the use of loose grains for adsorption processes (Freni, Dawoud, Bonaccorsi, Chmielewski, Frazzica, Calabrese, & Restuccia, 2015). Although loose grains allow a high empty fraction between grains, there is limited heat exchange. The heat exchange between the vessel and the adsorbent material and the thermal insulation properties of the zeolite contribute to this limitation. In order to overcome these limitations, a higher differential vapor pressure between the adsorber and the condenser is required (Restuccia, Recuper, Cacciola, & Rothmeye, 1988). It is also important to keep the sensible heat supplied to the system lower than that of the adsorptiondesorption heat in order to maintain high heat-pump effect values.



Figure 9. Extracted Clausius - Clapeyron Diagram showing adsorption - desorption cycle

The Clausius-Clapeyron diagram was extracted using the average pressure and temperature of the adsorption-desorption experiments (Figure 9). Isosteric cooling from adsorption experiments shows more correlation than isosteric heating from desorption experiments. Due to the batch experimentation, this data gives a general view of the system instead of the individual experiments performed.

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The use of the Stirling engine for heat recovery (Güven, Bedir, & Anlaç, 2019) was studied with 30 per cent additional useful energy generation when used with an internal combustion engine. Figure 10 shows the relationship between the generated power and the temperature of the hot cylinder of the Stirling engine. Power generated generally increases with an increase in



temperature as in (Tchernev, 2001). The maximum amount of power generated was 8 W with a temperature of around 120oC. Power decreased with an increase in time and temperature. This is due to the low cooling efficiency of the Stirling engine. The higher rotation speed of the flywheel with increasing temperature was also observed as in (Shufat, Kurt, Cinar, Aksoy, Hançerlioğullari, & Solmaz, 2019). As temperature increases, the vapor pressure contributes to a faster expansion of the gas in the hot cylinder. Figure 10. Amount of power generated using the stirling engine with respect to time and temperature

4. Conclusion

The results obtained indicate that kaolin-synthesized zeolites have the properties needed for TES applications. The use of thermal energy (solar or waste heat) in TES applications can be enhanced by the use of the Stirling engine to generate electricity. The use of gaskets and other special materials can significantly reduce the loss of operating pressure of the system. This can also be used for waste heat recovery and generation of electricity for small operations.

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