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Membrane application in Fischer–Tropsch synthesis reactors—Overview of concepts

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Abstract

Different applications of membranes have been proposed for Fischer–Tropsch synthesis in recent literature. Across membranes, reactants can be fed along the reactor axis or the inhibiting by-product H_2O can be selectively removed. Here, the concept of enhanced conversion of CO_2 containing synthesis gases to long-chain hydrocarbons by in situ H_2O removal is introduced. Experimental results of in situ H_2O removal under reactive conditions with an Fe-based catalyst show positive effects on conversion and yield. Additionally, catalytic membranes can be used as a defined reaction zone. In so-called plug-flow contactor membranes, high specific production rates can be achieved. Finally, a catalyst encapsulated by a zeolite membrane layer is presented as a possibility to modify product distribution.

Keywords: Membrane reactors; Catalytic membranes; Fischer–Tropsch synthesis; H_2O removal; CO hydrogenation; CO_2 hydrogenation

1. Introduction

Different applications of membrane reactors have been proposed for Fischer–Tropsch (FT) synthesis in recent literature. This overview does not consider the application of oxygen transfer membranes in synthesis gas production or filter applications for slurry systems, as it focuses solely on the FT reactor unit. We apply the classification of catalytic membrane reactors according to Sanchez Marcano and Tsotsis [1] who categorize according to the type of membrane (permselective/non-permselective) and the location of the catalyst (within/outside the membrane).

Fig. 1 and Table 1 summarize the published concepts for membrane application in FT reactors without claiming that the list is complete. By the application of membranes, advanced feeding concepts (distributed feeding) may be realized to control the heat of the FT reaction and to enhance the selectivity to long-chain products (Eq. (1)). The selective removal of the by-product H_2O which deactivates FT catalysts and may inhibit the reaction rate can increase per-pass conversion, product yield and catalyst lifetime. Furthermore, in situ removal of H_2O enhances the conversion of CO_2 containing syngases to long-chain hydrocarbons by displacing the equilibrium composition of the water gas shift (WGS) reaction (Eq. (2)).

$$\text{FT}: \quad CO + 2H_2 \rightarrow (CH_2) + H_2O, \quad \Delta_r H = -158\,\text{kJ/mol}\,(T = 250\,^{\circ}\text{C}) \tag{1}$$

$$\text{WGS}: \quad CO + H_2O \leftrightarrow CO_2 + H_2, \quad \Delta_r H = -39.5\,\text{kJ/mol}\,(T = 250\,^{\circ}\text{C}) \tag{2}$$

A catalytic membrane can offer a defined reaction zone while the reactants are forced through the membrane by a pressure gradient. Depending on the properties of the membrane, very high gas–liquid mass-transfer rate can be obtained, resulting in high volume specific production rates. In a new concept, the products of the FT synthesis are forced through a catalytic membrane resulting in a modified product distribution. Hence, the motivations for membrane application are: higher specific production rates, increased catalyst lifetime, and increased product selectivities. Especially for future small/medium-scale FT units, e.g. for off-shore applications and biomass-to-liquids (BTL) processes, membrane reactors may have potential.

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Table 1
Concepts of membrane application in FT synthesis reactors

	References	Concept	Reactors	Membrane/support	Catalyst	X_{CO}	$S_{C_{2+}}$	$Y_{C_{2+}}$
a	Léonard et al. [2–4]	Distributed feeding	PBNMR PBCMR	γ-Al_2O_3/α-Al_2O_3 ZSM-5/α-Al_2O_3	Co/Al_2O_3	$+^a$ /$-^b$	−/+	−/+
b	Espinoza et al. [5]	Selective H_2O removal	PBMR	Mordenite/ZSM-5/silicalite/stainless steel	n.a.			
b	Rohde et al. [6]	Selective H_2O removal reactant distribution	PBMR	$Si(OH)_xO_y$/γ-Al_2O_3/α-Al_2O_3	Fe/Al_2O_3/5K/Cu	$+^c$		$+^c$
b	Zhu et al. [7]	Selective H_2O removal	PBMR	4A-zeolite/TiO_2/stainless steel	n.a.			
c1	Khassin et al. [8]	Forced-through flow catalytic membrane	CNMR	Porous catalyst/copper structure	Co/Al_2O_3	+	+	+
c2	Bradford et al. [9]	Forced-through flow catalytic membrane	CNMR	Catalyst/γ-/α–Al_2O_3	P/Pt-Co/Al_2O_3	+	−	+
d	He et al. [10]	Control of product traffic	PBCMR	ZSM-5/catalyst pellet	Co/SiO_2	−	$+^d$	$+^d$

PBNMR: packed-bed non-permselective membrane reactor, PBMR: packed-bed MR, CMR: catalytic MR, CNMR: catalytic non-permselective MR.

[a] CO fed across membrane.

[b] H_2 fed across membrane.

[c] Based on CO_2.

[d] For C_1–C_{10}.

2. Concept of distributed feeding

Significant axial and radial temperature profiles can occur in multitubular packed bed reactors (PBR). Membranes as reactant distributor along the reactor axis have been proposed to control the heat production of the FT reaction. As the activity and product selectivity depend significantly on the H_2/CO-ratio in the case of Co-based catalysts, distributed feeding can positively affect the gas phase composition. Léonard et al. [2], Vanhove and Léonard [3] and Guillou et al. [4] presented a conceptual study on distributed feeding of H_2 and CO along the reactor axis. One of the reactants was fed through a tubular membrane, while the other was led through the catalyst bed located inside the membrane. The membrane was either inert (γ-Al_2O_3 on α-Al_2O_3) or coated with a ZSM-5 zeolite layer. The results obtained in the PBNMR and PBCMR setups were compared to PBR experiments operated under similar conditions (180 °C, 0.1 MPa, Co/Al_2O_3).

The observed results are in accordance with general kinetics of Co-based catalysts and the influence of H_2/CO-ratio on product selectivity [11–13]. With H_2 as feed gas and CO as distributed reactant, the H_2/CO-ratio maintains extremely high along the reactor axis. Hence, the inhibition of the FT reaction rate due to CO remains low and increased conversions were measured compared to the PBR. However, the formation of long-chain hydrocarbons is not favored and C_1–C_4 hydrocarbons were mainly recovered as product. Consequently, the distribution of H_2 into a CO feed stream resulted in lower conversions as the inhibition by CO is high. Due to the low H_2/CO-ratio, an increase in C_{10+} hydrocarbon yield and lower methane selectivity was observed. The application of the ZSM-5 membrane showed similar results, but it altered the product distribution additionally by secondary reactions at the acidic sites of the zeolite, resulting in higher yields of short-chain hydrocarbons. Another way of incorporating zeolites into FT reactors by means of membranes is the use of encapsulated catalysts (see further below).

3. Concept of H_2O removal

H_2O which is formed as a by-product during FT synthesis accumulates in the gas phase and decreases the partial pressures of the reactants. At high per-pass conversions, H_2O molar fractions of 40–50% for Co-based and as low as 8% for WGS active Fe-based catalysts can be met at the

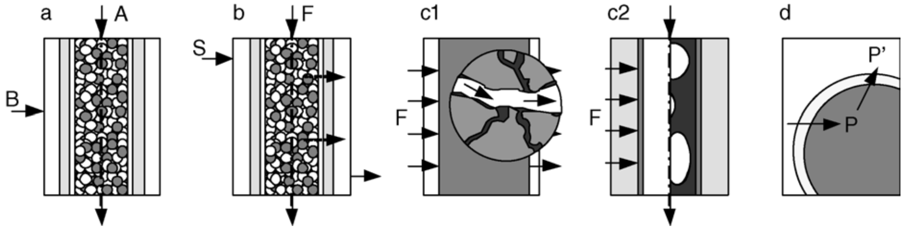

Fig. 1. Membrane reactors for FT synthesis proposed in literature. (a) Distributed feeding of the reactants A+B; (b) in situ H_2O removal by selective membrane, F: feed, S: sweep; (c1) plug-through contactor membrane (PCM) with wide transport pores; (c2) forced-through flow membrane contactor, product and heat removal by circulated liquid product; (d) zeolite encapsulated FT catalyst, P′: modified product. *Sources*: See Table 1.