MICROWAVE ASSISTED REGENERATION OF 3Å MOLECULAR SIEVES USED FOR ETHANOL DEHYDRATION

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The paper presents new methods for 3 Å molecular sieve regeneration using microwave energy. The experiments were performed under very strict conditions using a microwave generator, permitting the variation for the main parameters: temperature, microwave power, pressure and exposure time. Determining the amount of desorbed water from the molecular sieve during regeneration allowed correlating regeneration level with energy consumption. Also, the impact of vacuum pressure on the process efficiency has been studied. The purpose of the study was to determine optimal regeneration conditions that allow maximum regeneration level with minimum energy consumption.

Keywords: microwaves, molecular sieves, regeneration, ethanol drying

1. Introduction

For ethanol drying process, the most modern production units use technologies based on molecular sieves. 3Å zeolites are frequently used in ethanol drying processes because the pore dimension is 3Å, while water molecules have 2.8Å in diameter and ethanol molecules, 4.4Å. Thus, water molecules are adsorbed by the zeolites while ethanol passes trough [1].

The adsorbtion and the regeneration processes are linked together, the industrial process being made into 2 columns, one for ethanol drying and the other for the regeneration step. From the time and energy perspective, the regeneration step represents a critical process [2].

There are 2 major methods used for adsorbents regeneration [3, 4]:

- Regeneration trough pressure variation (PSR), used for removal of weakly adsorbed molecules;
- Regeneration trough temperature variation (TSR), used for removal of strongly adsorbed molecules;

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Modern plants use PSR processes for drying ethanol, water molecules being removed using vapor phase feed.

In a typical PSR process, the drying column operates at an almost constant temperature [4], the water adsorbed in the previous cycle is being desorbed by lowering operating pressure and by using a gas flow trough the adsorbent bed from the opposite direction. This helps removing water molecules desorbed from the zeolite.

Water has a high affinity for the 3Å molecular sieve, so for each kg of adsorbed water, 4186.8 kJ of heat are released (adsorption heat). When the same kg of water is removed during the regeneration step, the same quantity of heat must be provided, 4186.8 kJ (desorption heat). Thus, while the vapors are being dried, the adsorbent bed will heat up; by analogy, during the regeneration step the bed will cool down. 3Å molecular sieve is capable of adsorbing up to 22% of its weight in water, but the drying processes that use PSR operates at lower adsorbtion levels, thus limiting the drying step, preventing a high temperature variation between cycles [1].

By limiting the adsorption time, temperature variations are kept in reasonable limits and the adsorption heat is efficienty retained in the adsorber bed as sensitive heat. This heat is then available for supplying the energy needed for desorption during the regeneration step. The ability to use the recovered heat is the reason why molecular sieves are so energy efficient.

Assuming that the raw vapors come directly from the distillation column, the only extra energy sources used in the drying column come from the steam needed for overheating the vapors at the desired temperature in the adsorption process (12-24 kg steam/m^3 of dry ethanol) and from the electric energy used by the pumps (5-8 kW/m^3)

To refine the liquid which result in the regeneration step (ethanol with a low concentration), additional thermal energy and electricity are needed to operate the cooling system and also for the air compressor. A highly optimized system can have a total energy consumption of 1.115 kJ/m^3 of dried ethanol, assuming that the raw ethanol contains 5% water and the final product 0.25% water. In case of using higher water content in the feeding liquid or the final product is drier, a high quantity of energy will be needed [1].

Regeneration of the adsorbent by using the temperature variation (TSR) is an alternative of the PSR process and uses lower temperatures in the adsorption step while the regeneration step is operated at higher temperatures. The TSR process is usually less effective and much slower than the PSR process. This is because of high thermal inertia of the adsorbent and because of the low caloric capacity of the gases used for heating. Therefore, regeneration of the adsoption bed or of the adsorber is an important time consuming step, the products of the regeneration being highly diluted by the gas flow used for heating and implicitly

hard to recover. Because of these limitations, the processes that use TSR are less frequent than the PSR applications at industrial scale [2].

Summarizing these informations can be concluded that the TSR process is still entirelly unknown because no systematic studies regarding the kinetic of the process as well on energetic efficiency problems have been carried out [2].

Therefore, research activities focus on the development of new regeneration methods. Only a cheap solution alternative that can heat up the adsorption bed in the entire mass can ensure designing an efficient TSR process. One of the discussed solutions refers at using microwaves [2].

The advantages of using microwaves established at laboratory scale are [6, 7 and 8]:

- During dielectric heating, electromagnetic energy is directly converted by the material itself into heat. It provides a fast and volumetric warming of the material which limits heating the container;
- The temperature profiles are different from the ones obtained from the conventional heating (the temperature in the center of the adsorbent is higher than its surface temperature), which is a positive aspect in terms of energy savings;
- The regeneration of adsorbents with microwaves can be made repeatable without affecting them.

In gaseous phase, microwaves have a promising potential due to larger penetration depths of electromagnetic waves in gas-solid systems. The penetration depth (d_E) defined as the distance from the surface of an infinite plate at which the power of the electromagnetic field has decreased to 1/e (~/37%), can be calculated with the following simplified formula [9]:

$$d_E \approx \frac{\lambda_0}{2 * \pi} * \frac{\sqrt{\varepsilon'}}{\varepsilon''} \tag{1}$$

The penetration depth is dependant on the wavelength in vacuum (λ_0) and on the dielectric constants (ε' and ε'').

In liquid systems, containing water or other polar liquids, the penetration depth is limited to a scale of 1-2 cm. Beyond this diameter microwaves heat up only small zones on the edge of the layer [2].

In contrast to this aspect, most gases are microwave transparent. Zeolites used as typical catalysts or adsorbents allow penetration between 10 and 100 cm depending on water content and chemical composition [9].

Microwave desorption strongly depends on the electromagnetic properties of the adsorbent and solvents adsorbed. If microwave transparent adsorbents like dealuminated zeolites are used, polar solvents are easily desorbed while non-polar solvents stay in the adsorbed state. The energy is absorbed by the system as long as polar compounds are still adsorbed. When they are totally desorbed the whole system is microwave transparent and consequently temperature will decrease [2].

If adsorbents which absorb well the energy from the microwaves are used, like silica for example, the energy is retained by the adsorbent and the removal of the solvent mixture is similar with the desorption of a single component. There is no difference in desorption behavior of polar or non-polar solvents [2].

If the adsorbent's dielectric properties lie in between those two analized, a combination of both mechanisms can be foreseen.

Dielectric properties (permittivity) depend on the composition, temperature and on microwave frequency. In poly phased systems with the adsorbate in contact with a solid adsorbent, dielectric permittivities are not easily deduced from the permittivity values of the pure components. During desorption applications, they are modified by the changing temperature and composition [6].

Adsorbents as well as adsorbates themselves can exhibit very contradictory permittivity behaviors during temperature variations. Thus, each adsorbent–adsorbate system will possess its own variation of the dielectric properties during microwave desorption, leading to difficulties in predicting the overall behavior of the system.

Desorption under microwave is a complex process involving many stages [6]:

- Conversion of the electromagnetic energy into heat which is affected by the overall dielectric properties of the adsorbent and adsorbate materials and by the electric field distribution in the microwave applicator;
- Thermodynamic adsorption/desorption equilibrium which is temperature dependant;
- Mass transport phenomena in the pellets depending on the solid material structure and on the dimension and shape of the desorbed molecule;
- Mass and heat transfer in the entire system which depends on the hydrodynamic conditions.

The aim of this study is to point out the key parameters controlling desorption under microwave exposure. By measuring the amount of desorbed water during microwave regeneration, the (current) energy consumption can be correlated with regeneration level and finally optimum conditions for the regeneration step can be set.

2. Materials and methods

For regeneration experiments, saturated 3Å molecular sieve Grace Davison SYLOBEAD MS 564 C has been used. The adsorption capacity (0.14 kg water/kg dry solid) was determined by thermal regeneration of saturated sieve for 2h at 190^0C.

For microwave regeneration the Biotage Initiator device was used, which allowed conducting the experiments under well controlled conditions of temperature and microwave power. During desorption process, a mass balance was used for continuous measurements of the desorbed water. This allowed determining the variation of the specific energy and the regeneration level during regeneration process (see **Fig.1**).

During each experiment, 4 g of saturated molecular sieve was used and the microwave power was limited at 75 or 90 W to avoid overheating.

The regeneration under microwave exposure was studied under different conditions (see **tables 1**, **2**):

- atmospheric pressure and carrier gas –Ar (3-4 L/h);
- low pressure (6.7 kPa or 33.3 kPa), with or without carrier gas, with the low pressure applied from the beginning or after the set temperature was reached;
- MW power used: 75 and 90 W.

When the low pressure is applied from the beginning of the heating, a lot of water is removed from the sample before it can reach 190°C, and because the dry 3Å molecular sieve absorbs very few of the microwave energy it cannot longer heat, the maximum temperature being below 190°C (exp. 5 and 6, **table 1**). For this reason experiments were conducted with the low pressure applied after the temperature of 190°C was reached (exp.8, 13, 14, and 15). The mass measurements were made every 20 seconds, allowing determining the efficiency of the process depending on the amount of water desorbed.

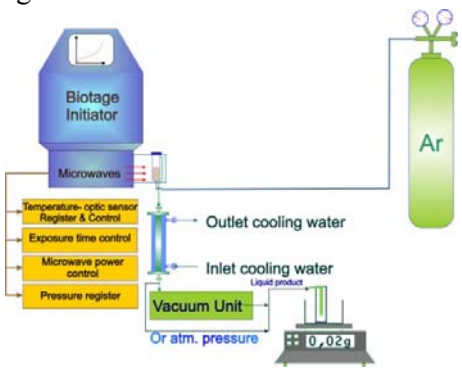

Fig. 1 Microwave regeneration unit at low or atmospheric pressure

Table 1

Conditions used for regeneration of 3A molecular sieves, MW power 75W

No.	Set temp, (°C)	Conditions			Heating time, (s)	Exposure time at max. temp., (s)	Δg (g)	Regeneration degree, (%)
		Pressure, (kPa)	Carrier gas	Vacuum application				
1	190	101.31	Ar	-	180	30	0.27	55.10
2	190	101.31	Ar	-	180	300	0.28	57.14
3	210	101.31	Ar	-	200	30	0.28	57.14
4	230	101.31	Ar	-	280	30	0.3	61.22
5	190[a]	6.7	-	From the beginning	260	-	0.24	48.98
6	190[b]	6.7	Ar	From the beginning	360	-	0.32	65.31
7	190	33.3	Ar	From the beginning	260	30	0.37	75.51
8	190	33.3	Ar	After reaching 190°C	180	300	0.37	75.51

[a] **– maximum reached temperature** 173°C;

[b] **- maximum reached temperature** 175°C;

Table 2

Conditions used for regeneration of 3A molecular sieves, MW power 90W

No	Set temp, (°C)	Conditions			Heating time, (s)	Exposure time at max. Temp., (s)	Δg (g)	Regeneration degree, (%)
		Pressure, (kPa)	Carrier gas	Vacuum application				
9	190	101.31	Ar	-	130	30	0.25	51.02
10	190	101.31	Ar	-	130	300	0.29	59.18
11	190	6.7	Ar	From the beginning	190	300	0.37	75.51
12	190	33.3	Ar	From the beginning	140	300	0.35	71.43
13	190	6.7	Ar	After reaching 190°C	130	30	0.28	57.14
14	190	33.3	Ar	After reaching 190°C	130	30	0.27	55.10
15	190	6.7	Ar	After reaching 190°C	130	300	0.37	75.51

3. Results and discussions

Tables 3 and 4 show the results from 3Å molecular sieve regeneration, sieve that was initially saturated in the drying of 95 % wt. ethanol process.

The supplied energy - E_f was determined from the power-time diagram given by the Biotage initiator apparatus (see eq. 2). By dividing the supplied energy to the amount of desorbed water, specific regeneration energy is obtained - E_s (see eq. 3).

$$E_f = P \times t \div 1000, \quad [w \times s \div 1000], \quad [kJ] \tag{2}$$

$$E_s = E_f \div m_{desorbed\_water}, \quad [kJ / g] \tag{3}$$

Because in the heating stage a lot of water is removed, supplied energy, regeneration level and specific regeneration energy were determined relating to heating time (until the set temperature is reached) and to the total regeneration time.

Analyzing the data presented in tables 3 and 4, some observations can be made:

- During regeneration at atmospheric pressure and in presence of Ar as carrier gas (exp. 1-4 and 9-10), the regeneration level reached is limited at 60% (because of the short heating time). At low MW power (75W), during heating stage most of the water is removed during all treatment period. At higher MW power (90W), the heating is faster and a smaller part of the water is removed during the heating time;

- When the process is conducted at low pressure (6.7 kPa) from the beginning of the process, at smaller MW power (75W) the water is removed mostly during the heating stage and the zeolite with low content of water has a low absorption capacity of the MW radiation. This limits the maximum temperature that can be reached at only 173-175°C (exp. 5-6). In this case, the regeneration level that can be achieved is 49% without a carrier gas and 65% with a carrier gas;

- At moderate pressure (33.3 kPa), the heating of the sample can be achieved even if the low pressure is applied from the beginning of the process. The regeneration level depends on the MW power and treatment time. In this case it was between 49-75%.

Table 3

Results obtained in regeneration of 3 Å molecular sieves at MW power of 75 W

Working conditions			Heating parameters				Results obtained					
No.	Max. temp. (°C)	Exposure time (s)	Heating time (s)	Total time (s)	Supplied energy (kJ)		Removed water, (g)		Regeneration level, (%)		Specific regeneration energy (kJ/g)	
					Until temp is reached	Final	Until temp is reached	Final	Until temp is reached	Final	Until temp is reached	Final
1	190	30	180	210	13.5	15.8	0.24	0.27	49.0	55.1	56.3	58.3
2	190	300	180	480	13.5	36.0	0.24	0.28	49.0	57.1	56.3	128.6
3	210	30	200	230	15.0	17.3	0.26	0.28	53.1	57.1	57.7	61.6
4	230	30	280	310	21.0	23.3	0.29	0.3	59.2	61.2	72.4	77.5
5	173	-	260	260	19.5	19.5	0.24	0.24	49.0	49.0	81.3	81.3
6	175	-	360	360	27.0	27.0	0.32	0.32	65.3	65.3	84.4	84.4
7	190	30	260	290	19.5	21.8	0.366	0.37	74.7	75.5	53.3	58.8
8	190	300	180	480	13.5	36.0	0.24	0.37	49.0	75.5	56.3	97.3

Table 4

Results obtained in regeneration of 3 Å molecular sieves at MW power of 90 W

Working conditions			Heating parameters				Results obtained					
No.	Max. temp. (°C)	Exposure time (s)	Heating time (s)	Total time (s)	Supplied energy (kJ)		Removed water, (g)		Regeneration level, (%)		Specific regeneration energy (kJ/g)	
					Until temp is reached	Final	Until temp is reached	Final	Until temp is reached	Final	Until temp is reached	Final
9	190	30	130	160	11.7	14.4	0.22	0.25	44.90	51.0	53.2	57.6
10	190	300	130	430	11.7	38.7	0.22	0.29	44.90	59.2	53.2	133.4
11	190	300	190	490	17.1	44.1	0.32	0.37	65.31	75.5	53.4	119.2
12	190	300	140	440	12.6	39.6	0.29	0.35	59.18	71.4	43.4	113.1
13	190	30	130	160	11.7	14.4	0.22	0.28	44.90	57.1	53.2	51.4
14	190	30	130	160	11.7	14.4	0.22	0.27	44.90	55.1	53.2	53.3
15	190	300	130	430	11.7	38.7	0.22	0.37	44.90	75.5	53.2	104.6

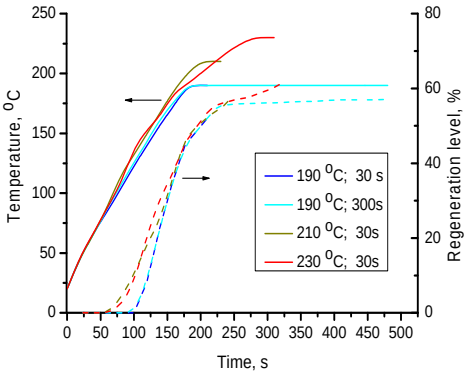

Fig. 2 Temperature (solid line) and regeneration degree (dash line) variation with exposure time during MW regeneration; P_{MW}=75W, Pressure=101.31 kPa, carrier gas -Ar.

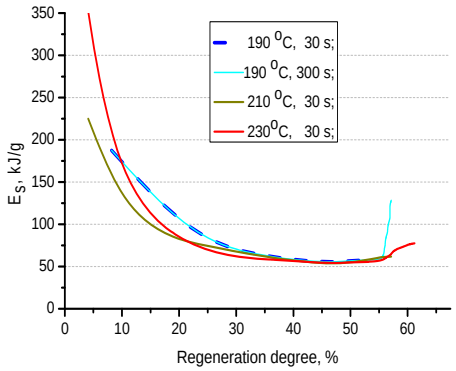

Fig. 3 Specific regeneration energy variation with regeneration degree during MW regeneration; P_{MW}=75W, Pressure = 101.31 kPa, carrier gas-Ar;

In fig. 2, 4 and 6, the time evolution of the temperature and regeneration level is presented. Fig. 3, 5 and 7 show the specific regeneration energy variations relating to regeneration level.

From the analysis of fig. 2, 3, the temperature influence on regeneration process at atmospheric pressure conducted with Ar as carrier gas and at MW power of 75W can be noticed.

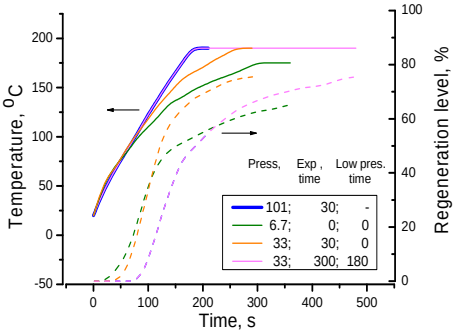

Fig. 4 Temperature (solid line) and regeneration degree (dash line) function of exposure time during MW regeneration; P_{MW}=75W, Pressure 6.7 or 33.3 kPa, Temp. 190°C, carrier gas-Ar.

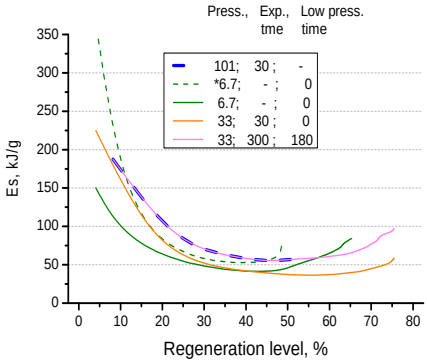

Fig. 5 Specific regeneration energy function of regeneration degree during MW regeneration; P_{MW}=75W, Pressure 6.7 or 33.3 kPa, Temp. 190°C, carrier gas-Ar; (*-without Ar).

Increasing the set temperature determines a slightly increase of the heating speed and for this reason the specific regeneration energy slightly decreases. Optimal regeneration level that can be reached in these conditions is limited at

55%, increasing regeneration time will lead to an increase of the specific regeneration energy.

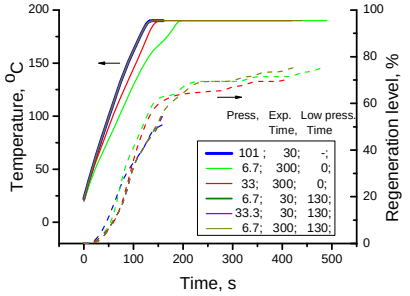

Fig. 6 Temperature (solid line) and regeneration degree (dash line) function of exposure time during MW regeneration; P_{MW}=90W, Pressure 6.7 or 33.3 kPa, Temp. 190°C, carrier gas-Ar.

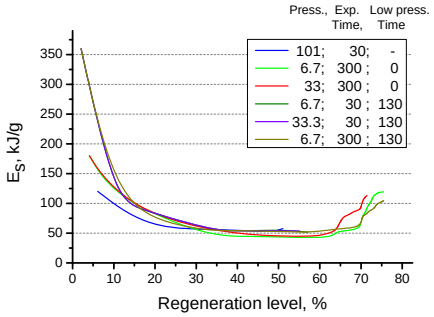

Fig. 7 Specific regeneration energy function of regeneration degree during MW regeneration; P_{MW}=90W, Pressure 6.7 or 33.3 kPa, Temp. 190°C, carrier gas-Ar;

In fig. 4 and 5 the results obtained from low pressure regeneration are presented, by using a MW power of 75W. Applying a low pressure from the beginning of the heating process determines a decrease in heating rate and even limitation of the temperature (at 6.7 kPa, the maximum temperature was 173°C). Regarding specific regeneration energy, at low values of pressure, lower values of Es can be reached in a wider range of regeneration levels (30-70%). In this MW heating conditions, the best results are obtained at 33.3 kPa pressure, applied from the beginning of the heating.

Fig. 6 and 7 show the results obtained from low pressure regeneration, at a MW power of 90W. In this case also, heating rates are slightly smaller once the pressure is decreasing, but the differences from the sample heated at atmospheric pressure are slightly lower than those registered in case of using less MW power. The smallest values for the Es can be obtained by using a vacuum pressure (6.7 or 33.3 kPa) applied from the beginning of the heating stage, for regeneration levels in range of 40-60%. To obtain higher regeneration levels, the specific regeneration energy is increasing rapidly.

6. Conclusions

Microwave regeneration can be used for water desorption from the molecular sieves. By increasing the exposure time and also the regeneration temperature, higher regeneration levels are achieved but the real efficiency depends on the energy consumed for water elimination. In all studied cases, the specific regeneration energy was higher at smaller or very high regeneration

levels. The best results for the specific regeneration levels can be obtained for medium regeneration levels (30-60%).

The specific regeneration energy can be reduced by increasing the regeneration temperature (but this is limited by the stability of the molecular sieve) or by applying a low pressure during regeneration process. Optimal working pressure has been determined to be 33.3 kPa, at even lower pressure water is removed too quickly and the heating with microwaves becomes ineffective.

MW power is also very important. Using a greater MW power can lead to overheating and even damaging the zeolite. Moderate MW power (75 W for a 4 g of molecular sieve sample) allows achieving the lowest values of Es when the regeneration process is conducted at low pressures (33.3 kPa).

Microwave regeneration of the molecular sieve used for bioethanol drying solves only a part of TSR issues. Thus, heating time is much shorter than conventional heating time, the regeneration temperature being lower than the conventional one which use hot carrier gases and by using moderate pressure, higher regeneration levels can be achieved.

For using this process at an industrial scale, constructive solutions must be found to make heating of large volumes of zeolite possible, even if the depth of penetration of the microwaves in the zeolite is limited.

Acknowledgments

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Nomenclature

d_E	penetration depth of an electromagnetic wave [m]
ε_0	dielectric constant (vacuum) [(A·s)/(V·m)]
ε’	1. dielectric constant
ε”	2. dielectric constant
λ_0	wavelength in vacuum [m]
μ_0	permeability in vacuum [(V·m)/(A·s)]
ω	frequency [1/s]
Es	specific regeneration energy [kJ/g]
Ef	supplied energy [kJ]
PSR	pressure swing regeneration
TSR	temperature swing regeneration
MW	microwave

R E F E R E N C E S

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