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Concentration and residence time effects in packed bed membrane reactors

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Abstract

A fixed bed reactor (FBR) and a packed bed membrane reactor (PBMR) were compared with respect to their performance in the oxidative dehydrogenation of ethane over $VO_x/\gamma\text{-}Al_2O_3$ catalyst. The experiments were carried out at high space velocities and under oxygen excess conditions. In the PBMR, the oxidant air was distributed from the shell side of the membrane.

At similar overall feed configurations, the conversion of ethane was found to be higher in the PBMR. This effect was most pronounced at the highest space velocity. Mostly ethylene yield was higher in the PBMR than in the FBR. However, the yield of carbon oxides increased more. Thus, an improvement of olefin selectivity was not observed. There were even sets of experimental conditions, where the ethylene yield in the PBMR fell below the corresponding value for the FBR. In the PBMR under oxygen excess conditions, the consecutive oxidation of ethylene is more favoured than in the FBR.

Two essential reasons for the observed differences in the reactor performances are discussed. At first, there are different local reactant concentrations. Secondly, there are essential differences in the residence time behaviour of the reactants in the FBR and PBMR. In order to exemplify the latter aspect additional experiments have been carried out using a cascade of three identical PBMRs. Varying the specific oxygen flow rates over the individual membrane segment walls different dosing profiles were implemented. The results obtained in this study emphasise the general potential, but also the limits of membrane reactors compared to the FBR.

Keywords: Membrane reactors; Oxidative dehydrogenation

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1. Introduction

Membrane reactors have been studied intensively in the last two decades in order to improve yields in selective oxidation reactions. Because of the fact, that selective and high temperature resistant membranes capable to extract intermediates as olefins and oxygenates are currently not yet available, ceramic membranes are mostly used for a distributed dosing of the oxygen into the reaction zone. Recently, a number of comprehensive reviews about membrane reactors was published, e.g. by Macano and Tsotsis [1], Saracco et al. [2], Sirkar et al. [3], Julbe et al. [4] and Coronas and Santamaría [5]. All these authors reported that the use of membrane reactors in selective oxidation reactions can result in an increase of selectivity of the desired intermediates and a suppression of the deep oxidation. This effect was usually attributed to a lower

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average oxygen partial pressure in the reaction zone by distributed insertion of the oxygen via the membrane. A lot of further experimental and theoretical studies performed in this field were published in [6,7].

Based on theoretical investigations of Lu et al. [8,9] and on the traditional knowledge of reaction engineers (summarised e.g. by Levenspiel [10]) it is well known that a distributed dosing of oxygen (i.e. a lower oxygen partial pressure in the reaction zone) could lead to an enhanced selectivity of an intermediate product provided the reaction orders with respect to oxygen are lower for the desired intermediate formation than for the undesired deep oxidation. Kinetic data published by several authors show that this condition is typically fulfilled in the case of oxidative dehydrogenation (ODH) and partial oxidation reactions of hydrocarbons ([11–14] for the oxidation of C_2 hydrocarbons). The successful use of membranes for distributed oxygen dosing is reported in several experimental studies [15–18]. Tonkovich et al. [15] stressed another important feature of membrane reactors, the possibility to operate them even at explosive hydrocarbon oxygen ratios.

In [16–18] there is reported, that membrane reactors show their best performance, in case where the ratio between shell and tube side flow rates was high, whereas Ramoz et al. [19] gave opposite results. Tonkovich et al. [15] pointed out, that in membrane reactors not only the concentration profiles of the reactants are different from profiles in classical fixed bed reactors (FBRs), but there additionally exist differences in residence time behaviour. These authors also mentioned that by dosing the oxidant via a membrane the contact time of hydrocarbon molecules with the catalyst increases and the contact time of the oxygen molecules decreases. Longer hydrocarbon contact times result in higher conversion rates. The lower contact times of oxygen in connection with its reduced average concentration yield to a higher intermediate selectivity. The authors also reported, that in case of ODH of ethane the ethylene yield could be increased by a factor of up to 4 compared to the results achieved in an FBR.

A systematic analysis of the effects of the interaction between changed concentration and residence profiles in membrane reactors is currently still missing. There is still a lack of reliable experimental data concerning the internal flow profiles. In our opinion this is the key aspect, which influences essentially local oxygen–hydrocarbon ratio and contact times and thus the conversion and the product distribution.

The objective of this study is twofold. Firstly, the available data basis should be enlarged by studying a packed bed membrane reactor (PBMR) under oxygen excess conditions in a large range of temperatures and space velocities in comparison with a conventional FBR. The ODH of ethane over a $VO_x/\gamma\text{-}Al_2O_3$ catalyst was chosen as model reaction. Moderate, but well quantifiable olefin yields were reported for this reaction performed in the FBR [20,21]. The reaction products can be quantified accurately and fast by GC analysis. Secondly, to study the residence time behaviour of the reactants in the PBMR we implemented a stage-wise membrane reactor arrangement consisting of three consecutive segments (3-PBMRC). By operating this cascade of membrane reactors with various distributions of dosed oxidant flow rates between the individual reactor stages the overall residence time behaviour was altered systematically.

2. Experimental

2.1. Catalyst preparation and membrane structure

The $VO_x/\gamma\text{-}Al_2O_3$ catalyst used in this study in all reactors was prepared by soaking impregnation of $\gamma\text{-}Al_2O_3$ with a solution of vanadyl acetylcetonate in acetone followed by a calcination step. 1.78 g of $VO(acac)_2$ (Merck) were solved in acetone, then 18.22 g of dried alumina (balls with a diameter of 1.8 mm, BET surface 200 m^2/g, Condea Chemie, Germany) were added. The suspension was heated up slowly to boiling temperature in a water bath under continuously stirring and refluxing of the solvent. After 2 h, the refluxing condenser was replaced by a Liebig condenser to remove the acetone. The impregnated alumina balls were dried at 130 °C overnight, than sieved to remove excessive vanadyl acetylacetonate crystals and at last calcinated in a muffle kiln at 700 °C for 4 h. The vanadium content of the catalyst was 1.4% V, measured by AAS analysis (Varian SpectrAA 250 plus) after microwave extraction in HNO_3. The surface of the calcinated catalyst was 167 m^2/g, measured by single point BET method with nitrogen as adsorbate (Ströhlein Instruments Areameter II).

The colour of the fresh catalyst was yellow, indicating vanadium was mainly in the +5 oxidation state. After the measurements, the catalyst colour had changed to a light blue-green. This can be attributed to a significant reduction of V(V) to V(IV), the species responsible for a high ODH selectivity [22].

The tubular ceramic composite membranes used for feeding air as the oxidant were provided by Hermsdorfer Institut für Technische Keramik (hitk/inocermic, Hermsdorf, Germany). They consisted of a mechanically stable α-Al_2O_3 support (average pore diameter: 3 μm) on which were deposited three more α-Al_2O_3 layers (pore diameters: 1, 0.2 μm, 60 nm; thickness of all: 25 μm) and finally one γ-Al_2O_3 layer (pore diameter: 6 nm; thickness: 2 μm). The whole membrane tube had a length of 300 mm, an inner diameter of 7 mm and a wall thickness of 1.5 mm. Both ends of the membrane were vitrified, leaving in the centre of the membrane a permeable zone of 60 mm. The mass transport properties of this membrane type were characterised by the authors in a previous study [23]. During assembling of the membrane reactor, the membrane tube was filled with inert material in the non-permeable zones and with the above described VO_x/γ-Al_2O_3 catalyst in the porous reaction zone.

2.2. Experimental setup

The setup used consisted of several units: three reactor modules, a catalytic afterburner and a GC-MSD (Agilent 6890 GC with 5973 MSD) with a 8 port multiposition valve (SIM, Germany) for reactant and product stream analysis. The reactor modules could be operated alternatively and will be described below. The catalytic afterburner had to prevent hazardous emissions to the laboratory air. A SIMATIC S7 (Siemens, Germany)-based process control system was implemented to run the unit automatically and store all process data.

Feed mixtures and flow configurations were realised by using electronic mass flow controllers (Bronkhorst HITEC FC 201 series). Gas samples were taken from different positions of the reactors as described below by switching the multiposition valve. They transferred via a heated line to the sample valve of the GC-MSD to prevent condensation. The GC was operated alternately with HP PLOT Q and GS CarbonPLOT capillary columns (Agilent), both allowing the separation of air, carbon dioxide, ethylene, ethane, water and acetaldehyde. Nitrogen and oxygen were analysed by the GC-MSD software, integrating the 14 and 32 ion masses from air peak separately. Carbon monoxide could not be quantified directly with the one-column GC-MSD used, since its GC peak could not be fully separated from the air peak and the signal intensity of the only specific 12 ion mass was too poor for an accurate quantification. For this reason, the deficit in the carbon balance was taken as the measure of CO production (as done e.g. also by Mills et al. [24]). This was possible because only non-quantifiable traces of acetaldehyde (in the range of 30 ppmv) and no other by-products (as acetic acid or higher hydrocarbons) were found. Carbon balance was checked by measuring CO_2 at the outlet of the catalytic afterburner, which correlates well to the amount of ethane inserted.

2.3. The reactors

2.3.1. Fixed bed reactor

The FBR applied was made from stainless steel and had an inner diameter of 15 mm. The catalyst zone had a length of 30 mm and was filled with 3.1 g (5.3 cm^3) of the prepared catalyst which was fixed by metal wires. All reactants were inserted together at the reactor inlet (Fig. 1a). The reactor could be heated electrically up to 700 °C.

In the middle of the catalyst bed, a thermocouple was installed in contact with the catalyst particles to measure the reaction temperature. Gas samples were taken via three sample capillaries (a) at the reactor inlet, (b) at the catalyst bed inlet to check for wall and gas phase reactions and (c) directly after the catalyst bed. Comparing the chromatograms from the reactor inlet and from the catalyst bed outlet conversion, selectivity and yield data were calculated in the conventional manner.

2.3.2. Packed bed membrane reactor

The PBMR consists of a steel tube ($d = 16$ mm) in which the membrane tube filled with the catalyst was inserted. The reactor was heated by an electric heating sleeve outside the steel tube. Hydrocarbon, for safety reasons diluted 1:15 in nitrogen, was fed on the tube side of the membrane. Air was dosed from the shell side over the membrane into the reactor (Fig. 1b).

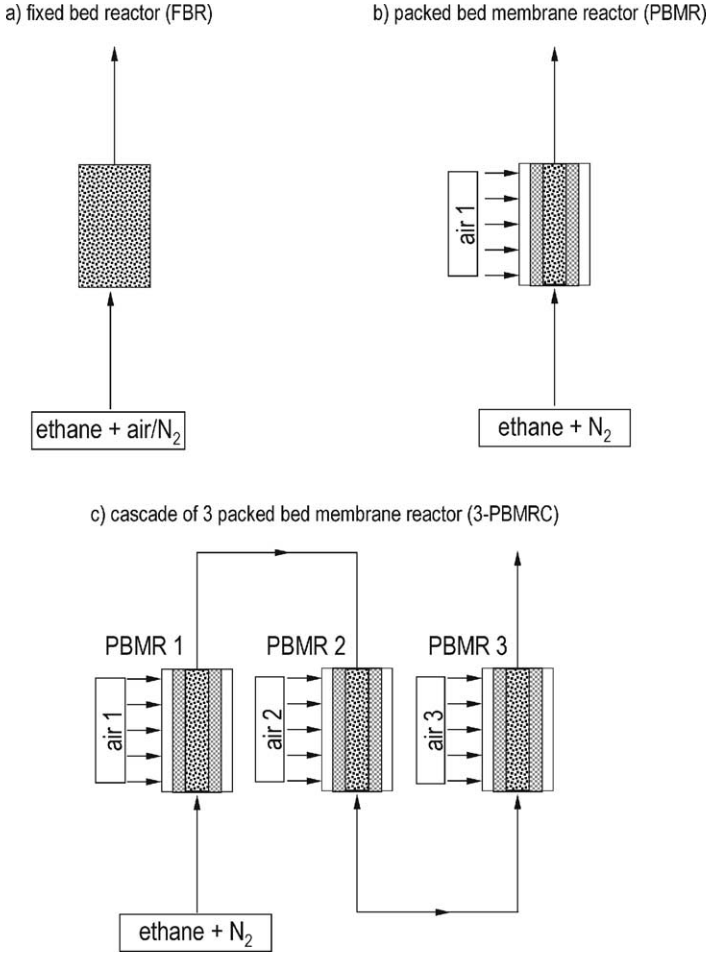

Fig. 1. Flow configurations for the different reactors used in this study (see Table 1).

The shell side outlet was closed so that all air dosed was pressed via the membrane into the catalyst bed. This configuration is similar to that reported mostly in the recent literature, e.g. as by Tonkovich et al. [15], Mallada et al. [17] and Ramoz et al. [19]. However, it differs from that studies, where the shell side outlet was open, so that oxidant transfer over the membrane is influenced by diffusion [25,26]. Pressing all air over the membrane has the advantage of an easy control of the amount of air inserted. In this way the membrane was used as a non-permselective oxidant distributor in a dead end configuration. This concept allows further to suppress the permeation of the hydrocarbon to the shell side effectively.

During assembling of the reactor the membrane tube was filled with inert material in the vitrified zones and with the $VO_x/\gamma\text{-}Al_2O_3$ catalyst (1.25 g, 2.3 cm^3) in the permeable section ($l = 60$ mm). As in the FBR, one thermocouple was placed in the centre of the catalyst bed and gas samples were taken at the tube side inlet and directly after the end of the catalyst bed.

The membrane tube was fixed in air cooled head segments. These head segments had a distance of 80 mm from the hot reaction zone. Both membrane sides were sealed gas-proof by viton O-ring seals. Because of the material of the seals the head segment temperature was limited to 150 °C. It was possible to operate the reactor at catalyst temperatures up to 650 °C without any damage of the seals or the membrane itself.

2.3.3. Cascade of 3-packed bed membrane reactors (3-PBMRC)

The membrane reactor cascade applied for studying the residence time behaviour of the PBMR consists of a serious connection of three identical membrane reactors, as described in the previous section. The catalyst masses inserted in every PBMR were 1.25 g. The tube side outlet of each reactor was connected with the tube side inlet of the following reactor. The hydrocarbon (again diluted 1:15 in nitrogen) was inserted on the tube side inlet of the first reactor. Air was introduced from the shell sides of all reactors. To realise different air dosing profiles, the distribution of the air flows between the reactors was changed systematically (Fig. 1c). Further each reactor could be heated separately by an electrical heating sleeve. However, for the experiments reported below the temperature was kept equal in all the reactors. Gas sampling was possible at the tube side inlet of the first reactor and at each tube side outlet.

2.4. Measuring conditions

In all reference studies of membrane reactors summarised in Table 1 oxygen was inserted in amounts near the ODH stoichiometric ratio (hydrocarbon:oxygen = 2:1) or in only small excess. The flow rates were relatively low. Typical contact times were normally in the range of 1 s and longer. For industrial applications such feed configurations are only of minor interest. In our investigations (Table 2), much higher space velocities were applied, closer to the requirements set by the industry.

Additionally, in our study overall oxygen hydrocarbon ratios were below the lower explosion limit, what favours safety of operation. This is in contrast to the literature cited in Table 1, where an operation with much higher hydrocarbon–oxygen ratios is preferred. The latter has the advantage of a higher olefin selectivity but it can cause explosions if the membrane is damaged. For this reason we decided to use lean hydrocarbon–oxygen mixtures, for which there is still no quantitative comparison between FBR and PBMR available.

Table 1
Summary of selected membrane reactor studies

Authors	Reaction, catalyst and temperature range	Reactor configuration	Overall hydrocarbon–oxygen ratio	Shell/tube side ratio of flow rates	weight of catalyst (g)/overall total flow (l/h)	Ref.
Tonkovich et al.	ODH of ethane on $LiSmO_x/MgO$ at 590–630 °C	PBMR	1:4–2.5:1	20:1–2:1	1.7/9.2[a]	[15]
Alfonso et al.	ODH of propane on $VO_x/\gamma\text{-}Al_2O_3$ at 550 and 600 °C	CMR	1:1.5–2:1	1:11.5–24:1	–/3.0	[16]
Mallada et al.	Oxidation of butane to maleic anhydride on VPO_x at 375–450 °C	PBMR	1:2	9:1–3:2	2.5–3/6.0–12.0 (1500–3000 h^{-1})	[17]
Xue and Ross	Oxidation of butane to maleic anhydride on VPO_x at 350–450 °C	PBMR	4:3	9:11	2/6.0[a]	[18]
Ramoz et al.	ODH of propane on $VO_x/\gamma\text{-}Al_2O_3$ or VO_x/MgO at 450–600 °C	PBMR	2:1–1:5	1:11.5, 24:1	3.1/12[a]	[19]

[a] Catalyst volume, density or GHSV values were not reported. Usually densities of layers of supported transition metal oxide catalyst particles are in the range of 0.6–0.8 g/cm^3.

Table 2
Conditions of the measurements performed

Measurement no.	GHSV (h^{-1})	Total overall flow rate (l/h)	Overall inlet concentrations (%)[a]		Tube side flow rates (l/h)[b]			Shell side flow rates (l/h)[b]		
			Ethane	Oxygen	Ethane	Air	Nitrogen	Air 1	Air 2	Air 3
FBR, 3.1 g/5.3 cm^3 catalyst										
A1[c]	6000	30	0.7	20.3	0.20	28.8	–	–	–	–
A2[c]	19000	100	0.7	20.3	0.68	99.3	–	–	–	–
A3[c]	38000	200	0.7	20.3	1.36	198.6	–	–	–	–
A4[d]	6000	30	0.7	0–20.3	0.20	Varying	Balance	–	–	–
A5[d]	19000	100	0.7	0.20.3	0.68	Varying	Balance	–	–	–
A6[d]	38000	200	0.7	0–20.3	1.36	Varying	Balance	–	–	–
PBMR, 1.25 g/2.3 cm^3 catalyst										
B1[c]	6000	15	0.7	18.4	0.10	–	1.90	13	–	–
B2[c]	19000	45	0.7	18.2	0.31	–	4.69	40	–	–
B3[c]	38000	89	0.7	17.7	0.62	–	8.38	80	–	–
Cascade of 3 packed bed membrane reactors (3-PBMRC), 3 × 1.25 g/2.3 cm^3 catalyst										
C1[e] (5/25/70)	18000	125.6	0.7	18.2	0.88	–	13.12	5.6	28.1	77.9
C2[e] (33/33/33)	18000	125.3	0.7	18.2	0.88	–	13.12	37.1	37.1	37.1
C3[e] (70/25/5)	18000	126.4	0.7	18.2	0.88	–	13.12	78.7	28.1	5.6

[a] Percentages of ethane and oxygen concentrations from the membrane reactor and the membrane reactor cascade refer to the overall feed, as all gases were premixed at the reactor entrance.

[b] A legend for flow configuration is given in Fig. 1.

[c] Catalyst temperature was increased from 400 to 650 °C in steps of 25–30 K.

[d] Catalyst temperature was kept constant at 590 °C.

[e] Catalyst temperature was increased from 400 to 650 °C in steps of 40–50 K.

Before the measurements were started the catalyst was equilibrated in mixtures of 0.7% ethane in air by heating it up from room temperature to 650 °C for several times until conversion and yields gave stable and reproducible values. The reproducibility was checked by conducting product stream analysis more than three times on every set of experimental parameters and additionally by twice or thrice repeating every complete run to examine changes of the catalyst itself. The plots given below contain only data from runs where both the reactor and the catalyst were in steady state and represent the average of the collected data.

The basic reference used to compare the performance of the reactors is the gas hourly space velocity. Thus, the absolute overall flow rates of the PBMR and of the 3-PBMRC were related to the flow rates of the FBR by considering the ratio of the different catalyst bed volumes. The three series of measurements performed are described below.

2.4.1. *FBR (measurements A1–A6)*

The objective of measurements A1–A3 was to evaluate the activity of the $VO_x/\gamma\text{-}Al_2O_3$ catalyst in the FBR. Subsequently measurements A4–A6 were performed to study the influence of oxygen supply on conversion and product distribution. Three GHSV levels were used in this study: 6000, 19 000 and 38 000 h^{-1}. Under these conditions, the pressure drop over the catalyst bed was always less than 0.3 bar.

During the measurements A1–A3, the overall feed composition was kept constant at 0.7% ethane in air (20.5% oxygen). At the beginning of these experiments, the catalyst was equilibrated with the reaction mixture at 400 °C for 1 h. The catalyst temperature was increased in steps of 25 K until a final temperature of 650 °C was reached.

During the measurements A4–A6, the catalyst temperature was kept constant at 590 °C and the amount of oxygen supply was changed. Here the preheating of the catalyst under the reaction mixture (0.7% ethane in air) was done at 590 °C. During each run, the air was replaced step by step by nitrogen. Thus, the oxygen supply was decreased, whereas the total flow remained constant.

2.4.2. *PBMR (measurements B1–B3)*

The general procedure in the PBMR experiments was the same as described for the FBR above. Again the ethane feed concentration was kept constant at 0.7%, and the space velocity levels were 6000, 19 000 and 38 000 h^{-1}.

The ethane–nitrogen mixtures (∼1:15) were fed on the tube side, the much larger amounts of air were dosed from the shell side of the membrane into the reactor. The resulting shell to tube side ratio of flow rates was approximately 9:1. At this feed configuration, the pressure differences between tube side inlet and reactor outlet were $<0.1/<0.1/0.25$ bar and between shell side of the PBMR and reactor outlet (tube side outlet) 0.15/0.5/0.9 bar for 6000, 19 000 and 38 000 h^{-1} (600 °C), respectively. The overall oxygen concentration was with 19% a little bit lower than in the FBR. This was due to the small nitrogen flux introduced on the tube side for safety reasons. Thus, also in the PBMR runs there was a large excess of oxygen.

2.4.3. *3-PBMRC (measurements C1–C3)*

The goal of the final 3-PBMRC measurements was to study effects of concentration and residence time profiles. The experiments further served to detect the probable shape of the air dosing profile along the catalyst bed axis established in the PBMR. During the experiments, the overall concentrations of ethane and oxygen were kept constant at 0.7 and 18.2%, but the distribution of the inserted air between the different reactors was changed. We performed three measurements: (a) with an increasing profile (measurement C1, distribution of air amounts between the first, second and third segment $= 5/25/70$), (b) with equal distribution (measurement C2, 33/33/33) and (c) with a decreasing profile (measurement C3, 70/25/5). The total flow in the 3-PBMRC was nearly three times higher than in the single PBMR, restricted by a much larger pressure drop. A GHSV of 18 000 h^{-1} was the maximum reachable value.

The general procedure was in principal the same as for the measurements A1–A3 and B1–B3. There were three small changes. Firstly, GC samples were taken at the tube side inlet of the first reactor and at the tube side outlets of all reactor segments to create a balance over the individual reactor stages and over the entire cascade. Secondly, the temperature was increased in larger steps (∼50 K, simultaneously in all reactors), because of the increased number of sampling sides. Finally, the three times higher flow rates (to keep overall space velocity constant) caused an increased heat transfer from the reaction zone to the seals. That is why the restriction to the catalyst temperature was stronger than for the single PBMR. For this reason not in all cases measurements at temperatures of 600–650 °C could be performed.

3. Results

3.1. Comparison between the FBR and the PBMR

Fig. 2 gives an overview of the obtained ethane conversion and the yield and selectivity data of all products for the FBR (measurements A1–A3) and for the PBMR (measurements B1–B3). As can be seen in Fig. 2a, the PBMR gives higher conversions than the FBR in general. It can be further observed that the difference between the reactors increases with increasing space velocity. In case of 6000 h^{-1}, the conversion rate ratio between the PBMR and the FBR is 1.1–1.5, at 19 000 h^{-1} it is enhanced to a level of near 2 and at 38 000 h^{-1} the conversion rate in the PBMR is almost three times higher. The conversion increases in both reactors continuously with increasing temperature.

The ethylene yield (Fig. 2b) shows the typical parabolic curves with a pronounced maximum, related to a certain temperature. With increasing GHSV the parabola becomes broader. The position of the yield maximum shifts to higher temperatures and lower amounts of ethylene formed. This behaviour is typical for both reactors. In case of measurement A3 (38 000 h^{-1}), the maximum was not reached in the investigated temperature range. Comparing the FBR and the PBMR, at 6000 h^{-1} the difference of the ethylene yields is rather small. The plot for the PBMR is shifted 50 K downwards related to corresponding curve for the FBR. Consequently, at temperatures below 550 °C the ethylene yield in the PBMR is higher than in the FBR, whereas at temperatures above 600 °C the opposite holds true. At 19 000 and 38 000 h^{-1}, the ethylene yield is twice as high in the PBMR as in the FBR. However, it is worthy to mention that this increase is smaller than the increase of conversion. Thus, the corresponding ethylene selectivity values (Fig. 2e) are generally lower in the PBMR than in the FBR and decrease continuously with increasing temperature. The ratio between both reactors decreases with increasing GHSV (1:1.5 at 6000 h^{-1}, 1:2 at 19 000 and 38 000 h^{-1}). The advantage of higher ethylene yields discussed above is coupled with the disadvantage of higher losses of ethane to carbon oxides.

In case of carbon monoxide, we can observe a similar behaviour as reported for the ethylene formation. Again parabolic curves with maximums and the same trends related to temperature and GHSV were found. Comparing the reactors, the yield ratio of CO between PBMR and FBR increases very fast with increasing GHSV. At 6000 h^{-1}, the plot for the PBMR is shifted 50 K downwards related to the FBR as in case of ethylene. At 19 000 h^{-1}, the ratio of PBMR to FBR is 2:1 and at 38 000 h^{-1} the ratio is 6:1 (Fig. 2c). This increase is much larger than the increase of conversion rate ratio. Consequently, the CO selectivity ratio increases with increasing GHSV, too (1:1–1.5 at 6000 and 19 000 h^{-1}, 1:3 at 38 000 h^{-1} — see Fig. 2f).

The carbon dioxide formation as the final reaction in the network shows the opposite trends. It enhances in both reactors with increasing temperature, especially at temperatures higher than 550–600 °C, but it is suppressed by increasing GHSV. The CO_2 yield ratio between the reactors decreases with increasing GHSV, too. At 6000 h^{-1}, the ratio of PBMR to FBR is 2:1, at 19 000 h^{-1} 1.5:1 and at 38 000 h^{-1} both reactors give almost identical yields. The selectivity ratio between PBMR and FBR is larger than 1 at 6000 h^{-1} (1.3:1). At 19 000 h^{-1}, it shifts from smaller than 1 at lower and larger than 1 at high temperatures (the plots meet at 550 °C). At 38 000 h^{-1}, CO_2 selectivity in the PBMR is only half of that in the FBR.

Summarising the above we have to note, that conversion in general and intermediate yields mostly were increased in the PBMR. But there were also sets of flow parameters and temperatures found, where ethylene yield was lower in the PBMR than in the FBR. Related to ethylene, no selectivity advantage could be determined for the PBMR under the conditions studied. This observation is in contrast to the data from the cited publications [15–19]. Below it is attempted to explain the reasons for the differences.

3.2. Concentration versus contact time effects—the dependence of conversion and product distribution on oxygen supply and GHSV

In the recent literature, usually the potential of membrane reactors to perform selective oxidation is

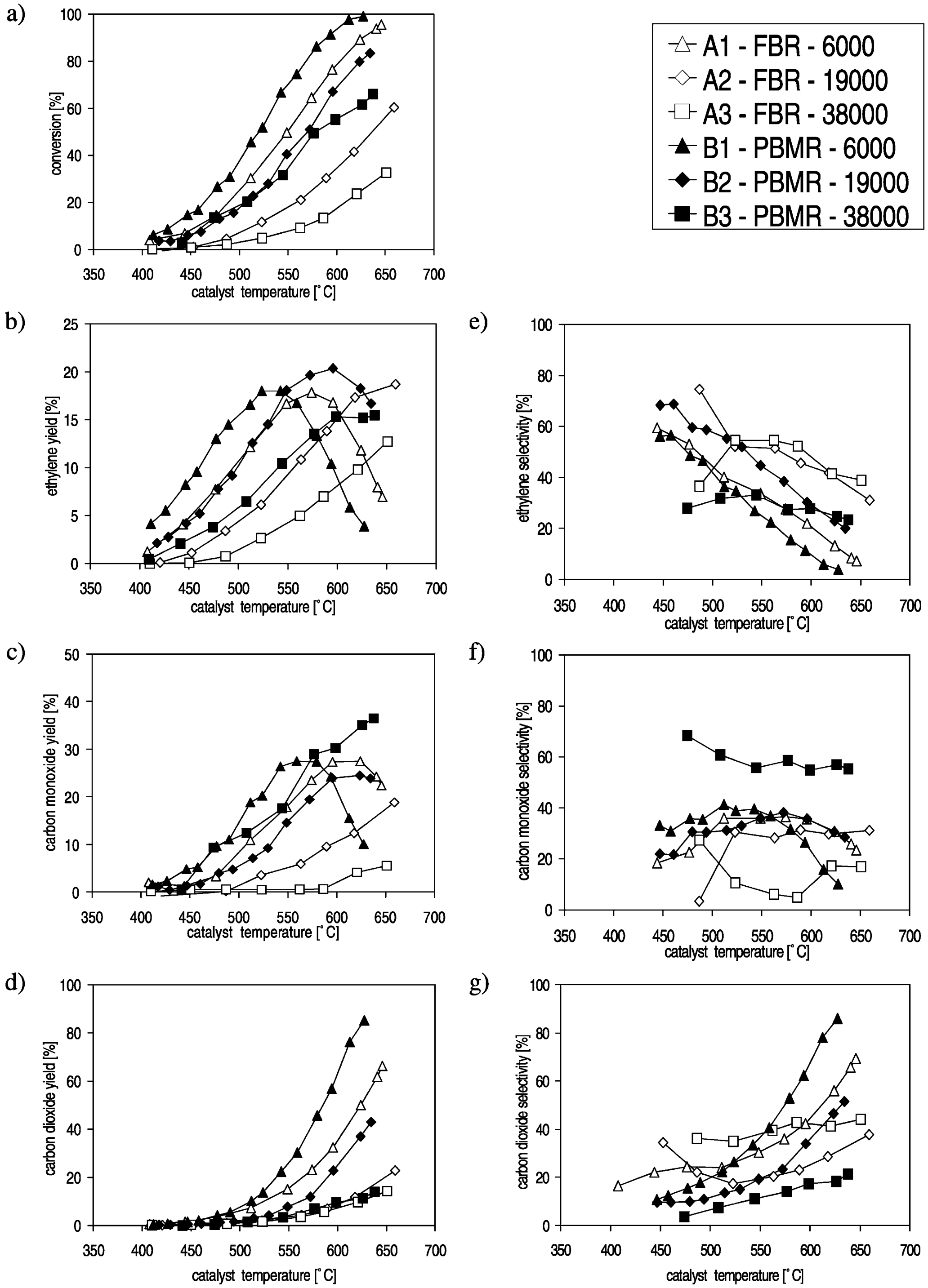

Fig. 2. Ethane conversion (a), product yields (b–d) and selectivities (e–g) in FBR and the PBMR as a function of catalyst temperature for GHSV levels of 6000, 19 000 and 38 000 h^{-1}. Key to legend (Table 2): measurement number; reactor; GHSV.

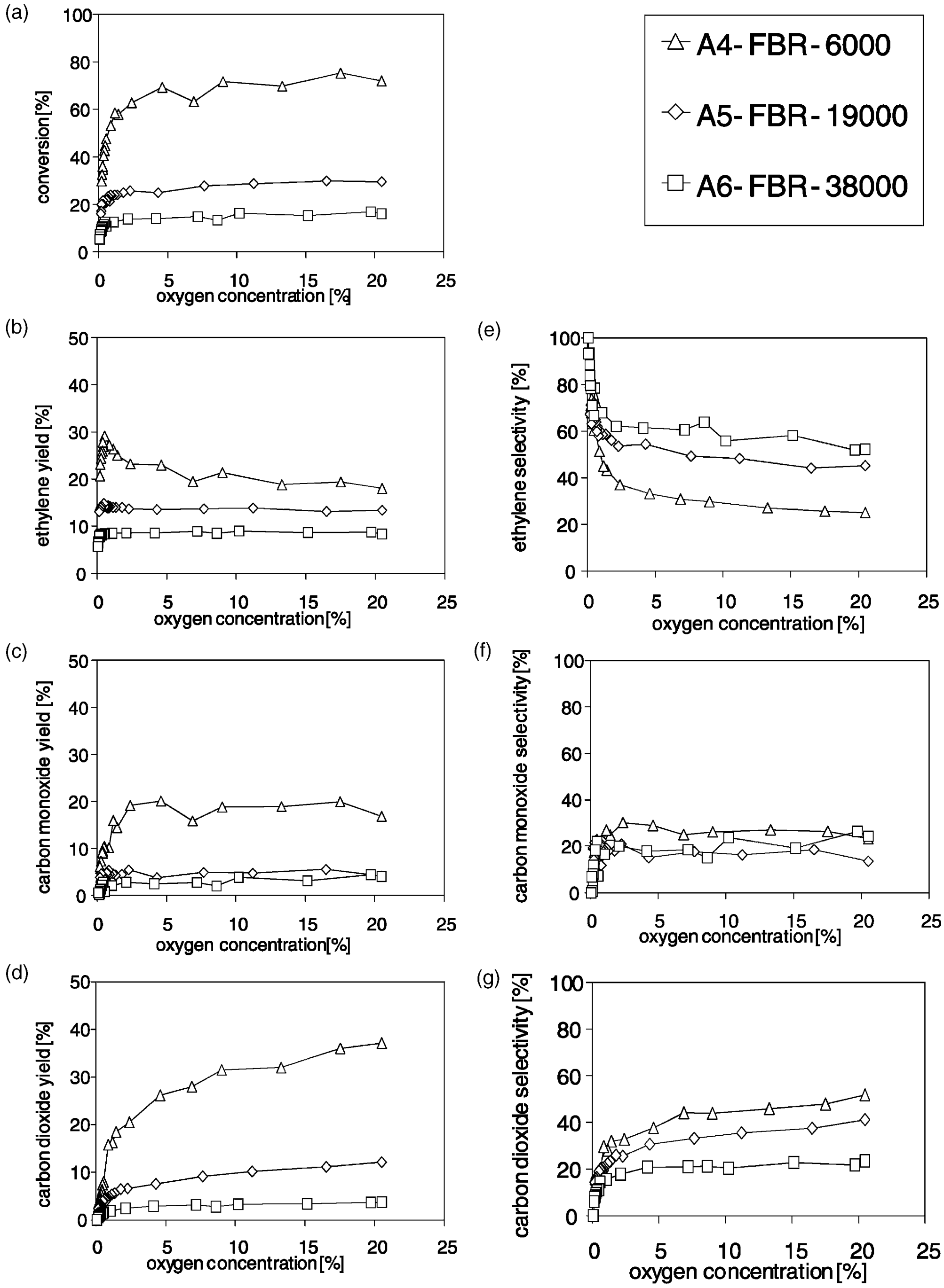

Fig. 3. Dependence of ethane conversion (a), product yields (b–d) and selectivities (e–g) on oxygen feed concentration at GHSV levels of 6000, 19 000 and 38 000 h^{-1} measured in the FBR. Key to legend (Table 2): measurement number; reactor; GHSV.

discussed in terms of an increase of intermediate selectivity by lowering the oxygen partial pressure. For this reason, we firstly studied the influence of the oxygen feed concentration on conversion and product distribution. These measurements were performed at all GHSV levels to include also the aspect of contact time. The experiments were done in the FBR (measurements A4–A6). Their results are given in Fig. 3.

At near zero oxygen level (above 0.1% O_2 remained in the technical grade nitrogen used), conversion rates of 30% ($6000\,h^{-1}$), 16% ($19\,000\,h^{-1}$) and 5% ($38\,000\,h^{-1}$) were measured. The reaction goes at all GHSV levels near completely to ethylene. Only traces of both carbon oxides and no evidence for soot formation were found. A small increase in oxygen supply up to 0.5% results in a very rapid increase of ethane conversion and carbon oxide formation. The ethylene selectivity decreases in the same rapid way, whereas selectivities of both carbon oxides increase continuously. Ethylene yield is enhanced, too, but much weaker. It reach its maximum value for 0.5% oxygen what is near to the ODH stoichiometric point at 0.35%.

With further increasing the oxygen supply to reach the excess region up to full air atmosphere, changes in conversion and product distribution become weaker. At all GHSV selectivity of ethylene decreases further, CO selectivity remains near constant and CO_2 selectivity increases with increasing oxygen supply. In the oxygen excess region the product distribution is more and more determined by the GHSV.

At $6000\,h^{-1}$, ethylene yield decreases over the whole oxygen concentration range between 1 and 20.5%, whereas the amount of formed CO is rather high and CO_2 yield shows a continuous increase. This indicates that significant amount of the desired ethylene is over-oxidised by the oxygen excess in consecutive reactions. This explanation is supported further by experiments concerning oxidation of ethylene under identical feed configurations, where a selectivity of 60–80% to CO was observed, but these results will not be presented here in detail. The consecutive oxidation of ethylene seems to be the main source for CO. Thus, the amount of formed CO is a good indicator to estimate the amount of ethylene losses by over-oxidation, which is favoured especially by long contact times.

At 19 000 and $38\,000\,h^{-1}$ ethylene yield remains nearly constant, the CO yield is diminished to 5% and the CO_2 formation is suppressed, too. Here the consecutive ethylene oxidation plays obviously only a minor role. A resulting reaction order of ethylene formation with respect to oxygen close to zero is consistent with the literature ([11], 0.12; [12], 0.16; [13], 0.1; [14], 0.04). We have to conclude that in the oxygen excess region the influence of contact time changes on the performance of our membrane reactor is much larger than the contribution of oxygen supply.

Thus, in a membrane reactor the concentration effect will be only significant if the oxygen supply is close to the selective oxidation stoichiometric ratio. In case of the oxygen excess situation concentration effects lose their importance, especially at high GHSV. Consequently, the aspect of oxygen supply alone does not give a satisfying explanation for the above-discussed conversion and selectivity behaviour of the PBMR. Especially, the high CO formation in the PBMR indicates that consecutive over-oxidation of ethylene plays a more important role than in the FBR. Because CO formation is a sensitive indicator for long contact times, as shown above, we have to conclude that the residence times of the reaction mixture in the catalyst bed, including a significant part of inserted oxygen, is prolonged in the PBMR than in the FBR. Thus, a second aspect needs a more detailed investigation in order to understand the effects occurring in membrane reactors. This is the residence time behaviour of the components in the PBMR. A systematic analysis of the effects of the interaction between changed concentration and residence profiles seems to be absolutely necessary.

3.3. Contact time profiles in membrane reactors — experiments with the 3-PBMRC

A first hypothesis concerning the possible residence time profiles could give an analysis of the pressure drops in the single stage PBMR studied (Fig. 4). The hydrocarbon molecules are introduced at the tube side inlet and pass subsequently the whole catalyst bed. All air inserted has to overcome the pressure drop of the membrane barrier. Inside the tube flow rate is continuously increasing along the catalyst bed axis by the amount of air, which had just passed the membrane. Thus, the local pressure drop is also increasing along the catalyst bed.

Since the pressure at the shell side is constant, the pressure gradient over the membrane forming the

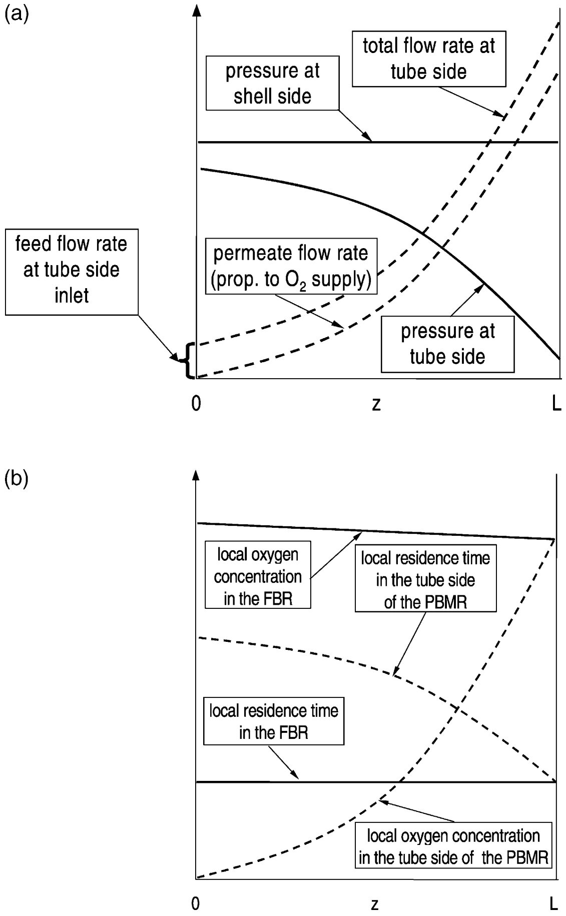

Fig. 4. (a) Schematic representation of assumed pressures and flow rates in the single stage PBMR over reactor length, (b) assumed oxygen concentration and residence time profiles in the FBR and in the tube side of the PBMR.

driving force for the air transport through the membrane increases along the reactor axis. Consequently, the amount of air dosed also increases along the membrane tube, an increased air dosing profile establishes. Typically, this causes a rather long zone with low oxygen concentrations and low gas velocities on the beginning of the catalyst bed, where high conversions with a high intermediate selectivity should be expected. Most of the air reaches the reaction zone only at the end of the catalyst bed. Consequently, here both oxygen concentration and gas velocity increase rapidly. Therefore, in the short oxygen-rich zone at the end of the catalyst bed, only a limited ethane conversion occurs and deep oxidation should be also suppressed. But under equal overall GHSV, the gas velocity in the tube side of the PBMR reaches that from the FBR first at the exit of the catalyst zone for $z = L$ (Fig. 4b). For this reason, conterminous to longer contact times along the overall catalyst bed in the PBMR, it seems possible, that in case of oxygen excess the amount of the over-oxidation in the membrane reactor can be even larger than in the FBR.

For verifying the above hypothesis, we studied ethane oxidation in a cascade of three identical membrane reactors (3-PBMRC) with the option of realising a distributed air insertion over the membranes of the single reactor stages. Experiments with an increasing (C1, 5/25/70), an uniform (C2, 33/33/33) and a decreasing (C3, 70/25/5) air dosing profile were performed. The results obtained under identical overall flow conditions (0.7% ethane, 18.2% O_2, GHSV $=$ $18\,000\,h^{-1}$) are summarised in Figs. 5 and 6.

Fig. 5 presents a comparison between the FBR, the PBMR and the 3-PBMRC with all tested air dosing profiles. Concerning the conversion and product yields the PBMR and the 3-PBMRC operated with an increasing air dosing profile (measurement C1) show the highest performance. The performances of the 3-PBMRC with uniform (measurement C2) and with decreasing air dosing profiles (measurement C3) are lower and closer to the results of the FBR, which exhibits the lowest conversions and ethylene yields. Because of the low differences between the individual plots and due to their larger errors selectivity values are not plotted here. From the data given in Fig. 5 it can be concluded, that the assumption that there is an increasing air dosing profile in a single PBMR segment (Fig. 4a and b) is correct.

Fig. 6 shows the conversion and yield profiles along the membrane reactor cascade during measurement C1, i.e. for the increasing air dosing profile. As expected most part of conversion occurs already in the first reactor segment, whereas the increase of conversion in the second reactor is rather small and in the third reactor it is even close to zero. In the first reactor primarily ethylene is formed. These results are consistent with the arguments given above.

In the second reactor carbon monoxide is the main product. Here the residence time is still relatively large, but oxygen concentration is higher than in the first stage of the cascade. Remember, that carbon monoxide is formed primarily in case of simultaneous

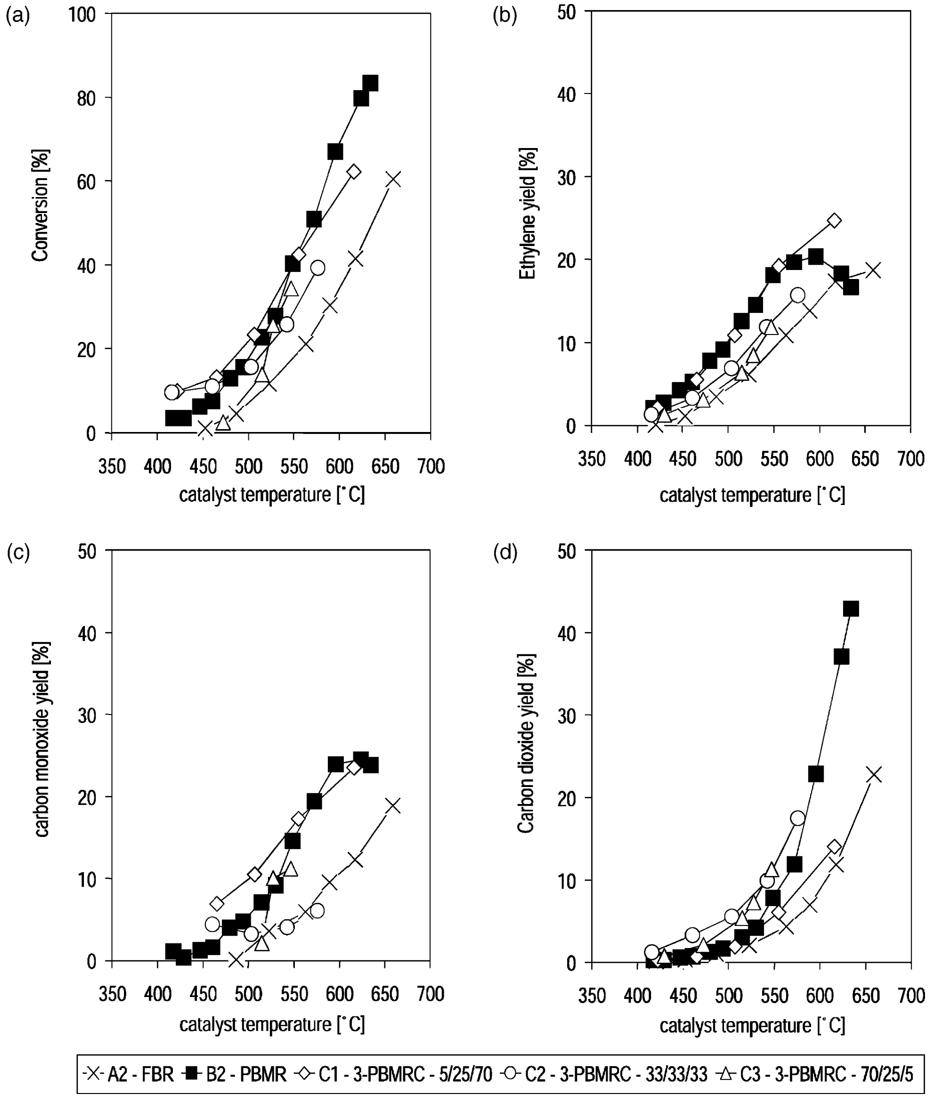

Fig. 5. Comparison of the conversion and yields between the FBR, the PBMR and the 3-PBMRC as a function of catalyst temperature, overall feed concentrations: 0.7% ethane, 19–20% oxygen, GHSV = 18 000–19 000 h^{-1}. Key to legend (Table 2): measurement number; reactor (air distribution between the reactors at the 3-PBMRC).

presence of low gas velocities and of a significant oxygen excess related to ODH stoichiometric ratio (ethane:O_2 = 2:1). To reach the oxygen excess region (>0.35% oxygen, respected to 0.7% ethane) for our feed configuration only 1.75% of the inserted air have to pass the membrane. If this level is exceeded, what happened here already at the end of the first stage, than the conditions are very favourable for the consecutive ethylene oxidation to CO. In the third reactor, CO_2 formation is the dominant reaction because of the large excess of oxygen here. Consequently, the effective ethylene yield shows a decrease from reactor segment to reactor segment during the measurement C1, whereas the CO yield has a maximum in the second stage and the CO_2 yield increases progressively. Similar results as described above, but at a lower levels

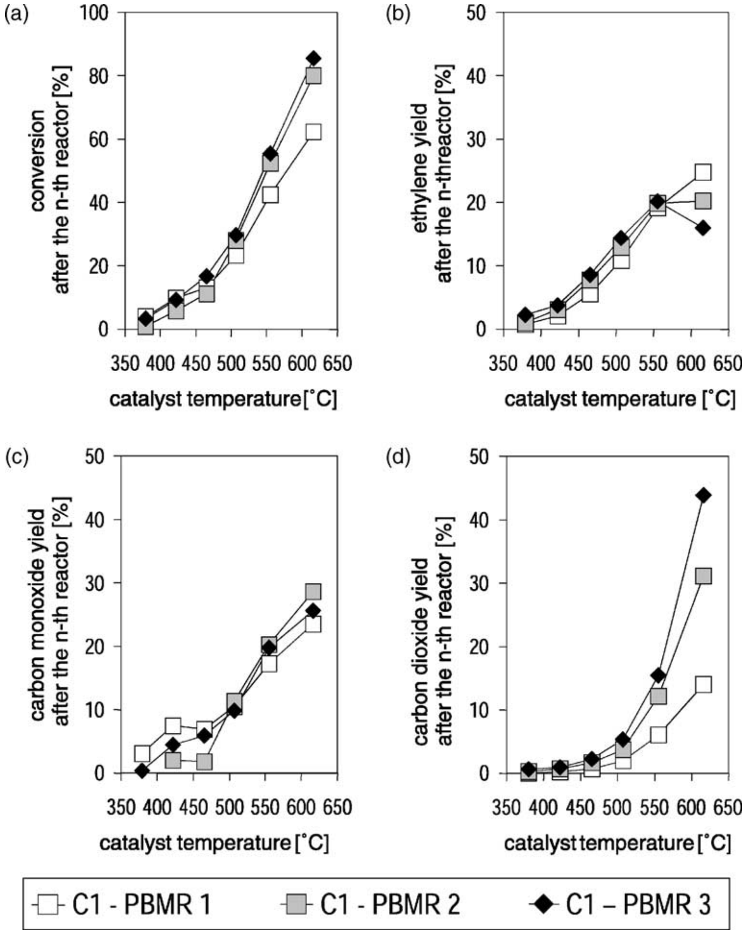

Fig. 6. Profiles of conversion and yields of all products along the reactors of the 3-PBMRC at air distribution 5/25/70; overall feed: 0.7% ethane, 19% oxygen, GHSV $= 18\,000\,h^{-1}$. Key to legend (Table 2): measurement number; reactor; position in the 3-PBMRC.

of conversion and yields than at the measurement C1 were found for the measurements C2 and C3 for which the data are not plotted here.

4. Discussion and conclusions

Finally, we want to analyse our results and compare it with the data from the cited literature. Concluding from the higher conversion rates, we agree with Tonkovich et al. [15] regarding to the prolonged contact time of ethane molecules in the PBMR. Additionally we agree, that overall oxygen concentration is lowered in the PBMR, deduced from the lower CO_2 selectivity which was found (Fig. 2g). But our results indicate clearly, that the residence time effects plays the primer role in the PBMR, especially in case of the favourable high to shell to tube side flow ratios. The relative gas velocity in the reaction zone on the tube side is much lowered by the distributed oxidant insertion via the membrane over the whole catalyst bed (see Section 3.3.). Only the interaction of the changed residence time behaviour (corresponding to the relative gas velocity) with the changed amount of local oxygen supply gives the key to explain our PBMR results and the observed contrast to the data from literature. This effect should be never neglected in the further discussion.

To evaluate the potential of membrane reactors applied for partial oxidations, there it should distinguished between the oxygen stoichiometric and the oxygen excess case. Due to the changes in concentration and contact time profiles in the PBMR, a completely different performance results compared to the FBR. Concluding from data given in Fig. 3 at low overall hydrocarbon oxygen ratios (close to ODH stoichiometric ratio of 2:1), the higher contact times in the PBMR increase conversion and in parallel, because of the local oxygen shortage it can be expected, conversion goes near completely to ethylene, until all available oxygen is consumed. Here deep oxidation is suppressed more effective in the PBMR because the local oxygen concentration level is kept at a low level along the whole catalyst bed axis. In contrast, the local inlet oxygen concentration is higher in an FBR (connected with shorter contact times), resulting in the formation of significant amounts of carbon oxides at lower conversion levels. A supply of oxygen close to ODH yields an increase of conversion and additionally a selectivity improvement as is described already by Tonkovich et al. [15] and Mallada et al. [16].

In the oxygen excess case in the PBMR, the ethylene formation is the primer reaction at the beginning of the catalyst bed, too. In an intermediate zone with oxygen concentrations corresponding to a small excess related to ODH stoichiometric demand the still low gas velocities favour the consecutive oxidation of ethylene, resulting in a much higher CO production. At the end of the catalyst bed in the oxygen richest zone only a minor part of ethane conversion occurs, but a significant part of ethylene and CO is over-oxidised to CO_2. This is due to the gas velocity is lower compared to the FBR operating at the same overall GHSV. Feeding air in excess via the membrane results in a complete loss of the desirable selectivity advantage by the changed residence time behaviour in the PBMR.

It should be noted that an operation under hydrocarbon excess, what is the alternative to overcome the residence time determined olefin combustion can cause hard explosions in case of membrane damage or other reactor leakages and for this reasons it correlates to much higher safety requirements. In our opinion, this can be a high barrier for the membrane reactor concept to find the way to an industrial application. A promising perspective is also to look for catalysts showing a stronger correlation between oxygen supply and their selectivity behaviour in particular under oxygen-rich conditions. Our results demonstrate, that a good catalyst for the FBR should not be the best choice in a membrane reactor. We want to emphasis that a detailed quantitative knowledge of the reaction kinetics over a wide range of contact times and oxygen concentrations is necessarily for a proper design of membrane reactors. Only the consideration of concentration and contact time effects together might promote a successful realisation of the membrane reactor concept.

Acknowledgements

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