ENVIRONMENTALLY FRIENDLY CHEMICAL SYNTHESIS AND CATALYSIS FOR IMPROVED POLYETHYLENE PRODUCTS

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Summary

Environmentally–friendly polymer processes have been developed for polyethylene product synthesis and catalysis. The developed processes seek ethylene and energy conservation coupled with elimination of toxic and hazardous solvents, catalysts and other byproduct reaction media. Increased polyethylene yields, ethylene recycling within the process, reduction in hazardous waste generation, reduction of process equipment and of capital and operational costs (including monomer and energy costs) are some of the improvements of the new processes. Ethylene can come from a variety of sources including a dehydrogenation membrane reactor which produces increased yields of the valuable monomer. Hydrogen or hydrogen and ethylene separation can occur via the walls of the catalytic dehydrogenation membrane reactor. Related modeling and optimization of the multiphase polyethylene reactor in the downstream is also underway to describe its functionality, operational range, capacity and polymer selectivity. The models used can simulate relevant acquired laboratory and industrial data. They describe numerically reaction, transport, recycling, polymerization, and polymer separation operations in the polyethylene reactor. Relative compositions of feedstock ethylene diluted with other components can be used in this reactor to produce polyethylene of variable molecular weight, structure, and tensile properties. Moreover, some forms of copolymers can be also produced directly during ethylene polymerization by adjusting the operation conditions and temperature of the upstream membrane dehydrogenator.

Process and Materials Description

This new communication reports current research analysis on reaction-separation systems for polymer-grade ethylene production via initial ethane based dehydrogenation reactions [1-4]. We present new process designs based on ethane dehydrogenation processes including work in design of experiments, operation and best parameter selection and optimization of such systems. These processes are of current significance in ethylene processing and conversion to valuable chemicals such as polyethylene and its copolymers [1-4,6]. This is because of the unique design characteristics of the examined reactor-separator systems to perform multiple operations. Among others, permeable catalytic carriers (membrane reactors) can be utilized by applying the equilibrium shift principles in ethane conversion and ethylene yield through the rapid removal of permselective species (mainly hydrogen) out of the catalyst and reaction zones.

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In the downstream, the ethylene products are used for direct polyethylene production through successive polymerization reactions [1-4,6].

Further, the work targets to develop efficient reactors and systems with increased processing capacity, conversion and selectivity, separation, and additional utilization (e.g., via recycling and side-feed flows) of primary and secondary ethane based streams. Ethane can come from a variety of sources including fossil and renewable resources after passing the proper purification steps and is directed in the entrance of the catalytic dehydrogenator. There is a substantial effort today to increase conversion of renewable ethane feedstocks into valuable end products such as polymers, from an engineering, economic, and environmental point of view [1,6].

Various combinations of permselective materials, including metals, inorganics, and composites can be used if a membrane reactor or a membrane permeator is selected for the operation. In these cases the hydrogen, or hydrogen and ethylene separation from the ethylene-hydrogen-unreacted ethane mixture is the operation that needs to be optimized in terms of the separative products yield and selectivity [1-4,8-11].

The use of such integrated systems of membrane reactors and permeators in comparison with previous impermeable-tubular reactors and separators, are well suited for low molecular weight alkane dehydrogenation reactions for production and separation of the corresponding olefins. These can be also considered sample reactions for stoichiometric hydrogen production from low-carbon alkane molecules. According to the proposed integration, product H_2 can be recovered/separated via the membranes from ethylene and ethane molecules and used in successive chemical synthesis (e.g., various hydrogenations) or as clean additive fuel in power generation equipment, such as turbines and fuel cells [1,6,10,11]. PEM and Alkaline fuel cells as example, are well suited to operate with the separated hydrogen from the membranes, and even SOFCs can operate within an acceptable thermal framework [6]. Further, the separated ethylene can be fed in polymerization reactors (such as coordination-catalysis type vessels) for direct polyethylene production, [7].

Related modeling of such multifunctional membrane dehydrogenation and polymerization reactors for the described applications is underway to describe their function, operational range, capacity, and product yield and selectivity. The models used can simulate relevant acquired laboratory and industrial data and predict the conditions for best dehydrogenator, separator, and polymerization reactor operation by variation of the process key-intrinsic parameters [1,6,11].

Kinetic and transport parameters used in the reaction/separation modeling can be obtained experimentally by separate kinetic and transport experiments or calculated by empirical correlations [6-11]. Moreover, the modeling of permeable and tubular reactors shows how the ethane conversion and ethylene yield is affected by varying key-design parameters such as the extent of the catalytic ethane dehydrogenation reaction, the permeability and selectivity factors of the membrane reactor wall material, the magnitude of the equilibrium constant for the dehydrogenation reaction, the ratio of pressures and flowrates of the reactive and inert gases within the catalytic bed and in the external side of the membrane reactor. Variations in the composition of the exit product stream from the dehydrogenator-separator assembly affects the polymerization in the consecutive

reactor and the range of molecular weight, structure, and properties of the produced polyethylene. Moreover, copolymers can be also produced directly in polymerization by adjusting the operational conditions of the catalytic membrane dehydrogenator.

As a conclusion, the proposed membrane based dehydrogenation-polymerization configurations for ethylene and polyethylene production from ethane based streams seek to perform multiple and combined unit operations by using single type or integrated membrane reaction-separation modules. These effects/operations make them advanced in comparison with up to now utilized conventional dehydrogenation reactors. Thus, the introduced membrane catalytic systems project a promising replacement technology for currently utilized ethane to ethylene production reactors (such as crackers or catalytic dehydrogenators) and in conjunction with downstream polyethylene yield reactors. Economic and environmental advantages are also applicable and promising.

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