

Regeneration of Weak and Medium Absorbing Molecular Sieves (3Å vs 4Å) under Microwave Exposure

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This paper presents the study of the regeneration process in microwave field of molecular sieves used for bioethanol drying. The study was carried on two types of molecular sieves with different pore sizes: 3Å and 4Å. The equipment used for microwave generation allowed a strict control of the process parameters and the determination of the necessary power consumption for the regeneration process. The regeneration was made in identical conditions for both types of sieves, studying the energy efficiency in correlation with the desired regeneration degree. The data regarding the incident and reflected microwave power evolution during the exposure in microwave field, allowed finding of an optimal regeneration degree from power consumption point of view. Although they have a reduced efficiency in the drying process of bioethanol, 4Å molecular sieves can be regenerated at a higher degree (80%) than 3Å sieves. The specific energy consumption for regeneration of 4Å sieves by microwaves is also lower when compared to 3Å molecular sieves.

Keywords: molecular sieves, microwaves, energy efficiency, bioethanol, regeneration

In the last years, the fuel market registered an opening to the reduction of the pollution degree and inherently to the usage of renewable resources. Biofuels are promoted by the EU directives. All fuel producers from EU are obliged to use bioethanol in mixture with gasoline, beginning with 2008. Starting with January 2013, the minimum quantity of bioethanol added to gasoline is set to 6% [1, 2].

These legislative modifications were an impulse for the bioethanol producers and also for the research departments that oriented themselves towards new technology development and power consumption optimization [3]. In Brazil, for instance, research is being carried out for the integration of bioethanol production with biodiesel production, this being the concept for future bio-refineries [4]. The ethanol has a huge potential in the chemical and petrochemical industry, being raw material also for polymers, but environmental impact studies are still in research [5].

There are several technologies used for water removal from ethanol to fulfil the requirements regarding water content (max 0.3% wt.) [6]. Power consumption necessary to obtain bioethanol reflects different energetic costs according to the type of process used. The water removal from ethanol can be carried out through classical distillation processes (max 96.4%), azeotropic distillation with volatile compounds (min 99.5%), extractive distillation with different agents - solvents, salts, ionic liquids, polymers- (min 99.5%), extractive distillation with dissolved salts (min 99.5%) or adsorption with molecular sieves (min 99.5%) [7, 8].

The molecular sieves are used for the selective water adsorption out of different organic compounds (e.g. out of bioethanol). The sieves selectivity depends on the pore geometry. Also, molecular sieves with a small Si/Al rate present a higher affinity towards water in the adsorption stage (in comparison with ethanol) [9]. After the adsorption process, in order to recover the adsorptive properties, the water must be eliminated from the pores, the regeneration

being obtained with energy consumption. There are two main methods used for the adsorbents regeneration:

- pressure swing regeneration (PSR) used for the desorption of weakly adsorbed molecules [10];
- temperature swing regeneration (TSR) for strong adsorbed components.

In TSA type processes case [11, 12], the regeneration degree can be limited not only by the molecular sieve characteristics or by technological parameters, but also by the energy consumption. In order to obtain a high regeneration degree of molecular sieves, supplementary energy consumption is required. To reduce operational costs, the process can be managed at lower regeneration degrees, but this means multiplying of the adsorption-regeneration cycle number for the same operation duration. This has as effect reducing the adsorption and regeneration duration per stage.

When the regeneration is not being carried out through heating with microwaves, the properties of microwave energy absorption depend on the sieve's chemical composition and its water content.

In water desorption case, when the saturated sieves are exposed to microwaves, the water is heated selectively due to radiation and less to the adsorbent, this leading to a reduced energy consumption usage [13].

The purpose of this study is to establish the correlation between the microwave energy absorption properties and the regeneration specific energy for molecular sieves under microwave heating.

Experimental part

Materials and methods

The experiments were carried out on two types of molecular sieves, with different pore dimensions: 3Å and 4Å (table 1, 2). There have been used activated sieves (dry) and saturated sieves (used in the process of water removal from ethanol under controlled conditions).

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3Å Grace Davison SYLOBEAD MS 564 C		
Property	Unit	Value
Bulk density	kg/m ³	689
Resistance to compression	kgf	3.15
Total volatiles at 954.4 °C	%	2.0
Water adsorption capacity*	% wt.	22.0
Water adsorption heat	kJ/kg	4186.8

*Calculated in conditions of 80% humidity at 25°C

Table 1
TYPE 3Å MOLECULAR SIEVE
CHARACTERISTICS [14]

4Å Laboratory BDH reagent						
Property	Unit	Grains		Pellets		Obs.
		Min.	Max	Min.	Max	
Diameter/Dimension	mm	1.6-2.5	3-5	1/16"	1/8"	
Water adsorption capacity	%gr	21.5		21.5		Humidity 50%, t - 25°C
Bulk density	g/ml	0.70		0.65		Stable
Loss at calcination	%gr	1.50		1.5		t - 575°C, 1h
Loss through granulation	%gr	0.10		0.2		
Resistance to compression	N	40	80	35	80	

Table 2
TYPE 4Å MOLECULAR SIEVES
CHARACTERISTICS [15]

The heating of the molecular sieves was done using 2 types of microwave generators:

- Biotage – Initiator;
- MicroFlow 200ss.

The ethanol concentration of the desorbed samples was determined indirectly, through the determination of the relative refractive index using a Waters 410 RI detector connected to a HPLC (model series 20xx, JASCO) system [16].

Heating with Biotage – Initiator

The regeneration was done in microwave field in conditions of constant power (75W), the process variables

being the regeneration time or the regeneration temperature.

The amount of desorbed product has been registered during the desorption process (fig. 1). This allowed the determination of the specific energy function of regeneration degree. For each experiment it was used a sample of 4g of molecular sieve saturated or dry and the microwave power was limited to 75W in order to avoid overheating the molecular sieve. To favor the desorbed vapour elimination out of the sieve pores, an inert gas (argon) was injected in the adsorbent mass throughout the entire microwave heating process.

When the dry molecular sieve was heated with microwaves, the analytical balance was not used, due to the fact that there was no mass loss registered.

Heating with MicroFlow 200ss

The MicroFlow equipment allows the recording of both incident power and reflected power. These measurements offer clues referring to microwave energy absorption capacity of the treated sample.

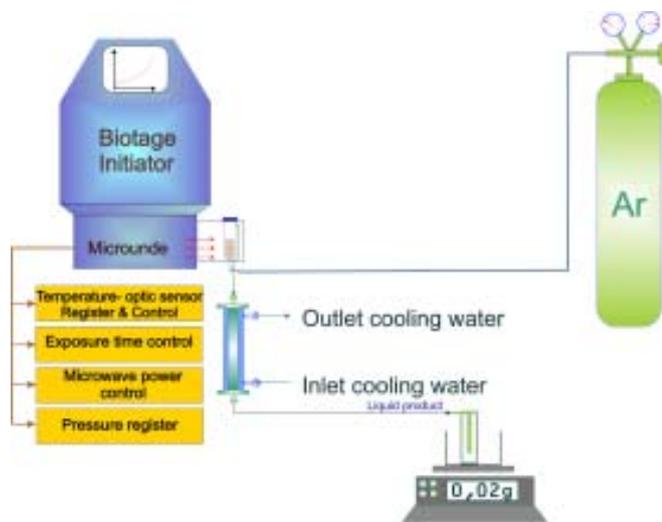


Fig.1. Microwave heating equipment using Biotage – Initiator microwave generator

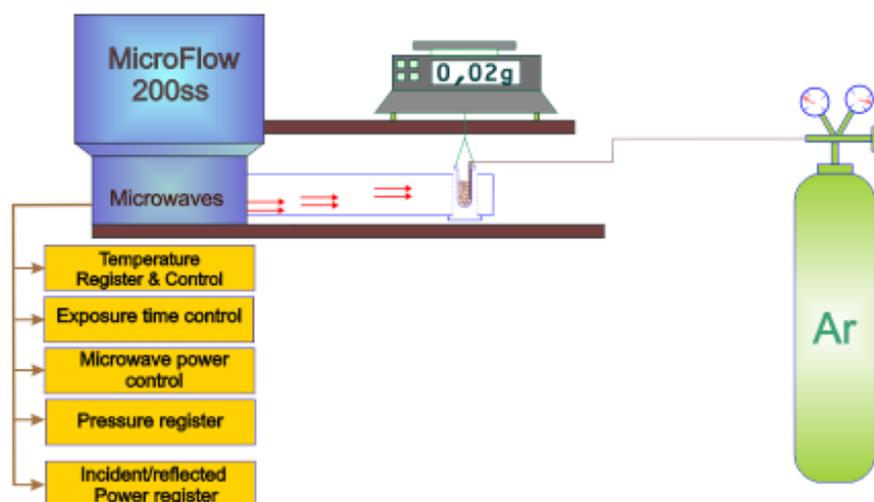


Fig. 2. Microwave heating equipment using MicroFlow 200ss as microwave generator

The working procedure was similar to the one followed with Biotage microwave generator (fig. 2), the difference being the possibility to obtain information on the emitted heating power, but also on the reflected power that its not absorbed by the molecular sieve.

Water saturation of molecular sieves

Saturation with water of molecular sieves was carried out by vaporization of 95% ethanol into a glass column with fixed molecular sieves [16]. The obtained vapours were condensed, cooled and analyzed to determine the water content in the ethanol. The obtained saturated molecular sieves were used for the determination of the efficiency for the microwave regeneration process.

Results and discussions

Ethanol (95% conc.) drying on molecular sieves

The treated ethanol concentration maintains a constant value as long as the adsorption front is inside the adsorbent column. After the breakthrough point is reached, the concentration decreases up to a point when the sieve cannot adsorb more water, and the ethanol concentration that exits the column is equal to the initial ethanol concentration (fig. 3). Due to higher selectivity, 3Å molecular sieve is capable of drying a higher volume of ethanol in the same conditions.

Molecular sieves behaviour at microwave heating (Biotage – Initiator)

The heating of the sieves was made in the Biotage – Initiator equipment, using enclosed vials, in order to determine the microwave energy absorption capacity (reflected in the temperature rise) for the two types of sieves, dry and saturated with water.

Analyzing the data from figure 4, it can be observed a very different behaviour between the dry sieves and similar

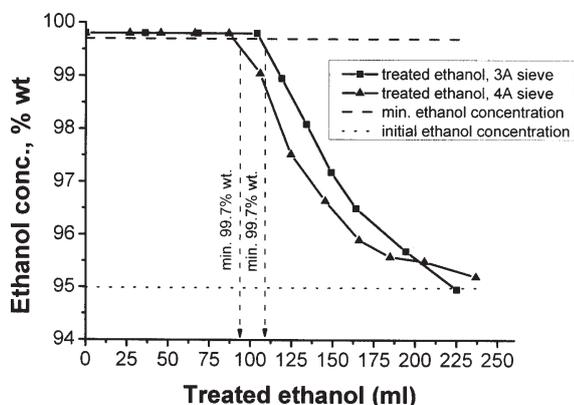


Fig. 3. Efficiency of water removal process, 3Å sieve vs 4Å sieve (45 g of sieves)

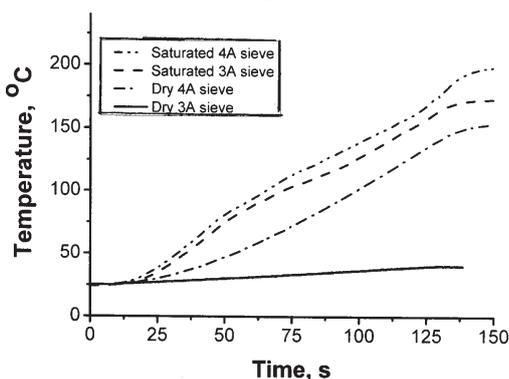


Fig. 4. Temperature variation with exposure duration in microwave field (Biotage Initiator) - 3Å and 4Å molecular sieves, dry and saturated

behaviour between the sieves with water content. The saturated sieves absorb better the microwave energy, thus heating up to a higher temperature than the dry sieves. To determine the degree of the heating in microwave field, all types of sieves were tested in the same conditions:

-Sample weight:	4.00 g
-Initial temperature:	25°C
-Heating time in microwave field:	2 min
-Microwave field power:	75W

Through the study of the behaviour at microwave heating we can deduct the sieve regeneration degree. A sieve with higher water content will heat up more than a sieve that contains lower water content. The complete regeneration can be achieved when the regenerated sieve heating curve coincides with the dry sieve heating curve.

Regardless of the temperature at which the regeneration takes place, the yielded energy for the 4Å sieve needed to reach the same temperature will be smaller than the yielded energy needed to heat the 3Å sieve (fig. 5). This is caused by the fact that the 4Å sieve absorbs better the microwave energy because of its different chemical composition. This fact is explained in figure 5, where it is presented the evolution of the supplied power by the magnetron for the two sieves.

Through the integration of the values from figure 5 we can obtain the following values: 27846 J to heat the 3Å sieve and 18547 J to heat the 4Å sieve.

When the heating under MWs has been done using an open vial in argon flow, the desorbed mass has been measured. In the first measurement set, the evolution of the desorbed mass due to heating up to 190°C of the two types of saturated sieves has been tracked (fig. 6). In the first minutes after MW exposure, the desorption is more

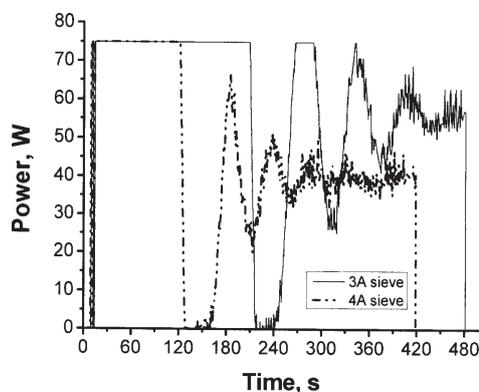


Fig. 5. Generated power used for regeneration of saturated sieves in microwave field, heating up to 170°C

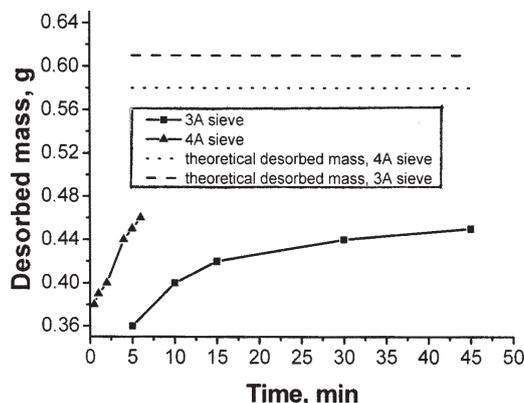


Fig. 6. Mass variation with exposure duration, in microwave field, up to 190°C (in argon flow)

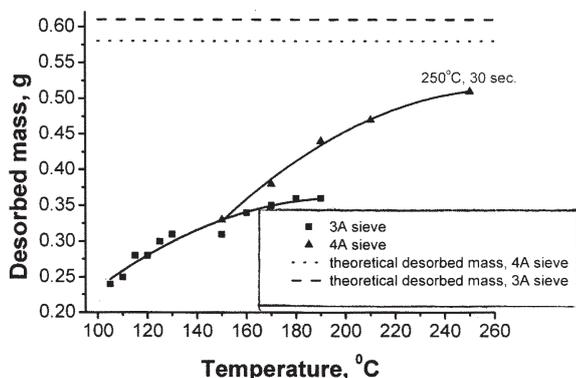


Fig. 7. Variation of desorbed mass with the regeneration temperature (heating time: 5 min, in steady argon flow); Note: the equipment protection did not allow the exposure to 250°C for longer than 30 s

pronounced, afterwards tending to reach a limit. For the same exposure durations, 4Å molecular sieve desorbs more water compared to 3Å sieve. In the following experimental set, the evolution of the desorbed mass out of the saturated molecular sieves was observed during heating for 5 min. The analysis of the data presented in figure 7 shows the fact that as the regeneration temperature increases the desorbed mass out of the sieve's pores also increases. We can also observe the fact that the 4Å sieve desorbs a much larger quantity than the 3Å sieve at a similar regeneration temperature. This is due to the more efficient microwave power absorption of the 4Å sieve.

During the regeneration with microwaves, the product obtained prior to desorption was collected. These samples were analyzed and depending on the refractive index, using the calibration curve, the solution concentration was determined.

During desorption, there can be noticed that, at first, a mixture richer in ethanol is desorbed, after which, as the regeneration temperature or time increases, the ethanol content becomes constant, more and more water being removed (tables 3-4). Because of the larger pore dimensions the water desorption selectivity in the 4Å sieve is smaller in comparison with the 3Å sieve.

The determination of the efficiency of the regeneration process

For the calculation of the regeneration process of molecular sieves with microwaves it was used the MicroFlow 200ss equipment. This equipment allows the registration of both incident and reflected power. Because of the fact that the heating chamber has a different configuration than the one used in the Biotage – Initiator, the temperature evolution in time charts are different.

The following parameters were determined:

$$C_{\text{ads}} - \text{molecular sieves adsorption capacity}$$

$$C_{\text{ads}} = (m_2 - m_1) / m_1 * 100, [\%] \quad (1)$$

$$P_{\text{ef}} - \text{effective transferred power to the molecular sieves}$$

$$P_{\text{ef}} = P_i - P_r, [\text{W}] \quad (2)$$

E_r – Energy delivered by the microwave generator to the molecular sieves (provided power)

$$E_r = P_i \times t, [\text{kJ}] \quad (3)$$

E_{sI} – Specific regeneration energy, in relation with the desorbed water (E_{sI}) or with the quantity of molecular sieve put into regeneration (E_{sII}).

$$E_{sI} = E_r / m_{\text{desorbed water}}, [\text{kJ/g water}] \quad (4)$$

$$E_{sII} = E_r / m_{\text{sita}}, [\text{kJ/g sieve}] \quad (5)$$

$C_{u.MW}$ – usage coefficient of microwave energy, offers indications on the sieve capacity to absorb microwave energy

$$C_{u.MW} = 100 - P_r / P_i \times 100, [\%] \quad (6)$$

Because of a higher microwave energy absorption level, the 4Å molecular sieves have a higher effective power value, the microwave heating taking place easier and with continuity (fig 8a). For the 3Å sieves there appears to be bigger effective power fluctuations, mostly at drying times greater than 300s. This aspect has direct influences on the process, the microwave power coefficient having fewer fluctuations for the 4Å sieve than for the 3Å sieve (fig 8b). From temperature evolution point of view, it can be observed in figure 8c that the 4Å sieves heat up without temperature fluctuations, this meaning that the number of

Regeneration temperature	Refractive index	Concentration in ethanol (% wt)	Component mass (g)	
			Ethanol	Water
150	1.3538	31.6	0.10	0.23
170	1.3525	29.1	0.11	0.27
190	1.3511	24.7	0.11	0.33
210	1.3485	22.2	0.10	0.37
250*	1.3481	21.5	0.11	0.40

*regeneration time: 30 s.

Table 3
CONCENTRATION OF THE RESULTED PRODUCT AFTER REGENERATION WITH MICROWAVES OF 3Å SIEVE AT DIFFERENT TEMPERATURES, FOR 5 min, P=75W

Regeneration temperature	Refraction index	Concentration in ethanol (% gr)	Component mass (g)	
			Ethanol	Water
150	1.3542	32.8	0.13	0.26
170	1.3546	33.2	0.13	0.27
190	1.3542	32.8	0.13	0.27
210	1.3506	25.7	0.11	0.33
250*	1.3490	22.9	0.11	0.35

*regeneration time 30 s.

Table 4
CONCENTRATION OF THE RESULTED PRODUCT AFTER REGENERATION WITH MICROWAVES OF 4Å SIEVE AT DIFFERENT TEMPERATURES, FOR 5 min, P=75W

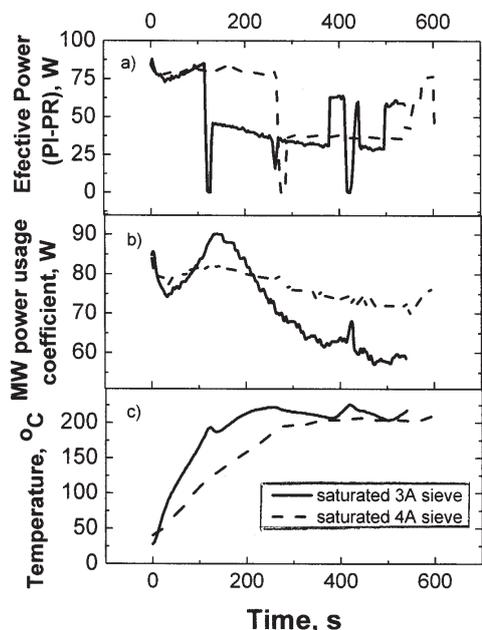


Fig. 8. Heating behaviour and the usage level of MW by the saturated sieves; a) effective transferred power variation in time; b) MW power usage coefficient variation in time; c) temperature variation with time.

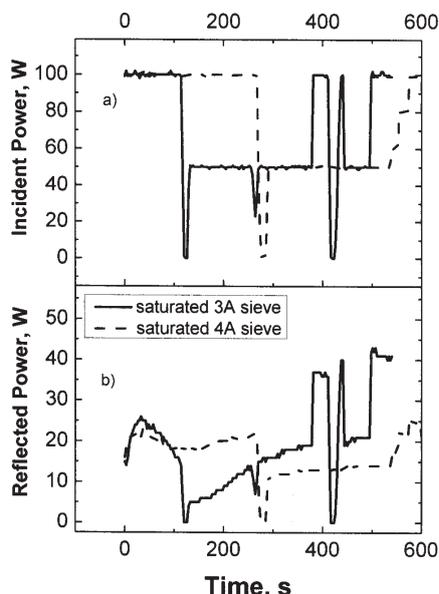


Fig. 9. MW power variation during the regeneration of saturated molecular sieves: a) Incident MW Power b) Reflected MW Power

regenerations that can be made without affecting the structure of the sieve is higher.

As the water is being desorbed out of the molecular sieve pores, the reflected power rises, the increase being more intense for the 3Å sieves with a lower microwave energy absorption degree (fig. 9b). The 4Å sieve did not register a significant modification in the reflected power because of its good capability of absorbing microwave energy, even in dry state.

From energy consumption point of view, the regeneration process with microwaves is not a big consumer when considering the molecular sieves regeneration up to 50-60% regeneration degree (15-50 kJ) for the 3Å sieves and even more (80%) for the 4Å sieves (fig. 10a).

The regeneration process efficiency is highlighted very well in the diagrams showing consumed energy depending on desorbed water. The specific energy has been calculated dividing the supplied energy by the desorbed water/ethanol

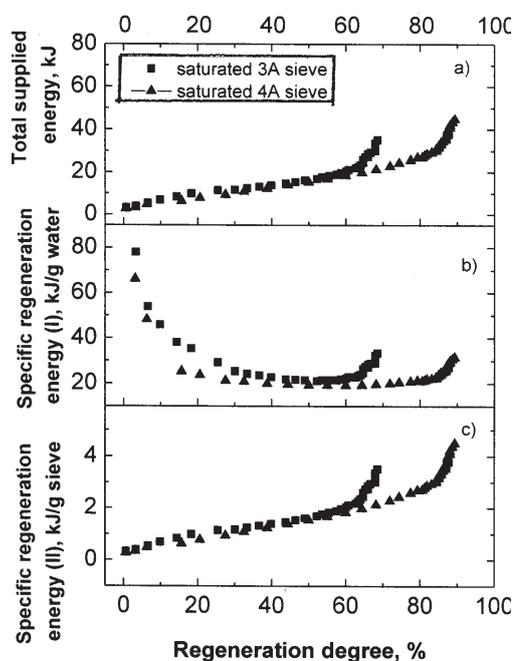


Fig. 10. Efficiency of the regeneration process depending on the regeneration degree of saturated sieves; a) Supplied energy (kJ); b) Specific regeneration energy I (kJ/g water); c) Specific regeneration energy II (kJ/g sieve)

mass, and the specific energy II was calculated dividing the supplied energy by the heated sieve mass. The specific energy I decreases (fig. 10b) as the regeneration process continues, reaches a minimum and start rapidly to increase, indicating that the process becomes ineffective from energy consumption point of view.

For the 3Å molecular sieve, due to its low microwave absorption rate in dry state, the maximum efficiency can be achieved at regeneration degree values up to 55-60%. The 4Å sieve, because of its higher microwave absorption rate, can be efficiently regenerated to even bigger values of the regeneration degree (80%).

In the case of specific energy (II), related to the molecular sieve mass, this energy slightly increases in the first region and when high values of the regeneration degrees are achieved, the increase becomes more rapidly.

Conclusions

The 4Å molecular sieve can be a good alternative to the classic 3Å sieve used for ethanol drying processes in terms of regeneration under MW exposure;

- due to the different chemical composition, 4Å molecular sieve absorbs easily the generated microwave energy, making possible a faster energy transfer to the ethanol/water mixture. Nevertheless, it has to be mentioned that the bigger pore size allows adsorption of a higher ethanol quantity in the drying (adsorption) phase, compared with 3Å molecular sieves;

- because of the increased water retention selectivity, the 3Å sieve is capable of drying a bigger quantity of ethanol, in the same conditions of temperature and exposure time;

- the increasing of temperature and exposure time under microwave field accelerates the desorption process, but the regeneration efficiency is given by economical factors such as energy consumption;

- the saturated 3Å sieves heat up faster at the beginning of the exposure, but as the water is being desorbed, the power usage coefficient decreases along with the decrease of the effective power;

- because of a better MW energy absorption, the 4A^o molecular sieves have higher effective power values, improving the heating efficiency. The 4A^o sieve did not register a significant modification in the reflected power because the MW absorption takes place also in dry phase;
 - taking into consideration the supplied energy, the regeneration process with microwaves is not such a big consumer considering the regeneration of the molecular sieves up to a regeneration degree of maximum 50-55% (15-20 kJ) for 3A^o sieves and even up to 80% for 4A^o sieves.

Notations

m_1 - weight of dry molecular sieve, [g]
 m_2 - Weight of saturated molecular sieve, [g]
 Es_1 - Specific regeneration energy I, [kJ/g water desorbed]
 Es_2 - Specific regeneration energy II [kJ/ g of treated sieve]
 $C_{u,MW}$ - MW Power usage coefficient, %
 P_i - Incident Power, W
 P_r - Reflected Power, W
 P_e - Effective Power, W
 MW - Microwave
 PSA - Pressure swing adsorption
 TSA - Temperature swing adsorption

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