Microwave Desorption for Flexible Sorption-Heat Storage Application

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Abstract

Microwave desorption is a highly efficient method for thermochemical heat storage, surpassing conventional drying. Zeolite desorption experiments showed material-dependent efficiencies: 4ABF reached 70%, 13XBF 30%, and 4AK 15%, compared to a 30% maximum for conventional methods. Sample weight influenced performance, with 13XBF maintaining efficiency across 262g to 869g, though larger masses required longer drying times. The porous structure of 4ABF enhanced vapor transport, achieving superior results. Challenges included non-uniform heating and thermal runaway in samples over 700g, with hotspots exceeding 500°C. Microwave desorption's flexibility in power adjustment (100%, 75%, 50%) makes it a promising approach for sorption heat storage, requiring further optimization to mitigate risks and enhance scalability.

Keywords: Thermochemical heat storage, sorption heat storage, zeolite desorption, microwave desorption

1. Introduction

In order to achieve efficient thermo-chemical heat storage, it is necessary to utilize sorption storage materials that have undergone complete desorption. The rate of desorption is dependent upon the specific material in question, the temperature, the duration of the desorption process, and the process vapor pressure (in a vacuum or in an atmosphere). Mineral sorption materials (e.g., zeolite) necessitate high maximum desorption temperatures; insufficient desorption results in diminished reaction kinetics and energy yield during storage discharge. In contrast, hygroscopic salts require a meticulously regulated desorption process over time to prevent melting and the formation of solutions.

Microwave desorption, which involves the conversion of electromagnetic wave energy directly into heat within the storage material, represents a highly flexible energy conversion option for this application, like reported in Dinglsreiter (2000) and Kraus (2010). Studies demonstrate that microwave irradiation significantly enhances the desorption rate of water vapor from zeolites. For instance, Watanabe et al. (2009) observed a 2.22-fold increase in water desorption rate from zeolite 4A using microwave heating compared to conventional hot-air methods. Similarly, Zhang and Hu (2011) reported that microwave-assisted regeneration of zeolites 13X and 4A for water desorption achieved superior efficiency and speed relative to traditional techniques. These findings are corroborated by Yasin and Martin (2020), who highlighted the enhanced energy efficiency and accelerated desorption process facilitated by microwave heating, particularly in humidity control applications.

The process of heating zeolite using microwaves is initiated by the application of microwave energy, which triggers a series of chemical and thermal interactions within the zeolite structure. Initially, hydrated zeolite absorbs microwave energy through its adsorbed water, resulting in a temperature increase. The adsorbed water desorbs from the zeolite at temperatures between 150 and 250°C, completing its contribution to microwave absorption. At higher temperatures (300–400°C), the zeolite itself begins to absorb microwaves directly, with absorption efficiency increasing as the temperature rises. A critical threshold (approximately 400–500°C) may result in thermal runaway, depending on the cation composition of the zeolite lattice. For example, ion-exchanged 5A zeolite does not experience thermal runaway due to the absence of cations in specific lattice positions, unlike 4A zeolite (Thiebaut, 1988; Ogishi, 2001).

This paper presents a concept of a multimode microwave desorption process, offering an efficient and highly flexible desorption method for energy storage using fluctuating sources. To capture the special conditions of this process, a demonstration setup is being implemented to compare desorption via infrared and microwave heating. By leveraging findings from prior research, such as those by Watanabe et al. (2009), Zhang and Hu (2011), and Yasin and Martin (2020), this study aims to further optimize desorption efficiency and evaluate its scalability for practical applications.

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2. Material and Methods

Several commercial materials were employed in the experimental investigations. Zeolites in granulated form, each exhibited distinctive behaviour contingent on their crystal structure, ion content, and binder content. The zeolites were procured from the supplier Chemiewerke Bad Köstritz: 4AK (1.6-2.5mm granules containing binder, LTA-Type, 0.4nm pore size), 13XK (1.6-2.5mm granules containing binder, Faujesite-Type, 0.9nm pore size), 13XBF (2.5-5mm granules, no binder, Faujesite-Type, 0.9nm pore size).

Two different measurement techniques were employed, including (a) a multimode microwave oven with a wave stirrer and internal weight measurement and temperature control, and (b) conventional drying in a hot air oven

Fig. 1: Multimode fixed-bed microwave oven with balance and power-meter (left), conventional hot-air drying oven (right)

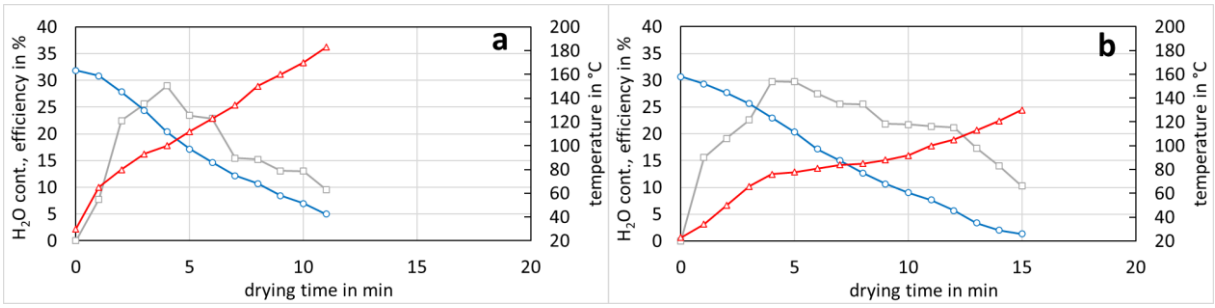
A weighing device was incorporated into the design of the multimode microwave oven (Fig.1, left) in order to facilitate the monitoring and recording of the weight loss of the material sample. The magnetron has a maximum output of approximately 1000W, with typical conversion losses of 35%. The emitted wave has a frequency of 2.45GHz. An infrared temperature sensor is positioned above the material undergoing drying, allowing for the monitoring of the temperature. A power meter is employed to quantify the electrical power consumption of the microwave. Comparative measurements in a conventional drying oven (Fig. 1, right) are conducted to facilitate a comparison of the efficiency of the two desorption routes. The measurements in the drying oven were determined with other sample weights due to the size of the oven. The electrical power was only measured during the desorption process, and the heating of the empty oven was not taken into account in the efficiency comparison.

3. Results

3.1. Microwave batch heating

Several different experiments were carried out. Different types of zeolite were tested, different sample weights were used and finally the microwave power was varied. For analysis, both the material temperature and the material weight were recorded to evaluate the drying progress of the zeolites.

The figures below show the results.



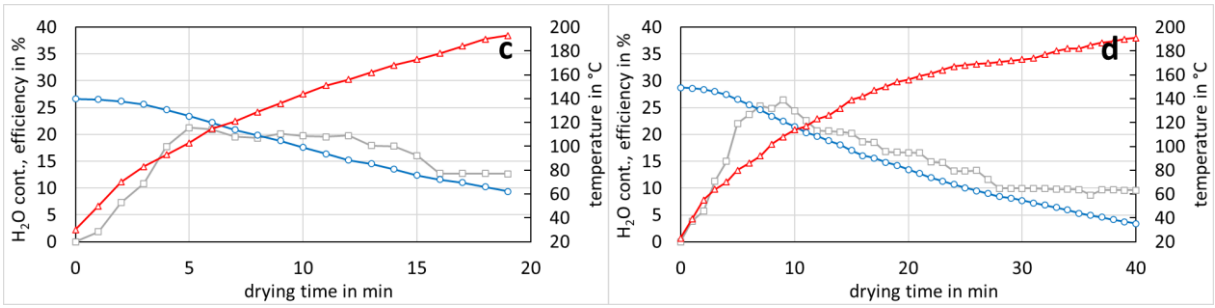


Fig. 2: Microwave desorption on 13XBF material with different masses: (a) 262g, (b) 408g, (c) 640g, (d) 869g. Material water fraction (blue) and drying efficiency (grey) refers to the left axis, material temperature (red) to the right axis.

In Fig 2 the material 13XBF was desorbed and the sample mass increased in steps from 262g to 869g. All weights are dry mass. The red line is the temperature of the material as measured by the infrared sensor, the blue line is the water content of the material as a percentage of the dry mass and the grey line is the drying efficiency.

The drying efficiency represents the current enthalpy per time required to cause the weight loss of the sample by desorption, compared to the total current power consumed.

The time required to heat and dry the material varies according to the weight of the material. The drying tests were carried out at a temperature of max. 200°C and the residual moisture of the material was determined in a conventional oven by heating (1h@350°C) and weighing. Heating of the zeolite fill was not always uniform; sometimes a hot spot pattern was formed, indicating that the wave-stirring function is inadequate. Prolonged heating (above 200°C) leads to thermal runaway in some areas of the material, the granules begin to glow, indicating temperatures >500°C.

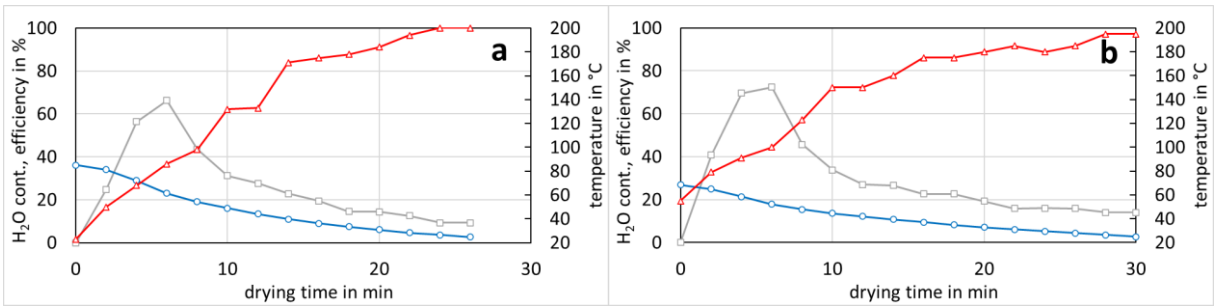


Fig. 3: Microwave desorption on 4ABF material with different masses: (a) 300g, (b) 550g. Material water fraction (blue) and drying efficiency (grey) refers to the left axis, material temperature (red) to the right axis.

In Fig. 3, 4ABF was desorbed. The drying efficiency is significantly higher for this material, with values of over 70% being achieved at times.

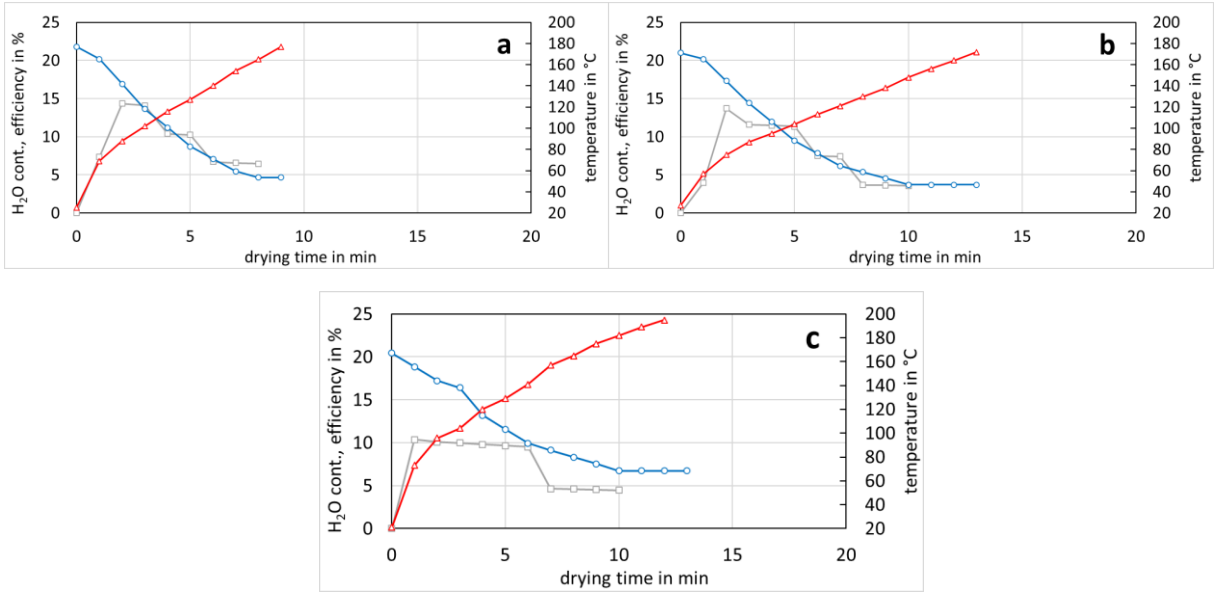


Fig. 4: Microwave desorption on 4AK material with similar masses but different microwave power: (a) 100% power, (b) 75% power, (c) 50% power. Material water fraction (blue) and drying efficiency (grey) refers to the left axis, material temperature (red) to the right axis.

In Fig. 4, the material 4AK was used, the microwave power was varied in this test. The sample mass of all measurements in Fig. 4 is 120g, the heating time is longer for lower powers, the drying efficiency is comparatively low for this material.

3.2 Conventional heating oven

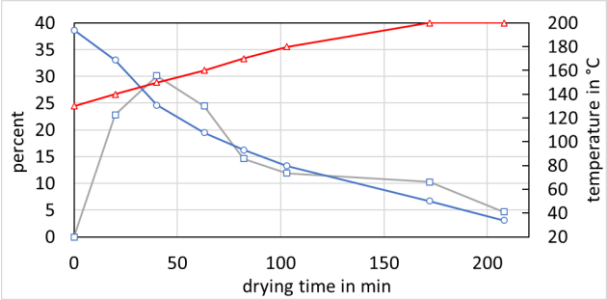


Fig. 5: Oven desorption of 13XBF material with a mass of 2800g. Material water fraction (blue) and drying efficiency (grey) refers to the left axis, material temperature (red) to the right axis.

To compare microwave drying with the conventional method, tests were carried out in a hot air oven. The weight of the sample was chosen to make good use of the space and electrical power of the oven and to avoid problems with moisture removal. The oven was preheated to 200° and from the time the sample was placed in the oven, the weight loss was determined by weighing at intervals and the drying efficiency was calculated.

4. Discussion

All tests show a temperature rise and mass loss due to desorption. The drying efficiency, defined as the ratio of the enthalpy required to cause sample weight loss through desorption to the total current power consumed, is initially low as the material heats up. Maximum drying efficiency is highly material-dependent, with values ranging from 15% for 4AK to 70% for 4ABF and 30% for 13XBF. However, at low material moisture levels, efficiency drops significantly and eventually reaches zero when no further drying is achieved. The ability to desorb a wide range of sorbent materials with high efficiency is a critical advantage of microwave drying, but it is contingent upon the specific zeolite structure and granule composition.

The granules 4AK and 4ABF, composed of identical zeolite crystals, differ in binder type: 4AK uses an attapulgite clay binder, while 4ABF incorporates an organic binder thermally converted into a porous zeolite-like structure. The BF-bonded materials exhibit significantly higher drying efficiencies due to enhanced vapor transport and faster desorption facilitated by the porous binder layer. When comparing 4ABF and 13XBF granules, the differing zeolite structures necessitate higher temperatures for 13X crystals than 4A crystals to achieve similar material moisture contents (Zettl et al., 2015).

Material quantity also influences the drying process. Larger quantities necessitate longer heating times, and for samples exceeding 700 g, temperature distribution fluctuations in the zeolite bed may lead to thermal runaway. However, for material quantities between 100 and 700 g, consistent temperature profiles, residual moisture values, and drying efficiencies are observed, apart from test duration.

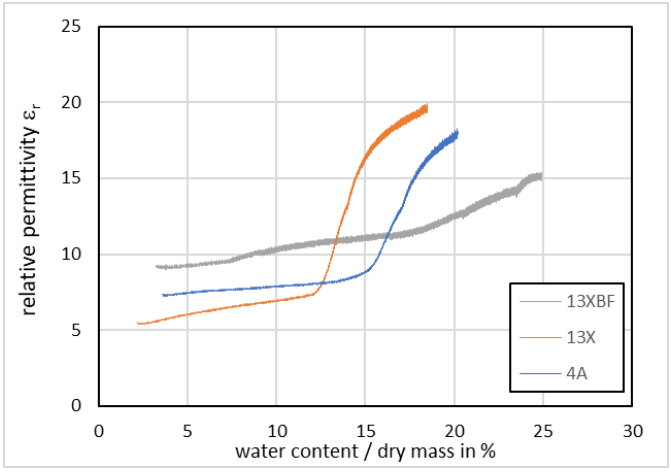


Fig. 6: Relative permittivity of commercial zeolites depending on material water content (Zettl et al. 2023)

The relative permittivity (dielectric conductivity) of zeolites varies with material water content and provides critical insights into absorption behaviour. Dielectric properties, including polarizability, ion oscillations, and water molecule displacement, are influenced by temperature and excitation frequency. Zettl et al. (2023) demonstrated a correlation between permittivity and humidity levels, showing that higher water content initially facilitates efficient microwave absorption. However, as desorption progresses and moisture decreases, permittivity declines, slowing temperature increases until thermal runaway thresholds are surpassed.

The experimental results corroborate the advantages of microwave heating observed in previous studies, such as its ability to accelerate desorption rates and enhance energy efficiency. Notably, our findings reveal material-dependent variations in drying efficiency, with 4ABF exhibiting significantly higher performance due to its porous binder structure. These results align with the reported improvements in desorption efficiency for similar materials (e.g., Zhang and Hu, 2011; Yasin and Martin, 2020), suggesting that microwave heating's volumetric and selective energy delivery plays a pivotal role.

However, challenges such as non-uniform heating patterns and thermal runaway risks persist, particularly in larger sample volumes. These issues resonate with findings by Nigar et al. (2019), who highlighted the influence of dielectric property changes and binder composition on heating behaviour. Addressing these through optimized system design, as suggested in prior research (e.g., Demir, 2013; Watanabe et al., 2009), and innovations in binder materials could further enhance the scalability and practicality of microwave-assisted desorption in energy storage applications.

The studies collectively emphasize the potential of microwave heating to achieve volumetric and selective heating, reducing cycle times and improving energy efficiency. Nonetheless, challenges such as thermal runaway, non-uniform temperature distribution, and material-specific performance variations persist. Addressing these through cavity optimization, binder innovations, and precise power control is vital for advancing the application of microwave desorption in thermochemical storage systems.

5. Conclusion

The study underscores the potential and challenges of employing microwave desorption in thermo-chemical heat storage applications, emphasizing its material-specific efficiency and operational characteristics. Key findings and numerical results from the experiments and referenced studies are summarized as follows:

Material-Specific Efficiency:

- Maximum drying efficiency varied significantly across zeolite types: 15% for 4AK, 30% for 13XBF, and 70% for 4ABF.
- BF bonded materials such as 4ABF have demonstrated superior drying efficiency due to the porous binder structure, which allows for faster vapor transport and desorption compared to conventional bonded materials using attapurgite clay as a binder.

Temperature and Moisture Dynamics:

- Microwave desorption exhibited a clear dependency on the zeolite structure. For instance, 13X crystals required higher temperatures (300–400°C) compared to 4A crystals (150–250°C) to achieve comparable residual moisture levels.
- At higher material temperatures (above 400°C), thermal runaway occurred in some samples, particularly those exceeding 700 g, emphasizing the need for careful temperature regulation.

Scale and Uniformity:

- Larger sample masses required extended heating times. Consistent drying efficiency and moisture reduction were observed for samples between 100 and 700 g, whereas 869 g samples exhibited non-uniform temperature distribution and thermal runaway.
- Comparison with conventional drying highlighted the superior energy efficiency of microwaves in smaller samples, though oven drying managed larger sample masses (e.g., 2800 g) more uniformly.

Permittivity and Dielectric Properties:

- The relative permittivity of zeolites decreased significantly as water content reduced, slowing desorption. For example, NaY zeolite exhibited a rapid temperature rise to 180°C within 5 minutes at 30 W microwave power, with its loss factor exponentially increasing above 200°C (Nigar et al., 2019).
- The permittivity changes align with reduced microwave absorption efficiency at lower moisture levels, a limitation for further optimization.

Microwave vs. Conventional Heating:

- Microwave heating consistently outperformed conventional methods in speed and energy efficiency, with faster desorption in zeolite 4A compared to hot-air drying.
- However, challenges such as non-uniform heating, partly low energy absorption efficiency, and thermal runaway risks were noted.

Implications and Recommendations

Microwave desorption proves advantageous in terms of speed, energy efficiency, and material-specific optimization for small-to-medium sample sizes. However, scaling up and ensuring uniform heating remain key challenges. Innovations in cavity design, power control, and binder composition are necessary to mitigate risks like thermal runaway and non-uniform heating. Addressing these will pave the way for efficient and scalable microwave-based desorption systems in thermo-chemical storage applications.

6. Acknowledgement

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