

## Article

# Investigating the Physical and Operational Characteristics of Manufacturing Processes for MFI-Type Zeolite Membranes for Ethanol/Water Separation via Principal Component Analysis

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**Abstract:** In this study, Principal Component Analysis (PCA) was applied to discern the underlying trends for 31 distinct MFI (Mobil No. 5)-zeolite membranes of 11 textural, chemical, and operational factors related to manufacturing processes. Initially, a comprehensive PCA approach was employed for the entire dataset, revealing a moderate influence of the first two principal components (PCs), which collectively accounted for around 38% of the variance. Membrane samples exhibited close proximity, which prevented the formation of any clusters. To address this limitation, a subset acquisition strategy was followed, based on the findings of the PCA for the entire dataset. This resulted in an enhanced overall contribution and the revelation of diverse patterns among the membranes and the considered manufacturing factors (total variance between 55% and 77%). The segmentation of the data unveiled a robust correlation between silica (SiO<sub>2</sub>) concentration and pervaporation conditions. Additionally, a notable clustering of the chemical compositions of the preparation solutions underscored their significant influence on the operational efficacy of MFI zeolite membranes. On the other hand, an exclusive chemical composition of the preparation solution was noticed. This highlighted the high influence of the chemical composition on the operational efficiency of MFI zeolite membranes. The coupling of PCA with experimental results can provide a data-driven enhancement strategy for the manufacturing of MFI-type zeolite membranes used for ethanol/water separation.

**Keywords:** MFI-type zeolite membranes; ethanol/water separation; Microporous materials; pervaporation; Principal Component Analysis



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## 1. Introduction

Fossil fuels such as coal, oil, and natural gas have long been relied upon as primary sources of energy, powering economic expansion and technological progress. Unfortunately, their widespread usage has produced various harmful environmental and human health consequences; with climate change concerns intensifying, as well as resource scarcity increasing rapidly, the inspection for alternatives which align with sustainability goals has become ever more imperative [1]. Biofuels have emerged as an attractive alternative to fossil fuels in recent years. Composed largely of organic matter, biofuels offer several advantages over their fossil-based counterparts; they are renewable as they derive from living or recently living organisms. Their production could originate from crops, agricultural residues, or even algal sources, providing a potentially sustainable energy solution,

with reduced environmental impacts. Biofuels play an essential part in helping to achieve the United Nations Sustainable Development Goals (SDGs), which aim to environmental sustainability [2].

Ethanol has gained significant attention as a biofuel, due to its high capacity to address environmental concerns and reduce the dependency on fossil fuels. Derived from renewable biomass sources, such as corn, sugarcane, or cellulosic feedstocks, ethanol is a promising alternative to conventional gasoline. With its widespread production and use, ethanol has emerged as a key player in the transition towards a more sustainable and cleaner energy future [2]. One of the biggest challenges in ethanol production is acquiring the proper purification techniques. Membrane technology has presented promising findings in this matter. Following this strategy, zeolite membranes offer an interesting option for ethanol separation and purification [3–5].

Significant research has been conducted on the advancement of zeolite membranes, owing to their potential utilization in various industrial applications like separation membranes (various hydrocarbon molecules and organic/water mixtures), membrane reactors, and catalysis [6,7]. In biodiesel production, MFI (Mobil No. 5) zeolite membranes act as an effective catalyst in the transesterification reaction, converting triglycerides into biodiesel [3–5]. Their unique structure and acidity enhance the reaction efficiency. In bioethanol production, MFI zeolite membranes are utilized for the dehydration process, selectively adsorbing water and increasing ethanol concentration. Additionally, MFI zeolite membranes play a role in biomass conversion, facilitating biomass pyrolysis, cracking, and hydrodeoxygenation, resulting in the production of valuable biofuels and chemicals. Their shape and catalytic properties improve the yield and selectivity of the desired products [3–5].

MFI zeolite membranes possess a well-defined crystalline structure with interconnected channels and a high surface area, which makes them good adsorbents and catalytically active; they can enable acid-catalyzed reactions. The shape of MFI zeolite membranes restricts the size and shape of molecules, enhancing selectivity and control in several processes. They exhibit thermal stability, maintaining their structure and activity at high temperatures [8]. MFI zeolite membranes also possess ion exchange capacity and exhibit high chemical resistance and corrosion, which makes them versatile materials for applications such as adsorption, catalysis, and separation in various industries [9].

Numerous investigations have thoroughly presented the latest advances in the synthesis, characterization, and applications of zeolite membranes. Neel et al. focused on the fabrication techniques of zeolite membranes, including seed assembly and secondary growth methods, with a particular emphasis on oriented films/membranes [10]. The secondary-growth method involves separating the nucleation and growth stages of crystal formation, which requires lower temperatures and shorter synthesis times compared to the in situ crystallization approach. Consequently, this method allows for improved control over the microstructure of membranes [11]. Various techniques have been employed to apply zeolite seeds onto porous supports, including rub coating [12], spin coating [13], dip coating [14], vacuum coating [15], electrophoretic deposition [16], among others. Additionally, studies have explored the applications of zeolites in membrane reactors, delving into the distinctions between metal-organic frameworks (MOF) and zeolite membranes [10]. Kosinov et al. provided a summary of the recent developments in zeolite membranes for gas separation, highlighting the exceptional separation performance of 8-MR (membered ring) zeolite membranes [17]. Algieri et al., on the other hand, reviewed the processes involved in synthesizing zeolite membranes for pervaporation and desalination [18]. Another study conducted by Li et al. delved into the preparation, functional mechanism, and applications of oriented MFI zeolite membranes [5].

Principal Component Analysis (PCA) is a powerful statistical tool widely used in membrane sciences for various critical applications [19–21]. One major application of PCA in this field resides in the analysis and interpretation of complex datasets, such as those obtained from spectroscopic measurements, and operational conditions [22,23]. By reducing

the dimensionality of the data, PCA helps in identifying the most significant variables, thus simplifying the analysis without significant loss of information [19–23]. This simplification is particularly valuable in the quality control and optimization of membrane fabrication processes, where multiple variables need to be monitored simultaneously [19–21]. Additionally, PCA is employed in the study of membrane fouling, enabling researchers to distinguish between different fouling mechanisms and to identify key factors contributing to fouling [24]. This insight is crucial for developing more efficient cleaning protocols and improving membrane longevity [24]. PCA is also used in the field of membrane performance prediction, where it assists in correlating various operational parameters with membrane performance metrics such as flux and selectivity, facilitating the design of better-performing membranes [19,22,23]. On the other hand, PCA can be adopted to validate the comparison of several experimental sets, aiming to uncover rheological properties of composite materials [25,26]. Overall, PCA is an indispensable tool in membrane sciences, aiding in data analysis, process optimization, fouling management, and performance prediction.

As can be seen from previous investigations, MFI zeolite membranes' application involves a wide range of physical/chemical characteristics, from one side, and operational features, from another side. In order to cope with these various distinctions and seek a more structured optimization of membrane conditions and operations, the application of data-driven machine learning techniques could be of potential benefits [21]. In this study, we investigated the application of PCA in order to reveal the most influencing variables in MFI zeolite membrane synthesis and operation [27].

## 2. Materials and Methods

### 2.1. Data Collection and Normalization

Data were collected from the published study of Lu et al. [27]. Table 1 presents the inventory of the different investigated MFI-type zeolite membranes, along with their physical properties, synthesis conditions, and pervaporation (PV) performance. Each of the investigated variables has a different weight. In order to remove any bias induced by magnitude differences, a normalization step similar to the one used by Murshid et al. [28] was applied as follows:

$$Y_{st} = \frac{\text{Value} - \text{Mean}}{\text{Standard Deviation}} \quad (1)$$

where  $Y_{st}$  represents the standardized dataset values.

### 2.2. Principal Component Analysis (PCA)

After the normalization process, the PCA results were obtained using XLSTAT 2014 software, following a similar approach as that adopted by Murshid et al. [28]. The missing data were estimated using the XLSTAT 2014 built-in feature that replaces a missing value with the "Mode" associated with its respective variable.

In this study, we exploited the PCA output to visualize certain phenomena and revealed hidden patterns through analyzing correlations (negative or positive) and the representative principle components (PCs) for the population in hand. The  $j^{\text{th}}$  PC matrix ( $Fi$ ) was expressed using a unit-weighting vector ( $U_j$ ) and the original data matrix  $M$  with  $m \times n$  dimensions (where  $m$  is the number of variables, and  $n$  is the number of datasets), as follows [29–32]:

$$Fi = U_j^T M, \quad (2)$$

where  $U$  is the loading coefficient, and  $M$  is the data vector of size  $n$ . The variance matrix of  $M$  ( $\text{Var}(M)$ ), obtained by projecting  $M$  to  $U$ , should be maximized, as follows:

$$\text{Var}(M) = \frac{1}{n} (UM)(UM)^T = \frac{1}{n} UMM^T U, \quad (3)$$

$$\text{Max}(\text{Var}(M)) = \text{Max} \left( \left( \frac{1}{n} \right) UMM^T U \right). \quad (4)$$

Since  $\frac{1}{n}MM^T$  is the same as the covariance matrix of  $M$  ( $\text{cov}(M)$ ),  $\text{Var}(M)$  can be expressed as follows:

$$\text{Var}(M) = U^T \text{cov}(M) U. \quad (5)$$

The Lagrangian function can be defined by the Lagrange multiplier method as follows:

$$L = U^T, \quad (6)$$

$$L = U^T \text{cov}(M) U - \delta (U^T U - 1). \quad (7)$$

In (7),  $U^T U - 1$  is considered to be equal to zero, since the weighting vector is a unit vector. Hence, the maximum value of  $\text{Var}(M)$  can be calculated by equating the derivative of the Lagrangian function ( $L$ ) with respect to  $U$ , as follows

$$\frac{dL}{dU} = 0, \quad (8)$$

$$\text{cov}(M)U - \delta U = (\text{cov}(M) - \delta I)U = 0, \quad (9)$$

where  $\delta$  and  $U$  are the eigenvalue and eigenvector of  $\text{cov}(M)$ , respectively.

The aim of this study was to apply PCA to the dataset obtained from the preceding research carried out by Lu et al. [27] (Table 1), in order to uncover hidden patterns between physical/chemical properties on one side and synthesis conditions and PV performances on the other side. If these patterns are identified, they will provide more comprehensive understanding and interpretation of the various factors influencing the application of specific MFI zeolite membranes. The insights derived from PCA could enhance several stages of the ethanol production process, ranging from the manufacturing approach and experimental conditions to the separation efficiency of ethanol/water mixtures for a selected membrane.

In this study, we applied PCA to 11 different factors that influenced the 31 investigated zeolite samples (Table 1). PCA, being a technique with the broad scope of unsupervised machine learning, is extensively utilized to reduce the dimensionality of a given dataset. It has consistently demonstrated its efficiency in recognizing patterns of data variability within multivariate matrices. One intriguing feature of PCA is its ability to visualize data variability and subsequently present the obtained information in an easy-to-understand graphical form [33].

### 2.3. PCA Interpretation and Application

Along with seeking a better understanding of the physical and operational features of MFI-type zeolite membranes, this research aimed to enhance the understanding of experimentalists regarding the application of PCA in handling their datasets. In brief, the investigated dataset consisted of multiple variables ( $x_1, x_2, \dots, x_n$ ); visualizing these variables would typically involve numerous graphs ( $n$ , number of graphs), with each graph plotting the studied population (membranes, in our case) against individual variables (pore size,  $\text{SiO}_2$ , temperature, etc.). PCA simplifies this process by consolidating the information into a singular plot comprising  $\text{PC}_1$  and  $\text{PC}_2$  [28,33].

Regarding the PCs, they represent the output of PCA. PCA transforms the original variables ( $x_1, x_2, \dots, x_n$ ) into principal components ( $\text{PC}_1, \text{PC}_2, \dots, \text{PC}_n$ ), where each PC is a combination of all the original variables. The distinction between the PCs and the original variables lies in their independence (described statistically as orthogonal). Each PC captures a portion of the “truth” in the data, defined as variance in statistical terms.  $\text{PC}_1$  exhibits the highest variance, which makes it the most representative of the variables, followed by  $\text{PC}_2$ , and so forth. This approach enables PCA to convey the predominant portion of the truth by depicting  $\text{PC}_1$  vs.  $\text{PC}_2$  [28,33]. In this context,  $\text{PC}_1$  and  $\text{PC}_2$  serve as tools for experimentalists to determine which variables merit their attention for more effective process optimization, particularly in the context of optimizing the manufacturing of membranes and prioritizing their operational features. The variables contributing the most to  $\text{PC}_1$  and  $\text{PC}_2$  should be given priority in the optimization process [28,33].

**Table 1.** Synthesis conditions for MFI zeolite membranes and their pervaporation (PV) performances with ethanol/water mixtures [27].

| No. | Support                                       | Support Pore Size (μm) | Growth Type <sup>b</sup> | Synthesis Solution Composition <sup>c</sup><br>(TPA <sup>+</sup> :<br>SiO <sub>2</sub> :H <sub>2</sub> O:OH <sup>-</sup> :Na <sup>+</sup> | Synthesis Conditions |          | Membrane Thickness (μm) | PV Conditions |           | Flux (kg m <sup>-2</sup> h <sup>-1</sup> ) | α <sup>d</sup> (–) | Ref. |
|-----|-----------------------------------------------|------------------------|--------------------------|-------------------------------------------------------------------------------------------------------------------------------------------|----------------------|----------|-------------------------|---------------|-----------|--------------------------------------------|--------------------|------|
|     |                                               |                        |                          |                                                                                                                                           | Temp. (K)            | Time (h) |                         | Feed (wt%)    | Temp. (K) |                                            |                    |      |
| M1  | PAD                                           | 1.25                   | In situ                  | 0.1:1:80:0.1:0.1 <sup>c1</sup>                                                                                                            | 443                  | 48       | 400–500                 | 4             | 303       | 0.10                                       | 24                 | [34] |
| M2  | PSSD                                          | 1.25                   | In situ                  | 0.1:1:80:0.1:0.1 <sup>c1</sup>                                                                                                            | 443                  | 48       | 400–500                 | 4             | 333       | 0.76                                       | 58                 | [34] |
| M3  | PST                                           | 0.3                    | In situ                  | 0.1:1:(60,100):0.05:0.05 <sup>c2</sup>                                                                                                    | 453                  | 14 + 10  | ~40                     | 3             | 333       | 0.47                                       | 89                 | [35] |
| M4  | PST                                           | 0.3                    | In situ                  | 0.1:1:(80,100):0.05:0.05 <sup>c2</sup>                                                                                                    | 453                  | 22 + 10  | 30                      | 3             | 333       | 0.87                                       | 69                 | [36] |
| M5  | PAT                                           | 0.3                    | In situ                  | 0.1:1:(80,100):0.05:0.05 <sup>c2</sup>                                                                                                    | 453                  | 22 + 10  | 50                      | 3             | 353       | 0.35                                       | 33                 | [36] |
| M6  | PMT                                           | 1                      | In situ                  | 0.17:1:120:0.17:0 <sup>c3</sup>                                                                                                           | 448                  | 16       | ~20                     | 5             | 333       | 0.93                                       | 106                | [37] |
| M7  | PAT <sup>a1</sup>                             | 1                      | In situ                  | 1:6:571:5:1                                                                                                                               | 448                  | 24       | 2.5                     | 5             | 348       | 1.36                                       | 58                 | [38] |
| M8  | TiO <sub>2</sub> disk <sup>a1</sup>           |                        | In situ                  | 1:6:571:5:1                                                                                                                               | 448                  | 24       | 3                       | 5             | 348       | 2.56                                       | 103                | [38] |
| M9  | Zeolite–Cal/Al <sub>2</sub> O <sub>3</sub> HF |                        | In situ                  | 0.17:1:120:0.17:0                                                                                                                         | 448                  | 20       | ~15                     | 5             | 333       | 5.1                                        | 74                 | [39] |
| M10 | PAHF                                          | 0.15                   | SG                       | 0.17:1:165:0.17:0                                                                                                                         | 448                  | 6        | 5                       | 5             | 333       | 9.8                                        | 58                 | [40] |
| M11 | YSZ HF                                        | 0.75                   | SG <sup>b1</sup>         | (0.17–0.39):1:176: (0.17–0.39):0                                                                                                          | 453                  | 8        | ~3                      | 5             | 333       | 7.40                                       | 47                 | [41] |
| M12 | YSZ HF                                        | 0.75                   | SG                       | 0.2:1:1.76:0.2:0.08:0.04WO <sub>4</sub> <sup>2–</sup>                                                                                     | 413                  | 8        | 3                       | 5             | 333       | 2.81                                       | 32                 | [4]  |
| M13 | PAHF                                          | 0.2                    | SG <sup>b2</sup>         | 0.9:4:1000:0.9:0.9                                                                                                                        | 398–448              | 3–3      | 4                       | 5             | 298       | 2.9                                        | 160                | [42] |
| M14 | PAHF                                          | 0.15                   | SG <sup>b1</sup>         | (0.12–0.32):1:165:(0.12–0.32):0                                                                                                           | 448                  | 12       | 12                      | 3             | 333       | 2.90                                       | 66                 | [43] |
| M15 | PAT                                           | 2                      | SG <sup>b3</sup>         | 0.17:1:120:0.17:0                                                                                                                         | 458                  | 5.5      | ~20                     | 5             | 333       | 1.81                                       | 89                 | [44] |
| M16 | PAT                                           | 2.5                    | SG <sup>b4</sup>         | 0.17:1:120:0.17:0                                                                                                                         | 413                  | 20       | 10                      | 5             | 333       | 1.38                                       | 45                 | [45] |
| M17 | PSST                                          | 1                      | SG <sup>b5</sup>         | 0.15:1:158.3:0.15:0                                                                                                                       | 448                  | 48       | N/A                     | 5             | 333       | 1.00                                       | 23                 | [46] |
| M18 | PSS net                                       |                        | SG <sup>b6</sup>         | 0.32:1:165:0.32:0                                                                                                                         | 443                  | 72       | ~7.5                    | 5             | 298       | 11.50                                      | 20                 | [47] |
| M19 | PAT                                           | 1                      | SG <sup>b7</sup>         | (0.2 + 0.2):1:180:0.2:0 <sup>c4</sup>                                                                                                     | 433                  | 24       | 8.5                     | 5             | 333       | 1.4                                        | 54                 | [48] |
| M20 | PAT                                           | 1                      | SG <sup>b7</sup>         | (0.2 + 0.2):1:180:0.2:0 <sup>c4</sup>                                                                                                     | 433                  | 24       | 9.2                     | 8             | 333       | 1.52                                       | 86                 | [49] |
| M21 | PMT                                           | 1                      | SG <sup>b3</sup>         | 0.17:1:120:0.17:0                                                                                                                         | 448                  | 8        | N/A                     | 10            | 333       | 2.55                                       | 72                 | [50] |
| M22 | PAT                                           | 2                      | SG                       | 0.2:1:600:0.2:0:0.06H <sub>3</sub> BO <sub>3</sub>                                                                                        | 448                  | 24       | 15                      | 5             | 333       | 2.6                                        | 55                 | [51] |
| M23 | PMT                                           | 1                      | SG <sup>b1</sup>         | 0.4:1:800:0.2: 0:(0–0.25)NH <sub>4</sub> F                                                                                                | 453                  | 20       | ~6                      | 5             | 333       | 2.85                                       | 60                 | [52] |
| M24 | PMT                                           | 1                      | SG <sup>b1</sup>         | (0–0.8):1:(120–1000):(0–0.7):(0–0.3) <sup>c4</sup>                                                                                        | 453                  | 16       | ~10                     | 5             | 333       | 1.91                                       | 66                 | [53] |
| M25 | PAT                                           | 0.3                    | SG                       | 0.1:1:165:0.1:(0–0.5)                                                                                                                     | 448                  | 4        | 3                       | 5             | 333       | 1.05                                       | 76                 | [54] |
| M26 | PA capillary                                  | 0.8                    | SG <sup>b1</sup>         | 0.12:1:60:0.12:0                                                                                                                          | 428                  | 16       | ~5                      | 5             | 338       | 1.50                                       | 54                 | [55] |
| M27 | PAT                                           | 1                      | Gel-free                 | N/A                                                                                                                                       | 423                  | 24       | 0.5                     | 5             | 333       | 2.3                                        | 136                | [56] |
| M28 | PST                                           | 0.5                    | SG                       | 0.05:1:75:0.08:0.08                                                                                                                       | 433                  | 8        | 12                      | 10            | 323       | 3.16                                       | 120                | [57] |
| M29 | PAT                                           | 1                      | SG                       | 0.15:1:135:0.15:0.12:0.06WO <sub>4</sub> <sup>2–</sup>                                                                                    | 393                  | 24       | 3.5                     | 5             | 333       | 2.5                                        | 69                 | [58] |
| M30 | PAT                                           | 0.3                    | SG                       | 0.005:1:100:0.05:0.05                                                                                                                     | 433                  | 24       | 7                       | 10            | 323       | 0.85                                       | 52                 | [59] |
| M31 | PAT                                           | 0.3                    | SG                       | 0.05:1:165:0.1:0.05                                                                                                                       | 448                  | 16       | 4                       | 5             | 333       | 1.22                                       | 88                 | [8]  |

<sup>a1</sup> 1H,1H,2H,2H perfluoroalkyltriethoxysilane-modified supports. Seed assembly techniques: <sup>b</sup> SG secondary growth, <sup>b1</sup> dip coating, <sup>b2</sup> dual-seed layer, <sup>b3</sup> rubbing a water slurry, <sup>b4</sup> vacuum seeding, <sup>b5</sup> sonication seeding, <sup>b6</sup> casting, <sup>b7</sup> varying-temperature hot-dip coating (VTHDC). Silica source: <sup>c1</sup> colloidal silica, <sup>c2</sup> silica solution, <sup>c3</sup> colloidal silica, TEOS, Ludox AS30 (40), fumed silica; <sup>c4</sup> templates (TEABr/TBAOH = 0.2/0.2). <sup>d</sup> Separation factor (ethanol/water).

### 3. Results and Discussion

#### 3.1. PCA Approach for the Entire Dataset

Figure 1 presents the PCA output for the previously published data of chemical components, physical properties, and operational conditions involved in the manufacturing process of MFI zeolite membranes, as well as their pervaporation (PV) performances with ethanol/water mixtures [27]. The first two PCs accounted for only 38% of the total variance (21.4% and 16.6% for the first and second PC, respectively (Figure 1a)). This value is lower than those reported in previous PCA investigations concerning materials' characterization [20,21,23,28,60]. For the investigated variables, most properties had moderate to low contributions to PC<sub>1</sub>, with insignificant influence of pore size, flux, and synthesis and pervaporation temperature. The highest contributions were scored for synthesis time and materials' thickness (yielding 23% and 17.6%, respectively (Figure 1b)). Several investigations emphasized the optimization of the synthesis time, highlighting the relevance of this factor. Peng et al. [8] investigated the crystallization time for pure silica MFI-type zeolite membrane preparation, achieving pervaporation separation factors higher than 85 for five wt% ethanol/water mixtures at 333 K. Their study revealed that parasitic twin crystals in the zeolite membrane significantly influenced the separation process [8]. Additionally, rapid thermal processing (heating rates of 973 K/min and an isothermal process at 973 K for 0.5 min) was introduced for the removal of organic structure-directing agents (OS-DAs) to minimize grain boundary defects in *c*-oriented silicalite-1 membranes [61]. This technology enabled the development of silicalite-1 membranes with superior separation performance by strengthening grain bonding at the grain boundaries (condensation of Si–OH groups) and reducing grain boundary defects, compared to conventional calcination methods (heating rates of 1 K/min and an isothermal process at around 673–823 K for several hours) [61].

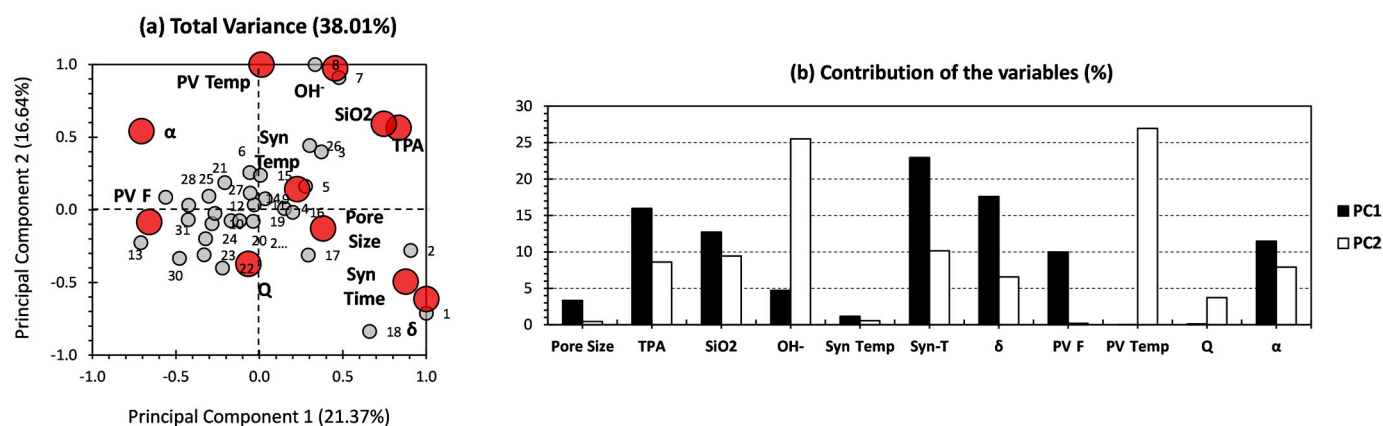


**Figure 1.** PCA biplot for the whole dataset (data originated from the investigations of Lu et al. [27]). The grey bullets indicate the individuals in the population (different investigated MFI zeolite membranes). The red bullets represent the variables (different used chemical components, physical properties, and operational conditions).

Efforts over the last few decades focused on decreasing the thickness of zeolite membranes to increase their permeability while maintaining selectivity. In addition, attempting to decrease the thickness of zeolite membranes would make their use more economically viable [3]. This involved synthesizing smaller and thinner zeolite seeds, from the micrometer to the nanometer size, or even ultrathin zeolite sheets, which are then coated and assembled on porous supports to form thin membranes [4–6]. Additionally, hierarchical zeolites with moderate mesopores have been created through confined synthesis, dual-templating strategies, or post-etching techniques, obtaining membranes with ultrathin dense layers [7].

As for PC<sub>2</sub>, most variables showed low to negligible contributions, with the exception of OH<sup>-</sup> and pervaporation temperature (accounting for 25.5% and 26.9%, respectively

(Figure 1b)). Interestingly, the primary contributors to the first two PCs displayed a positive correlation with each other when viewed in a biplot representation (Figure 1a), signifying that a positive correlation existed. This indicated that the pervaporation temperature was directly proportional to the concentration of  $\text{OH}^-$  in the synthesis solution. In addition, the synthesis time had a substantial direct impact on the thickness of the membrane. The pervaporation temperature plays a crucial role in the performance of MFI zeolite membranes, as it significantly influences separation efficiency and flux. Pervaporation is a process where a liquid mixture is separated by partial vaporization through a selective membrane [18]. Hence, it heavily relies on temperature to drive an efficient separation [42,62]. MFI zeolites are known for their uniform pore structure and high thermal stability, which allows them to operate at high temperatures, typically enhancing their separation performance [63–65]. In fact, high temperatures increase the vapor pressure of the components, thereby improving their diffusivity through the membrane's pores. Consequently, an increase in temperature can lead to higher permeation rates and improved selectivity, particularly in separating components with similar molecular sizes [42,62]. However, the temperature must be carefully optimized, as excessively high temperatures could potentially damage the membrane structure or lead to undesirable phase changes [63–65]. For instance, Peng et al. [8] demonstrated that operating at 333 K resulted in a high impact of the separation factors in the pervaporation of ethanol/water mixtures, showcasing the importance of selecting an appropriate temperature to achieve optimal separation outcomes [42,62]. Thus, controlling the pervaporation temperature is vital to maximizing the efficiency and lifespan of MFI zeolite membranes in practical applications [63].

The relationship between alkalinity and pervaporation temperature is critical in optimizing the performance of MFI zeolite membranes. Alkalinity, often quantified by the  $\text{OH}^-$ /Si ratio during the synthesis of MFI zeolites, significantly affects a membrane's structural properties, such as pore size and defect density [27,66,67]. These structural properties, in turn, influence the membrane's performance at various pervaporation temperatures [66,67]. High alkalinity can promote the formation of more defined and interconnected pores, which enhances the diffusivity of molecules through the membrane. When combined with elevated pervaporation temperatures, this can lead to improved separation efficiency and flux [27,66,67]. For instance, operating at high temperatures increases the vapor pressure and mobility of molecules, which synergizes with the enhanced pore structure created by optimal alkalinity levels, thus boosting the overall pervaporation performance [27,42,62]. However, it is crucial to balance alkalinity, as excessive levels can cause the formation of defects or reduce the thermal stability of zeolite membrane [27]. Therefore, understanding and controlling the interplay between alkalinity and pervaporation temperature is essential for maximizing the separation efficiency, stability, and longevity of MFI zeolite membranes in various industrial applications, as too low or too high alkalinity would result in the loss of b-orientation [27,68].

When observing all the membranes, a significant agglomeration around the node was evident (Figure 1a). The highest factor loading was noticed for membranes 1, 2, 7, 8, and 18. This pattern suggested three possible interpretations: (a) Most of the investigated samples presented the same behavior towards the investigated physical, chemical, and operational properties, regardless of their extensive difference. (b) The investigated properties had minimal influence on the different types of studied membranes. (c) The samples that exhibited the highest factor loading skewed the dispersion of the clustered samples at the node. In order to confirm or reject these possibilities, a data partitioning technique was adopted following the position of the samples along the four sides of the PCA biplot. Hence, the dataset was divided into four subsets, according to the following behavior: (a) positive membrane behavior for the first two PCs (Figure 2); (b) negative and positive membrane behavior for  $\text{PC}_1$  and  $\text{PC}_2$ , respectively (Figure 3); (c) negative membrane behavior for the first two PCs (Figure 4); (d) positive and negative membrane behavior for  $\text{PC}_1$  and  $\text{PC}_2$ , respectively (Figure 5). The purpose of this separation was to seek a higher variance in the dataset, therefore reaching more reliable findings with the PCA.

Separation into multiple subsets was obtained following the positive/negative behavior of different membranes for PC<sub>1</sub> and PC<sub>2</sub>, as shown in Figure 1. Although a certain bias was noticed for the whole-dataset approach, we observed that the membrane samples 7 and 8 presented a high positive loading for PC<sub>2</sub>, and a negligible positive one for PC<sub>1</sub>. These two membranes showed a high positive influence of the highest contributors to PC<sub>2</sub> (pervaporation temperature and OH<sup>−</sup> concentration in the synthesis solution). As for the samples 1, 2, and 18, they were clustered along the positive side of PC<sub>1</sub> and the negative side of PC<sub>2</sub>. These membranes showed a high positive influence of the highest contributors to PC<sub>1</sub> (synthesis time and membrane thickness).

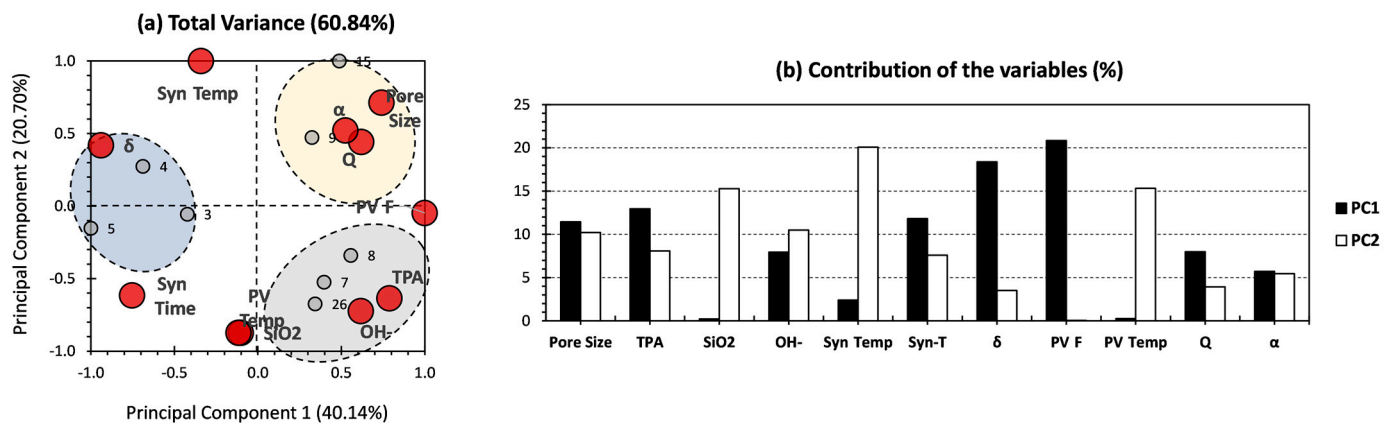


**Figure 2.** PCA biplot for the positively correlated dataset for the first two PCs of Figure 1 (data were obtained from Lu et al. [27]). The grey bullets represent the individuals in the population (different investigated MFI zeolite membranes). The red bullets represent the variables (different used chemical components, physical properties, and operational conditions).

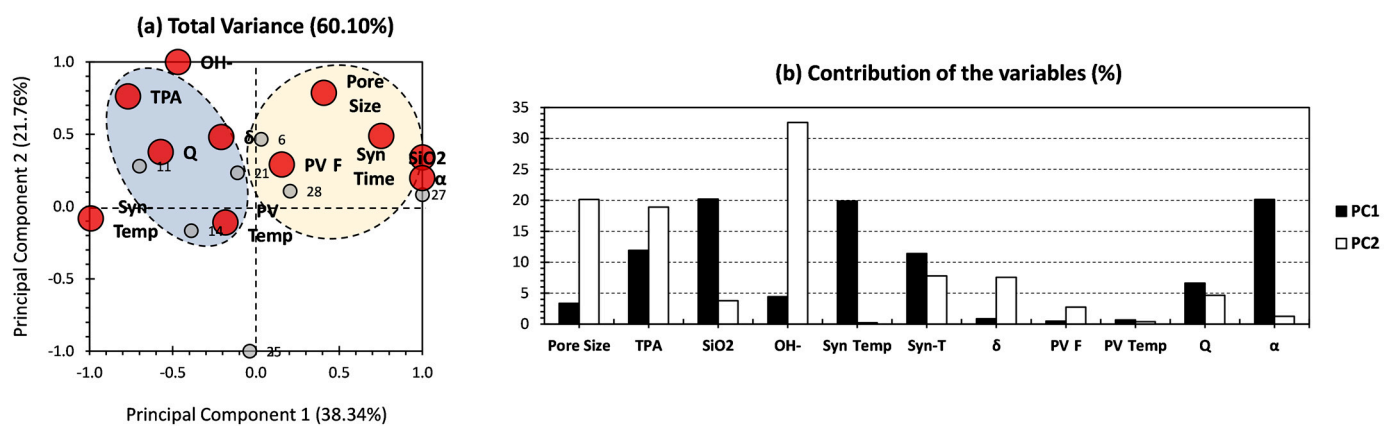


**Figure 3.** PCA biplot for the negatively correlated dataset for PC<sub>1</sub> and the positively correlated dataset for PC<sub>2</sub> shown in Figure 1 (data were obtained from Lu et al. [27]). The grey bullets represent the individuals in the population (different investigated MFI zeolite membranes). The red bullets represent the variables (different used chemical components, physical properties, and operational conditions).

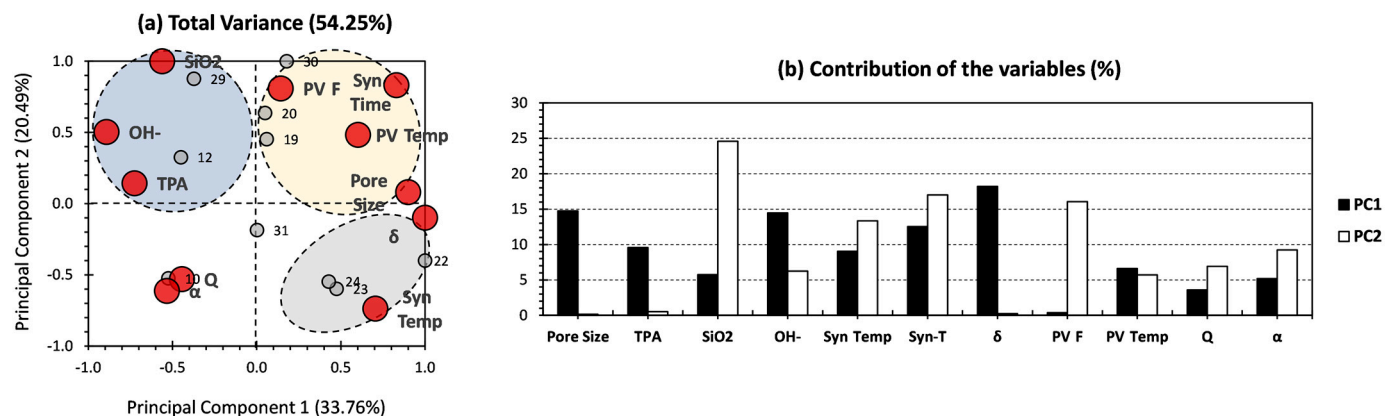


**Figure 4.** PCA biplot for the negatively correlated dataset for the first two PCs of Figure 1 (data were obtained from Lu et al. [27]). The grey bullets represent the individuals in the population (different investigated MFI zeolite membranes). The red bullets represent the variables (different used chemical components, physical properties, and operational conditions).

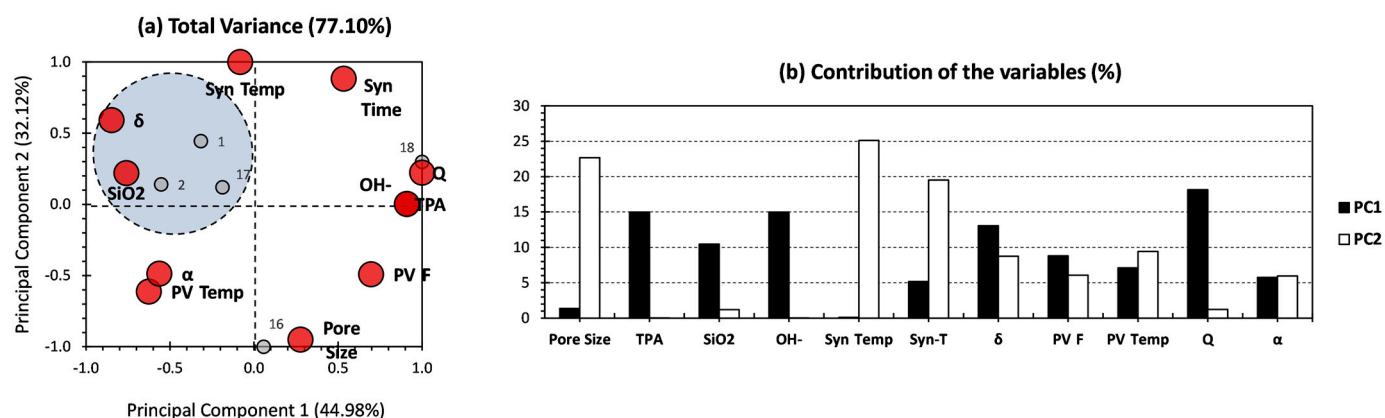


**Figure 5.** PCA biplot for the positively correlated dataset for PC<sub>1</sub> and the negatively correlated dataset for PC<sub>2</sub> shown in Figure 1 (data were obtained from Lu et al. [27]). The grey bullets represent the individuals in the population (different investigated MFI zeolite membranes). The red bullets represent the variables (different used chemical components, physical properties, and operational conditions).

### 3.2. PCA Approach for the Subsets

Figure 2 illustrates the PCA results for the positively correlated samples for the first two PCs shown in Figure 1. Hence, this PCA focused exclusively on membranes 3, 4, 5, 7, 8, 9, 15, and 26. Interestingly an increase in total variance was noticed, as a value of 60.8% was determined (40.1% and 20.7% for the first two PCs, respectively (Figure 2a)). These trends ascertained the efficiency of the adopted methodology, as a more informative fact representation was obtained. For the investigated variables, most properties showed a high to moderate contribution to PC<sub>1</sub>. In fact, pervaporation feed and membrane thickness showed the highest contribution, accounting for 20.8% and 18.4%, respectively (Figure 2b). Interestingly, these two factors were situated on opposite ends with respect to PC<sub>1</sub>, indicating an inverse correlation between them. These trends are in total accordance with previous reports (check Section 3.1).

Regarding PC<sub>2</sub>, several factors showed a high to moderate contribution. In particular, the properties/conditions mostly contributing to PC<sub>1</sub> showed a negligible contribution to PC<sub>2</sub>, indicating that only the first PC represented the trends of these factors, without any contribution originating from the latter. On the other hand, the temperature of both pervaporation and synthesis exhibited the highest contribution to PC<sub>2</sub>, scoring 15.3% and 20.1%, respectively. SiO<sub>2</sub> showed a high contribution as well, corresponding to 15.3% (Figure 2b). These trends indicated that the pervaporation conditions were the dominant operational

factors, along with  $\text{SiO}_2$  as a chemical component of the solution. The aforementioned factors influenced the membrane thickness in a similar manner. The  $\text{SiO}_2$  content is a critical factor in the synthesis of MFI zeolites, as it influences the membrane framework density, pore size, and surface properties [16]. A high  $\text{SiO}_2$  content typically results in a more hydrophobic membrane, which is advantageous for the separation of organic compounds from aqueous solutions [7,17,18]. This is particularly relevant under various pervaporation conditions, where the operating temperature and feed composition can significantly impact the separation efficiency [7,18]. For example, a high  $\text{SiO}_2$  content can enhance the selectivity and permeability of a membrane for organic molecules at elevated temperatures, where the vapor pressure and diffusivity of the components are increased [7,14,18]. Conversely, a low  $\text{SiO}_2$  content can result in a more hydrophilic membrane, which might be beneficial for different separation tasks but could also lead to increased water permeation and reduced selectivity for organic compounds [18,19]. The optimization of the pervaporation conditions and  $\text{SiO}_2$  content must be carefully handled to tailor a membrane's properties for specific separation requirements, ensuring high performance and stability in practical applications [14].

For the selected membranes, three clusters could be identified in the PCA biplot (Figure 2a). The cluster depicted in yellow is located on the positive axis of both PCs and contains membranes 9 and 15. These membranes were positively correlated with flux, pore size, and retention factor. Interestingly, these two membranes exhibited a high dissimilarity in their chemical composition, which could probably indicate that their high proximity originated from similarities on the textural and mesoscopic scales. Hence, the mechanism involving molecular sieving interactions might provide a more appropriate explanation for contaminant retention in this case, rather than the diffusion–adsorption mechanism. The blue cluster is located on the negative side of  $\text{PC}_1$ , with a low influence with respect to  $\text{PC}_2$ . It contains membranes 3, 4, and 5 and showed a high positive influence on membrane thickness, with a moderate influence on synthesis time. The grey cluster is plotted along the positive and negative sides of  $\text{PC}_1$  and  $\text{PC}_2$ , respectively, and contains membranes 7, 8, and 26. These membranes showed a high positive influence of  $\text{TPA}^+$  (tetrapropylammonium) and  $\text{OH}^-$  in the synthesis solution. This indicated that these samples were more likely influenced by the chemical features of the preparation procedure rather than the physical conditions of the preparation and the physical properties of the membranes themselves.

Figure 3 shows the PCA results for the samples that were negatively correlated with respect to  $\text{PC}_1$ , and positively correlated with respect to  $\text{PC}_2$  (Figure 1). Hence, this PCA visualization exclusively targeted membranes 6, 11, 14, 21, 25, 27, and 28. In comparison to the PCA approach involving the whole dataset (Figure 1), this approach encompassed 60.1% of the total variance for its first two PCs. Interestingly, this trend is similar to the one shown in Figure 2. For the investigated variables, most properties exhibited a negligible influence with respect to  $\text{PC}_1$ , with moderate contributions for  $\text{SiO}_2$ , synthesis temperature, and retention factor, yielding 20.2%, 19.9%, and 20.1% of the variance, respectively (Figure 3b). For  $\text{PC}_2$ , the highest contribution was recorded for the  $\text{OH}^-$  concentration in the synthesis solution, accounting for 32.6% of the variance (Figure 3b). On the other hand, a moderate to high contribution was recorded for the pore size and  $\text{TPA}^+$  concentration in the preparation solution (corresponding to 20.1% and 18.9%, respectively; Figure 3b). As for the remainder of the variables, they showed a low to negligible contribution with respect to  $\text{PC}_2$ . These findings show some similarities to those of the PCA investigations shown in Figure 2, as a high simultaneous influence of  $\text{SiO}_2$  and the temperature of synthesis was noticed. On the other hand, an exclusive chemical composition of the synthesis solution was distinguished for  $\text{PC}_2$ . These findings peculiarly indicated the high influence of the chemical composition on the investigated membranes shown in Figure 3. This could signify that the retention capacity of this set of membranes would more likely be controlled by a diffusion–adsorption mechanism, due to the fact that the major contributors were the chemical composition and the pore size.

For the selected membranes, two clusters were distinguished within the PCA biplot in Figure 3a. Interestingly, all of the investigated membranes and properties were positioned on the positive side of PC<sub>2</sub>, indicating the high relevance of their molecular composition compared to those excluded from this particular PCA investigation (Figure 3). The yellow cluster was located on the positive side of PC<sub>1</sub> and contained membranes 6, 27, and 28. These membranes were most likely positively correlated with factors such as pore size, pervaporation feed, SiO<sub>2</sub>, and retention factor (Figure 3a). Conversely, the blue cluster was located on the negative side of PC<sub>1</sub> and contained membranes 11, 14, and 21. These membranes were most likely positively correlated with flux, pervaporation temperature, membrane thickness, and TPA<sup>+</sup> concentration.

Figure 4 displays the PCA results for the negatively correlated samples, for both PC<sub>1</sub> and PC<sub>2</sub>, shown in Figure 1. This PCA analysis exclusively targeted membranes 10, 12, 19, 20, 22, 23, 24, 29, 30, and 31. In this case, the first two PCs accounted for 54.2% of the total variance (33.8% and 20.5% for the first two PCs, respectively (Figure 4a)). The lower total variance, in comparison to that measured in the PCA with the separated samples approach (Figures 2, 3 and 5), could be explained by the greater number of samples in this third subset. Yet, these findings are still reliable for unveiling various patterns and distinguishing hidden features. Regarding the investigated variables, most properties presented low to moderate contribution to PC<sub>1</sub>. Pore size, OH<sup>−</sup>, and membrane thickness exhibited the highest contribution to PC<sub>1</sub>, accounting for 14.7%, 14.5%, and 18.2% of the variance, respectively (Figure 4b). For PC<sub>2</sub>, SiO<sub>2</sub> showed the highest contribution, corresponding to 24.6%, and most likely moderate contributions were noticed for synthesis temperature (13.4%), time (17%), and pervaporation feed, corresponding to 16% (Figure 4b). These patterns indicated that elevated amounts of SiO<sub>2</sub> might influence the pervaporation conditions. On the other hand, high amounts of OH<sup>−</sup> might potentially influence the physical properties of the membrane, such as pore size and membrane thickness.

For the selected membranes, three different clusters could be identified within the PCA biplot (Figure 4a). The yellow cluster was located on the positive sides of both PCs and contained membranes 19, 20, and 30, which were positively correlated with synthesis and operational conditions. The blue cluster was located on the negative side of PC<sub>1</sub> and the positive side of PC<sub>2</sub>. It contained membranes 2 and 9. These membranes showed a high positive influence of the three investigated chemicals in the synthesis solution. This indicated that these samples, in comparison to the other samples in this PCA (Figure 4), were more likely influenced by the chemical features of the membrane rather than by its physical properties. This could indicate a predominance of the diffusion–adsorption mechanism in ethanol removal for this set of membranes compared to the other membranes investigated in Figure 4.

Figure 5 illustrates the PCA results for the positively correlated samples with respect to PC<sub>1</sub> and the negatively correlated ones with respect to PC<sub>2</sub>, shown in Figure 1. This PCA analysis exclusively targeted membranes 1, 2, 16, 17, and 18. In this case, the first two PCs accounted for 77.1% of the total variance (45% and 32.1% for the first two PCs, respectively (Figure 5a)). The elevated total variance, compared to those determined in the other PCAs with the separated sample approach (Figures 2–4), could be explained by the lower number of samples considered in this case. Hence, quite interesting findings could be revealed, given the advantage of having such limited data coupled with a high total variance. For the investigated variables, for PC<sub>1</sub>, most of the properties and features had moderate to low contributions. The highest contributions were those of TPA<sup>+</sup> and OH<sup>−</sup>, each accounting for 15% of the variance, and of the flux, accounting for 18.1% (Figure 5b). For PC<sub>2</sub>, the greatest contributions were obtained from pore size, synthesis temperature, and time, accounting for 22.7%, 25.1%, and 19.5% of the variance, respectively (Figure 5b). These trends indicated the highest influence of the flux operative condition, following the chemical composition of the investigated membranes, and the high influence of the synthesis operative conditions, followed by the pore size. For the selected membranes, the samples 1, 2, and 17 were clustered (blue cluster) along the negative and positive sides

of the PC<sub>1</sub> and PC<sub>2</sub>, respectively (Figure 5a). These membranes showed a high positive influence of SiO<sub>2</sub> and thickness. Only membrane 16 was located on the far negative side of PC<sub>2</sub>, with a negligible influence with respect to PC<sub>1</sub>. This membrane showed a high positive influence of the pore size. Conversely, membrane 18 was the only one located on the far positive side of PC<sub>1</sub>, with a negligible influence with respect to PC<sub>2</sub>. This membrane was notably influenced by the chemical composition of the solution (OH<sup>−</sup> and TPA<sup>+</sup>) and the membrane flux.

The different PCAs of the subsets exhibited higher variance than the all-in-one data set approach (Figure 1) and different relevance of the different variables depending on how the dataset was considered (Table 2). Hence, this would indicate that the PCA trends strongly depended on the examined zeolite membrane. In other words, the selection of membranes to be compared and optimized is very important. In our case, the synthesis temperature and the chemical composition were found to be the most significant factors, as they repeatedly showed the highest percentage contributions in the four PCAs of the subsets (Table 2).

**Table 2.** Summary of the PCA findings for the subsets (Figures 2–5).

| PCA <sup>a</sup> | Total Variance (%) | PC <sub>1</sub> (%) | PC <sub>2</sub> (%) | Highest % Contribution Variables                                                                                      | Number of Clusters |
|------------------|--------------------|---------------------|---------------------|-----------------------------------------------------------------------------------------------------------------------|--------------------|
| ++               | 60.8               | 40.1                | 20.7                | δ, PV F (PC <sub>1</sub> )<br>Syn Temp, SiO <sub>2</sub> (PC <sub>2</sub> )                                           | 3                  |
| −+               | 60.1               | 38.3                | 21.8                | α, Syn Temp, SiO <sub>2</sub> (PC <sub>1</sub> )<br>OH <sup>−</sup> , TPA <sup>+</sup> , Pore Size (PC <sub>2</sub> ) | 2                  |
| −−               | 54.3               | 33.8                | 20.5                | δ (PC <sub>1</sub> )<br>SiO <sub>2</sub> (PC <sub>2</sub> )                                                           | 3                  |
| +−               | 77.1               | 45.0                | 32.1                | Q, TPA, OH <sup>−</sup> (PC <sub>1</sub> )<br>Syn Temp, Syn T (PC <sub>2</sub> )                                      | 1                  |

<sup>a</sup> the two signs respectively show the positive/negative plotting of the individuals for PC<sub>1</sub> (left sign) and PC<sub>2</sub> (right sign) in the PCA of the whole dataset (Figure 1).

#### 4. Conclusions

In this study, Principal Component Analysis (PCA) was used to investigate the inter-correlations between 11 variables of 31 MFI (Mobil No. 5)-zeolite membranes, including chemical composition, physical properties, and synthesis and operational features. The first two principal components (PCs) accounted for 38% of the total variance, indicating moderate to low contribution. Notably, the synthesis time had a direct impact on membrane thickness (for PC<sub>1</sub>; see Figure 1). Additionally, a high proximity was observed between pervaporation temperature and OH<sup>−</sup> concentration in the synthesis solution (for PC<sub>2</sub>; see Figure 1).

In order to seek higher variance, the data were divided into four subsets, following the trends for the first two PCs in the whole-dataset approach. Following this separation, higher variance was obtained in all four attempts (55–77%). The separation resulted in a high correlation between SiO<sub>2</sub> concentration and pervaporation conditions, highlighting the dominance of these conditions and the significant influence of the chemical composition. A high SiO<sub>2</sub> content typically resulted in a more hydrophobic membrane. This is beneficial for separating organic compounds from aqueous solutions. The chemical composition of the synthesis solution, including the SiO<sub>2</sub> and OH<sup>−</sup> concentrations, greatly influenced the operational efficiency of the MFI zeolite membranes, affecting properties such as membrane thickness (Figures 2 and 3). The synthesis temperature and chemical composition consistently emerged as significant variables across the subsets, which emphasizes the importance of a careful membrane selection for comparison and optimization. This study suggests that the trends in PCA are highly dependent on the specific zeolite membrane examined, with the synthesis conditions playing a crucial role in its performance.

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