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New Integrated Catalytic Membrane Processes for Enhanced Propylene and Polypropylene Production

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Newly reported integrated processes are discussed for aliphatic (paraffin) hydrocarbon dehydrogenation into olefins and subsequent polymerization into polyolefins (e.g., propane to propylene to polypropylene, ethane to ethylene to polyethylene). Catalytic dehydrogenation membrane reactors (permreactors) made by inorganic or metal membranes are employed in conjunction with fluid bed polymerization reactors using coordination catalysts. The catalytic propane dehydrogenation is considered as a sample reaction in order to design an integrated process of enhanced propylene polymerization. Related kinetic experimental data of the propane dehydrogenation in a fixed bed type catalytic reactor is reviewed which indicates the molecular range of the produced C_1-C_3 hydrocarbons. Experimental membrane reactor conversion and yield data are also reviewed. Experimental data were obtained with catalytic membrane reactors using the same catalyst as the non-membrane reactor. Developed models are discussed in terms of the operation of the reactors through computational simulation, by varying key reactor and reaction parameters. The data show that it is effective for catalytic permreactors to provide streams of olefins to successive polymerization reactors for the end production of polyolefins (i.e., polypropylene, polyethylene) in homopolymer or copolymer form. Improved technical, economic, and environmental benefits are discussed from the implementation of these processes.

Keywords catalytic membranes; dehydrogenation membrane reactor; hydrogen separation; pollution reduction; polyolefins-polypropylene; propylene yield; recycling; separative membranes

INTRODUCTION

New processes for the production of chemicals or materials must demonstrate certain improvements from existing ones in order to be accepted for commercialization in industrial chemical process engineering. Materials and energy conservation coupled with environmentally benign process modification (e.g., elimination of toxic or hazardous solvents, catalysts or other media) are key factors to be considered. Increased product yields, recycling of reactants and intermediate products for utilization within the process, reduction in waste generation, reduction of process steps and of capital and operational costs (including materials and energy costs), are such necessary improvements. An improved process for integrated olefin, polyolefin production from the dehydrogenation of alkanes (paraffinic streams) is discussed below. Polyolefins such as polypropylene (PP), polyethylene (PE) and their copolymers, poly(butene-1), polyisobutylene, poly(4-methylpentene-1) are high value commodity polymers. They are produced in high capacity annually and used in the manufacturing of plastics, medical/industrial parts and tools, chemicals, and household products. Polypropylene alone has a production capacity of about 8.5 million m.t. annually in North American and 44 million m.t. globally (1). Polyethylene has a higher global capacity in annual production. Both are predicted to grow in the years to come.

The new process proposed here uses the permeable reactor concept (membrane reactor or permreactor) in order to design a catalytic dehydrogenation membrane reactor (CDMR) of paraffins (alkanes) to olefins (alkenes). The process integrates the CDMR with a polymerization reactor (PR) (gas phase or slurry type) for polyolefin production in a two-step reactor process (2). A third vessel, a separator (or permeator), complements the flow chart to separate, in gas phase, the unreacted olefin from the paraffin at the exit of the polymerization reactor. Olefin (e.g., propylene) is fed back into the PR inlet and the paraffin (e.g., propane) is recycled into the CDMR inlet. Thus, the entire process consists of an integrated reaction-separation-recycling system for the production of polymer grade olefins and subsequently of polyolefin products through a first step catalytic dehydrogenation process of paraffin-feedstocks.

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DESCRIPTION OF THE PROCESS, EQUIPMENT, AND OPERATIONS

Production of polymer grade olefins through polymerization reactions usually requires pure monomers as feedstocks to avoid catalyst and solvent contamination and rapid loss of catalyst activity during polymerization. Depending on the type of the downstream utilized polymerization reactor and process (e.g., solution, bulk, suspension, emulsion, gas phase) and the type of the polymer chain propagation reactions (i.e., step-reaction, radical-chain (addition), ionic, coordination) the purity, flowrate, and concentration of the monomers (olefins) may vary in the reactor feed. These feed parameters for the monomer are coupled with the polymerization temperature, pressure, and reactor volume to make for the production of specific polymers within the desired range of molecular weight, structure, and properties (i.e., crystallinity, transparency, viscosity, tensile, and impact strength). Specifically, most of the aforementioned commercially available polyolefins are produced with coordination type polymerization and catalysts. Both stirred bed (slurry-multiphase type) reactors and fluid bed (gas phase type) reactors can be used in coordination polymerization employing coordinated complex catalysts (of Ziegler-Natta type) or supported metal oxide catalysts (3,4).

Hydrocarbon type solvents are used in the slurry process (e.g., hexane, heptane). Commercially established reactors and reactor modifications of both types operate at conditions which usually range from $T = 50–250°C$ and $P = 1–30$ atm (3,4). The exothermic heat of the polymerization reaction is removed by cooling the reactor externally or internally (i.e., by vaporizing a suitable solvent or diluent) or by circulating the unreacted gas through external cooling devices. The above-described coordination type polmerization reaction can utilize hydrogen product from the CDMR within the reactor as a chain transfer agent to reduce the polymer molecular weight (MW) and achieve branching which contributes to a decreased crystallinity product wherein such an end polymer is required. Moreover, the olefin monomer can be diluted with a paraffin or cycloparaffin during the polymerization in both types of reactors mentioned above. The proposed processes seek to utilize as part of the diluent or solvent in the polymerization reactor the unreacted (non-consumed) paraffin from the CDMR (e.g., propane for polypropylene, ethane for polyethylene, n-butane for poly(butene-1, etc.) to increase the process efficacy and economy. The unreacted paraffins can remove the exothermic heat of polymerization by vaporization at the reaction conditions. As an example, propane and propylene have low boiling points and under usual polymerization conditions (25–35 atm, 55–70°C) they can be transferred from the liquid to the gas phase through boiling. Mixing with a higher paraffin such as hexane or heptane in the slurry process is also possible in order to increase the solvent efficiency towards the formed polymer and promote mixing in the reactor. By utilizing propane in the polypropylene reactor, the propane/propylene separation cost before polymerization can be eliminated. Further, the use of propane or the corresponding higher carbon paraffins (e.g., butane, pentane) as solvents in polymerization, minimizes the use of higher priced organic solvents and provides an environmentally benign process modification. However, the non-utilized propane or higher carbon paraffins exiting from the PR have to be recycled into the CDMR in order to keep the operation cost low and the continuous production of propylene or higher olefin monomers as shown in Fig. 1 below. Thus, the solvent-like initial paraffin needs to be separated from the unreacted olefin at the top exit of the polymerization reactor. The proposed separator/permeator (E) as shown in the flow chart of Fig. 1 can operate based on dense or nanoporous solid type polymer reactive membranes, or liquid membranes, containing activated metal ions such as Cu (copper), Ag (silver), Zn (zinc), Cr (chromium), Fe (iron), Ni (nickel), Co (cobalt). These ions have a degree of affinity to form a transporting complex with the permeating olefin (e.g., propylene, ethylene) and to facilitate its transport via the membrane. Moreover, facilitated transport of olefins via metal coated and metal-ion exchange membranes can be also used as separation candidates in the separator E (5,6). The described membrane based separation processes compete well energetically and economically with currently applied separation techniques such as the low temperature hydrocarbon distillation. Furthermore, our long term goal is the development of more stable membranes to perform

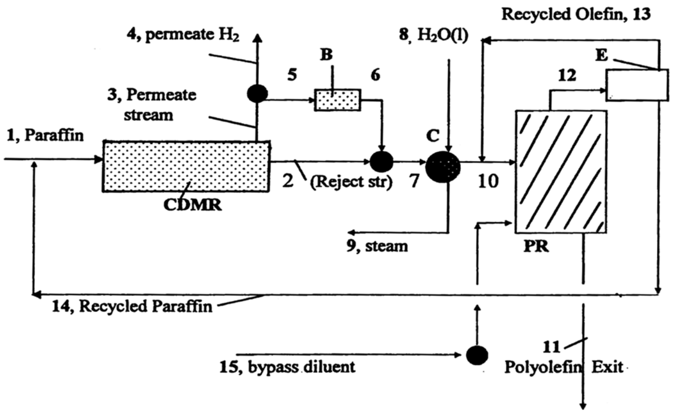

FIG. 1. Flow chart of the new production process for propane to propylene to polypropylene conversion (with a separate hydrogen generation stream from the dehydrogenation reactor). -CDMR: Catalytic Dehydrogenation Membrane Reactor, -PR: Polymerization Reactor, -C: Heat Exchanger, -E: Membrane Permeator/Separator, -B: Pressure compressor. - ●: Ball (Flow) Valves.

this separation. Such new membranes can be based on composite metal-polymer, metal-inorganic, or polymer-inorganic materials, stable at higher temperatures and pressures for the separation of olefins (2,7–13).

Key variables for the consecutive PR are the molar flowrate (throughput) and concentration of the olefinic monomer stream exiting from the CDMR. These parameters together with the reaction conditions (i.e., temperature, pressure, reactor volume, solvent/diluent type, catalyst type, and reaction efficiency) define the rate of monomer (e.g., propylene) consumption, which in turn affects the degree of polymerization, molecular weight, structure, and density of the formed polymer. Use of membrane reactors (permreactors) as dehydrogenators provides beneficial increases in paraffin (e.g., propane) conversion and olefinic monomer (e.g., propylene) yield per reactant (propane) pass. This beneficial effect contributes to subsequent increases in polypropylene yields in the consecutive PR. Another benefit of using the CDMR is the supply of regulated mixtures of propylene, propane, and hydrogen in the polymerization (which make for the monomer, diluent, and chain transfer agent respectively) by adjusting the reaction conditions in the dehydrogenator. As an example, an increase in dehydrogenation temperature or a decrease in pressure will increase the amount of propylene at the exit of the dehydrogenation reactor. Special emphasis will be given subsequently on the design and operation of the CDMR, by describing analytical experimental sample studies on catalytic propane dehydrogenation reactions (Fig. 1). The hydrogen (H_2) gas which permeates via the membranes in the CDMR can be used in several applications when it is utilized as a separate stream. These include direct feed as fuel in hydrogen based fuel cells, in chemical synthesis, and other energy applications (7–13).

PROCESS DESIGN, MODELING AND ANALYSIS

Membrane Reactor/CDMR Modeling

Detailed experiments, modeling, and design analysis of catalytic membrane reactors for propane and other alkane dehydrogenation reactions have been reported in earlier communications (7,8,10,12,13). There are also reports on the ethane, butane (n- and i- monomers), and higher hydrocarbon dehydrogenation reactions and on related new processes (14–16). According to Ziaka and co-workers (7,8,10,12,13), on the propane dehydrogenation reaction to propylene, different catalytic membrane reactors were made and tested in variable composition propane streams, by using Pt-Mg catalysts (magnesium enriched platinum catalysts) and alumina based mesoporous membranes (40–50 Å pore size, 5 μm thickness in the inner most permselective layer). A one-dimensional model was developed and tested for the CDMR by integrating the mass conservation equations for the reactive species along the fixed-bed plug flow reactor length (z). Isothermal and steady state conditions are assumed. The model consists of a set of equations representing the catalyst bearing side (reaction side) and the gas permeate side created by the mesoporous alumina membrane, as shown below (7,8): Mass balances in the reaction side are as follows:

$$\mathrm{dX^{HC}/dz} = (\pi \mathrm{d}_T^2/4n^{\mathrm{R}}_{\mathrm{HCo}})\rho_{\mathrm{B}}\mathrm{R_{HC}} - (2\pi/\mathrm{n^R_{HCo}})\mathrm{P_{HC,e}}[(p^R_{HC} - p^P_{HC})/\ln(\mathrm{r_T}/\mathrm{r_{T+t}})] \tag{1}$$

with: $\mathrm{R_{HC}} = -\mathrm{R_1}$ for HC = paraffin, $\mathrm{R_{HC}} = \mathrm{R_1}$ for HC = olefinand $\mathrm{d_T}$, $\mathrm{r_T}$, $\mathrm{r_{T+t}}$, are the inner reactor diameter in reaction side, the inner reactor radius in the reaction side, and the inner the reactor radius plus the membrane thickness respectively.

$\mathrm{n^R_{jo}}$, $\mathrm{n^P_{jo}}$, ρ_{B}, are the molar flow rate of reactant j at the reaction and permeation side inlets, and the catalyst bed density, respectively. $\mathrm{P_{j,e}}$ (gmol/h.atm.cm), $\mathrm{p^R_j}$, $\mathrm{p^P_j}$, are the effective permeability through the membrane of species j, and the partial pressures of j in the reaction (R) and permeation (P) sides respectively. $\mathrm{R_j}$ is the rate of dehydrogenation reaction which in the general simplified case is given as:

$$\mathrm{R_1} = \mathrm{k_1}\{[C_nH_{2n+2}] - (1/K_{eq})[C_nH_{2n}][H_2]\} \tag{2}$$

with $\mathrm{k_1}$ and $\mathrm{K_{eq}}$ being the rate of the forward reaction and the equilibrium reaction constant, respectively. Also the remaining mass balance for the hydrogen product becomes:

$$\mathrm{dX^{H2}/dz} = (\pi\mathrm{d_T^2}/4\mathrm{n^R_{HCo}})\rho_{\mathrm{B}}\mathrm{R_{H2}} - (2\pi/\mathrm{n^R_{HCo}})\mathrm{P_{H2,e}}[(\mathrm{p^R_{H2}} - \mathrm{p^P_{H2}})/\ln(\mathrm{r_T}/\mathrm{r_{T+t}})] \tag{3}$$

with: $\mathrm{R_{H2}} = \mathrm{R_1}$

The total pressure drop $\mathrm{P^R_T}$ along the fixed catalyst bed (reaction side) is given by the general one-dimensional equation:

$$\mathrm{dP^R_T/dz} = -(2\ \mathrm{f}\ \rho_{\mathrm{g}}\ \mathrm{u_s^2}/\mathrm{g_c}\ \mathrm{d_p}) \tag{4}$$

with f, ρ_{g}, $\mathrm{u_s}$, $\mathrm{g_c}$ (g/h^2.cm.atm), $\mathrm{d_p}$ to be the dimensionless friction factor along the bed of catalyst particles, the gas density, superficial gas velocity, conversion factor, and equivalent particle diameter, respectively. Equations (1) to (4) are complemented by the inlet conditions:

$$\text{At z} = 0 \text{ (reactor inlet):} \qquad \mathrm{X}^j = 0, \qquad \mathrm{P^R_T} = \mathrm{P^R_{To}}$$

For the permeating species j in the empty external conduit (permeate side) the general equations are given below: Mass balances in the permeate side:

$$\mathrm{dn}^{\mathrm{P}}_j/\mathrm{dz} = -(2\pi\mathrm{P}_{j,e})[(\mathrm{p}^{\mathrm{R}}_j - \mathrm{p}^{\mathrm{P}}_j)/\ln(r_{\mathrm{T}}/r_{\mathrm{T+t}})] \tag{5}$$

The total pressure drop balance in the permeate side, assumes an empty permeable reactor shell. Further, the gas flow is assumed laminar-incompressible which follows the Hagen-Poiseuille equation in this side, as given below:

$$\mathrm{dP_T^P/dz = -[128\ R\ T\ \mu_m\ n_T^P/\pi(d_{TO} - d_{T+t})^4 P_T^P\ g_c]} \quad (6)$$

with the inlet conditions: at $z = 0$ (inlet): $n_j^P = n_{jo}^P$, $P_T^P = P_{To}^P$

with μ_m, d_{TO}, d_{T+t}, being the viscosity of the gas mixture, the overall outer reactor diameter wherein the membrane is enclosed (reaction plus permeate sides), and the inner tube diameter including the thickness of the membrane; T and R are the respective reactor temperature in K, and the gas constant in atm.cm^3/gmol.K, respectively. The set of equations described above is integrated numerically and solved to obtain the species conversions, molar flow rates, and pressure values along the reactor length z, and their final values at the two CDMR exits.

In the case in which the membrane material in the CDMR consists of a metal membrane such as palladium, palladium-silver, or palladium-platinum alloys (11), the driving force for the single hydrogen atom permeation between the reaction and permeation sides in the above equations becomes as follows, based on hydrogen atom solution and transport across the metal lattice: $[(p^R H)^{0.5} - (p^P H)^{0.5}]$.

Polymerization Reactor/PR Modeling

For the polymerization reactor (PR), we will apply the assumption of using a fluidized bed instead of an agitated well stirred bed which will lead to expressions of two phase type models for the mass continuity equations. The bubble-emulsion two phase type models describe flow and reaction along the bed height (17), with the following equations:

$$\text{Bubble phase: } f_b U_b (dC_{Ab}/dL) + k_i (C_{Ab} - C_{Ae}) + R_A \rho_b f_b = 0 \quad (7)$$

$$\text{Emulsion phase: } f_e U_e (dC_{Ae}/dL) - k_i (C_{Ab} - C_{Ae}) - f_e D_e (d^2 C_{Ae}/dL^2) + R_A \rho_e (1 - f_b) = 0 \quad (8)$$

The concentration of the monomer in the gas phase exiting from the polymerization reactor PR is given as follows:

$$U_s C_A = (f_b U_b C_{Ab}) + (f_e U_e C_{Ae}) \quad (9)$$

with the boundary conditions: Bubble phase, $L = 0$

$C_{Ab} = (C_A)_i$

Emulsion phase, $L = 0$ $\quad -D_e (dC_{Ae}/dL) = u_e (C_{Ai} - C_{Ae})$

$z = L$ $\quad dC_{Ae}/dL = 0$ (10)

where f_b is the bubble bed-volume fraction, U_b the bubble phase velocity, k_i(m^3/m$_b^3$ hr) the coefficient of interchange, ρ_b the bulk density of the bubble phase, R_A is the rate expression for the polymerization reaction with propylene as monomer A; C_{Ab}, C_{Ae}, are concentrations of the monomer in bubble and emulsion phases, respectively. Also, f_e is the emulsion gas bed-volume fraction, U_e is the interstitial velocity of emulsion gas, U_s is the superficial total bed velocity, ρ_e the bulk density of the emulsion phase, D_e the effective diffusivity for transport in the emulsion phase (17). The fluidized bed usually can achieve operation at isothermal conditions and thus no heat balance is needed in the PR. Such two phase models have been developed, analyzed, and tested by several investigators since 1960s (18,19). The models are able to predict the exit conversion (or concentration) of the monomer (e.g., propylene) and the necessary bed height or amount of catalyst used, together with the mass and heat transfer coefficients between the different phases. For example, if a first order kinetics is assumed for propylene polymerization in the PR, the final derived vertical concentration variation from the above equations becomes:

$$-U_b (dC_{Ab}/dL) = K_R C_{Ab}$$

which after integration over the bed height L_t becomes:

$$1 - X_A = \exp(-K_R L_t / U_b) \quad (11)$$

Detailed analysis of the PR operation and yield is the subject of continuous work.

The permeability of the polymer-metal or other composite type membranes used in permeator E can vary over a wide range, depending on the preparation of the polymer membrane solution and the membrane treatment, drying, casting, and deposition on support conditions. As an example, the permeability of a 2 µm thickness membrane can vary from $2 \times 10^{-9}\,\mathrm{cm^3 \cdot cm^{-1} \cdot s^{-1} \cdot cmHg^{-1}}$ for a propylene-propane mixture to $4 \times 10^{-9}\,\mathrm{cm^3 \cdot cm^{-1} \cdot s^{-1} \cdot cmHg^{-1}}$ for an ethylene-ethane mixture at 25°C, according to the values reported by Kim and co-workers (20). The corresponding reported maximum attainable selectivities (ratios of permeabilities) vary from 8:1 for the ethylene-ethane mixture to 10:1 for the propylene-propane mixture. This membrane was based on a copper/poly(vinyl pyrrolidone) composite membrane stabilized with trimethyl phosphite and deposited on a porous asymmetric polysulfone support (20). An Ag$^+$ enriched sulfonated polyphenylene oxide membrane was reported by Leblanc et al. (21) which was used in ethylene-ethane separation with a 288:1 selectivity for ethylene. Use of cuprous diketonate in an a-methylstyrene solvent (and not as membrane) was reported by Ho et al. (6) for olefin separation. Selectivities of 17:1 for an ethylene-ethane mixture to 10:1 for a propylene-propane mixture were reported based on a chemical absorption mechanism. Use of copper-I chloride on a polystyrene resin derived from amino groups yielded a 5.9:1 ethylene-ethane selectivity based on chemisorption, as reported by Hirai et al. (22).

RESULTS AND DISCUSSION

The plots below refer to permeation and reaction data for the propane dehydrogenation reaction in mesoporous alumina membrane based reactors (7,8,10,12,13) packed with catalyst particles of about 2–3 mm diameter (FBP configuration: fixed bed permreactor). Some of the alumina membrane tubes may have additionally modified with a catalytic Pt, Mg based metal solution (CFBP configuration: catalytic fixed bed permreactor) for better catalytic and permeation activity. These experimental results refer to the CDMR reactor operation which is shown in the process chart of Fig. 1.

Figure 2, refers to the permeability of the reactive and inert gases through the alumina membranes at 200°C for various transmembrane pressure drops. The catalytic modification of the blank alumina membrane with 0.2 g of catalyst (Pt-Mg solution) by an incipient wetness impregnation technique, resulted in lower permeabilities as shown in the plot. The drop in permeability by impregnation was more than two folds. Experiments with a higher catalytic load modification in the membrane resulted to a higher drop in permeability of all gases. Assuming a $d = 5\,\mu m$ thickness membrane, the permeability of propylene in the catalytically modified membrane, from Fig. 2, was calculated at about $1.1 \times 10^{-5}\,cm^3 \cdot cm^{-1} \cdot s^{-1} \cdot cmHg^{-1}$. The permeability of propane is very close to this of propylene, with that of hydrogen to be higher at about: $4.3 \times 10^{-5}\,cm^3 \cdot cm^{-1} \cdot s^{-1} \cdot cmHg^{-1}$ for the same membrane. Figure 3, refers to the kinetic study of the catalyst used in the CDMR operation, by measuring the yield to propylene product as a function of the reactor residence time (V_r/n_{To}) and the temperature (T). Vr is in cm^3 and n_{To} in cm^3/s. n_{To} (the total flowrate at the reaction side inlet), was measured with a wet bubblemeter located after the exit of the reaction system. The composition of the species at the exit mixture and in the inlet of the reactors was measured by using a mass spectrometer working under high vacuum. High vacuum was obtained using an interconnected turbomolecular pump. More details on the experimental flow apparatus and procedures are available elsewhere (8). The permreactor was also utilized by closing the valves in the permeate side and by operating it with a single inlet and outlet both located in the catalyst reaction side. This operation is similar to a plug flow tubular reactor (PFR) with no permeation effect. This is the configuration applied to obtain the results of Fig. 3. The amount of catalyst particles was about 0.7 g which was a 5% Pt/γ-Al_2O_3 enriched with Mg for better deactivation stability. Mg was added in the particles as $Mg(NO_3)_2 \cdot 6H_2O$ in a NH_4OH solution by dry impregnation. The composition of the feed mixture was $C_3H_8:H_2 = 1:0.2$ and the pressure in the reaction side was maintained at 2 psig. The hydrogen gas was added in the feed to suppress the coke formation on the catalyst, especially at the inlet of the reactor. The experiment with the residence time variation was repeated at several temperatures in the range of 480–625°C. In the so-called low temperature range of 480–540°C no significant

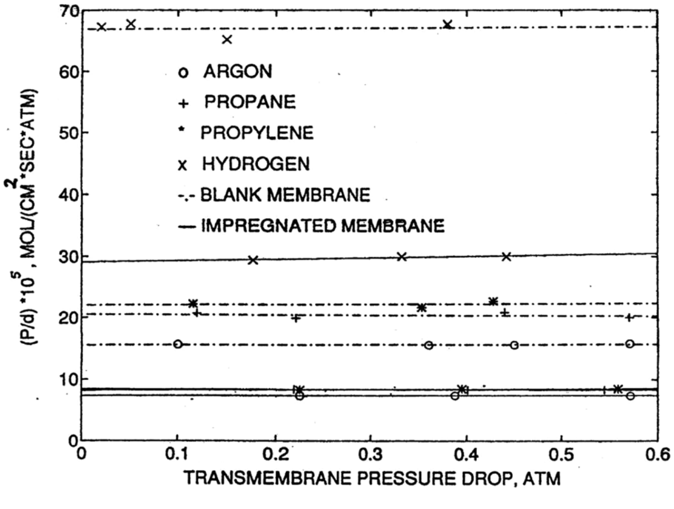

FIG. 2. Permeability over membrane thickness (P/d), versus transmembrane pressure drop for various gases; $T = 200°C$, membrane impregnation with 0.2 grams of catalyst.

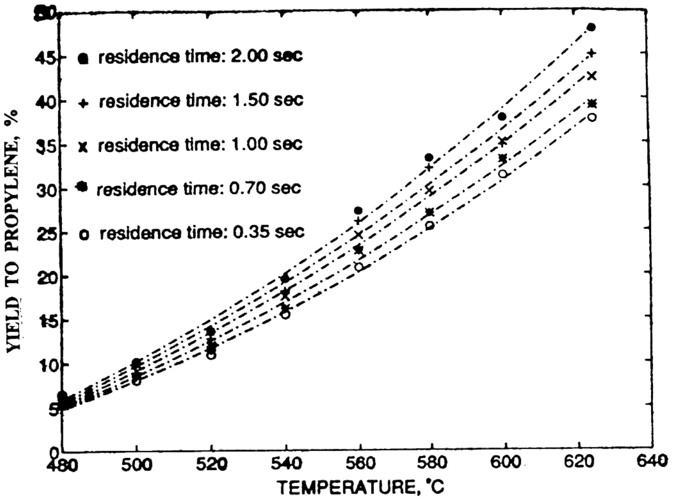

FIG. 3. Propylene yield versus reaction temperature at various PFR-reactor residence times. Reactor pressure (P_T^R) = 2 psig.

amounts of byproducts were detected with propylene being the main hydrocarbon product exiting from the reactor. However, at the higher temperature range (560–625°C), ethylene and methane were also detected as dehydrogenation byproducts which were coming from the direct decomposition (cracking) of propane (Eq. 13, below). The product distribution is plotted in Fig. 4, for the 2 sec residence time case. The lines passing through the experimental points in Fig. 4, are simulation results obtained by use of the PFR model by a combined integration and non-linear data regression technique, based on numerical mathematical library routines (IMSL library). Based on the data of these plots the kinetic constants for the reactions occurring in the catalyst were calculated and used later in the CDMR modeling (8). In this work a third reaction was also considered for interpreting the kinetic data, that is the recombination of propane with methane to yield ethylene and hydrogen (Eq. 14, below). These reactions are written below:

$$C_3H_8 = C_3H_6 + H_2, \quad \text{with}$$

$$(\Delta H^o_{298} = 124.3\,\mathrm{kJ/mol}), \quad k_{r1} = 17.848 \times 10^7 \exp(-29,048/RT), \quad (12)$$

$$\text{Also,} \quad C_3H_8 \rightarrow C_2H_4 + CH_4, \quad (13)$$

$$\text{and,} \quad C_3H_8 + CH_4 \rightarrow 2C_2H_4 + 2H_2, \quad (14)$$

the main olefin hydrocarbons produced in the CDMR, propylene and ethylene, can be used in the next polymerization reactor PR for PP, PE, homopolymer, or copolymer production. The flow chart of the new process including the reaction vessels under review and the flow lines are shown in detail in Fig. 1 above. The CDMR can be an inorganic based permreactor utilizing membranes similar to the ones described above. A tube/shell configuration can be assumed as this is described in the model above. The tubeside is filled with catalyst particles while the inorganic membrane can be blank (FBP: fixed bed permreactor) or catalytic (CFBP: catalytic fixed bed permreactor). The inorganic membrane can be assumed to be of mesoporous or microporous structure made by alumina, titania, silica, zirconia type oxides, and more permselective to hydrogen than to olefins and paraffins as shown in Fig. 2 above (7–13,16). Moreover, metal dispersed inorganic or inorganic-metal composite type membranes can be used to enhance the hydrogen separation factor and increase the catalytic propane conversion. Such micro-metallic based membranes can act also as dehydrogenation catalysts. The reject feedside and permeate side streams (streams 2 and 3 in Fig.1) can be combined in the downstream of the CDMR into a single stream (stream 7) and after proper cooling at the polymerization temperature by flowing through the exchanger C, can be fed in the inlet of the PR (stream 10). The compressor B can be used in the permeate stream (streams 3, 5, and 6) to increase its pressure at the pressure level of the reject exit stream 2. The permeate stream 3 is rich in hydrogen but also may contain substantial amounts of propylene and unreacted propane as well as permeate ethylene and methane byproducts when the CDMR operates at higher temperatures. Increases in paraffin (e.g., propane) conversion and olefin (e.g., propylene) yield at the permreactor exit are due to the equilibrium shift of the reaction (12) towards the product side which is caused by the permeation of mainly hydrogen and olefins through the membrane walls. Olefin (e.g., propylene, ethylene) yield increases by use of permreactors are translated into a richer olefin feed than the one obtained by the use/operation of the fixed bed (no permeation) plug flow reactor (PFR). This effect in turn results in higher polymer (e.g., polypropylene) yields in the adjacent polymerization reactor. Both fluid-bed and stirred bed coordination type polymer reactors can be used to convert the exit olefin mixture into a polyolefin. The described process configuration is suitable for the production of polyolefins (such as polypropylene, polyethylene, polybutylene) with medium to low molecular weight due to the strong presence of hydrogen as a chain transfer agent in the polymerization reactor feed. High paraffin conversions and olefin yields are desirable in order to increase the polymer production efficiency per pass of paraffin feed (e.g., lb/hr of polypropylene produced over kmol/hr of propane feed). Higher dehydrogenation temperatures and lower pressures are necessary conditions in the CDMR to increase paraffin conversion and olefin yield, with the temperature to stay usually below 550°C for pure olefin production. The permreactor in Fig.1 can be replaced by a conventional fixed-bed (non-permeable) catalytic reactor

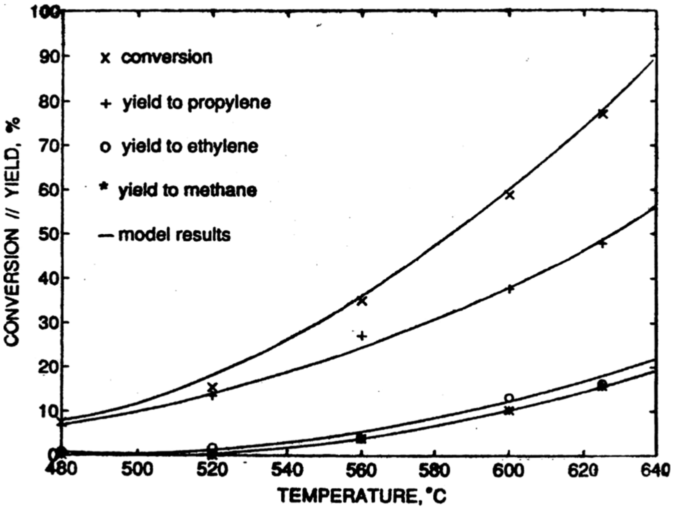

FIG. 4. Propane conversion and propylene, ethylene, and methane yields in the PFR reactor versus temperature; 2 sec residence time, $P^R_T = 2$ psig, feed ratio: C_3H_8:H_2 = 1:0.20.

(a PFR dehydrogenator) for the production of similar propylene-propane-hydrogen mixtures (7–9,12,13).

Another possible process configuration of Fig. 1 utilizes a metal membrane type CDMR instead of an inorganic or a composite one. This ensures the removal of only pure hydrogen out of the dehydrogenation zone (streams 3 and 4). Various hydrogen permselective metals and metal alloys can be used as permreactor wall materials (i.e., Pd, V, Pd/Ag, Pd/Pt). If no hydrogen is allowed to flow in the reject exit stream 2, the olefin rich feed in the PR is suitable for the production of higher molecular weight polyolefins (usually linear crystalline materials) due to the absence of the chain transfer effect in polymerization. The permeated H_2 from the CDMR can be directed separately as a fuel feed in hydrogen type fuel cells. This consists an efficient use of the separated hydrogen for auxiliary energy usage, such as this in fuel cells (7,11).

Alternatively, if hydrogen is diverted into the reject stream 2 (via streams 5 and 6) the process can again produce polyolefins of controlled MW (molecular weight) due to the chain transfer effect, similarly with the inorganic membrane permreactor described above. The described process designs in Fig. 1 can work as well for the production of propylene-ethylene copolymers when the described permreactors operate at higher reaction temperatures as aforementioned (i.e., Fig. 4). Further, the use of a mixed propane-ethane feed in the initial CDMR will yield dehydrogenated exit streams rich in both propylene and ethylene which can be used for the direct production of block or random copolymers in the PR. Different paraffin flowrates and composition in the feed, and different reaction conditions in the CDMR are controlling the final flowrate and composition of homopolymer or copolymer produced from the polymerization. Further, the process shown in Fig. 1 can be as well applied in the dehydrogenation of higher paraffins (e.g., n-butane, i-butane, 4-methylpentane-1) to yield olefins which can be used for the production of corresponding higher-monomer polyolefins in homopolymer or copolymer state (2,7,16). Figure 5 reports a combined experimental conversion and selectivity data from a catalytic permreactor (CFBP) and a plug flow reactor (PFR) for reaction temperatures between 480–540°C. Use of the CFBP module improves the propylene selectivity and the total propane conversion over the PFR values.

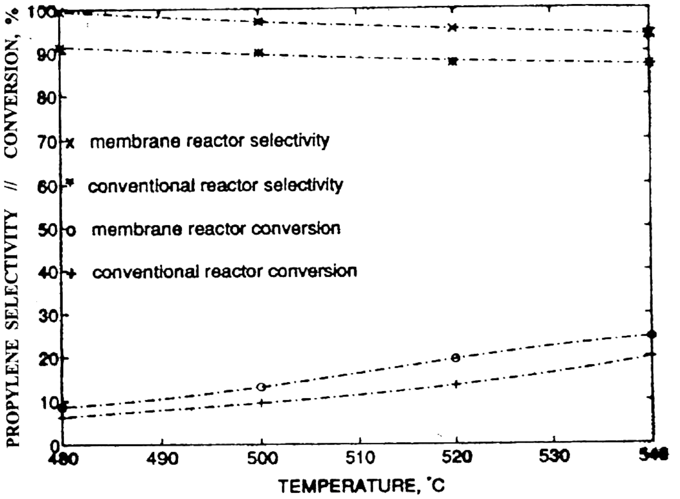

FIG. 5. Propane conversion and selectively to propylene versus temperature in the CFBP and PFR reactors. 2 sec residence time, $P_T^R = 6$ psig, $P_T^P = 3$ psig, lack of sweep gas, feed ratio: C_3H_8:H_2 = 1:0.20.

Figure 6 reports on the yield to propylene for a number of different reactor configurations versus the propylene to propane ratio in the feed. Two types of reactors were applied to the reaction, the FBP and PFR types. The propylene to propane ratio in the reactor feed varies from 0.1–0.43, at $T^R = 560$°C, $P_T^R = 2$ psig, for a 2 sec residence time. In these experimental runs, some hydrogen was added in the reactor feed at the same ratio as the propylene feed, (i.e., $H_2/C_3H_8 = C_3H_6/C_3H_8$). The membrane reactor was operated without sweep gas. The improvement in propylene yield by the use of the CDMR (FBP type) is plotted in comparison with the calculated equilibrium and the conventional PFR yields. The results of the model from the FBP operation, as described above, are also plotted in the same figure in order to depict the improvement in propylene yield. Such type of mixed feed in the first CDMR (or FBP) is obtained during the recycling of the reject propane stream from permeator E, which also contains some non-permeate propylene. As the time on stream increases in the process, the amount of propylene in the mixed feed stream stabilizes until it reaches its steady-state

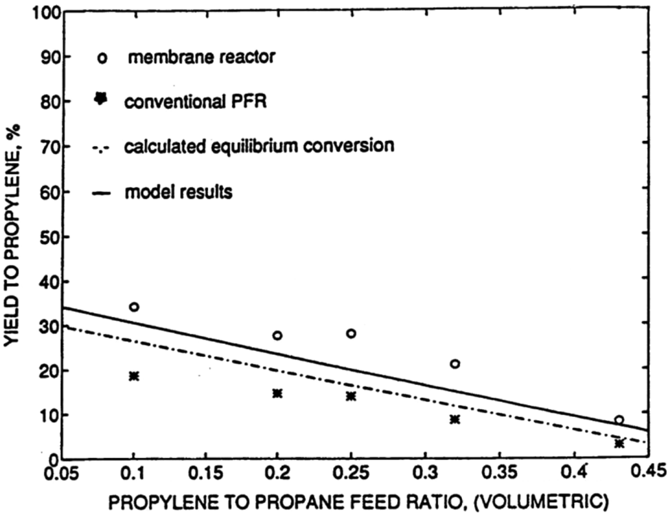

FIG. 6. Yield to propylene versus propylene to propane feed ratio by comparing the FBP, the PFR, and the calculated-equilibrium yield values; $T_r = 560$°C, 2 sec residence time, $P_T^R = 2$ psig, $P_T^P = 0$ psig, lack of sweep gas, feed ratio: C_3H_6:C_3H_8 = H_2:C_3H_8.

concentration. We can further assume that there is a direct proportion between the produced polypropylene yield in the PR and the propylene yield in the FBP. Thus, the measured propylene yield improvements at the FBP exit can be translated into the respective polypropylene yield improvements for the two different reactors and the equilibrium yields shown in Fig. 6.

Finally, a projected design plot is shown in Fig. 7, which assumes different values for the design parameter K_R/U_b of the fluidized bed reactor according to Eq. (11). K_R (1/s) is a lump kinetic constant and U_b the bubble rising velocity (cm/s). The simplified plot assumes direct first order propylene consumption kinetics, and shows the bed height (L_t, cm) required to obtain a fixed PP yield (%) in the PR. Values for the rate constants of the propylene to polypropylene polymerization, according to the pertinent literature, are reported. Supported metal oxides catalysts (i.e., $TiCl_3$, $TiCl_4$, $MgCl_2$) increase propylene conversion by 1–1.5 orders of magnitude in comparison with unsupported Ziegler-Natta catalysts (e.g., conventional $TiCl_3$, $TiCl_4$ catalysts). By utilizing the propylene polymerization data reported by Soga and Shiono in 1988 (23), values for the rate constants of supported catalysts can be obtained. The rate constants are calculated based on a first-order kinetics for the rate-time profiles of the polymerization of propylene for various supported catalysts. Using the first-order polymerization decay approximation as described by Galli et al. in 1981 (24), values for kp are calculated. A value of kp = 2.06 (kg-PP/g-Ti.h^2) was calculated for the $TiCl_4$/EB/$MgCl_2$ catalyst and this of kp = 1.83 (kg-PP/g-Ti.h^2) for the $TiCl_4$/DNBP/$MgCl_2$ catalyst. The calculated polymerization rate constants (kp) are lumped together with the resistances of the fluid-bed reactor (e.g., the Kunii and Levenspiel model) (18) to yield values for the K_R which is the combined kinetic rate constant for the fluidized type propylene polymerization reaction as shown in Fig. 7.

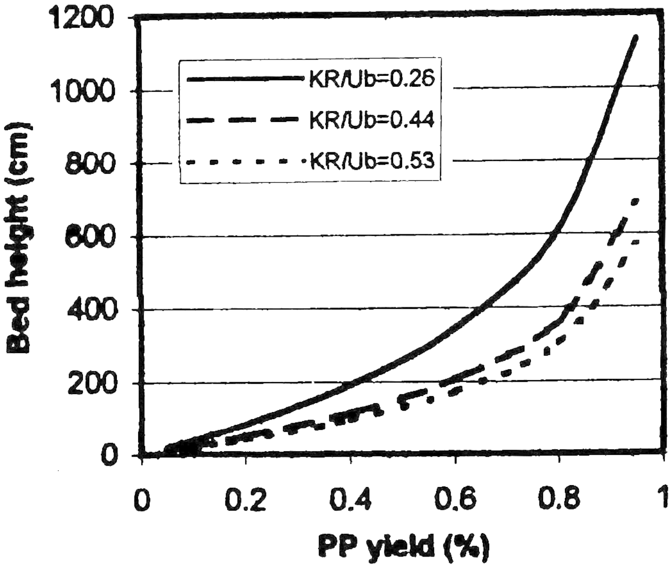

FIG. 7. Estimated polypropylene yield variation at various fluid bed heights (cm), in the PR (polymerization reactor) for different K_R/U_b values.

In the following table (Table 1), we briefly summarize the effect of the type of the dehydrogenation reactor used for propylene production and the hydrogen chain transfer effect, to the molecular weight and the chemical structure characteristics of the produced polyolefin (i.e., polypropylene) polymers (7,8,10).

High MW polypropylene (homolpolymer: pure polymer) is a crystalline dense material with a high T_m (melting point temperature) and mainly of isotactic (linear) stereoregular configuration. On the contrary, low to medium MW polypropylene (caused by chain transfer agents such as hydrogen) and copolymerization of propylene with ethylene decreases the crystallinity and linearity of the material and shifts it towards the amorphous and branched domain. Block copolymers of propylene with ethylene have a higher degree of crystallinity than random copolymers due to their ordered structure.

Some additional comments on the described integrated membrane processes are as follows:

One primary focus area of this technology is in the use of alternative solvents and reaction conditions for environmentally benign process and green chemistry.

This selection is supported by the alternative reaction conditions used in the polymerization vessels to polymerize the produced olefins into polyolefins. These conditions utilize non-toxic hydrocarbons as solvents in the process. Thus, the process achieves substantial pollution reduction. Also it utilizes the product hydrogen inherently, as a chain transfer agent to control nicely the degree of polymerization in the produced phasma of polymers (several polyolefin products). The produced final materials are polypropylene, polyethylene, poly(butene-1), polyisobutylene, and other polymers. They can be produced as pure polymers or copolymers depending on the feed composition of the paraffins and the resulting olefin products.

Another important focus area of this technology is in the use of alternativesynthetic pathways for environmentally benign (i.e., green) chemistry.

The use of dehydrogenation reaction routes in this process for the production of olefins from paraffins is an alternative pathway from the conventional cracking and refining of paraffins which are more energy demanding. This technology also reduces process steps by combining reaction and separation in a single reactor by using permreactors as alternative reactors for hydrogen production and separation and for olefin purification. Also, the polymerization occurs with alternative reaction pathways and chemistry routes, and with paraffin hydrocarbon recycling which makes for a more environmentally benign and less toxic

TABLE 1
Effect of reactor and membrane type on the polymer characteristics

Parameters	DRT	DRP	MW of	(PP)	(PP-PE)
Type of Dehydr.	°C	atm	Polymer	Homopolymer	Copolymer
Reactor type					
Inorganic based	<550	1–30	low to medium	Yes	No
Permreactor (CDMR) or conventional catalytic reactor (PFR):	>550	1–30	low to medium	No	Yes
(H_2 present as chain transfer gas in the next PR);					
Metal based	<550	1–30	high	Yes	No
Permreactor (CDMR) (no H_2 present in the next PR);	>550	1–30	high	No	Yes

DRT: Dehydrogenation Reaction Temperature; DRP: Dehydrogenation Reaction Pressure.

and costly process. Thus, the overall process achieves substantial pollution reduction as well.

REMARKS AND CONCLUSIONS

New integrated process designs are described and analyzed for continuous dehydrogenation of paraffin hydrocarbons to olefins and subsequent polymerization to polyolefins (e.g., propane to propylene to polypropylene). The main points of the described processes are the following:

The analyzed technology eliminates the use of toxic organic solvents in polyolefin production. It uses catalytic dehydrogenation effectively instead of thermal cracking or refining. It reduces process steps by combining reaction and separation in a single reactor by using permreactors/(membrane type reactors) as the main reactors for hydrogen-product generation and separation and for olefin purification. Therefore, the operation of those processes by the industry staff becomes safer and more effective.

The release of toxic materials and toxic spills (i.e., toxic/liquid organic solvents and catalysts) by those chemical production processes are eliminated.

The chemistry of the technology involves primarily the endothermic, catalytically assisted dehydrogenation of paraffins into olefins. Use of catalysts such as chromium and platinum is effective in higher olefin yields. The main reactions include dehydrogenation of propane into propylene, also ethane into ethylene, butane into butylenes, and other related ones.

The consecutive reactions occur in gas phase and multiphase type polymerization reactors and involve the efficient polymerization of olefins into polyolefins (i.e., propylene into polypropylene) by the catalytic polymerization activity of coordination type metal catalysts (such as $TiCl_3$ and others).

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