Study of membrane system performance and HAZOP analysis in gas separation and reaction

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Introduction

In order to separate efficiently a mixture, the designer has to create the conditions in which the components behave drastically different. These conditions depend mainly on chemical and physical properties of the species. Separation and purification methods take advantage just from differences concerning some specific properties of the mixture components that can be enhanced acting on temperature and pressure or modifying the system by means of an additive.

Membrane technology is an innovative method to carry out fluid separations without the addition of external components to the mixture and less affected by scale factors with respect to the traditional separation methods. The effective combination of engineering and chemical aspects determines the achieving of good results in membrane operations. Flux velocity and selectivity of the membrane represent the main variables of interest for the identification of the more proper material. With reference to the engineering aspects flow pattern, module configuration, stage arrangement determine completely the performance of the membrane separation system. Each of these aspects must be optimised according to the requirements of the process and operating conditions as safety aspects have to be also considered before proposing an alternative to a traditional process. Membrane reactors (MRs) are a practical example of membrane application suitable to combine reaction and separation steps in a single unit, simplifying the process. The membrane provides a selective removal of one or more products simultaneously with the reaction, thus the chemical equilibrium is continually shifted to the products formation. MRs allow to operate in continuous mode, to increase the concentration of the reference species in a gas mixture reducing the presence of noxious species in the downstream; these devices avoid further separation steps, with energetic and environmental advantages.

The Hazard and Operability analysis (HAZOP) identifies in a systematic way all the possible causes and consequences for a system due to each hypothesized deviation of one of the process variables by applying a set of “guide words” and it suggests the recommendations more proper to limit the effect of the specific event [Swann and Preston, 1995; Khan and Abbasi, 1997; Bartolozzi et al., 2000].

Basic aspects of membrane gas separation systems

The transport of each species in a membrane unit can be described by means of a mass balance equation (Eq. 1) and an equation that measures the permeation rate through the membrane medium (Eq. 2).

$$x_{f_i} \cdot F = y_{p_i} \cdot P + x_{r_i} \cdot R \quad \forall i \qquad \text{Eq. 1}$$

$$-dF_i = \frac{P_i}{l} \cdot dS \cdot \left(a_i^F - a_i^P\right) \qquad \text{Eq. 2}$$

where x_f, y_p, x_r represent the composition of the i species in feed (F), permeate (P), and retentate (R) streams respectively, dF_i the differential amount that leaves the feed side through the differential membrane surface (dS) under a driving force represented by an activity difference $\left(a_i^F - a_i^P\right)$. Finally, $\frac{P_i}{l}$ is the permeance of the i species through the membrane. The main variables involved in a membrane gas operation are the composition of the feed, permeate and retentate streams, the membrane surface area, the intrinsic membrane properties (permeation rate and selectivity), the driving force available for the separation process, the fraction of the feed recovered as permeate (stage cut, θ). Membrane properties are significantly influenced by operating conditions (e.g. temperature and pressure).

By using these fundamental equations it is possible to evaluate, as demonstrated in literature [Hwang and Kammermayer, 1975], some variables relating to the separation when the others are known. The modality of integration of the differential equation with the proper boundary conditions is representative of the different flow patterns inside membrane unit.

A separation is typically evaluated in terms of purity and recovery of the product. These targets move in opposite directions, thus a trade off of their values is necessary. As consequence of a better use of the applied driving force, in analogy with the heat exchangers, counter-current flow is the better solution in terms of purity level and recovery of the more permeable species at the permeate side; co-current flow is the intermediate configuration while complete mixing for both feed and permeate streams, often a real condition and not only a theoretical example, represents the worse situation. However it is important to put in evidence how the differences of the performance among the flow modes are significant operating in an intermediate range of stage cut, while at low and high stage cut values the results of the three configurations are similar. Therefore it is important to design properly the membrane unit with reference to the feed flow-rate and product recovery (optimal separation load) to take advantage from the flow pattern.

The maximum purity level of the species is mainly affected by two concurrent parameters: the intrinsic selectivity of the material and the applied driving force, expressed as pressure ratio between permeate and feed streams (PR). These two variables have to be considered not independently since the analysis of the influence of only one of these can determine not appropriate operating conditions. As shown in figure 1a, where a gas mixture containing 10 mol % of the more permeable component is considered, when the driving force is low (PR$\rightarrow$1) an increase of selectivity (α) does not change the purity while α becomes determinant in correspondence of a high driving force (PR$\rightarrow$0). Thus the selectivity influence rises with a decrease of PR. The effect of the selectivity becomes, however, relatively less significant at higher feed concentrations (figures 1b-d). Thus the use of a very selective material is justified only if a significant driving force can be applied. The increase of the feed concentration (x_f) tends to shift toward pressure ratios close to 1 the advantage of high selectivity values. An increase of x_f determines in all cases an increase of the maximum achievable purity value for each pressure ratio but, at the same time, the purity percentage increment measured with respect to the feed concentration (y_p/x_f) decreases with feed concentration independently by the selectivity value.

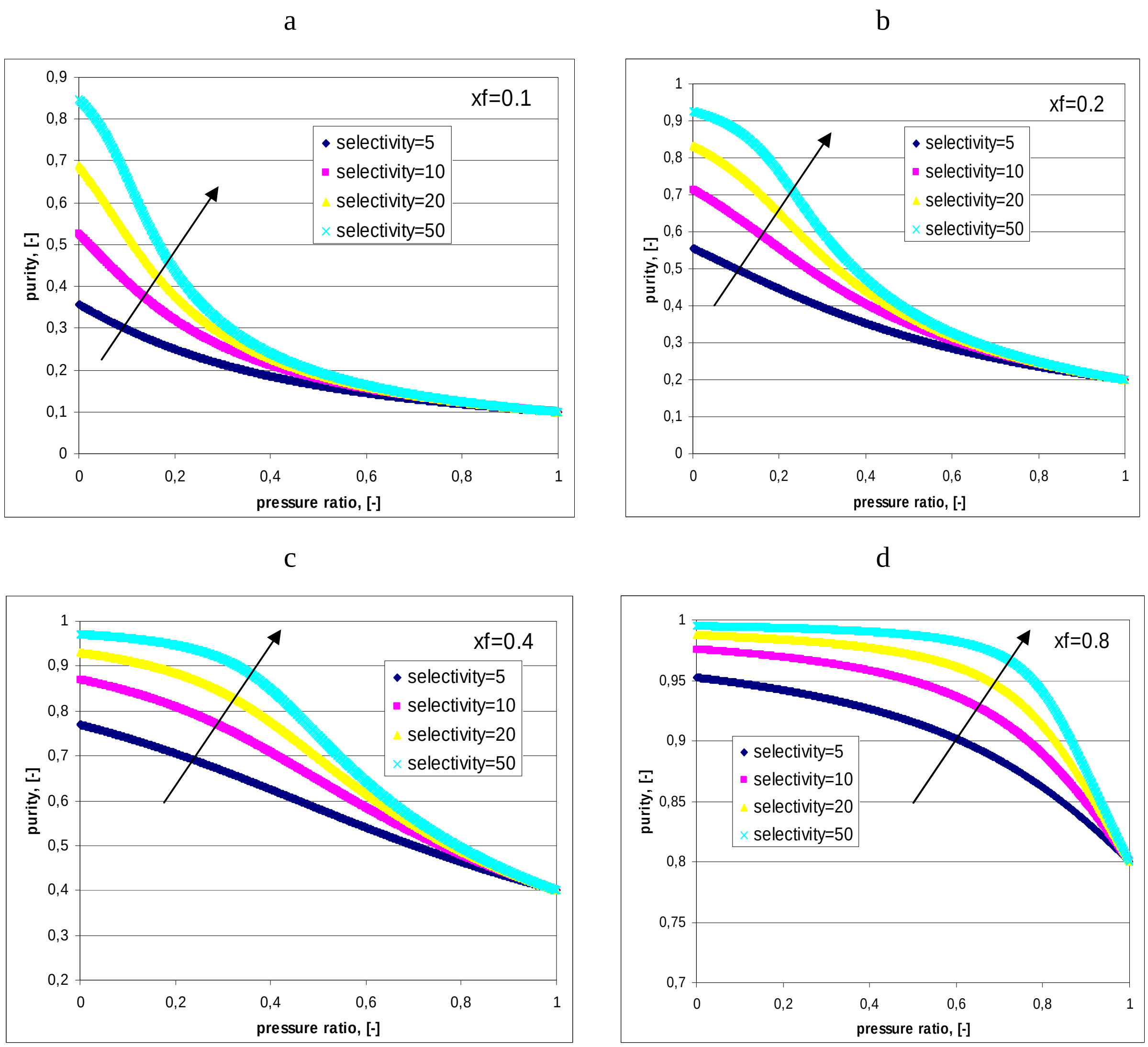

Figure 1. Purity level vs. pressure ratio at different selectivity values for a fixed feed composition

Figures 2 shows how in a single membrane stage the purity changes as function of the pressure ratio at different feed concentrations in correspondence of a fixed selectivity value. A single membrane stage is capable to realize only a limited enrichment of the more permeable component in the permeate stream; in order to meet the requirements of separations of industrial interest it is necessary to operate in multi stage configurations. For example, starting from a x_f=10% a single stage equipped with a membrane characterised by a selectivity value of 50, assures a max purity of 20% if a pressure ratio of 0.45 is applied; two membrane stages in cascade allow to reach a 40% of purity while a combination of three membrane stages is characterised by a purity value of 80%. Finally, the permeate concentration of the fourth membrane stage is equal to 99.5%. Vice versa for a single membrane stage the maximum purity available if a pressure ratio PR~0.001 will result less than 85%.

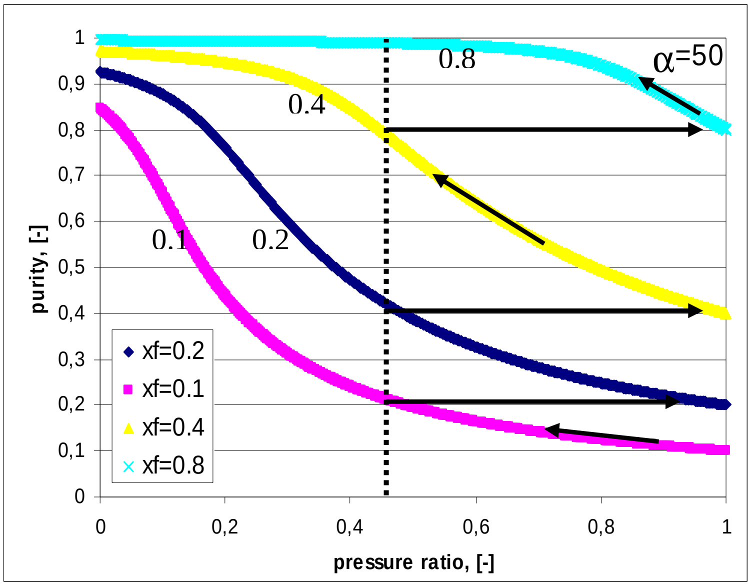

Figure 2. Purity level vs. pressure ratio at different feed compositions for a fixed selectivity value

The advantage of multi stage configurations in terms of purity is paid by higher energy costs to assure the necessary driving force on the membrane.

Membrane units for gas reactions

The basic principle of a MR is profitably used in the dehydrogenation reactions since hydrogen highly selective membranes are capable to operate at high pressures and temperatures. However homogeneous defect-free films are still characterised by a low permeation rate due to the membrane thickness.

In analogy with a traditional reactor, MR performance, in equilibrium reactions, are mainly influenced by the temperature, pressure, residence time, dilution phenomena but their effect is different. An increase of operating pressure is more beneficial than in a traditional reactor because the volume reduction is accompanied by the further advantage relative to the product permeation through the membrane and the consequent removal from the reaction ambient. This aspect becomes specially important for the reactions involving an increase of the number of the moles that are thermodynamically favoured by low pressure conditions. Also the temperature affects both the reaction and the permeation rates. For what concerns the endothermic reactions, the increase of the temperature has a positive effect on the reaction rate and thermodynamics (traditional reactor) but also on the permeation rate that is an activated process (MR). Thus at fixed operating temperature the conversion in MR is always higher than that one estimated for a conventional reactor [Assabumrungrat and White, 1996]. For the exothermic reactions, the kinetics is still favoured by the temperature rise while the thermodynamics suggests to operate at low temperature in order to improve the conversion. The possibility to remove selectively one product from the reactor, operation favoured by the temperature, partially balances the negative effect of the temperature on the thermodynamics.

Another important parameter is represented by the residence time. In order that a MR can express its distinctive properties, it is necessary that the reagents have time to convert themselves, also allowing the preferential permeation of the product. For this reason it is very important to design properly the MR as function of the optimal space velocity. Dilution effects due to the presence of inert species or products in the feed mixture are more important than in conventional reaction systems. In fact the presence of inert species at the same pressure lowers the partial pressure of the permeating component reducing the driving force of the permeation process.

The conversion of the limiting reagent (e.g. CO in water gas shift reaction) can be enhanced operating on feed molar ratio; this solution could be used favourably when the reagent is also involved in a side reaction producing an undesired species not permeable through the membrane. In figure 3, it is possible to observe that the conversion increases with the temperature for each feed molar flow rate. The conversion decreases when the limiting reagent molar flow rate increases, at constant temperature, due to reduced residence times. At low temperature the performance of the membrane reactor are lower than the thermodynamic equilibrium because the reaction and permeation are too slow to improve significantly the conversion. Although a temperature increase is disvantageous for thermodynamics, the conversion increases in a MR for the contribution of the higher product permeation.

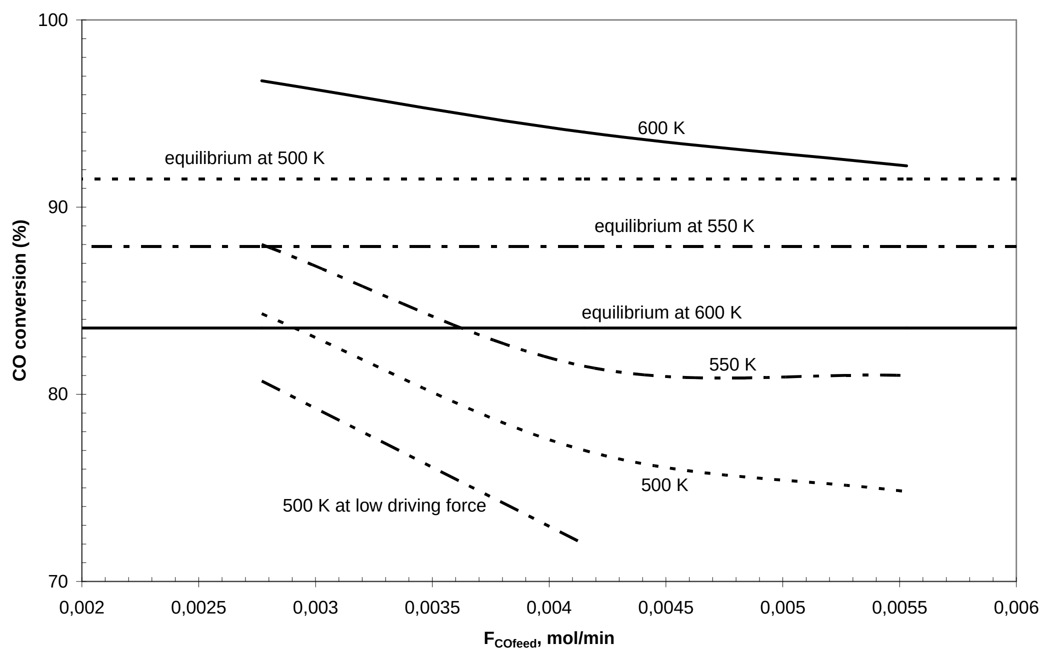

Figure 3. Effect of feed flow rate on limiting reagent conversion at different temperatures

A MR is more sensitive to fouling problems (e.g. coke formation by the reactions of hydrocarbons) with respect to a traditional fixed bed reactor because besides the negative effects on the catalyst also a reduction of active membrane surface occurs. This drawback is still more marked when the membrane itself acts as catalyst (catalytic membrane reactor) [Saracco et al., 1999].

Hazard and operability preliminary analysis

In addition to the aspects that control the separation performance, a complete analysis has to consider safety conditions of a membrane unit. HAZOP technique, widely applied in industrial process design, has been used in this study to analyse a membrane gas separation/reaction unit (figure 4). The analysis of all possible deviations from the intention of the designer, the identification of the different causes and the relative consequences and the indication of the possible solutions have been the main steps of the followed approach. In the scheme of the membrane plant, it is possible to distinguish a prefiltration unit (F1), a compression section (C), a fine filtration section (F2), a heating section (H) and, finally, the membrane separation unit (MS/MR). A section that provides the evaporation of a liquid reagent (EV) by using the hot gas retentate stream is also represented. The main critical points for these units are an adequate pre-treatment system and a proper temperature and pressure control. The pre-treatment of feed stream in membrane operations is a fundamental step because it keeps constant the separation performance, preserving the integrity of the membrane. This is particularly important in gas separation where the hollow fiber configuration is, in general, the obliged choice for maximizing the surface/volume ratio.

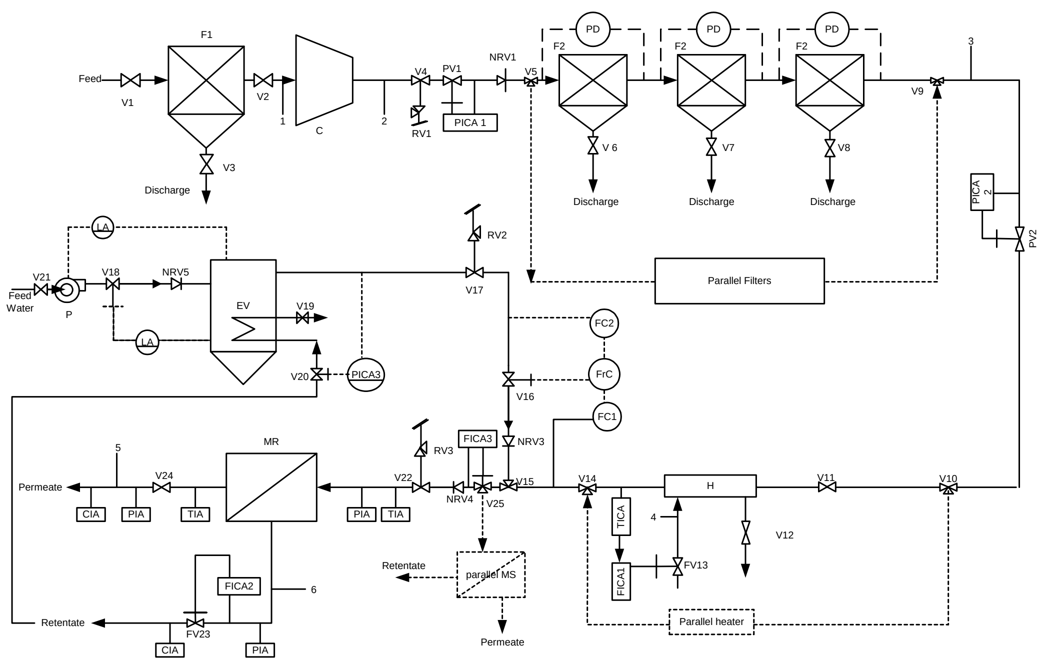

Figure 4. Scheme of membrane separation/reaction process plant

In the following some significant results of this preliminary analysis are summarised in form of graphical representation (Pressure variation for a MR, figure 5) and input-output variable table (Flow and Temperature changes for a membrane separation unit, table 1).

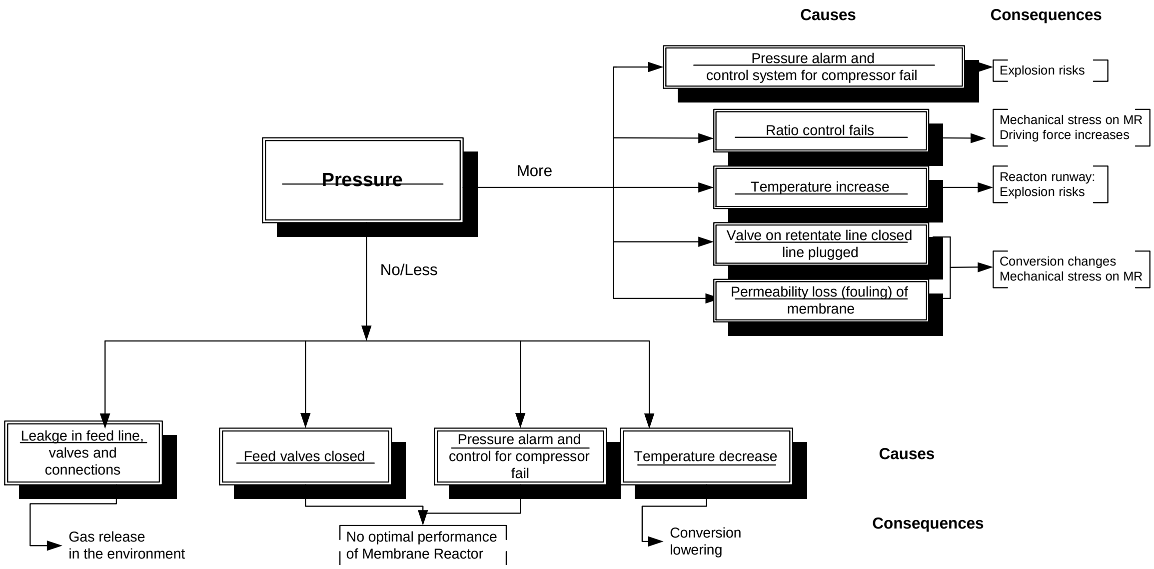

Figure 5. A graphical representation of pressure deviations in MR

Table 1. Input-output table for flow and temperature deviations in gas separation unit

Process parameter	Guide Word	Causes	Consequences	Recommendations
Flow	NO/ LESS	Feed line/valves blocked	No separation, overpressure	Maintenance of lines/valves, fit a relief valve and a pressure alarm
		Gas leakage	Gas release in atmosphere	Check of valves and lines
		Particulate or condensate film on the membrane	No efficient separation	Check the filtration system, clean membrane and fit a low temperature alarm
		Aging of the membrane		Membrane substitution
		Valve on retentate side open		Maintenance of valve and instrumentation
		Temperature decrease, Joule-Thomson effect	Condensate on membrane surface	Fit a control and a low temperature alarm
	MORE	Membrane failure	No separation	Membrane substitution
		Feed flow-rate increase	Purity loss, overpressure	Fit a relief valve Maintenance of instrumentation Split the feed stream on parallel modules
		Temperature increase	Recovery increase Purity loss	Fit a high temperature alarm
		Valve on retentate side partially closed	Recovery increase Purity loss	Maintenance of valve and instrumentation
T	LESS	Steam feed valve in heat exchanger partially closed	Condensate film on membrane surface. No efficient separation	Fit a low temperature alarm Membrane cleaning Maintenance and check of feed steam and gas valves
		Increase of gas flow-rate fed into heat exchanger		
		Heat exchanger control fails		Maintenance of instrumentation
	MORE	Steam feed valve in heat exchanger sticks open	Membrane can be damaged. Higher permeate flow-rate	Fit a control and a high temperature alarm
		Decrease of gas flow-rate fed into heat exchanger		
		Heat exchanger control fails	No efficient separation	Maintenance of instrumentation

Variations of the flow depend directly on mechanical and electric failures of valves, lines and control instrumentation and only indirectly on membrane damages due to an uncontrolled change of temperature and pressure or a non efficient filtration system. Alterations of the temperature with respect to the set point value are exclusively attributed to a not appropriate thermal load in the heat exchanger as consequence of deviations of feed gas and/or heating fluid from the planned flow rates. Sudden uncontrolled pressure deviations can determine severe problems for the membrane integrity and the safety of the ambient.

Relief valves, control and alarm instrumentation with a systematic check and maintenance protocol can reduce significantly the risk for people and environment especially when hazardous species are involved in the reaction process. Membrane units for their simplicity need only few auxiliary units and relating instrumentation that introduce a little complexity in the whole system. Thus a correct analysis of the operating tasks allows to individuate the more frequent problems during the operation.

The absence of additive species to perform the separation and the possibility to remove quickly a product from the reaction zone limit the explosion risk by means of intrinsic control of operating temperature and pressure. Furthermore the controlled reagent feeding avoids the flammable limit of specific mixtures.

Conclusions

An efficient use of a membrane unit in production cycles requires a in-depth knowledge of the variables that influence the separation/reaction performance. Many variables are common to the traditional technologies but their influence in membrane units is more significant. Moreover the link of some parameters such as membrane selectivity and driving force in gas separation or temperature influence combined to dilution effect and space velocity in MR suggests specific operation modalities for improving the performance of the whole process.

The occurring of the specific membrane phenomena (e.g. fouling, presence of micro-defects, swelling, aging) can be readily detected by means of the HAZOP methodology. In order to limit the incidence of the causes and the propagation of the consequences, the introduction of a specific instrumentation and its periodic maintenance is recommend.

However it must be put in evidence how the membrane unit presents also advantages in terms of safety with respect to a conventional equipment, in particular for exothermic reactions. The membrane allowing the selective removal of a product from the reaction ambient lowers, for example, the thermal load and reduces the risk of runway of the reaction.

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