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Membrane pilot reactor applied to selective oxidation reactions

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Abstract

The partial oxidation of butane to maleic anhydride was studied in a conventional fixed bed as well as a novel reactor configuration consisting of a porous metallic membrane immersed in a gas–solid fluid bed. The diameter of both reactors was at a commercial scale greater than 30 mm. A range of gas flow rates, temperatures and butane concentrations were tested. Maleic anhydride yield was generally higher in the membrane reactor due to higher butane conversion. Maleic productivity in the fixed bed equalled that observed in the membrane reactor when the gas–solid fluid bed was maintained at a higher temperature of as much as 30 °C. The butane feed rate to the membrane reactor was limited by hot spots. These hot spots were unanticipated and underscore the importance of increasing heat transfer in order to commercialize this technology.

Keywords: Pilot plant inert membrane reactor; Fluid bed; Butane oxidation; Maleic anhydride; VPO catalysts

1. Introduction

Maleic anhydride (MA) is a multi-functional compound and is an important monomer for various non-saturated polyester resins. Several reactor technologies have been commercialized to produce MA including fixed beds, fluid beds and transport beds [1]. Membrane reactors have also been considered and several researchers have described their functional qualities for partial oxidation reactions [2–6]. For example, they claim increased selectivity of the desired intermediates due to the lower average concentration of oxygen in the reaction zone. Our earlier study [7] showed a clear advantage of this reactor configuration over conventional fixed beds due to a reduced hot spot; the temperature profile was flat implying that higher feed rates and thus production rates were possible.

Several limitations of membrane reactors have been cited recently [8,9]. Higher product yields are attained due to the longer contact times resulting in increased conversion. Selectivity in the membrane reactor are equivalent to those achievable in fixed beds but with higher temperatures. Furthermore, two recent reviews [3,10] have pointed out the lack of data in large-scale equipment. Typical inner diameters of experimental membranes are around 7 mm.

The scope of this work is to quantitatively compare membrane reactor performance versus conventional fixed bed reactors at a commercial scale diameter of 32 mm using the same catalyst and operating conditions.

2. Experimental set-up

A schematic diagram of the reactor configuration is shown in Fig. 1 and Fig. 2 illustrates the instrumentation including the feed manifold, reactor and analysis section.

2.1. Feed section

Gas mixtures of butane, air and nitrogen are metered into the reactor using three Brooks mass flow controllers. Liquid

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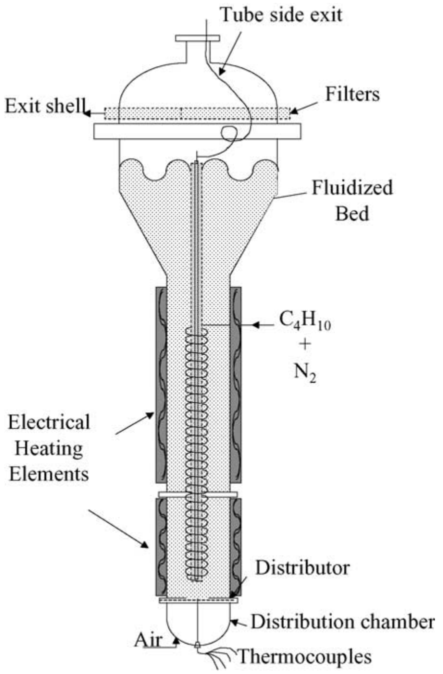

Fig. 1. Design of the membrane reactor.

n-butane at 2.2 bar is vaporized by heating the pipe to 60 °C before entering the gas mass flow controller. The mixture (butane, air and nitrogen) is pre-heated by passing the feed through a coil in the heated fluid bed. The exit of the coil is connected to the entrance of the membrane at the bottom of the reactor. Due to the inherent risks associated with mixing butane and oxygen, the system is equipped with various security measures. Air and butane lines are equipped with electro-pneumatic valves with interlocks for low air pressure, low N_2 pressure, high temperature and high line pressure. In case of pressure build-up in the reactor or overheating, a programmer logic controller switches to safety mode until the condition is solved.

2.2. Fluid bed shell

The shell is made of carbon steel with an inner diameter of 127 mm in the lower section and flanges out to 318 mm in the transport disengagement section. Its total length is 1.8 m and a Geldart A powder (FCC catalyst) was used as the fluidizing medium in which the reactor (fixed bed or membrane containing the VPO catalyst) is immersed. The function of the fluidized bed is two fold: In the first case, the air used for fluidizing the FCC powder is the primary source of oxygen for the reaction. Secondly, two electrical band heaters are mounted on the outer surface of the shell to control the reaction temperature. In a commercial reactor, steam cooling coils would be used.

2.3. Reactors

A stainless steel tube 32 mm ID and 1 m length was used as a fixed bed reactor (FR), while a porous metallic tube with a slightly larger diameter (34 mm ID) was used as a membrane reactor (MR). Catalyst was charged to the reactors to a height of about 500 mm. Note that before activation, the bed height was 565 mm. During the calcination and activation process, the precursor loses 15% weight due to water and organics. After the fixed bed tests, the same catalyst was charged to the membrane reactor. The resulting bed height was 485 mm. In the case of the membrane reactor, the upper part of the tube above the catalyst zone is made of non-porous stainless steel. A 17 multipoint thermocouple centred in the catalyst bed monitored the temperature profile along the reactor length. The pressure in both chambers was registered by relative pressure Keller Transmitters in both inlets and outlets.

2.4. On-line analysis

The effluent gas exited the top of the reactor through a line heated to a temperature of 200 °C to prevent maleic

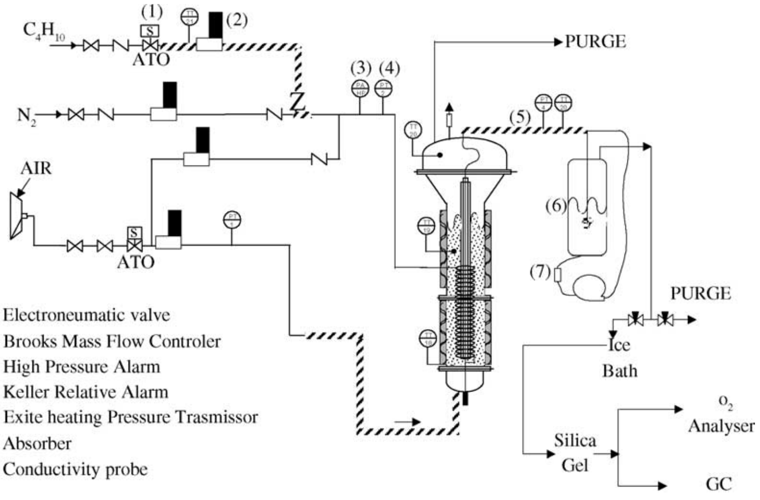

Fig. 2. Flow diagram of the experimental set-up.

anhydride from condensing. The product stream passed through an absorber containing distilled water where the condensable products (maleic anhydride and by-product acids) were retained. Water from the absorber was pumped to the effluent gas line to maximize the contact efficiency. A conductivity probe installed upstream of the pump monitored the acid evolution on-line. Liquid samples were recovered at the end of each experiment. In addition, the absorber was washed several times after each experiment to collect residual acids that deposited on the walls of the absorber. All the samples were subsequently analyzed by HPLC with an ION-300 column. Maleic anhydride (acid) was the main product and other acids included acetic, acrylic, methacrylic, fumaric, and phthalic. The measured concentrations were in line with the values reported by Lorences et al. [11].

The analysis of the non-condensable gases (feed and exit) was carried out by a Gas Chromatograph equipped with TCD and FID detectors, a Haysep R packed column and a Molecular Sieve 5A are attached to the TCD detector where O_2, CO, CO_2, N_2 and butane are quantified, a HP1 capillary column is attached to the FID detector in order to have a more reliable quantification of butane. The oxygen concentration was also monitored on-line via a paramagnetic oxygen analyser.

2.5. Catalyst

The VPO precursor was synthesized in an organic medium (chemical composition close to a commercial VPO catalyst with a P:V of 1.1) and then made into ring shaped tablets (4 mm OD × 4 mm height × 1 mm hole). The density of the tablets was optimized to achieve the strength required to avoid crushing of the tablets during the operation. The precursor was calcined and activated in situ in the fixed bed reactor under specific operating conditions. It was then subjected to a net oxidizing environment of about 1% butane in air for 200 h to stabilize its catalytic performance. It was diluted 45:55 by weight with inert spheres.

3. Results and discussion

Together with the kinetic studies, several tests were conducted to assess the axial permeation rate, heat transfer characteristics, the steady state temperature profile and the gas residence time distribution. The operating variables studied in the fixed bed included temperature, contact time, and butane and oxygen concentrations. The degrees of freedom for the membrane reactor are significantly greater, resulting in a large number of operating variables and thus possible experiments. Together with the fixed bed operating conditions, we also varied the oxygen concentration in the shell, flow rate, temperature profile and pressure differential. Experiments labeled FR refer to the fixed bed reactor and MR refers to the membrane reactor.

3.1. Hydrodynamic studies

3.1.1. Pressure drop profile

The hydrocarbon feed gas enters the bottom of the reactor and thus the pressure drops from the bottom to the top, which is the same for the fluid bed: the pressure at the bottom equals the hydrostatic head of the solids. By selecting a moderate gas velocity (combined with the relatively large particles), we can operate the membrane reactor such that the pressure drop along its length equals the pressure drop across the fluid bed. Thus, the pressure differential between the membrane and fluid bed is relatively constant and the flow from the shell should be distributed uniformly.

We estimated the permeation rate applying the Dusty Gas Model [12] and estimated the pressure drop in the fixed bed using the Ergun equation. Fig. 3 shows the results at two experimental conditions (high and low permeation rates). The figure shows that the permeation flow rate is a little higher at the inlet of the bed, but is almost constant along the membrane length (due to the effect of the fluidized bed), confirming that that the flow from the shell is fairly evenly distributed.

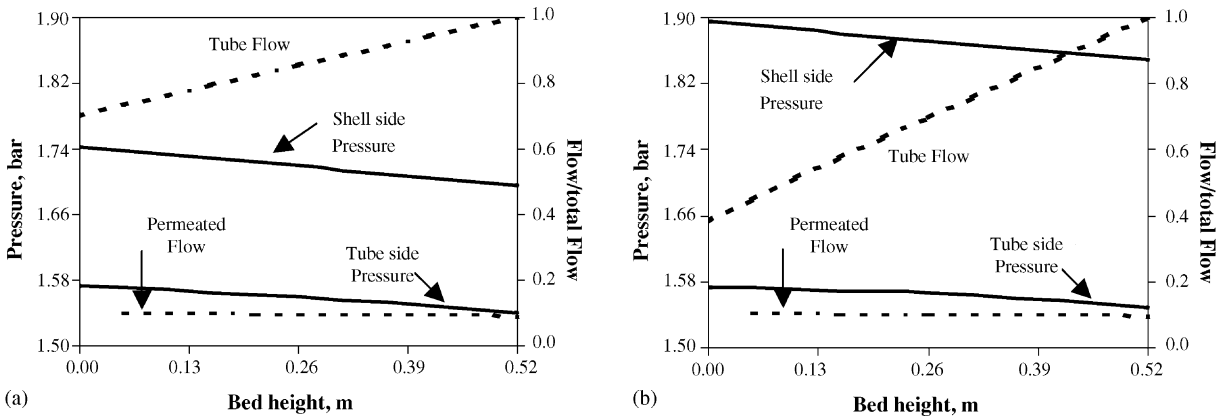

Fig. 3. Pressure profiles, tube flow, and permeated flow along the bed; bath temperature, 350 °C; total flow rate, 23 sL/min; (a) inlet flow, 19 sL/min; permeated flow, 8 sL/min; (b) inlet flow, 10 sL/min; permeated flow, 17 sL/min.

3.1.2. Transient response studies

Several types of experiments were conducted in order to assess mixing and heat transfer. Heat transfer rates were measured by imposing a temperature profile across the membrane by feeding a relatively high concentration of butane and then cutting off the butane feed and recording the change in temperature with time. Step tracer studies were carried out by feeding a constant rate of air, then switching a fraction of the air to nitrogen for 300 s, and then switching back to 100% air. For the case of the membrane reactor, we changed the feed conditions of the fluid bed and membrane independently. The paramagnetic oxygen analyser registered the oxygen concentration at the exit of the membrane reactor.

In general, the tracer response results of the fixed bed and membrane reactor were substantially similar in the aggregate. Axial dispersion of the feed gas in the membrane reactor is very low. However, the pulse experiments conducted by switching from air-to-N_2-to-air in the fluid bed (while monitoring the oxygen at the exit of the membrane) show a significant amount of axial dispersion.

3.2. Reactor performance

The entire fixed bed reactor performance data set includes 55 experiments at distinct temperatures, flow rates and butane and oxygen concentrations. The most relevant experimental conditions within the scope of the present work are summarized in Table 1. Compressed air was used as the fluidizing medium for the Geldart A powder in the shell. The air velocity was maintained at about 10 times the minimum fluidization velocity. This value was sufficient in order to maintain a constant temperature across the reactor.

The membrane reactor experimental conditions are also summarized in Table 1 and consisted of 20 conditions: two levels of temperatures, several levels of butane and oxygen concentration and several permeation flow rates. The flow rate and concentrations indicated as “Tube“ refer to the feed introduced directly into the membrane while the ones indicated as “Shell” refer to the permeation flow and gas concentrations permeating from the shell trough the membrane. The overall conditions are those of the membrane inside adding both contributions. The total flow entering the fluid bed (shell side) is the permeating flow plus the flow required for fluidizing the bed (corresponding to ten times the minimum fluidization velocity). The percentage of the total flow in the reactor that comes from the gas permeating across the membrane is also indicated in the table.

Experiments M1–M7 and M8–M14 are identical except for bath temperature. Air was used as the source of oxygen for most experiments and it was generally introduced into the fluid bed and permeated across the membrane to the catalyst. However, several experiments were conducted with enriched air and 100% oxygen (M19–M20 and M17–M18, respectively). In M4, M5 and M7 (and their homologous at 370 °C), air was co-fed to the tube side while in M6 air was diluted with nitrogen in the shell side in order to decrease the global oxygen concentration maintaining all flow rates constant. M15 and M16 were experiments designed to create a temperature gradient across the reactor in which the lower part of the shell was maintained at 370 °C and the upper part was held at 350 °C.

Table 1
Experimental conditions

Experiment	Temperature bath (°C)	Shell			Tube			Overall conditions		
		Flow (L/min)	O_2 (vol.%)	Permeation flow (%)	Flow (L/min)	Butane (vol.%)	O_2 (vol.%)	Flow (L/min)	Butane (vol.%)	O_2 (vol.%)
F1	370							24	0.5	19.9
F2	350							18	1.1	10.5
M1	350	5	21	28	13	1.4	0.0	18	1.0	5.5
M2	350	5	20	28	13	2.1	0.0	18	1.5	5.4
M3	350	10	20	53	9	2.0	0.0	19	1.0	10.5
M4	350	8	20	350	19	0.7	20.0	27	0.5	20.1
M5	350	17	20	63	10	1.3	20.1	27	0.5	20.3
M6	350	10	11	53	9	2.1	0.0	19	1.0	5.4
M7	350	7	21	37	12	1.5	5.4	19	1.0	10.8
M8	370	5	20	28	13	1.3	0.0	18	1.0	5.4
M9	370	5	21	28	13	1.9	0.0	18	1.4	5.5
M10	370	10	21	53	9	2.0	0.0	19	1.0	10.6
M11	370	8	20	30	19	0.6	19.6	27	0.4	19.8
M12	370	17	20	63	10	1.2	19.7	27	0.4	20.1
M13	370	10	11	53	9	1.9	0.0	19	0.9	5.6
M14	370	7	20	37	12	1.4	5.3	19	0.9	10.6
M15	370–350	10	20	53	9	1.9	0.0	19	0.9	10.6
M16	370–350	10	20	53	9	2.6	0.0	19	1.3	10.6
M17	370	4	100	17	19	0.6	0.0	23	0.5	17.0
M18	370	4	10,0	17	19	1.1	0.0	23	0.9	17.0
M19	370	7	28	37	12	1.5	0.0	19	1.0	10.0
M20	370	7	39	29	17	1.3	0.0	24	1.0	10.8

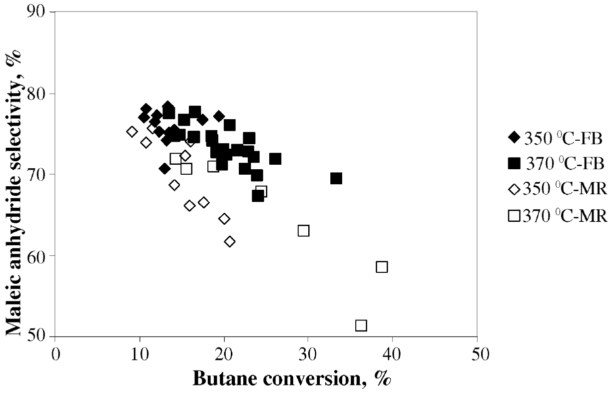

Fig. 4. Butane conversion vs. maleic anhydride selectivity for fixed bed and membrane reactor at different bath temperature.

3.2.1. Conversion versus selectivity

Fig. 4 provides a broad overview of the experimental data and compares the reactor performance–butane conversion versus maleic anhydride selectivity–of the fixed bed reactor versus the membrane reactor at 350 and 370 °C. Further experimental data are summarized in Table 2. In general, the figure shows that selectivity is higher in the fixed bed reactor compared to the membrane reactor when operated at the same level of conversion. However, the data also show that the membrane reactor has higher selectivity at a higher temperature, which is inconsistent with expectation.

A complementary method of comparing reactor performance, which may be more relevant from an industrial perspective, is to consider the maleic anhydride production rate under the same overall operating conditions (GHSV, bath temperature, %C_4 and %O_2).

3.2.2. Temperature profile under reaction conditions

Fig. 5 demonstrates the temperature profiles at steady state reaction conditions with 0.5% butane in air and a bath temperature of 370 °C (Experiments F1 and M17). In experiment M17, butane and nitrogen are co-fed to the membrane reactor and pure oxygen is the fluidizing gas in the shell. Under these conditions a low permeation flow rate is required to feed sufficient oxygen to react in the membrane. In the fixed bed, the temperature rises by about 10 °C in the first 0.2 m of the bed and remains constant thereafter. On the other hand for the membrane reactor, the temperature rises continually from the entrance until just before the exit–a rise of almost 70 °C! The maleic anhydride production rates for both reactors, included in the figure, are converted from the on-line conductivity measurements. The overall production rate of the membrane reactor at steady state is higher by approximately 21%.

Results of experiments F2 and M3 are illustrated in Fig. 6. In these tests, the ‘‘average’’ butane and oxygen concentrations are 1 and 10%, respectively. Air is the fluidizing gas in the shell and it was maintained at a temperature of 350 °C. Compared to experiment M17, the permeation rate across the membrane is much greater to achieve the oxygen concentration. However, despite the large difference in permeation rates, the general trends are similar but less accentuated. The temperature rises constantly along the length and reaches 380 °C, which is 30 °C hotter than the fluid bed temperature. The temperature rise across the fixed bed was a modest 10 °C. This experiment is an example where the performance of the membrane reactor is superior to the fixed bed in that conversion and maleic yield are higher yet maintaining the same selectivity of about 74%.

Table 2
Results for experiments in Table 1

Experiment	X (%)	S_{MA} (%)	S_{CO} (%)	S_{CO_2} (%)	Prod. (gMA/h/kg cat.)	Y (%)	CO/CO_2
F1	20	71	16	10	18	14	1.5
F2	13	74	13	11	18	10	1.2
M1	11	74	13	10	17	8	1.4
M2	9	75	12	9	21	7	1.3
M3	16	74	14	10	25	12	1.4
M4	16	66	16	16	16	11	1.0
M5	20	64	18	15	19	13	1.2
M6	12	76	13	9	19	9	1.5
M7	16	74	14	10	26	12	1.4
M8	16	71	16	10	22	11	1.5
M9	14	72	15	10	30	10	1.6
M10	29	63	21	13	38	19	1.6
M11	36	57	26	15	28	21	1.7
M12	39	59	25	15	31	23	1.7
M13	19	71	17	10	26	13	1.6
M14	24	68	18	11	55	17	1.6
M15	24	69	18	11	33	17	1.6
M16	24	62	22	13	39	15	1.6
M17	24	68	19	10	22	16	1.8
M18	25	58	28	11	32	14	2.4
M19	24	67	19	11	55	16	1.7
M20	18	69	19	10	32	12	1.8

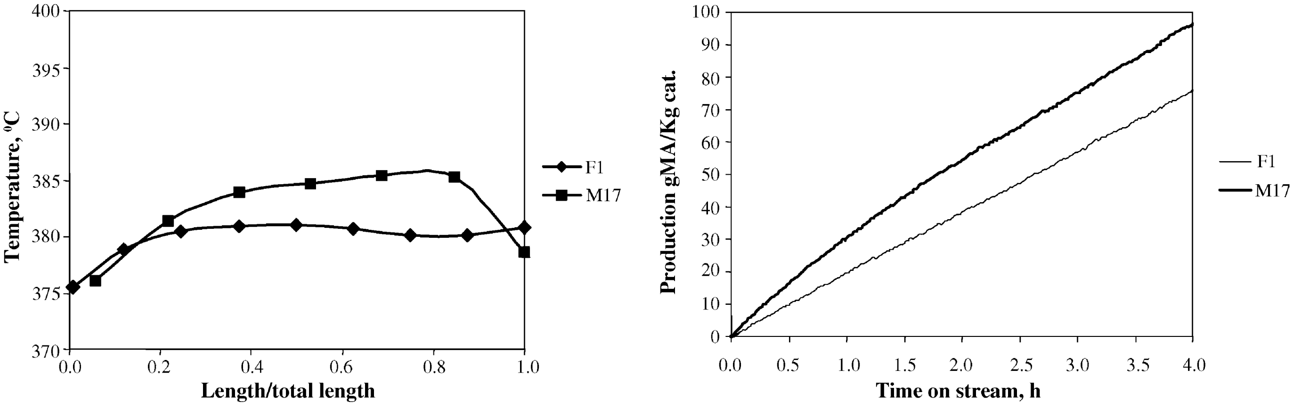

Fig. 5. Fixed bed and membrane reactor comparison at the same overall conditions: bath temperature, 370 °C; total flow rate, 23 sL/min; 0.5% C_4; 20% O_2 (pure oxygen).

3.3. Membrane parameters

3.3.1. Effect of oxygen distribution

Different feed modes in a membrane reactor have been previously reported [13]:

1. Co-feed: Oxygen and butane are co-fed to the tube side (fixed bed reactor),
2. Totally segregated feed: Butane is fed to the tube side and all the oxygen through the membrane,
3. Mixed feed: Part of the oxygen is co-fed to the tube side,
4. Mixed feed reversal: Including reversing of the feed containing *n*-butane.

A similar comparison has been performed in this work to evaluate the effect of distributing the oxygen (air in this case) between the shell and the tube side. F2 is the reference fixed bed experiment (conducted at 350 °C). M3 and M10 are experiments run at 350 and 370 °C, respectively, with air fed to the fluid bed and zero co-fed with butane to the catalyst. M7 and M14 were run at 350 and 370 °C. Air was fed to the fluid bed and 5% oxygen was co-fed with the butane to the membrane. Maleic anhydride productivity was higher with the membrane reactor; 40% higher at 350 °C and at least 80% higher for the experiments run at 370 °C. The temperature rise for M3 and M7 was on the order of 30 °C and it was 65 °C for M10 and 45 °C for M14. The tendency seems to be as follows: as more oxygen is fed through the membrane, lower temperatures are observed at the reactor entrance and higher temperatures at the exit.

Regarding the catalytic performance the following trend is observed related to the oxygen distribution at 350 °C:

Butane conversion	Co-feed < segregated feed < mixed feed
MA Selectivity	Mixed feed ≈ segregated feed ≈ co-feed

The difference in conversion by introducing 30% of the total oxygen in the tube side (mixed feed) or the totally segregated feed is less than 5% at 350 °C, while the selectivity seems to be independent of the oxygen feed mode. The same tendency is reported by [14]. However, Mota et al. found the highest conversion in the co-feed mode and the lowest in the segregated mode. In their results, the high conversion is accompanied by low selectivity. In this work, the differences between operating modes becomes accentuated at 370 °C.

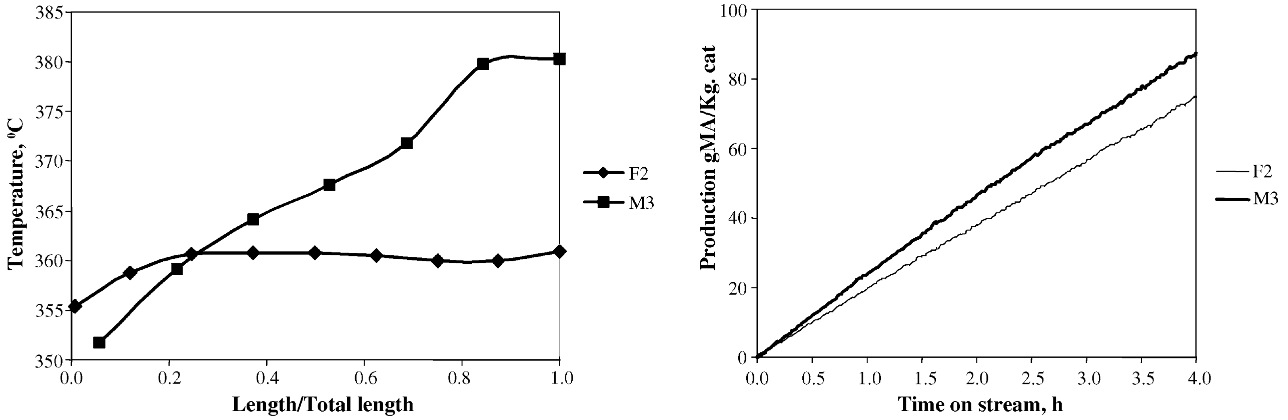

Fig. 6. Fixed bed and membrane reactor comparison at the same overall conditions: bath temperature, 350 °C; total flow rate, 19 sL/min; 1% C_4; 10% O_2 (using air).

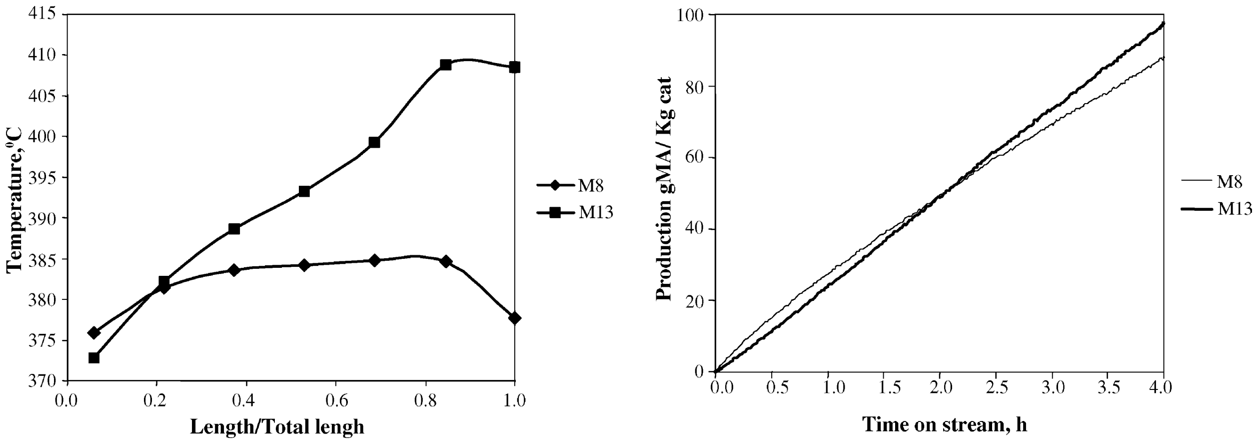

Fig. 7. Effect of the N_2 distribution at the same overall conditions: bath temperature, 370 °C; total flow rate, 19 sL/min; 1% C_4; 5% O_2.

3.3.2. *Effect of inert distribution*

The effect of the amount of nitrogen fed to the tube side has been studied at two overall oxygen concentrations: Case 1 includes experiments M10 and M13 when 50% of the nitrogen is introduced to the tube side. In Case 2–experiments M8 and M19–approximately 75% of the nitrogen comes from the tube side. Reducing the inert concentration of the membrane feed line increases the net butane residence time. As a consequence, higher butane conversion and lower selectivity are observed. These results are in agreement with data reported from other authors [15,16].

Figs. 7 and 8 illustrate the temperature distribution across the membrane together with the maleic anhydride evolution during the experiment. Note that in both cases MA productivity is higher for experiments M8 and M19 (higher dilution) during the first 1.5 h on-stream (transient). The temperature rise is also lower for M8 and M19, which is a reflection of the lower overall conversion at steady state.

Mallada [14] and Ramos et al. [16] reported an increase in the selectivity with the amount of inert introduced to the tube side, but less effect is attributed to the inert distribution in comparison with the oxygen distribution. The same conclusion could be drawn from the results reported in this work. This is most likely due to the important role that the oxygen concentration plays on the catalyst oxidation state in the first part of the bed.

3.3.3. *Effect of fluid bed temperature*

Experiments M8–M14 are replicates of M1–M7 but were conducted at a 20 °C higher temperature. Conversion and selectivity to combustion products were significantly higher at 370 versus 350 °C. On average, the rise in conversion was on the order of 11% (absolute and 26% relative) and the maleic anhydride selectivity dropped by about 6% absolute. However, due to the increased butane conversion (and low heat transfer rates) the average temperature difference between the experiments was often much larger than 20 °C.

The performance of the membrane reactor appears to be compromised by the lower than expected heat transfer rate. Several possible experiments were considered in order to increase the rate. One series of tests consisted of cooling the upper section of the bed. The temperature of the fluid bed was maintained by two externally mounted band heaters. Fig. 9 compares the results obtained under the same experimental conditions but 20 °C lower temperature in the upper part of the fluid bed (M10 at 370 °C constant fluid bed temperature and M15 at 370 °C in the bottom and 350 °C in the top half). In M15, the increase in the temperature is lower compared to M10. Butane conversion is lower and maleic

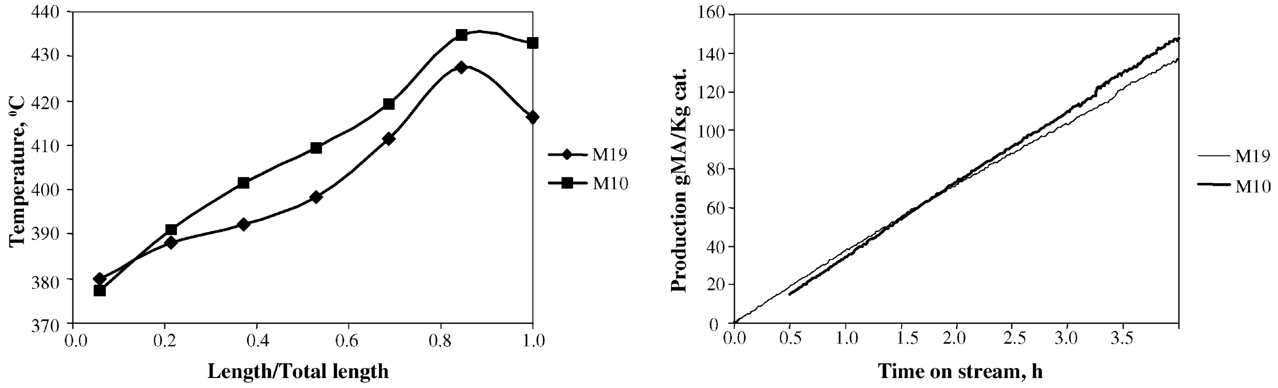

Fig. 8. Effect of the N_2 distribution at the same overall conditions: bath temperature, 370 °C; total flow rate, 19 sL/min; 1% C_4; 10% O_2.

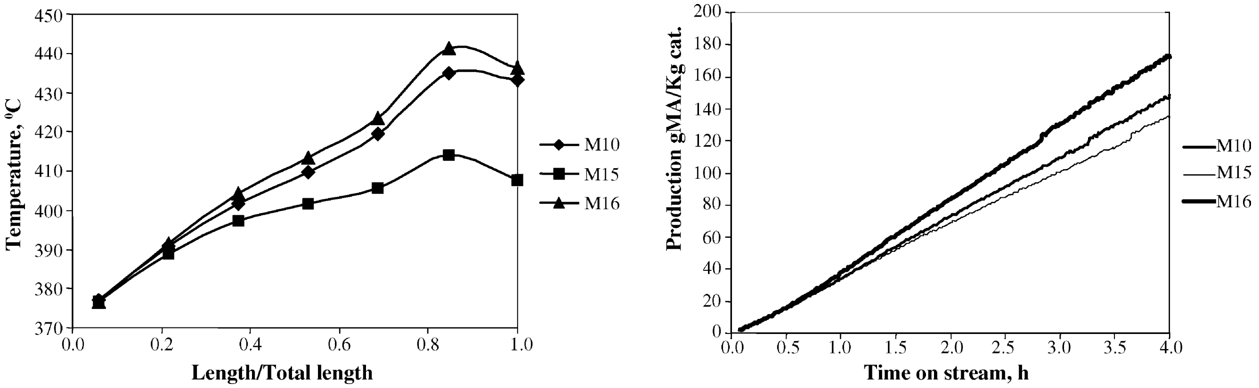

Fig. 9. Effect of the bath temperature at the same overall conditions: total flow rate, 19 sL/min; 10% O_2.

anhydride selectivity is higher for M15 with the reduced exit temperature. In M10 the maximum temperature allowed in the bed due to possible phosphorous depletion of the catalyst is reached. When the temperature is lower, it is possible to fed more butane. In M16 the permeation and tube flow rates as well as total flow rate and oxygen concentration are the same as in M10 and M15, bath temperature is reduced as in M15, but more butane is fed in order to reach this temperature limit. Maleic anhydride production is increased by 17%.

4. Conclusions

The membrane reactor discussed in this work has several advantages versus conventional fixed bed technology including safety. Under no conditions have we recorded back permeation of butane to the fluid bed shell and we have been able to control the addition of oxygen along the length of the catalyst bed. Separating the oxidant from the hydrocarbon in this manner is inherently safer compared to processes where they are mixed together at high temperature (and pressure). With respect to feed conditions, the membrane reactor may operate with higher butane feed concentrations since there is no restriction with respect to the lower explosion limit of 1.8% butane in air. Furthermore, several experiments demonstrated that under similar operating conditions, production of maleic anhydride is higher with a membrane reactor versus a conventional fixed bed. However, the data also show that on average, the reactor performance–conversion versus selectivity of the fixed bed reactor is superior than the membrane reactor for the conditions tested. On average, at equal conversion, the selectivity in the fixed bed is several percent higher. The lower than expected selectivity requires further investigation. One possible explanation relates to the poor heat transfer and increasing the heat transfer rate will be key to its commercial development. The difference in temperature profiles between both reactors is a complex combination of heat transfer, oxygen distribution, flow pattern, thermal conductivity and hydrocarbon residence time and it is difficult to attribute the contribution of each of these parameters to reactor performance at this time.

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References

[1] R.M. Contractor, D.I. Garnett, H.S. Horowitz, H.E. Bergna, G.S. Patience, J.T. Schwartz, G.M. Sisler, in: Corberan, Bellon (Eds.), New Developments in Selective Oxidation II, Elsevier, New York, 1994, p. 233.
[2] J.G.S. Macano, T.T. Tsotsis, Catalytic Membranes and Membrane Reactors, Wiley/VCH, Weinheim, 2002.
[3] G. Saracco, H.W.J.P. Neomagus, G.F. Veersteeg, W.P.M. van Swaaij, Chem. Eng. Sci. 54 (1999) 1997–2017.
[4] K.K. Sirkar, P.V. Shanbhag, A.S. Kovvali, Ind. Eng. Chem. Res. 38 (1999) 3715–3737.
[5] A. Julbe, D. Farrusseng, C. Guizard, J. Mem. Sci. 181 (2001) 3–20.
[6] J. Coronas, J. Santamaría, Catal. Today 51 (1999) 377–389.
[7] M. Alonso, M.J. Lorences, M.P. Pina, G.S. Patience, Catal. Today 67 (2001) 151–157.
[8] F. Klose, T. Wolff, S. Thomas, A. Seidel-Morgenstern, Catal. Today 82 (2003) 25–49.
[9] A.L.Y. Tonkovich, J.L. Zilka, D.M. Jimenez, G.L. Roberts, J.L. Cox, Chem. Eng. Sci. 51 (1996) 789–806.
[10] J.N. Armor, J. Mem. Sci. 147 (1998) 217–233.
[11] M.J. Lorences, G.S. Patience, F.V. Díez, J. Coca, I&EC Res. 42 (2003) 6730–6742.
[12] E.A. Mason, A.P. Malinauskas, Gas Transport in Porous Media: The Dusty Gas Model. Chem. Eng. Monographs, 17, Elsevier, Amsterdam, 1983.
[13] S. Mota, S. Miachon, J.C. Volta, J.A. Dalmon, Catal. Today 67 (2001) 169–176.
[14] R. Mallada, Estudio de la oxidación selectiva de butano a anhídrido maleico en reactores de membrana, Ph.D. Thesis, Zaragoza, 1999.
[15] R. Mallada, M. Menéndez, J. Santamaría, Catal. Today 56 (2000) 191–197.
[16] R. Ramos, M. Menéndez, J. Santamaría, Catal. Today 56 (2000) 239–245.