



Review

Steam separation enhanced reactions: Review and outlook

Jasper van Kampen^{a,b,*}, Jurriaan Boon^{a,b}, Frans van Berkel^a, Jaap Vente^a,
Martin van Sint Annaland^b

^a Sustainable Process Technology, ECN part of TNO, P.O. Box 15, 1755 ZG Petten, the Netherlands

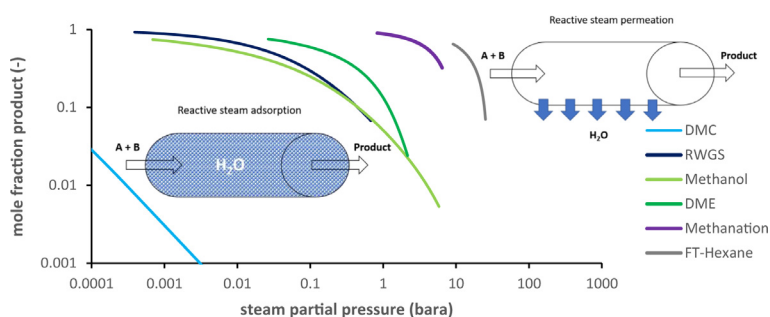
^b Chemical Process Intensification, TU/e, P.O. Box 513, 5600 MB Eindhoven, the Netherlands



HIGHLIGHTS

- Steam separation enhancement promising process intensification for CO₂ utilization.
- Reactive steam permeation processes require hydrothermal stability, permselectivity.
- Reactive steam adsorption processes require high working capacity, heat management.
- Progress in process development requires combination of theory and experiments.

GRAPHICAL ABSTRACT



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ABSTRACT

Enhancement by steam separation is a promising process intensification for many types of reactions in which water is formed as a byproduct. For this, two main technologies are reactive vapor permeation (membrane technology) and reactive adsorption. Both can achieve significant conversion enhancement of equilibrium limited reactions by in situ removal of the by-product steam, while additionally it may help protecting catalysts from steam-induced deactivation.

In general, reactive permeation or reactive adsorption would be preferable for distinctly different process conditions and requirements. However, although some advantages of reactive steam separation are readily apparent from a theoretical, thermodynamic point of view, the developments in several research lines make clear that the feasibility of in situ steam removal should be addressed case specifically and not only from a theoretical point of view. This includes the hydrothermal stability of the membranes and their permselectivity for reactive steam permeation, whereas high-temperature working capacities and heat management are crucial aspects for reactive steam adsorption. Together, these developments can accelerate further discovery, innovation and the rollout of steam separation enhanced reaction processes.

1. Introduction

Dehydration reactions are common in chemical industry, and similarly the utilization of carbon dioxide often starts with its chemical reduction with hydrogen and the formation of steam. In fact, the

effective handling of steam is one of the biggest bottlenecks for CO₂ utilization in industry [1,2]. Whereas H₂O is the main byproduct of many equilibrium limited reactions, such as the water-gas shift reaction and dimethyl ether synthesis, its in situ removal will result in significant conversion enhancements and thus process intensification. This is based

* Corresponding author at: ECN part of TNO, P.O. Box 15, 1755 ZG Petten, the Netherlands.

E-mail addresses: j.v.kampen@tue.nl, jasper.vankampen@tno.nl (J. van Kampen).

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Nomenclature

A_m	membrane area (m^2)
a_m	membrane area per reactor volume ($m^2 m^{-3}$)
Da	Damköhler number (–)
f	inhibition factor (–)
k	reaction rate constant (s^{-1})
K_{eq}	equilibrium constant (–)
P_i	partial pressure of component i (bar)
Pe	Péclet number (–)
Q_i	permeance of component i ($mol s^{-1} m^{-2} Pa^{-1}$)
q_i	adsorbent loading ($kg kg^{-1}$)
r	reaction rate ($mol m^{-3} s^{-1}$)
R_i	production rate of component i ($kg h^{-1} m^{-3}$)
R	steam removal (%)
S	selectivity (–)
t	time (s)
V_R	reactor volume (m^3)
w_{ads}	weight of adsorbent (kg)
X	conversion (–)

Abbreviations

CMR	catalytic membrane reactor
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COS	carbonyl sulfide
CSP	ceramic supported polymer
CZA	copper/zinc oxide/alumina
DMC	dimethyl carbonate
DME	dimethyl ether
FBMR	fluidized bed membrane reactor
FBR	fluidized bed reactor
FT	Fischer-Tropsch
LTA	Linde type A
MOR	mordenite
MR	membrane reactor
PBMR	packed bed membrane reactor
PBR	packed bed reactor
PI	process intensification
PSA	pressure swing adsorption
RD	reactive distillation
rWGS	reverse water-gas shift
SMBR	simulated moving bed reactor
SOD	sodalite
TMBR	true moving bed reactor
TSA	temperature swing adsorption
WGS	water-gas shift
ZSM-5	zeolite Socony Mobil-5

on Le Chatelier's principle, according to which the reactant conversion to products in an equilibrium limited reaction is increased by selectively removing reaction products. In chemical process intensification this concept is used in reactive separations, where reaction and separation take place in a single process step [3]. Another benefit of in situ steam removal involves the mitigation of catalyst deactivation. Thermally induced deactivation (such as sintering or phase transformation at high temperatures) is generally accelerated by H_2O [4]. For reactions in which H_2O is a main byproduct, such as Fischer-Tropsch synthesis, catalyst deactivation by the formed H_2O could be detrimental. On the catalyst level, tuning of catalyst support, promoters and crystallite size has been applied to the increase H_2O resistance and extend catalyst lifetime. Additionally, on a reactor and process level, in situ removal of steam would benefit catalyst stability, enhancing catalyst lifetime and process efficiency in these cases as well. While the advantages of process intensification through steam separation enhanced reactions has become apparent from several experimental and theoretical studies, a critical review is currently lacking.

Several possibilities exist to enhance process efficiency by steam separation. Staged ex situ separation, using for example interstage cooling and condensation, could be applied when the conversion per reactor stage is reasonably high. Otherwise, the required large number of sequential reaction and separation steps to achieve low steam levels makes this a less efficient approach [5,6], or entails the use of a large recycle stream. In situ steam separation by means of a reactive separation method is often required to achieve efficient process intensification.

Although reactive distillation (RD) is one of the best-known examples of integrated reaction and separation and therefore a widespread implemented method [7,8], its use is limited to systems with a product in the liquid phase. For gas phase systems, membrane (reactive vapor permeation) and (reactive) adsorption technologies are the most important separation methods that could be implemented.

Also membrane technology has been extensively studied and has found various commercial applications, for example in hydrogen separation and filtration applications. Many different types of membranes exist, which are applicable to gas and/or liquid processes. Key factors for application of membrane separation processes or membrane reactors, irrespective of the specific process or reactor, are permeability,

selectivity or separation factor and material stability [9]. Over the past decades dehydration of organic streams using membranes gained attention with the first steam selective membranes being reported [10]. This development has made membranes available for in situ H_2O removal during steam producing reactions, i.e. reactive vapor permeation.

Adsorption technology is widely used in pressure swing adsorption (PSA) applications, where high purity requirements have to be reached. While the concept of reactive adsorption had long been known [11], the use of an adsorbent and catalyst mixture in a reactor and its periodic operation have been studied in the open literature since the 1980s [12–15]. The most common application of this concept is the conversion enhancement in a reversible reaction to overcome equilibrium limitations. However, selectivity control could also be obtained by the selective removal of a byproduct. The use of a solid adsorbent requires periodic regeneration to regain the adsorptive capacity of the system. Several reactor and regeneration concepts exist for various adsorption technologies. Typically, a fixed-bed reactor configuration is combined with regeneration cycles. The method of regeneration can be divided into pressure swing, temperature swing, concentration swing, reactive regeneration, displacement regeneration or a combination of these operations [16–18]. In fact, in adsorptive reactors the regeneration process is often the rate determining step and the regeneration determines the cycle times and the required equipment, and therefore the efficiency and feasibility of the process. However, the regeneration procedure is determined by the requirements and the possibilities of the reactive separation system. Carvill et al. (1996) were the first to experimentally investigate the reactive adsorption of steam in the reverse water-gas shift reaction [19]. They showed the potential of reactive adsorption for the in situ removal of steam during a chemical reaction.

Thus, over the past decades the relevance of reactive separation has been established, as many authors have investigated the possibility of reactive steam separation for their studied processes by theoretical and experimental means. At this point in time, lessons can be drawn about the strategies for developing steam separation enhanced reactions, combining insights from experimental and modelling work in the literature. As the interest in the development of steam separation enhanced reactions is strongly increasing with the development of CO_2 utilization processes, these lessons may serve as a guidance for future

developments in this field.

In this paper the possibilities of in situ steam separation from dehydration reactions are reviewed. The advances in reactive steam separation by membrane and adsorption technologies are highlighted and the potential of both reactive separation methods is discussed, based on process requirements. Whereas the processes relevant in this field are operated at higher temperatures, a general temperature window starting from 200 °C up to maximally 400 °C is considered. Finally, critical aspects for future development and optimization of reactive steam separation technologies are identified.

2. Reactive separation of steam

2.1. General considerations

The conversion of equilibrium limited dehydration reactions can be enhanced due to an equilibrium displacement by selectively separating steam, resulting in lower remaining steam partial pressures. This is illustrated in Fig. 1, where on the left the thermodynamic carbon distribution for direct dimethyl ether (DME) synthesis is depicted and on the right the experimentally obtained results for sorption enhanced DME synthesis are shown [20]. Not only does the DME yield increase from a conventionally limited 9% for CO₂ feed, or 55% for CO feed, to more than 80%, also the CO₂ content in the product is decreased to less than 1%. This results in an increased single-pass conversion, less demand on downstream separation units, and smaller recycle streams for all CO₂ to CO syngas ratios and especially for CO₂ feed.

In Fig. 2 the yield as a function of the remaining steam partial pressure is shown for some important reactions studied in literature, clearly indicating the possible increase in equilibrium conversion at lower steam partial pressures for the different reactions. On the one hand, very low steam partial pressures are required to gain a high CO yield in the reverse WGS, or even extremely low partial pressures for the direct synthesis of dimethyl carbonate (DMC). On the other hand, for the Fischer-Tropsch synthesis of hexane a steam partial pressure of 10 bar would already result in significant conversion enhancement. Besides conversion enhancement due to equilibrium displacement, the decrease in the steam partial pressure by in situ separation can also affect the reaction kinetics, reaction selectivity, catalyst deactivation and thus catalyst lifetime. All these positive and/or negative effects are different for each case and must be addressed case specific. For

example, in the case of methanation, the primary advantage of employing sorption enhancement is not to increase the (already high) conversion, but to enhance product purity by converting remaining hydrogen [21] or carbon dioxide [22]. Other opportunities are operation at milder reaction conditions to achieve the same conversion and yield as conventional processes, such as in Ref. [19].

The sections below discuss adsorptive and membrane-based processes, respectively, for steam separation enhanced reaction processes. It is followed by a third section discussing their relative merits.

2.2. Reactive steam adsorption

Steam adsorption enhanced reverse water-gas shift experiments in a bench scale reactor by Carvill et al. were the first to be reported in the open literature [19]. Since then, in situ steam adsorption has been studied for various reactions, including the reverse water-gas shift, the Claus process, the Sabatier process, dimethyl ether (DME) synthesis and dimethyl carbonate (DMC) synthesis. A shortlist of steam adsorption studies is presented in Table 1.

Only few authors have conducted studies that combine theory and experiments in a fundamental way, which is crucial for a proper understanding of this type of process as argued below.

Essential for an adsorptive reactor is the capacity of the adsorbent and its affinity for separation of the desired component. However, the capacity of the adsorbent is finite, which makes periodic regeneration inherent to any adsorption process. The periodic regeneration restores the adsorptive capacity and therefore gives an extra degree of freedom to the process, making the method of regeneration another essential aspect for reactive steam adsorption. In this respect, a distinction has to be made between the total capacity and the working capacity of an adsorbent material. The working capacity of the material is its apparent capacity over many consecutive cycles of adsorption and regeneration, whereas the total capacity is a material characteristic given by its isotherm. A large amount of adsorbent material is necessary when its working capacity is low (while a large amount of steam has to be separated). Evidently, a large amount of adsorbent would make the implementation of an adsorptive reactor less feasible. Another factor of interest is the selectivity for the adsorption of steam relative to other components, which determines the loss of reactants and/or products. Non-selective adsorption results in an impure desorption gas stream, which can or has to be separated for economic or environmental

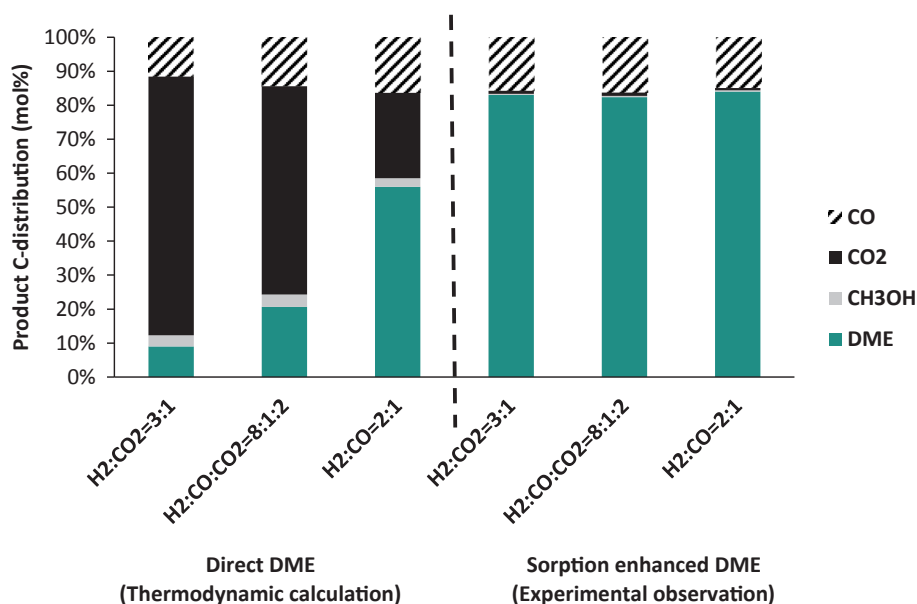


Fig. 1. Thermodynamic (maximally possible) carbon distribution versus experimentally obtained results for sorption enhanced DME synthesis. Conditions: stoichiometric H₂ to CO_x feed, CO_x feed is CO₂, CO₂:CO 2:1 and CO, including 30% inert, 275 °C & 40 bar [20].

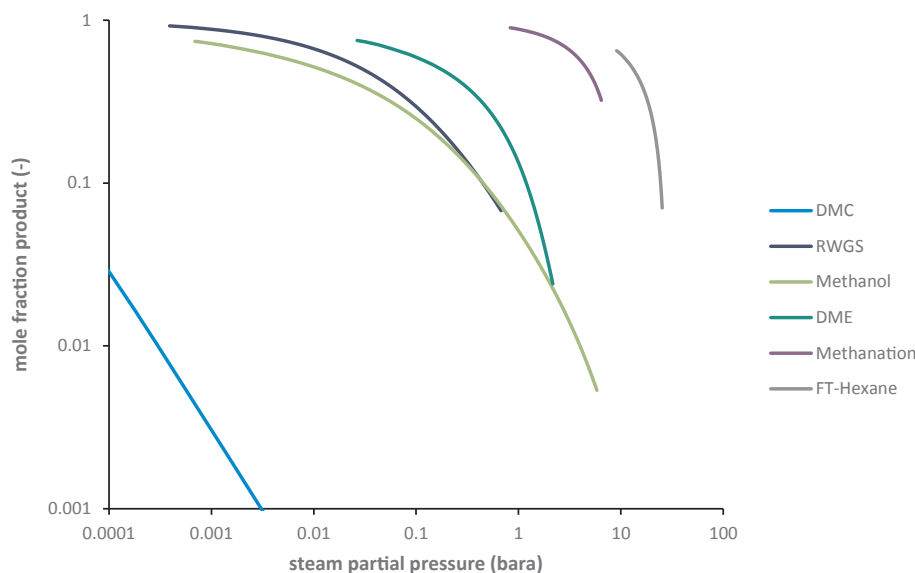


Fig. 2. Molar fraction of product, CO for RWGS, CH₃OH for methanol synthesis, DME for direct DME synthesis, CH₄ for methanation, hexane for Fischer-Tropsch and DMC for direct DMC synthesis, as a function of the remaining steam partial pressure based on minimization of the Gibbs free energy of reaction. Conditions: stoichiometric H₂, CO₂ feed for all reactions; RWGS 300 °C, 10 bar; methanol 250 °C, 30 bar; DME 275 °C, 30 bar; methanation 300 °C, 10 bar; FT 250 °C, 30 bar; DMC 200 °C, 30 bar.

Table 1

Shortlist overview of experimental work on reactive steam adsorption.

Reaction	Sorbent	Regeneration	Reference
r-WGS	13X	Pressure swing	Carvill et al. [19]
r-WGS	4A	–	Haije et al. [23]
r-WGS	13X, 4A, SOD	–	Ghodhbene et al. [24]
Claus	3A	Purge & Temperature swing	Agar [25]
Claus	3A	Purge & Temperature swing	Elsner et al. [26,27]
DME	MgSO ₄	–	Kim et al. [28]
DME	3A	Pressure swing	Ressler et al. [29]
DME	LTA	Temperature & Pressure swing	Boon et al. [5]
DME	LTA	Temperature & Pressure swing	van Kampen et al. [20,30]
Methanation	4A	Purge & Temperature swing	Walspurger et al. [21]
Methanation	3A, 5A	–	Borgschulte et al. [22,31]
Methanation	5A, 13X	Purge	Delmelle et al. [32,33]
DMC	3A	–	Choi et al. [34]
Glycerol carbonate	13X	–	George et al. [35]

reasons. Additional separation units and possible recycle streams make the process more complex, costly and less viable. Besides separation affinity and capacity, the kinetics of separation could also play an important role. Ideally, the rate of steam adsorption matches the rate of steam production. The latter, however, is influenced by the adsorption of steam due to the changed kinetics of the desired reaction and/or undesired side-reactions. Moreover, mass transfer limitations between catalytically active sites and adsorption sites could affect the outcome of a reactive adsorption process. In addition to mass transfer, heat transfer is often an important aspect in chemical reactors. Especially for highly exothermic or highly endothermic reactions heat transfer limitations could be problematic and heat management is essential. In addition to the heat of reaction(s), the heat of adsorption has to be managed as well for reactive adsorption processes. This makes the heat management possibly more complex. Consequently, the complexity of operating reactive adsorption processes has led to the proposal of very different contactor types for its implementation. Among others, these contactor types include a moving bed adsorptive reactor, a packed bed adsorptive reactor and a fluidized bed adsorptive reactor. The choice of contactor type influences all other aspects, from heat and mass transfer characteristics to possible regeneration modes. Therefore, one contactor type could be preferred over another depending on specific issues. For instance, a fluidized bed reactor could be beneficial in case of heat transfer limitations. However, a contactor type could also increase the complexity of the process, for example in the case of a moving bed reactor. These aspects of reactive adsorption processes are discussed in

more detail below.

2.2.1. Selectivity

For in situ steam removal by solid adsorbents, zeolite type materials are often preferred, as can also be deduced from Table 1. These structured materials have well-defined pore sizes and geometries. Because of their characteristics zeolite materials can have a high affinity and selectivity for the desired adsorbate. Zeolite types 3A and 4A are especially suitable for the removal of steam (~0.2–0.3 nm kinetic diameter [36,37]) due to their micropores with a diameter of around 0.3–0.4 nm [16], preventing the adsorption of other, larger components that are present during reaction. Conversely, Carvill et al. (1996) used zeolite NaX as water-selective adsorbent at moderately high temperatures for the reverse water-gas shift reaction [19]. Although zeolite NaX typically has a larger pore opening of 0.8 nm, possible co-adsorption of other components is not observed nor discussed. Similarly, zeolite 13X (NaX) is used as solid adsorbent for steam in the formation of larger, cyclic carbonates (e.g. ethylene carbonate, propylene carbonate and glycerol carbonate). Also in this study, enhanced product yields with almost 100% selectivity were obtained [35].

Although co-adsorption is not always observed nor discussed, competitive adsorption of steam and CO₂ is well-known for various materials [36,38]. In line with this, Walspurger et al. (2014) show competitive adsorption of CO₂ on zeolite 4A adsorbent. Although the adsorption capacity of CO₂ itself seems very low, the capacity for steam adsorption decreases significantly in the presence of CO₂ [21].

Recently, Delmelle et al. (2018) gave evidence of a decrease in water diffusion kinetics during adsorbent regeneration due to pore blocking by reaction intermediates and products [32]. Moreover, Vaporciyan and Kadlec (1987, 1989) even use the slightly larger pore zeolite 5A for the separation of CO₂ [14,15]. For zeolites 5A and 4A, authors also showed co-adsorption of other components, such as carbon monoxide, methanol and DME [36,39,40]. For zeolite type 3A adsorbent, co-adsorption is less well-known. Its smaller pore size (0.3 nm) physically restricts slightly larger molecules to adsorb, which is why zeolite type 3A is used for drying both polar gases and reactive gases [37]. However, other authors have shown that the presence of methanol influences steam adsorption, even for zeolite type 3A [41], and that DMC can also adsorb on 3A, although at high pressures (20 MPa) [42].

2.2.2. Capacity

Physical adsorption is an exothermic process, which makes that the capacity of all adsorbents decreases with an increase in temperature. A physical sorbent is typically characterized by a low adsorption heat, a low activation energy, high adsorption/desorption rates and excellent reversibility [43]. Contrastingly, chemisorption is characterized by the reaction between adsorbate and surface-active sites of the adsorbent. Therefore, chemisorption features high adsorption heat and activation energy compared to physisorption. Typical chemical adsorbents are base-metal oxides. Although steam will adsorb chemically on base metal oxides, at high temperatures and pressures carbonates will likely be formed in the presence of CO₂ [44,45]. Hydrotalcites, a class of double hydroxides with the general formula Mg_(1-x)Al_x(OH)₂(CO₃)_(x/2)nH₂O, are typically used for CO₂ adsorption. However, they show a capacity for steam adsorption as well [38,46]. With respect to the sorption capacity, it is important to focus on materials which retain sufficient capacity at elevated temperatures. The steam adsorption capacity of the hydrotalcites, as for the base metal oxides, is however limited [46,47].

In Fig. 3 (adapted from [48]) the water adsorption capacity of three physical adsorbents is plotted against temperature. Zeolites are well-known molecular sieves, and are used at relatively low to moderate temperatures. Possible steam separation enhanced reactions on the other hand are typically operated at higher temperatures (200–400 °C), which requires sufficient adsorption capacity at these temperatures. Although zeolite molecular sieves have an adsorption capacity for water at slightly elevated temperatures (Fig. 3), little information about the adsorption of steam on zeolite materials under higher temperatures is known in the open literature. Elsner et al. (2002) encountered this issue and experimentally determined a Freundlich isotherm for a zeolite type 3A under sorption enhanced Claus conditions [27]. Other authors, focusing on modelling a sorption enhanced reaction process, use a variety

of adsorption isotherm descriptions besides Freundlich models, such as Unilan and Langmuir models, derived from material studies [49–51]. Gabrus et al. (2015) experimentally studied the water adsorption isotherm for zeolite types 3A and 4A, and Mette et al. (2014) similarly performed a study on binderless zeolite type 13X up to 250 °C [52,53]. However, it was reported that the latter material has reduced hydrothermal stability at temperatures above 200 °C. Although the Langmuir-Freundlich and the dual-site Langmuir-Langmuir models proposed by Gabrus et al. (2015) are fitted for temperatures up to 250 °C, these, and other descriptions have been determined under different conditions than those of the studied sorption enhanced reactions, which means that the models have to be extrapolated to unverified conditions. In contrast, the more experimental studies regarding sorption enhanced reactions do not explicitly consider isotherm models for the used adsorbent material. The focus in these contributions is merely on the enhancement effect of the adsorbent on the reaction, not on a description of the intrinsic adsorption behavior of the material [19,22,28,29,34].

2.2.3. Regeneration

Besides the adsorption capacity at high temperature, the adsorbent material should also have good adsorption kinetics under the sorption enhanced reaction conditions [24]. Preferably the rates of adsorption and production of steam match. However, especially the desorption kinetics of the adsorbent material are of interest. The desorption rate is often the time-limiting step in a sorption enhanced reaction process, determining the length of the regeneration. The most common regeneration procedures are pressure swing, temperature swing or a combination of both operations, possibly with the use of a purge gas. In theoretical evaluations often pressure swing regeneration is considered [25,49,50], because its fast response and therefore short regeneration time is preferred over the slower temperature swing. However, in practical applications of zeolite molecular sieves, the drying beds at moderate temperatures are often regenerated by increasing the temperature [36,37]. For the use of a purge gas, a suitable stream must be available in the process and its partial back mixing must not cause complications.

In the study by Carvill et al. (1996) pressure swing regeneration is shown to be suitable for periodic regeneration of the zeolite NaX adsorbent [19]. Using product to repressurize the reactor they could achieve a high purity product, whereas reactant repressurization led to sorption enhanced conversions without high purity product. The product CO concentrations were initially low due to the displacement of the pressurization gas from the reactor and only reached a maximum of 80% before reaction equilibrium values were obtained. Although the benefits of sorption enhancement are demonstrated experimentally for

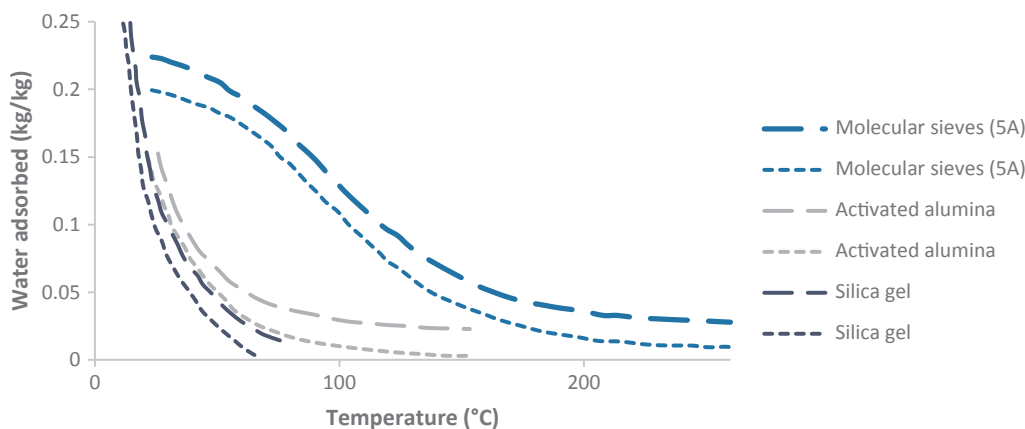


Fig. 3. Water adsorption capacity versus temperature in equilibrium with 13.33 mbar water vapor partial pressure for molecular sieves (zeolite 5A), silica gel, and activated alumina (striped lines). Dotted lines show the effect of the 2 wt% of residual water at the start of the adsorption (adapted from [48]).

the reverse WGS reaction, further optimization of the adsorption and regeneration process is required to roll out the sorption enhanced reverse water-gas shift process to achieve high conversion of CO₂ to CO, with high purity. To optimize the sorption enhanced reverse WGS in a solar fuel process Haije et al. (2011) suggest using the heat released from Fischer-Tropsch synthesis, downstream of the rWGS unit, to regenerate the adsorbent by temperature swing regeneration [23].

In the sorption enhanced methanation process temperature swing regeneration with the use of a purge gas has been applied in cyclic experiments, as reported by Walspurger et al. [21]. The regeneration temperature, ranging from 350 to 450 °C, had no significant effect on the working capacity of the used zeolite material, which could be due to either the extensive regeneration time or the excess of purge gas used. Delmelle et al. (2016) observed a significant improvement in regeneration for a hybrid Ni/13X adsorbent using air rather than hydrogen as purge gas in their sorption enhanced methanation process [33]. The purge gas did not affect the regeneration of hybrid Ni/5A, suggesting that the larger pores of 13X allow for faster transport and better regeneration. Whereas the methanation experiments have been performed at atmospheric pressure, the choice of regeneration method and appropriate conditions, however, is critical for the feasibility of the reactor concept. Design and optimization of the regeneration step will be key in optimizing the energy requirement and the associated operational costs.

In successive studies on the Claus process, the regeneration was analyzed in more detail [26,27]. Based on the thermal inertia of the fixed-bed, the study concludes that regeneration by temperature swing is not feasible. This makes pressure swing regeneration the most viable option, which is often preferred over TSA in the design of cyclic processes. Abufares et al. (2007) evaluate an optimization model for vacuum swing regeneration for the same Claus process [54]. They show that a high performance adsorptive reaction process is possible by means of optimized vacuum swing regeneration.

In addition to previous studies, van Kampen et al. (2017) also explicitly looked into the effect of the regeneration conditions on the sorption enhanced DME process [20,30]. They have shown that the used zeolite adsorbents can be readily regenerated by pressure swing regeneration. Increasing the temperature during regeneration (temperature swing) improves the extent of regeneration even further by increasing the working capacity of the adsorbent.

2.2.4. Catalyst activity, reaction kinetics, and mass transfer

Studies have clearly indicated that the adsorbent regeneration not only influences the adsorptive capacity of the system, but that periodic exposure to regeneration conditions may also affect the catalyst performance. In a study of the regeneration conditions in sorption enhanced DME synthesis, van Kampen et al. [20] have shown that periodic exposure to temperature swing conditions of 400 °C not only improves the performance of the adsorbent, which can be judged from the extended period before breakthrough, but also improves the activity of the Cu/ZnO/Al₂O₃ catalyst, which can be judged from the equilibrium conversion after breakthrough and stabilization (see Figs. 4 and 5).

Regarding the effect on catalyst activity and reaction kinetics, Reßler et al. (2005), employing adsorbent zeolite 3A in sorption enhanced DME formation, posit that the removal of steam has a conflicting role. Methanol and DME producing reactions are enhanced, but the opposite holds for the water-gas shift reaction [29]. It is widely known that a low content of CO₂ enhances the reaction kinetics for methanol synthesis over CZA catalysts, although CO₂ limits the reaction equilibrium [55]. Whereas the extent of regeneration in sorption enhanced DME synthesis influences the amount of CO₂ present, it also directly influences the reaction kinetics. This gives the regeneration of this reactive adsorption system extra importance, although it is an important parameter in adsorptive reactors in general.

Although sorption enhanced methanation is shown by Walspurger et al. (2014) for a physical mixture of a methanation catalyst and a zeolite adsorbent [21], there are indications that a hybrid catalyst adsorbent particle could perform better than a physical mixture [22,31]. It is clear that the effective transport of species between, and therefore the proximity of catalytically active sites and adsorbent sites can have an important role in sorption enhanced processes. In addition, this also suggests that the major mass transport resistance comprises the transport from the catalyst, via the bulk phase, to the sorbent. The relatively low space velocities for many adsorption processes increases the likelihood of mass transfer limitations. However, recent developments in rapid PSA cycling seem promising for improving these aspects.

As mentioned previously, by modification of the reaction conditions the conversion of the desired reaction can be enhanced, but undesired parallel or consecutive reactions may be enhanced as well. In the Claus process this aspect of reactive adsorption appears. To a small extent, the formation of undesirable carbonyl sulfide (COS) was observed. In the

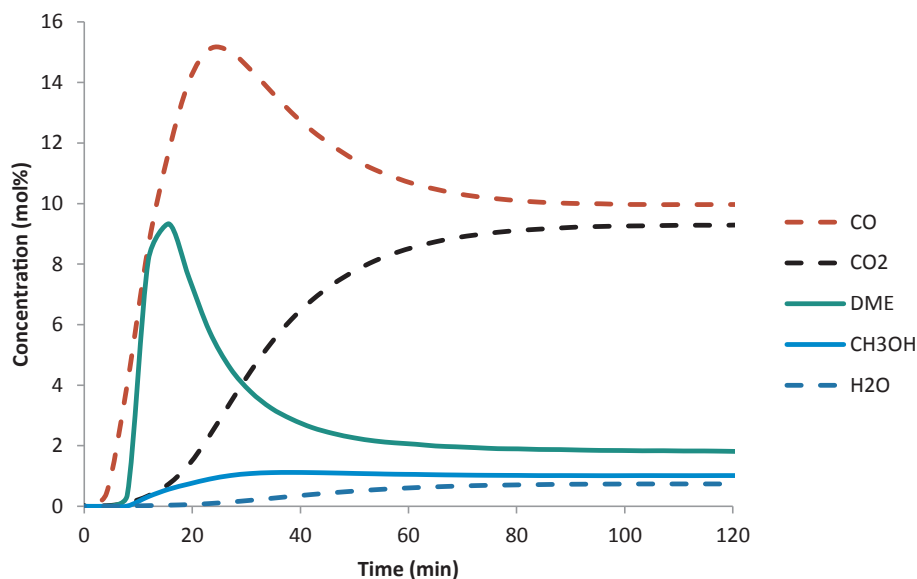


Fig. 4. Typical breakthrough profile for CZA catalyst + LTA adsorbent system. Conditions: stoichiometric H₂, CO, CO₂ feed for all reactions; CO₂:CO = 1:2; 275 °C, 25 bar(a); 300 °C regeneration [20].

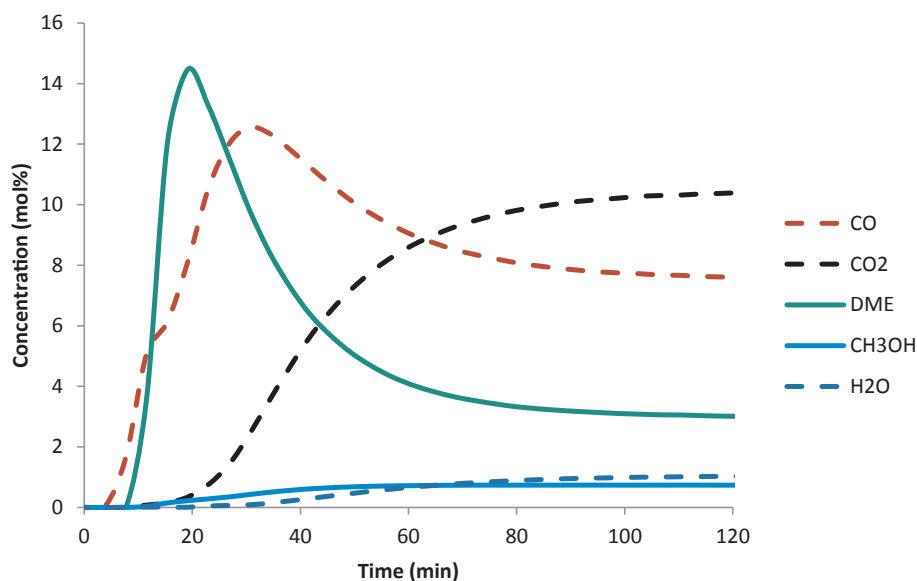


Fig. 5. Typical breakthrough profile for CZA catalyst + LTA adsorbent system. Conditions: stoichiometric H_2 , CO, CO_2 feed for all reactions; $CO_2:CO = 1:2$; 275 °C, 25 bar(a); 400 °C regeneration [20].

conventional Claus process COS is hydrolyzed by the steam present in the reactor. Whereas steam is selectively removed in the adsorptive reactor concept, this hydrolyzation is suppressed as well and even more COS could be formed compared to the conventional process [27]. This example of COS formation clearly illustrates the possible enhancement of undesired side-reactions due to inherent concentration or temperature profiles in reactive adsorption processes.

2.2.5. Heat management

Heat management is very important for chemical reactions, especially in the case of high exothermicity or endothermicity, and thus also for reactive adsorption processes. The adsorption of steam is an exothermic process, which is therefore favored at low temperatures (and high pressures). The adsorbent material requires a high affinity for steam to obtain sufficient working capacity and subsequent sorption enhancement at higher reaction temperatures (between 200 and 400 °C). This was shown for the zeolite type adsorbents used by various authors (Table 1).

For exothermic reactions, such as the methanation reaction, the Claus reaction and (direct) DME synthesis, the adiabatic temperature rise could be very high (up to 500 °C for methanation). Besides the influence this already would have on the conventional reactions, these temperature profiles affect the adsorption capacity of steam, the kinetics and the concentration profiles in adsorptive reactions. For this reason, Walspurger et al. (2014) considered an adsorptive reactor as a third reactor in a (conventional) series of three adiabatic reactors, in which the main part of the reaction heat is mitigated to the first and second reactor. In this way they motivate the use of an adiabatic reactor instead of a more complex and costly isothermal reactor [21]. Elsnér et al. (2003), on the other hand, claim that the thermal inertia of the fixed bed adsorptive reactor avoids interference of the reaction heat with the adsorption process [27], which would make adiabatic operation feasible. In addition, for a fixed bed reactor in chemical looping combustion it is shown that as long as the velocity of the reaction front is larger than that of the heat front, the maximum temperature increase is only effected by the gas and solid properties [56,57]. Also other authors assessed the possibilities of adiabatic and non-adiabatic reactor operation. Sorption enhanced reverse WGS couples the endothermic rWGS reaction with the exothermic steam adsorption, possibly minimizing external heat input required for rWGS [58]. In a fixed bed reactor Parra et al. (2017) show that in the optimal configuration the

temperature is close to the set maximum temperature of 260 °C. Although a higher temperature limits the adsorption capacity, the reaction kinetics are faster. For the adiabatic case this optimization towards the highest allowable temperature means that the feed temperature has to be low to not exceed 260 °C inside the reactor. In the non-adiabatic case a profile of the wall temperature allows for the highest productivity. Near the reactor inlet a lower wall temperature results in more adsorption due to the higher allowable heat of adsorption. Throughout the reactor the rates of reaction and adsorption converge, allowing operation at higher (wall) temperatures [58]. This shows the advantage of non-adiabatic operation, the temperature can be tuned to favor the dominant phenomenon, reaction or adsorption. Contrastingly, for adiabatic operation the temperature is determined by (the ex- or endothermicity of) the dominant phenomenon, which is also shown for sorption enhanced reverse WGS in a moving bed reactor [59].

2.2.6. Contactor type and reactor configuration

In the literature focusing on reactive steam adsorption, a packed bed adsorptive reactor is the most commonly selected reactor configuration [19–21,27]. This reactor configuration is relatively easy to implement compared to a less mature technology, such as a fluidized bed adsorptive reactor. By optimizing the reactor operation, the ideal performance of a moving bed reactor can be achieved. Parra et al. (2017, 2018) showed that a moving bed adsorptive reactor could be more beneficial than a packed bed adsorptive reactor for the reverse WGS reaction with an order of magnitude difference in space time yield [58,59]. Similarly, Santos et al. (2015) proved the potential of a moving bed chromatograph reactor for the separation of water and DMC, in its direct synthesis [60]. Although other contactor types are less apparent in research on reactive steam adsorption, they could be beneficial for specific steam sorption enhanced reaction processes. In the previous sections the importance of mass transfer and heat management is discussed. If transfer limitations are a serious issue for a process, fluidized bed technology would be a good candidate for its great mass and heat transfer properties. For these reasons Bayat et al. have suggested several configurations for sorption enhanced methanol synthesis and sorption enhanced Fischer-Tropsch synthesis [51,61], including a dual (moving) bed reactor and a fluidized bed reactor, thermally coupled to a fixed bed reactor.

2.3. Reactive steam permeation (membrane steam separation)

The second reactive steam separation method is reactive steam permeation or reactive membrane separation. Few studies have been published on steam separation enhanced reactions, including DME and DMC synthesis [62–72], however the Fischer-Tropsch (FT) reaction has received the most attention [73–78]. A shortlist is given in Table 2.

Espinoza et al. (1999, 2000) were the first to show that zeolite type membranes can selectively separate steam under FT-reaction conditions [73,74]. However, especially the selectivity tends to decrease at increasing temperatures. This brings us to the requirements for reactive steam separation by membranes. Similar to the capacity for reactive adsorption, the steam flux through the membrane (given by the membrane permeance) has to be sufficient. Whereas the rate of steam separation has to match the rate of steam production, the membrane permeance directly determines the required membrane area. The membrane area, however, is limited, depending on the membrane reactor configuration, and therefore defines the feasibility of the concept. As already mentioned in the example by Espinoza et al., another aspect determining the viability of the reactive steam permeation concept, is the permselectivity of the membrane. A low separation selectivity could result in a reduced separation enhancement and loss of reactants and/or product, which means that an extra, costly recovery is necessary for economic, legislative or environmental reasons. A third principal requirement for reactive steam permeation is the hydrothermal stability of the membrane. Many membranes typically operate at low to moderate temperatures [95]. In contrast, operation at high temperatures and high pressures is necessary for reactive steam permeation. Aside from these aspects, kinetic effects and mass and heat transfer limitations could be of importance. As already mentioned, the rate of steam separation should match the rate of steam production. However, the production rate could be influenced by the separation of steam due altered kinetics of the desired reaction and/or undesired side-reactions. Furthermore, mass and heat transfer limitations in the membrane reactor, and especially between catalytically active sites and the membrane, could largely affect the reactive steam permeation process. Finally, also for reactive steam separation by membranes several contactor types are possible for implementation. The fixed bed

membrane reactor, catalytic membrane reactor and fluidized bed membrane reactor are examples of the many possible types available. These contactor types have different characteristics and therefore influence all other aspects. For example, in case of mass transfer limitations due to the (non-)proximity of catalytically active material and the membrane a catalytic membrane would help to overcome this issue by bringing the functionalities closer together. A fluidized bed membrane reactor could also become an option in the case of (severe) mass or heat transfer limitations due to its good mass and heat characteristics.

2.3.1. Flux and permeance

Many authors who have theoretically evaluated membrane steam separation enhanced reactions have relied on permeance and permselectivity data taken from literature that has been obtained during membrane characterization studies [62,64,67]. Rohde et al. (2008) already have presented an overview of the state-of-the-art membranes for in situ H₂O removal, dividing them in three different types: zeolite membranes, amorphous membranes and polymer membranes [77]. Their work is used as a basis and extended to a summary on H₂O permeances at higher temperatures (200–400 °C) (Fig. 6).

As already mentioned, many membranes were applied at low to moderate temperatures. For example, Holtbruegge et al. (2014) gave a maximum temperature of 90 °C related to the polymer layers in PERVAP 1255 [88]. Due to these temperatures various membranes depicted in Fig. 6 have only been tested up to 200 °C, and only few membranes have been tested above 300 °C.

Although pervaporation, in which the liquid feed/retentate changes phase to the vapor permeate, is outside the scope of this article due to its temperature window (generally well below 200 °C), some membranes, that are in principle also suitable for reactive steam permeation, have only been tested for pervaporation applications. Rohde et al. (2008) and Khajavi et al. (2009) tested their hydroxy sodalite (H-SOD) membrane for steam pervaporation [77,89]. Although the membrane performed well for pervaporation and should be suitable for vapor permeation, the processes are different and their applicability in steam separation is not guaranteed. Both systems have different modes of operation. Where in vapor permeation the steam pressure difference determines the driving force, in pervaporation the liquid feed/retentate

Table 2

Shortlist overview of experimental and modelling literature on reactive steam permeation (and pervaporation). Membrane reactors (MR), packed bed membrane reactors (PBMR), catalytic membrane reactors (CMR) and simulated moving bed membrane reactors (PermsMBR) are listed.

Reaction	Membrane material	Process	Reference
FT	Zeolite: MOR, ZSM-5	MR: gas phase & slurry	Espinoza et al. [73,74]
FT	Ceramic (TEOS coated)	PBMR	Rohde et al. [75]
FT	Zeolite: H-SOD	MR	Rohde et al. [77]
FT	Ceramic supported polymer (CSP)	PBMR	Rohde et al. [76]
DME	Silica	PBMR	Lee et al. [79]
DME	NaA	MR & PBMR	Fedosov et al. [80]
DME	Zeolite model	PBMR model	Iliuta et al. [62]
DME	Microporous zeolite: ZSM5/MFI	PBMR model	De Falco et al. [64]
DME	Zeolite model: ZSM5, MOR or SIL	PBMR model	Diban et al. [63,69]
Methanol	Zeolite	PBMR & PBMR model	Gallucci et al. [81,82]
Methanol/ steam selective	Mordenite	MR (permeation)	Sawamura et al. [83]
Methanol	Nafion	PBMR & PBMR model	Struis et al. [84]
Methanol/ steam selective	Zeolite: A	MR	Gorbe et al. [85]
Methanol	Inorganic: carbon & zeolite	–	Gallucci [10]
Flue gas dehydration	SPEEK	MR	Sijbesma et al. [86]
DMC	SPEEK	MR & CMR model	Mengers et al. [66]
DMC	SPEEK model & SPEEK chitosan model (up to 200C)	(C)MR model	Kuennen et al. [67,68]
DMC	Composite membrane (PERVAP 1255)	MR assisted RD: methanol permeation	Holtbruegge et al. [87,88]
Water selective membranes	Zeolite: 4A	MR	Zhu et al. [39]
Water selective membranes	Zeolite: H-SOD	MR (pervaporation)	Khajavi et al. [89]
Water selective membranes	Zeolite: H-SOD	MR (permeation)	Lafleur et al. [90]
Steam selective membranes (methanol, DME, DMC)	Zeolite: SOD	MR (permeation)	Wang et al. [91,92]
Acetals	Silica	PermsMBR	Pereira et al. [93]
Acetals	Silica	PermsMBR	Silva et al. [94]

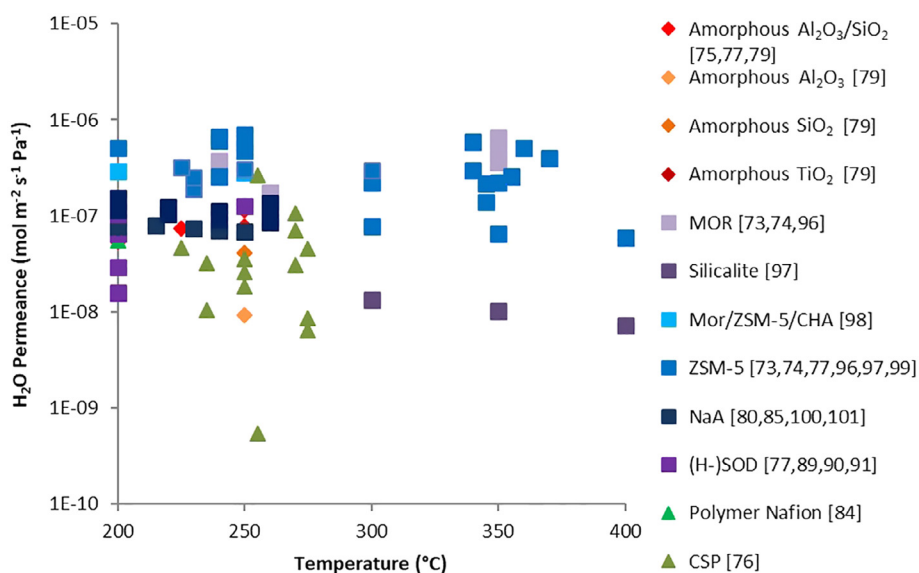


Fig. 6. H₂O permeances for zeolite, amorphous and polymer membranes between 200 and 400 °C [73–77,79,80,84,85,89–91,96–101].

changes phase to the vapor permeate driven by a concentration gradient. Wang et al. (2014) and Lafleur et al. (2017), however, developed (hydroxy) sodalite membranes suitable for steam permeation, indeed showing good permeances [90,91].

From Fig. 6 it can be seen that zeolite membranes, specifically ZSM-5 and mordenite type membranes, outperform the amorphous and polymer membranes in steam permeance at higher temperatures. In general, these zeolite membranes have a permeance between $1 \cdot 10^{-7}$ and $1 \cdot 10^{-6}$ mol Pa⁻¹ m⁻² s⁻¹. Except from Wang et al. (2012), who tested self-made membranes even up to 550 °C [97], no clear trend in steam permeance is observed for the mentioned zeolite membranes within this temperature range, which is promising for the thermal stability of these membranes. Although duration experiments are required for actual membrane stability measurements.

2.3.2. Permselectivity

Considering the permselectivities of the different membrane types, in general the selectivities of H₂O towards H₂ and of H₂O towards alcohols, such as methanol are considered critical [62,63,95]. The permselectivity of H₂O towards H₂ for various types of membranes at

elevated temperatures is shown in Fig. 7. Increasing the temperature results in a decreased permselectivity for all types of membranes. As discussed in the previous section on reactive steam adsorption, zeolite materials are well-structured with specific pore diameters. Both steam and hydrogen are small enough to enter these pores. However, the loading of steam on zeolite membranes is prone to block the permeation of hydrogen [39,83,85,97]. With increasing temperature both the steam loading and the permselectivity decrease. Polymer membranes tend to have a decrease in vapor permeance and an increase in gas permeance with increasing temperatures, resulting in a drop in the H₂O/H₂ permselectivity [86]. For amorphous membranes the decrease in H₂O/H₂ permselectivity is explained by an increase in the H₂ permeance due to degradation of the membrane at higher temperatures [77]. Again, the zeolite membranes seem to outperform the other membranes with permselectivities over 10, and even up to 1000, for the temperature range 200–300 °C. For example the permselectivities for the polymer membranes are in the range between 1 and 10. Although some higher values are obtained for ECN's ceramic supported polymer tested by Rohde et al. [76,77]. For even higher temperatures (> 300 °C) only data for zeolite membranes are available. And at these temperatures the

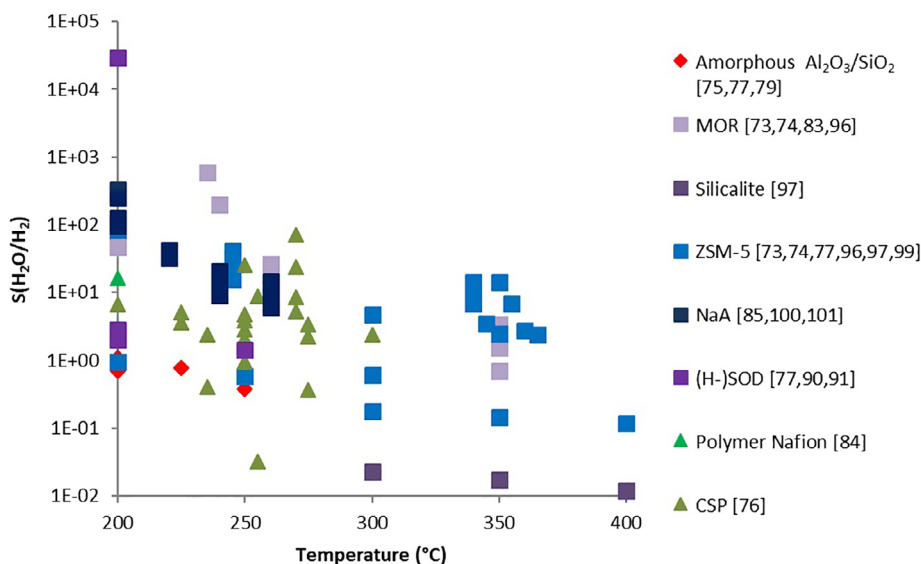


Fig. 7. Permselectivity of H₂O towards H₂ for zeolite, amorphous and polymer membranes between 200 and 400 °C [73–77,79,83–85,90,91,96,97,99–101].

permselectivity of the zeolite membranes drops to values ranging from 1 till 10, as explained above.

Another important aspect is the permselectivity of H₂O towards condensable (vapor) components in a reaction mixture. The separation enhanced yield for a PBMR can be even lower than the yield of a PBR due high losses over the membrane, as shown for methanol permselectivity in DME synthesis [63,69]. In Fig. 8 the permselectivity of H₂O towards methanol (as the hardest to separate alcohol) is presented for various types of membranes at elevated temperatures.

The first thing to notice from Fig. 8 is that the available data is limited and the temperature range only goes up to 250 °C. Secondly, relatively low permselectivities are achieved for the separation of steam and methanol. Although, more recent work on zeolite membranes shows more promising permselectivities of steam towards methanol [83,91,92]. The difficult separation, due to the preferential permeation of polar molecules, can be explained by a preferential adsorption mechanism rather than a size exclusion mechanism [95]. This supports the previous statement that the presence of steam limits the permeation of hydrogen in zeolite membranes, which is observed by several authors. Although not only the presence of steam limits hydrogen permeation, also the presence of methanol does.

Due to this difficult separation often the separation of condensables (vapor), such as steam and methanol, from non-condensable gases is considered [67,68,81,82]. Some authors even use these hydrophilic membranes to separate methanol in a process where they exclude the presence of steam, in particular for polymer membranes [87,88].

2.3.3. Stability

Also the hydrothermal stability of the considered membranes is of great importance. Zeolite type membranes are tested at higher temperatures (200–400 °C), as could be seen in Figs. 6 and 7. In contrast, polymer membranes are generally operated at lower temperatures and tend to break down at higher temperatures [88]. This is also the reason that there is little experimental data available for polymer membranes at elevated temperatures. The ceramic supported polymer membrane is a notable exception to this and this membrane was tested up to 300 °C and was reported to be stable under hydrothermal conditions, which would make it suitable for practical applications of in situ steam removal. Amorphous membranes are not tested over 250 °C. They are reported to degrade at higher temperatures and are therefore considered not suitable for operation at elevated temperatures [77]. Although zeolite type membranes are used at higher temperatures, also their stability is not always optimal. Thermal expansion, adsorbate-

induced structural changes and the effect of the framework cations influence membrane stability [102]. In line with these observations, LTA membranes have been stated to be unstable towards hydrolysis [103]. Therefore ZSM-5 membranes are dominant in the window between 300 and 400 °C. These membranes, however, often show less permeance due to reduced hydrophilicity [103,104]. Either increasing hydrophilicity, or increasing stability by Si enrichment are promising developments in further improving zeolite type membranes.

2.3.4. Mass transfer and kinetics

Besides permeance, permselectivity and stability, also kinetic effects and mass transfer limitations could be of importance. Some authors express the kinetic compatibility as the product of the modified Péclet number (Pe) and the Damköhler number (Da), and give a range between 0.1 and 10 for this expression [77,105]. The modified Péclet number relates the rate of transport by convection (and therefore the residence time) to rate of transport through the membrane, whereas the Damköhler number relates the rate of reaction to the rate of transport by convection. As the rate of reaction and the rate of separation have to be balanced, the product of Pe and Da should be balanced as well. Although this approach could work for many cases, the rate of reaction is evaluated with kinetics that do not account for separation enhancement conditions. Therefore, it neglects the possible influence of reactive separation on the kinetics of the system. Not only the kinetics, but also mass transfer limitations could affect the reactive steam permeation. In most cases the transport from the catalyst to the membrane via the bulk phase is rate determining. On the one hand, the relatively low space velocities for many separation enhanced processes adds to the probability of mass transfer limitations. On the other hand, radial convection can significantly contribute to the transport to/from the membrane [106,107]. Whereas transfer limitations between the different functional areas could influence the kinetics of reaction and separation, and the overall reactive separation performance, it is important to assess the limitations of the steam separation enhanced system, kinetics and/or mass transfer, so that the best configuration and reactor tuning can be applied.

2.3.5. Heat management

In addition, heat transfer limitations could have a large effect on the performance of reactive steam permeation. Heat management is important for chemical reactions in general, especially in the case of high exothermicity or endothermicity. Temperature profiles in reactive separation, however, does not only influence the local reaction rate, but

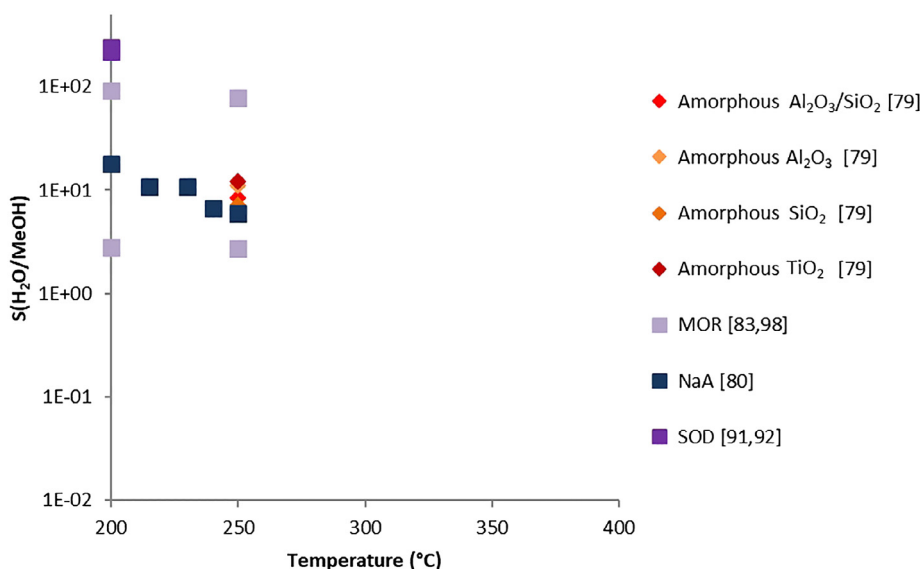


Fig. 8. Permselectivity of H₂O towards methanol for zeolite and amorphous membranes between 200 and 400 °C [79,80,83,91,92,98].

also the separation, thereby changing the overall behavior of the reactive permeation process. Gorbe et al. (2018) even suggest the application of a temperature gradient over their zeolite membrane to improve its performance [85]. In general, the behavior of a reactive permeation process can be controlled relatively easy by heat management due to the steady-state characteristics of a membrane reactor.

2.3.6. Contactor types and reactor configuration

The most common implementation of reactive steam permeation is as packed bed membrane reactor (PBMR), in which a membrane reactor is filled with catalyst material [66,70,71,73–76,78,80,108]. Although this is a relatively easy way to implement membrane separation, other contactor types could be beneficial for different reactions and operating conditions. For example, in case of mass transfer limitations due to the (non-)proximity of catalytic active material and the membrane a catalytic membrane could help overcoming this issue by bringing the functionalities closer together. A fluidized bed membrane reactor could also become an option in the case of (severe) heat transfer limitations due to its good heat transfer characteristics.

Besides the characteristics of the various membrane reactor types, also the choice of using a sweep determines the behavior of the reactive steam permeation system. Basically, the system is regenerated using a pressure swing, whereas the partial pressure difference over the membrane is the driving force for steam separation. Nevertheless, a degree of freedom remains in the choice for a vacuum or sweep gas at the permeate side. Sweeping the permeate side of the membrane with a low pressure, inert gas can increase the driving force over the membrane. On the other hand, diffusional resistances due to penetration of sweep gas into the membrane support can increase as well [107]. However, the increase in the driving force will be more dominant than the increase in mass transfer resistances and therefore the use of sweep gas can enhance steam separation. Another example is the recirculation of the sweep gas stream. In the case of a PBMR for DME synthesis, the recirculation of the sweep gas stream reduces the driving force for methanol over the membrane. The minimized loss of methanol across the membrane results in increased DME yields at high recirculation factors [69].

For the (reactive) separation of steam, although permeation was not used in all cases, many reactor configurations are reported. Hydrophilic membranes were tested in slurry, fixed-bed and fluidized-bed reactors [62,77]. Dual membrane reactors have been suggested, utilizing both a steam selective membrane and a hydrogen selective membrane [70,71]. A simulated moving bed membrane reactor was developed for acetal synthesis [93,94] and steam permeation was combined with reactive distillation [87,88]. All these configurations could result in potential benefits regarding the specific reactions and process conditions. Therefore, the optimal contactor type is case specific.

3. Selection of separation method

To benefit from the full potential of process intensification (PI), many ongoing research activities focus on new methodologies, frameworks and toolboxes for this level of process synthesis [3,109–112]. Although design methods for reaction-separation processes have been reviewed and revised [109,110], in practice a superstructure method is not applied in the design of completely new processes due to its high complexity [113,114]. Instead, process engineering decisions are often based on expert knowledge. Commonly this knowledge is formulated in so-called heuristic rules or rules-of-thumb [18,113]. The potential of in situ steam removal as PI is discussed with regard to selection criteria and process requirements.

3.1. Potential of in situ steam removal

3.1.1. Process selection criteria

In process selection, commonly a cost optimization is performed in

which the overall economy of the process is guiding the selection of the best option or configuration. This includes the material and energy efficiency, as well as the required separation technologies and recycles. In situ steam removal could result in a more complex reactor design by means of the implementation of membrane area or adsorbent in the reactor. However, the reduction of the downstream separation and recycle section, as well as possible operation at milder reaction conditions, could lower the capital expenditure significantly. The higher energy efficiency of an in situ steam removal process compared to the conventional process reduces the energy costs and therefore operational expenditure. The operational expenditure could be lowered as well by means of improved resource efficiency for in situ separation. Often such an energy (or resource) efficient process also results in reduction of the capital expenditure cost (satisfying the classic optimization equation), based on a reduction in the number of steps [112,114]. Moreover, not only costs can be a criterion for process selection, also its environmental impact can be a selection criterion. For such a ‘license to operate’ the energy efficiency and global warming potential of the process have to be assessed. The climate change mitigation potential of a process could be assessed by quantifying the CO₂ emissions avoided through a life cycle analysis [115]. This quantification could be a good method to evaluate different technologies and select an optimum process, especially for carbon capture and utilization technologies.

3.1.2. Criteria for in situ steam removal

For the feasibility of reactive steam separation, various aspects have to be evaluated. The first aspect to be addressed is the advantage of in situ steam separation in terms of reaction equilibrium and/or kinetics. Secondly, the steam concentration, which has to be reached, has to be evaluated and therefore the amount of steam that has to be separated. Thirdly, the technical aspect of the required in situ separation has to be attended. Finally, the process selection criteria such as the process economics and the reduction of the overall global warming potential can be addressed. The last aspects can only be fully considered if the first aspects have been evaluated and answered sufficiently.

Although the advantages of the first aspects for reactive steam separation may be apparent from a theoretical point of view, the developments in several research lines have demonstrated that the actual performance of the reactive steam adsorption system is often determined by the chemistry of the system and therefore impossible to be determined on a general level [20,30]. This makes clear that the feasibility of in situ steam removal should be addressed for each specific case and not only from a theoretical point of view. Nonetheless, some general aspects can be outlined.

3.1.2.1. General considerations: Impact of steam removal. To discuss general aspects for steam separation enhanced reactions a simple equilibrium reaction (1) is assumed:



In this reaction, reactants A and B form the desired product P and by-product H₂O, such as the reverse water-gas shift, etherification or esterification reactions. The impact of steam removal on this reaction can be assessed by the amount of steam present in equilibrium:

$$P_{H_2O} = \sqrt[d]{K_{eq} \frac{P_A^a P_B^b}{P_P^c}} \quad (2)$$

Secondly, reaction kinetics can be influenced by steam due to inhibition or even deactivation. This is generalized in Eq. (3) using a stoichiometry of one. The equation includes catalyst inhibition by H₂O as a surface coverage effect with an inhibition factor *f*.

$$r = k \frac{P_A P_B - P_P P_{H_2O} / K_{eq}}{(1 + f P_{H_2O})^2} \quad (3)$$

To evaluate the potential advantage of in situ steam removal Eqs.

(1), (2) and (3) are used in a simple plug flow reactor model [116]. Steam is removed instantaneous from the reaction mixture and the possible influence on the residence time is neglected for simplification. The parameters and conditions can be found in Table 3. The potential advantage of in situ steam removal is illustrated in Fig. 9, where the reactant conversion to product is shown as a function of the equilibrium constant which represents different type of reactions.

As can be expected, for reactions with large values for the equilibrium constant the conversion to product is significantly larger due to the equilibrium position. The effect of steam inhibition on the reaction rate, and therefore on the conversion is especially significant for a reaction with larger values for their equilibrium constant. The larger K_{eq} , the more favored is the formation of product and of steam. However, the formed steam inhibits the reaction and therefore suppresses the product yield. The Fischer-Tropsch synthesis is a typical example of this situation. In Fig. 10 the impact of in situ steam removal on reactions with and without steam inhibition is shown. Clearly in situ H_2O removal is an interesting option for a large range of conditions and therefore reactions. The conversion of reactions with a small equilibrium constant, such as the reverse WGS ($K_{eq}(300\text{ }^\circ\text{C}) \approx 2 \cdot 10^{-2}$), can be significantly enhanced by in situ separation, although low steam levels have to be achieved. At the other end of the range, for reactions with a large equilibrium constant, such as Fischer-Tropsch ($K_{eq}(250\text{ }^\circ\text{C}, H_2\text{-CO to } C_6H_{14}) \approx 1 \cdot 10^{20}$), the effect of steam removal is less pronounced, unless steam inhibition (Eq. (3)) plays a role, as is the case for Fischer-Tropsch. Whereas inhibition by steam has a large effect on the conversion for reactions with a large K_{eq} (Fig. 9), the impact of in situ steam removal increases if steam inhibition is more pronounced (Fig. 10).

3.1.2.2. Selectivity and permselectivity. Another aspect of the feasibility of reactive steam separation is the selectivity. Reactive steam permeation (membrane separation) requires high permselectivities and reactive steam adsorption requires high selectivity of the adsorbent material. As depicted in Fig. 11, the (perm)selectivity for steam separation (compared to reactant A) has only a limited influence on the conversion towards the product. For the case of a reaction with a K_{eq} of 10 and 90% steam removal, a selectivity above 30 hardly further improves the conversion and the largest improvement is already made towards a selectivity of 10. For the other cases shown in this figure, this threshold is even lower. This is different concerning the selectivity for steam separation compared to the product P: if product P is unselectively separated as well, this could improve conversion enhancement. However, not only the effect of the (perm)selectivity on the conversion is important. The impact on the process complexity and (economic) viability determines the requirements for the (perm)selectivity. The necessity of extra separation and purification due to economic (recovery of costly reactant/product), environmental and/or legislative (pollution) reasons, would make the process even more complex than reactive separation already can be and could reduce the (economic) viability of the reactive separation process. If for one, or more, of these reasons the reactant loss has to be limited to 5%, a (perm)selectivity higher than 15 is already sufficient for the depicted conditions, as shown in Fig. 12. However, if the loss has to be below 1%, (perm)selectivities of 100 or larger are required.

3.1.2.3. Kinetics and mass transfer limitations. Besides displacement of the reaction equilibrium, the removal of steam may also change the reaction kinetics. This has been discussed in Section 3.1.2.1. When the reaction is faster than the rate of separation, the separation enhanced process is limited by the separation and the enhancement could become minimal. Vice versa, with faster separation than reaction, not only the desired reaction could become separation enhanced. Even a conventionally insignificant side reaction could become the dominant reaction, as is the case for the formation of COS in the Claus process [27].

In addition to matching reaction and separation rates, also the proximity of reaction and separation plays an important role. It was observed that the performance of the reactive steam adsorption system is determined by the chemistry of local conditions in the system [22,30]. This close proximity reduces possible mass transfer limitations between reaction and separation which is the case for both adsorption and vapor permeation, and therefore improves the performance of the reactive separation process. The choice of contactor type/reactor configuration could help in this regard. An adsorption reactor, as well as a catalytic membrane reactor could provide a closer proximity of reaction and separation compared to a packed bed membrane reactor.

3.1.2.4. Capacity and permeance. The fourth aspect of the criteria for in situ steam removal to be considered is the capacity of separation. In the case of reactive adsorption this is the adsorption capacity of the adsorbent material, in the case of reactive membrane separation the membrane permeance determines the capacity of separation. As plotted in Section 2.3, membrane steam permeances range from 10^{-8} to $10^{-6} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$, and adsorbent steam capacities can range from 2 to 20 wt% [16,37]. The resulting capacity of separation should match the amount of steam produced, as was also shown by varying the sorbent volume capacity in a thermodynamic analysis of sorption enhanced methanol synthesis [117]. In order to match the steam production, the separation capacity determines the membrane area or adsorbent weight required. In its turn the required membrane area or adsorbent weight results in the size of the reactive separation system and therefore determines a large part of the capital costs.

3.2. System sizing: membrane area and sorbent weight

The rate of separation and the rate of formation have to be compatible to implement reactive separation. The necessary membrane area can be computed from the production rate, the membrane permeance and the steam pressure difference over the membrane:

$$a_m = \frac{A_m}{V_R} = \frac{R_{H_2O}}{Q_{H_2O} \Delta P_{H_2O}} \quad (4)$$

A maximum of 250 m^2 membrane area per m^3 reactor volume can be incorporated in a standard shell-tube reactor configuration [118]. Furthermore, zeolite-type membranes achieve permeance values of $1 \cdot 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ (cf Section 2.3.1). For a case of Fischer-Tropsch synthesis with in situ steam removal a production rate of $193 \text{ kg } H_2O/(\text{h } \text{m}^3 \text{ reactor volume})$ is assumed. For this rate together with 2.5 bar steam pressure difference over the membrane, almost 50% of the reactor volume would be occupied for in situ steam separation [77].

The current state-of-the-art membranes as discussed in Section 2.3, with a tenfold increased permeance, will drastically decrease the occupied reactor volume. Besides a good indication of the minimum permeance required for application of membranes for in situ steam separation, $1 \cdot 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$, this example also gives a good indication of a minimum steam pressure difference required over the length of the membrane. Rohde et al. [77] state that pressure differences less than 2.5 bar steam are technically not feasible. Depending on the specific conditions, it can be argued that a steam partial pressure of 1 bar is the minimum to be considered for membrane separation utilizing the maximum 250 m^2 membrane area per m^3 reactor in Eq. (4).

Table 3
Parameters and conditions for PFR model.

Operating conditions	Data	Operating conditions	Data
Reactor length	6 m	Superficial gas velocity	0.15 m s^{-1}
Reactor temperature	$250\text{ }^\circ\text{C}$	Kinetic rate constant	10^{-3} s^{-1}
Reactor pressure	50 bar(a)		

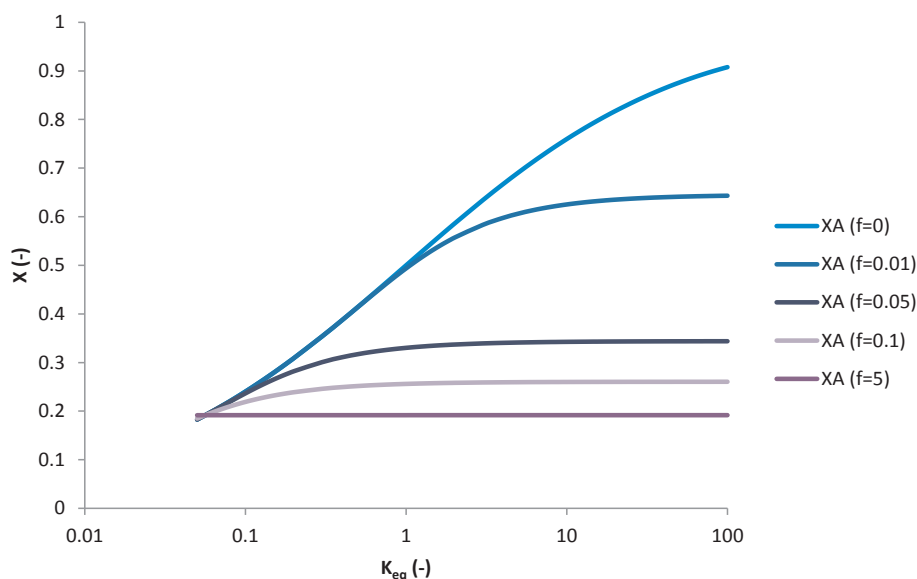


Fig. 9. Conversion X in a PFR reactor as a function of the equilibrium constant K_{eq} for different steam inhibition factors f (conditions listed in Table 3).

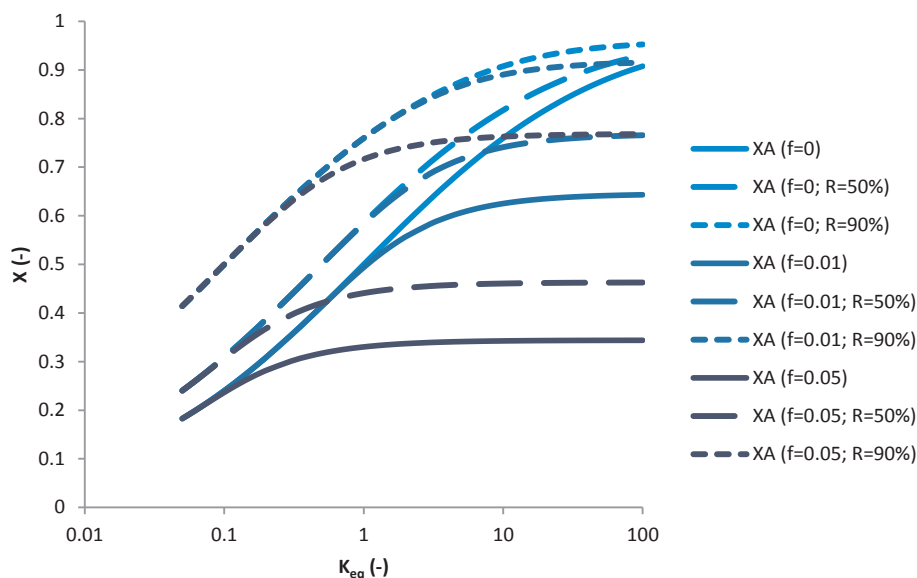


Fig. 10. Impact of 50 and 90% steam removal (instantaneous) on PFR conversion as a function of the equilibrium constant K_{eq} (conditions listed in Table 3).

Similar to the membrane area, the amount of adsorbent material required can be estimated. For this, one needs to know the production rate, the adsorption capacity and the adsorption (cycle) time.

$$\frac{w_{ads}}{V_R} = \frac{R_{H_2O}t}{q_{H_2O}} \tag{5}$$

Where for reactive vapor permeation (not for reactive pervaporation) the pressure difference over the membrane is an extra parameter influencing the system sizing and design, for reactive adsorption this is the adsorption (cycle) time. The cycle time gives an extra degree of freedom to reactive adsorption systems.

As an example, the same case of Fischer-Tropsch synthesis with in situ steam removal is considered, again assuming a 193 kg H_2O /($h\ m^3$ reactor volume) production rate. A typical working capacity for zeolite type adsorbents for gas drying is stated to readily be 10 wt% and a bulk density of 720 kg/m^3 is given [37]. Using short cycle times of 15 minutes already two-thirds of the reactor volume would be filled by adsorbent, leaving the remaining space available for catalyst material. To design a system with longer cycle times, more adsorbent material

and/or higher working capacities are required.

3.3. System: contactor type and regeneration

3.3.1. Regeneration

Another important degree of freedom for reactive steam adsorption is the method of sorbent regeneration, which can be divided into pressure swing, temperature swing, concentration swing, reactive regeneration, displacement regeneration or combinations of these operations [16–18]. Inherently, regeneration is slow compared to adsorption because of the shape of the isotherm [17]. Therefore, the regeneration determines the cycle times, the extent of equipment required, and therefore the efficiency and feasibility of the process. Pressure swing regeneration, possibly vacuum or in combination with a purge gas, is the most commonly used regeneration mode for reactive adsorption [19,20,26,27,29]. This operation is relatively easily implemented and fast in operation, making short cycle times and efficient use of adsorbent feasible [16]. Temperature swing on the other hand, commonly used for molecular sieves, is generally a slower method of

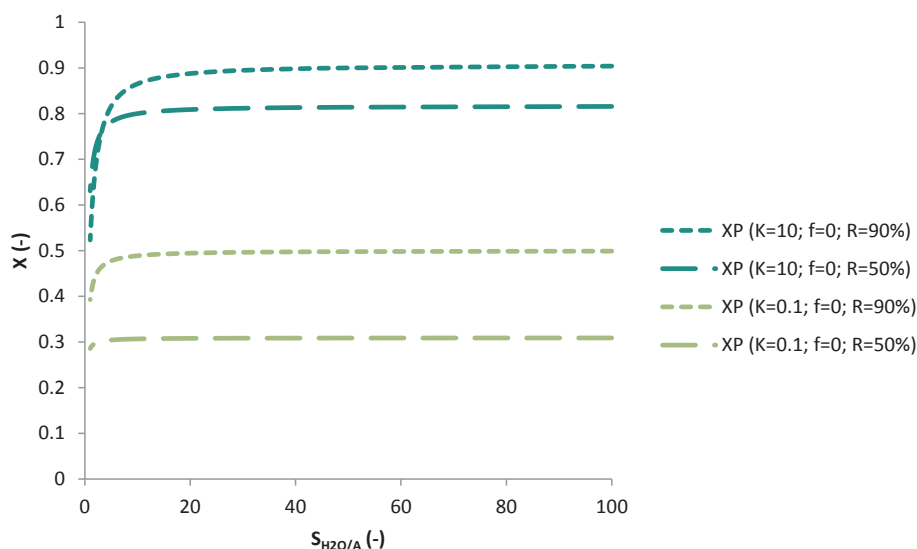


Fig. 11. PFR conversion as a function of (perm)selectivity of steam towards reactant A (conditions listed in Table 3).

regeneration and therefore results in less freedom for the selection of cycle times.

In contrast to reactive steam adsorption, reactive steam permeation has no extra degree of freedom in the choice of regeneration. Basically, membrane technology involves pressure swing regeneration by means of a partial pressure difference across the membrane. Restricting the operational choice to vacuum or sweep gas operation, where the use of a sweep gas can increase the driving force and therefore the separation, although diffusion resistances could arise (as discussed in Section 2.3).

3.3.2. Contactor type and reactor configuration

The contactor type is another variable in the design of a reactive separation process. Although different technologies have been developed for (reactive) separation by membranes and adsorption, analogies can be drawn. Implementation of membrane separation can be done in various contactor types, each with its own pros and cons. Among others, membrane contactors are a packed bed membrane reactor (PBMR), a catalytic membrane reactor (CMR) and a fluidized bed membrane reactor (FBMR).

The PBMR generally consists of a membrane reactor, standard shell-tube configuration, filled with a catalyst bed. This is the easiest

configuration to design and operate, therefore it is the most commonly used configuration in reactive steam permeation literature [66,73–76,78,80,108]. However, possible downsides include mass and heat transfer limitations. A CMR reduces mass transfer limitations between reaction and separation by integrating the catalytic functionality on the membrane. The performance of a catalytic membrane reactor is determined by the catalytic layer thickness, of which the optimum is a function of the reaction kinetics and the membrane permeability [119]. Where on the one hand the close integration could be beneficial, on the other hand membrane fabrication becomes more complex and the system loses degrees of freedom compared to a PBMR. In addition to PBMR, the FBMR integrates membranes in a fluidized bed reactor, which is especially suitable for situations in which mass and/or heat transfer limitations are important. This technology is still in early stages of development and main challenges include particle attrition and membrane deterioration due to the particle fluidization. Applications of FBMR technology for reactive steam separation are lacking in the open literature.

Similar to membrane separation, integration of adsorption is possible with various contactor types. Some possibilities include a packed bed reactor, a (simulated) moving bed reactor and a fluidized bed

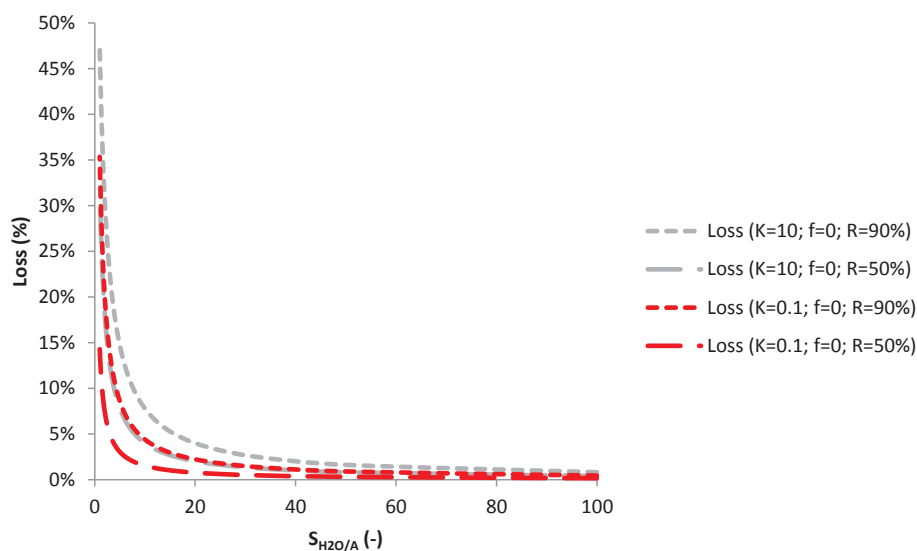


Fig. 12. Loss of reactant A as a function of (perm)selectivity of steam towards reactant A (conditions listed in Table 3).

reactor. The most commonly used configuration for (reactive) adsorption is a packed bed reactor. Inherent to the use of a solid adsorbent, periodic regeneration is required to regain the adsorptive capacity of the system. Typically, multiple fixed-bed reactor configurations are combined in a process cycle, switching between adsorption and regeneration steps, resembling a temperature or pressure swing adsorption system [16]. Examples of packed bed reactors in reactive steam adsorption show process considerations regarding regeneration, including heat management [21,27], separation enhanced kinetics [20] and repressurization [19]. Although the multiple reactor concept works well, the performance of a fixed-bed reactor could be improved by using a moving bed reactor as contactor type. In this reactor configuration the solids are circulated between adsorption and regeneration reactors, thus reducing the total solids inventory. The reactors can be operated continuously in the same mode of operation, removing the transient behavior which is typical for a fixed-bed configuration. Advantageous is also the decoupling of adsorption and regeneration, which therefore could be separately optimized. Parra et al. (2018) discussed the advantages of a moving bed reactor over a fixed-bed reactor for steam separation enhanced reverse WGS [59]. Santos et al. (2015) have demonstrated true moving bed reactor (TMBR) technology for the direct synthesis of DMC [60]. However, they also indicate a major drawback of the technology. Disadvantageous is the moving of solids, which would result in a more complex system with accompanying issues such as particle attrition and mechanical failure (solid transport). For these reasons the moving bed reactor can be simulated by means of a simulated moving bed reactor (SMBR), which retains the advantages of a TMBR without introducing the problems associated with the actual movement of solids [120]. In a conventional SMBR the solids are fixed in a packed bed and instead the feed is switched periodically to a different reactor to simulate the behavior of a moving bed reactor. This is most commonly done in a configuration of multiple packed bed reactors [93,94]. Finally, a fluidized bed reactor (FBR) can be considered as a type of moving bed reactor. The solids are generally well mixed due to fluidization, and by interconnection of two fluidized bed reactors adsorption and regeneration can be done in different reactors. This would assure continuous operation of a reactor and decoupling of adsorption and regeneration. The biggest advantage of fluidized bed reactors are the good specifications with regard to heat transfer, due to the well mixed particles. Whereas the gas phase is generally in plug flow, also good mass transfer is achievable. However, back-mixing of particles could be an issue. Applications of FBR for reactive steam adsorption have not appeared in the open literature, although these systems are studied for CO₂ adsorption [121].

3.4. Adsorption and membrane technology

Following the criteria for in situ steam removal, the first aspect to be discussed is the steam partial pressure difference: what amount of steam has to be removed and what remaining steam level is acceptable? For example, Rohde et al. [77] stated that at least a partial pressure difference of 2.5 bar steam is necessary for membrane technology to be feasible in Fischer-Tropsch synthesis. In addition, even with vacuum on the permeate side, a minimum achievable steam partial pressure in the reactor product arguably seems to be 1 bar. In situ steam removal by adsorption on the other hand does not have this minimum steam partial pressure difference and could be used to remove trace amounts of steam, provided sufficient regeneration is possible. This regeneration, however, results in the driving force for adsorption. Where the driving force for permeation is determined by the partial pressure difference, the driving force for adsorption is determined by the difference between the actual adsorbent loading and the equilibrium loading, defined by an isotherm [16,17]. Therefore the, often nonlinear, shape of the isotherm results in a different behavior compared to membrane separation.

Regarding selectivity, this has only a limited influence on the conversion towards the product. As discussed in Section 3.1.2.2, the

influence on the loss of reactant is probably more significant. For both technologies materials (adsorbents and membranes) are available which can achieve reasonable selectivity towards steam removal, although methanol selectivity is a well-known bottleneck. Unselective separation of the product together with steam could benefit conversion enhancement, for example in methanol synthesis [81,82]. Additional separation of product and steam would determine the viability in this case. Unselective separation of reactant could result in significant losses and/or costly recovery, definitively in the case of reactive steam permeation. For reactive steam adsorption, co-adsorption of reactant could possibly be handled by holding the reactant in the system, keeping it available for reaction. The required selectivity depends on the specific case however. Furthermore, the selectivity could be a trade-off with separation capacity, permeance and kinetics of the system. Examples are the use of large pore zeolites in adsorption [16,37] or reducing membrane thickness to reduce diffusion resistances [95,107], although losing some selectivity.

Some examples [27,30] show that the kinetics of in situ steam removal could also play an important role. In the case of mass transfer limitations between catalytic reaction and steam separation a catalytic membrane reactor could be beneficial compared to a packed bed membrane reactor. Reactive adsorption would be beneficial as well, whereas the catalytic and separation functionalities are closer together (depending on mixing scales).

The separation capacity, or permeance in the case of membrane technology, mainly determines the system sizing (as discussed in Section 3.2). Large amounts of steam produced help the separation via membranes due to a larger pressure difference over the membrane. For steam adsorption the capacity is limited, so the larger the amount of steam to be separated, the more adsorbent material is required. Although some extra degree of freedom is present in the form of cycle times, the required membrane area tends to be advantageous compared to the necessary adsorbent material for large amounts of steam to be separated. For this reason a large part of the literature on reactive steam permeation is dedicated to Fischer-Tropsch synthesis, where large amounts of steam have to be separated [73–78]. Whereas reactive steam adsorption literature mainly focuses on reactions where the remaining steam content is crucial, such as the reverse WGS and DME synthesis [5,19,20,24,28–30,58,59]. All of these reactions have great opportunities in the direct or indirect conversion of CO₂ towards fuels and chemicals in order to reduce CO₂ emissions and to create value [2].

In summary, membrane technology would be preferable for larger steam pressures (> 1 bar), where the remaining steam content is less restricted. Reactive adsorption would be preferable for lower steam pressure processes (< 1 bar) and particularly for steam level reduction as low as trace amounts. Finally, all aspects have to be evaluated case specific and supported by experimental corroboration.

3.5. Future developments in steam separation enhancement

Although reactive steam separation shows great potential for process intensification, and therefore energy efficiency and reduced environmental impact, currently limited industrial applications exist. In this section the main obstacles, bottlenecks and the directions for future developments in steam separation enhancement are elucidated.

3.5.1. Sorbents

Reactive steam adsorption requires a high working capacity of the adsorbent material at elevated temperatures. However, many adsorbents are used at relatively low to moderate temperatures. Although some materials, such as zeolite molecular sieves, still have a working capacity at slightly elevated temperatures (Fig. 3), in general little information about the adsorption of steam under high temperatures is known in the open literature. This makes the working capacity one of the main obstacles to overcome prior to industrial practice. Another bottleneck comprises heat management. The adsorption of steam is an

exothermic process, which is therefore favored at low temperatures. Hence, the requirement of sufficient working capacities at higher temperatures. In addition, many dehydration reactions, such as the methanation reaction, the Claus reaction and (direct) DME synthesis, are exothermic as well. The resulting temperature profiles could affect the adsorption capacity, the kinetics and the concentration profiles in adsorptive reactions. Again, case specific reaction, reactor and process conditions determine the importance of heat management and the best way to overcome possible obstacles. The combination of theory and experiments in a fundamental way is crucial for a proper understanding of steam adsorption enhanced processes and to overcome its bottlenecks. Although theoretical frameworks and model predictions give an overview of the potential of in situ steam adsorption (especially for the reverse WGS, DME synthesis and methanation reactions), often isotherm models are used that have not been validated under the actual reaction conditions and only provide indicative results. Therefore, closer investigation of steam adsorption at elevated reaction temperatures has to be performed. Secondly, although co-adsorption of various reactants may be suspected for regularly used adsorbents, it is rarely studied. Thus, improved understanding of selectivity and co-adsorption at reaction conditions are a second aspect that need to be addressed for the future development of reactive steam adsorption. Thirdly, kinetic and mass transfer behavior is different for sorption enhanced reactions compared to conventional reaction systems. Nevertheless, conventional descriptions are often used for reactive steam separation. Although it could possibly describe the system well, the difference between sorption enhanced and conventional kinetics need to be further investigated. Besides mass transfer, also heat transfer, and heat management in general, is a fourth aspect presently receiving little attention in studies on reactive steam adsorption. Whereas many steam sorption enhanced reactions, as well as steam adsorption itself, are exothermic, proper heat management will be of large significance in the further development of these processes. Furthermore, the regeneration of the reactive steam adsorption system will have a large impact on the overall process and its feasibility. On the one hand, the overall process design would benefit from a quick and energy efficient regeneration procedure, while on the other hand the reaction system could require a slow and energy intensive regeneration procedure. Interfering with all other aspects, regeneration is a fifth and important aspect for the future development of reactive steam adsorption processes. Finally, after all these aspects have been evaluated and answered sufficiently, criteria such as the process economics and the reduction of the overall global warming potential can be addressed.

3.5.2. Membranes

For reactive steam permeation hydrothermal stability is a major bottleneck for industrial application. Typically, amorphous membranes are reported to degrade at higher temperatures (over 250 °C) and are therefore considered unsuitable at these temperatures [77]. Polymer membranes tend to break down at higher temperatures as well [88], to which the ceramic supported polymer membrane is a notable exception with reported hydrothermal stability up to 300 °C. Although zeolite type membranes are tested at higher temperatures, thermal expansion, adsorbate-induced structural changes and the effect of the framework cations influence membrane stability [102]. Enhancing the flux by increasing hydrophilicity of stable membranes, or increasing stability by Si enrichment of less stable membranes are promising developments in further improving zeolite type membranes. In addition to the stability, the seal and the loading of membranes at high temperatures and pressures are an essential aspect for industrial application. However, detailed discussion on this aspect is often missing in the open literature [122]. In general, high pressures are not an issue at low temperatures and vice versa. The combination of high pressure and high temperature becomes increasingly challenging for more severe conditions and therefore could become a bottleneck. Another obstacle to overcome for reactive steam permeation is the permselectivity. In general, the

permselectivities of H₂O towards H₂ and of H₂O towards alcohols, such as methanol are considered most important [62,63,95]. For all types of membranes higher temperatures result in a decreased permselectivity. In addition to this, due to the difficult separation of steam and methanol, often the separation of condensables (vapor) from non-condensable gases is considered and even exploited [67,68,81,82].

Similar to reactive steam adsorption, several authors developing theoretical frameworks for reactive steam permeation rely on experimentally obtained membrane permeance and selectivity, that were not validated at reaction conditions. Other authors have focused on experimental work, specifically looking at membrane performance (permeance/flux) and less on the overall reactive separation system. Firstly, whereas experimental data at higher temperatures is limited, steam permeation at elevated reaction temperatures has to be investigated more closely. Permselectivity data is often limited to hydrogen and steam, up to moderate temperatures. Therefore, membrane selectivity for relevant reaction components (under reaction conditions) is a second aspect for the future development of reactive steam permeation. A third aspect is membrane stability. The hydrothermal stability of the membranes is often unknown or considered critical, making both duration tests under relevant conditions and the development of new stable membranes the third important aspect for future development. Kinetic and mass transfer limitations also play an important role in steam permeation enhanced reactions and therefore they are a fourth aspect requiring closer investigation. Similar to mass transfer, this also holds for heat transfer. Whereas the reactor configuration directly influences mass and heat transfer behavior, the benefits of (novel) reactor configurations, other than packed bed membrane reactors, for reactive steam permeation is a fifth important aspect in the development of these novel processes. Lastly, although the regeneration mode is fixed being a pressure swing over the membrane, the importance of the sweep gas or the choice for a vacuum affects the reactive steam permeation. Again, criteria such as the process economics and the reduction of the overall global warming potential can only be addressed after all other aspects have been evaluated and answered sufficiently.

4. Conclusions

In this review, reactive separation of steam has been discussed. The potential process for intensification and efficiency enhancement through in situ steam separation has been highlighted for both reactive steam adsorption and reactive steam permeation.

Reducing the steam partial pressure by in situ separation results in conversion enhancement due to equilibrium displacement. However, it could affect reaction kinetics, reaction selectivity, catalyst deactivation and therefore catalyst lifetime. All these opportunities (positive and negative) are case specific and have to be addressed as such. Nonetheless, some general aspects have been outlined in this review.

Membrane technology requires larger steam partial pressure differences (> 1 bar) and may be preferred when the remaining steam content is less restricted, when there are no kinetic and mass transfer limitations, and when the (perm)selectivity is high, at least of steam compared to the reactants. Reactive adsorption would be preferable to consider for achieving lower steam partial pressures (< 1 bar), for steam level reductions as low as trace amounts and if transfer limitations between catalytic activity and separation are important.

Before process design and selection criteria, such as the process economics, energy efficiency, and its environmental impact, can be regarded, various aspects of the reactive steam separation process need to be further addressed. Crucial aspects for reactive steam permeation are the hydrothermal stability of the membranes and their permselectivity, whereas high temperature working capacities and heat management are crucial aspects for reactive steam adsorption processes. Crucial to further our understanding of steam separation enhanced processes are studies that combine theory and experiments in a fundamental way. Not only material performance under relevant

conditions has to be investigated, but also different reactor and process configurations. Together, these developments in steam separation enhancement can accelerate further discovery, innovation and rollout of steam separation enhanced reaction processes, thereby offering possibilities to solve one of the biggest bottlenecks for industrial CO₂ utilization: the in situ separation of steam.

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