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Oxidative Coupling of Methane: A Design of Integrated Catalytic processes

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The development and improvement of processes for the selective activation and conversion of methane is one of the enormous challenges in fundamental and applied chemistry. If methane could be chemically converted into value-added substances, this would provide a significant time buffer before the inevitable departure from the use of oil. This would make also the transition to renewable energy sources significantly easier. On the other hand, novel catalysts are economically viable only if they can be used in industrial, large-scale processes. Scaling up from laboratory-scale experiments to industrial scale processes is not simply enlargement of a new catalytic reaction. Instead, many additional phenomena, such as heat and mass transfer, have to be taken into account. Thus, improved modeling, novel reactor geometries and concepts, and realistic cost estimates are required. In this work, modeling, design and the experimental verification of an integrated catalytic process is developed on the basis of the oxidative methane coupling (OCM) process. For this purpose, new reactor concepts and the integrated downstream process are presented. These concepts are embedded in a running research project within the Cluster of Excellence called "Unifying Concepts in Catalysis" - UNICAT, in which the OCM downstream process, the reactor and the catalyst are designed simultaneously. This strategy causes enhanced interactions between catalyst, reactor and the downstream process during the design.

1. Introduction

With a production of 112 Mt/y, Ethylene represents an important feedstock of the Chemical industry. More than 60 % is used for polyethylene and Vinylchlorid. Further synthesis products are Ethylenoxid and Acetaldehyd. The state of the art in ethylene production is via steam cracking of naphtha (Hugill et. al., 2005). Oxidative coupling of methane (OCM) is a promising route for the production of ethylene by utilizing methane, the main constituent of natural gas. OCM is a reaction of two methyl radicals coupled after the abstraction of one hydrogen atom from the methane molecule (Figure 1). This reaction is highly exothermic. The conventional processes are endothermic, energy intensive and low in C2 selectivity, depending on the choice of the feedstock. However, the development of the industrial process still remains in its very early stage with the main efforts focused on the search for a sufficiently selective, active, and stable catalyst. Conventionally, as part of a close collaboration between chemical and process engineering, models for the individual reaction and process steps are used that allow for static and dynamic simulations of the overall process. On the basis of simulations, new process designs are derived and evaluated with respect to their potential for industrial implementation and economic efficiency. For this purpose, model-based cost-estimating procedure for the early design stage has been established.

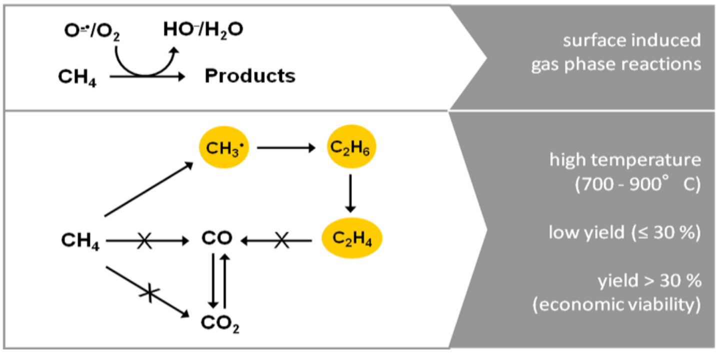

Figure 1: OCM reaction scheme.

In this work, we present the most promising concepts, which are tested by constructing mini-plants as an essential step towards further up-scaling for industrial applications. Furthermore, a central task in this research project concerns the screening of catalysts with respect to activity, stability and selectivity. For catalysts with promising performance, more detailed kinetic studies are being carried out. These investigations started with powder catalysts in order to obtain kinetic parameters for chemical reactions without any inference from heat or mass transfer limitations. For catalysts in homogeneous catalysis, tests are carried out and are expected to allow the design of appropriate reactors and process concepts. The integration of homogeneously catalyzed reactions, catalyst recovery and product isolation within the same process unit offers the advantage of recycling without loss of activity or material. Thus, a mini-plant and reactor set-up configurations are used in order to provide a setting for checking new process concepts and assessing catalyst performance, start-up behavior, recycling of feedstock and economy.

2. Process Concepts and Modified Design Procedure

Several concepts have been proposed for the OCM process in the last two decades. These are e.g. the OXCO Process, the UCC Process, the ARCO Process, the Suzuki Process, the Turek-Schwittay Process, and the Co-generation Process. All of them have a similar structure, high energy demand for product separation and purification in common (Figure 2). The challenge results in a concurrent design and improvement of catalyst, reactor unit, and the downstream process.

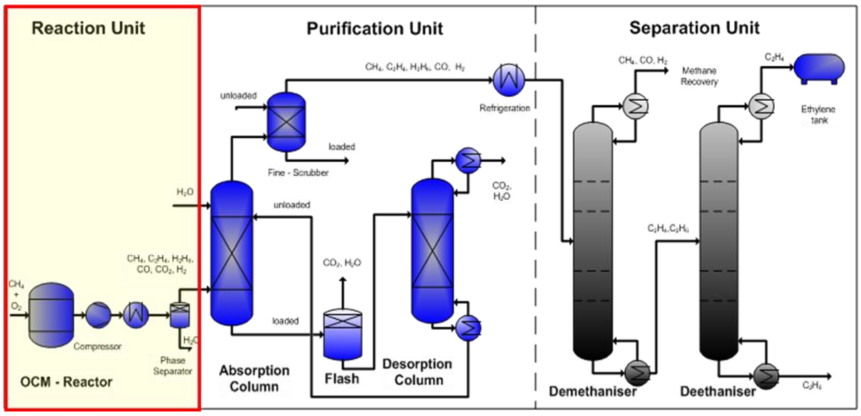

Figure 2: Basic Flowsheet of the OCM Process.

For the process synthesis, the whole OCM Process is divided into three general unit operations: the reaction unit, the purification unit and the separation unit (Figure 2). All of them are linked and investigated simultaneously. Therefore, a design case for each unit has been defined which shares the same range of process and stream conditions. The miniplant technique applied in this research project is a well known technique in the scope of process synthesis in order to obtain fundamental information and an experimental basis. Figure 2 shows also the basic miniplant layouts for each unit. However, due to the simultaneous process design and caused by economical reasons, additional requirements from the downstream are expected for the reaction unit and the catalyst, in particular related to yield, C_2 and CO_2 selectivity, as well as methane conversation rate and dilution concentration. Thus, the design procedure used in this work differs from the conventional one in the sense that the reactor design is first considered as a unique stage (Emets et al., 2006). We firstly focus in those alternatives, which are also relevant for an industrial application such as fixed bed reactor, fluidized bed reactor, as well as membrane reactors and their network applications. Furthermore, in this approach the consideration of the recycle stream is left to last stage (Figure 3).

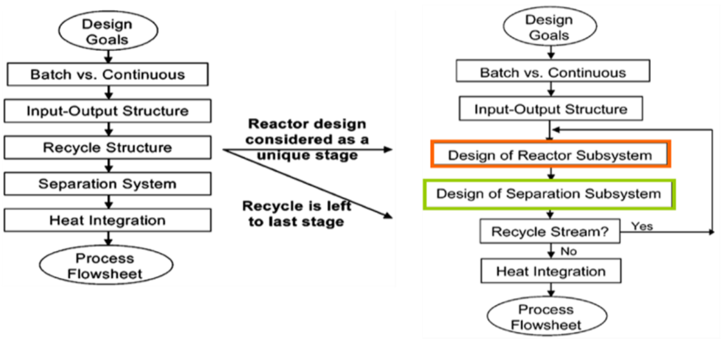

Figure 3: Modified Design Procedure (adapted from Emets et al., 2006).

3. Reactor Concepts and their Performance

Basic reactor types, used commonly in industry are fixed bed reactors, fluidized bed reactors and membrane reactors (Figure 4). The number of such devices in industry varies by orders of magnitute. Fixed bed reactor is the most common reactor type, used in almost all processes. Fluidized bed reactor is widely spread in petrochemical industry for FCC/amoxidation/oxidation reactions for removing huge amounts of heat and recycling and replacing deactivated catalyst. Nevertheless, it is still not well understood, and modeling and scale-up methods are still under development. Membrane reactors are not used so often in the industry because of their complex structure. However, they allow improved feeding policies and removal of some species from the reaction side therefore increasing reactor performance significantly.

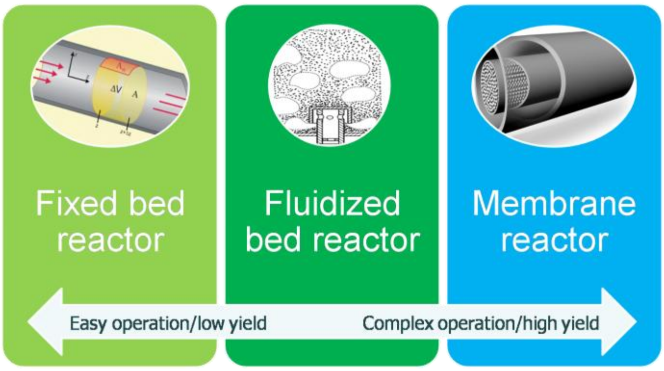

Figure 4: Investigated Reactor Concepts.

However, in this process, dealing with the huge amount of reported kinetic data and different proposed reactor concepts requires an efficient reactor synthesis for the OCM Process. Thus, in this work, new alternative operation modes of the Packed Bed Membrane Reactor (PBMR) are proposed in order to increase the efficiency of the OCM process. These structures have a high potential to improve the process performance in comparison to Fixed Bed Reactors (PFR) and even to a conventional PBMR design structure. The main drawbacks in operating PFR or PBMR have been to find suitable operation policies towards the enhancement of both yield and selectivity at the same time. We present a comparative study of the OCM process performance for those reactors types are presented including three types of catalysts, namely La_2O_3/CaO, Mn/Na_2WO_4/SiO_2 and PbO/Al_2O_3. For this purpose, the effect of oxygen accessibility in the different design structures is investigated. Basically, the new proposed feeding policy structures combine the advantages of PFR and the conventional PBMR so as to get a high yield amount by co-feeding methane and oxygen into the reactor entrance while guaranteeing an acceptable level of selectivity by reducing the accessibility to ethylene and oxygen, in particular, at the reactor end. Moreover, using the potential of the proposed operation mode it is now possible to build a reactor network consisting of the new proposed and the conventional PBMR in order to treat shell side streams, which result from each PBMR structure. Besides, a sensitivity analysis is performed in order to analyze the effect of reactant accessibility in the proposed feeding policy structure. The results are analyzed along with the study of the optimal operating range in order to conceptually design a membrane reactor network towards satisfying economical and industrial considerations in terms of selectivity, one pass yield and methane conversion.

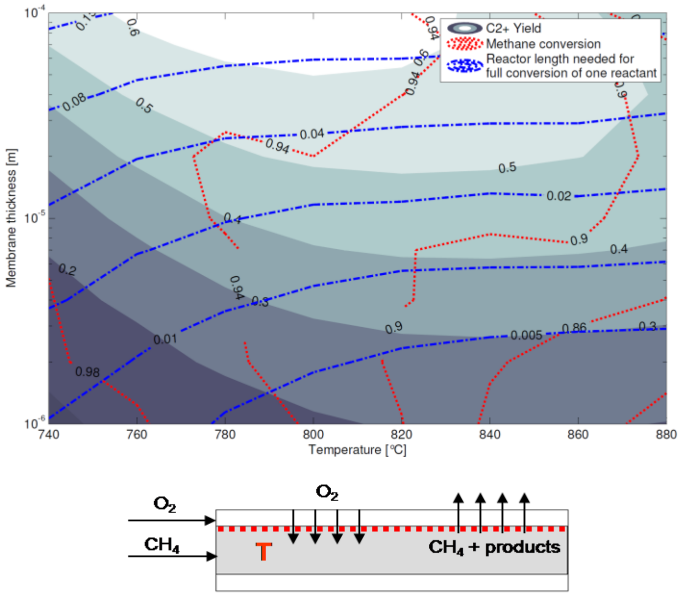

Figure 5: Membrane Reactor Performance Analysis

Figure 5 shows one of such investigations. The optimum feed ratio was applied with a fixed flowrate and temperature and the membrane thickness were manipulated simultaneously. Such manipulation gave overview of reactor operation under different conditions, and showed clearly the areas of highest attainable performance for this reactor type. Furthermore, methane conversion and reactor size corresponding to each operation condition are shown on Figure 5 as well.
In addition, a fluidized bed reactor is investigated as an alternative reactor concept for the OCM. Its advantages are possibility to operate isothermally under severe reaction conditions, and to enable efficient and continuous catalyst replacement or reactivation. Such features are crucial for the OCM, because of the deactivating catalyst and enormous heat effects. In order to resolve the underlying effect of complex hydrodynamics on the transport phenomena and reaction kinetics, this reactor type is investigated by both two-phase models as well as by means of CFD. Furthermore, using results of detailed hydrodynamics coupled with kinetics obtained by CFD it is possible to improve reactor design, and scale-up procedure. In order to validate simulation results, a miniplant scale reactor is being built in our chair. Such reactor is going to be implemented in already existing miniplant scale down streaming unit, in order to investigate the multiple dynamic effects on the global process behavior and performance.

4. Miniplant Technology in the OCM Process

The downstream of the OCM process consists of a phase separation unit, a carbon dioxide removal unit and a product separation unit (Figure 2). The purification unit consists of an amine based absorption process for the carbon dioxide separation. The separation unit consists of a cryogenic distillation for the product separation. Due to the high energy consumption of the cryogenic distillation, the pressure is increased up to 35 bar to increase the boiling point of the hydrocarbons. Considering the limitation by the laboratory conditions, the pressure increase is limited as well. Regarding the idea of using carbon dioxide as an inert gas for the dilution in the OCM reactor, the carbon dioxide removal step becomes even more important in the downstream process. Therefore, the purification section as the first downstream unit is first considered and the carbon dioxide removal is investigated in detail (Figure 6).

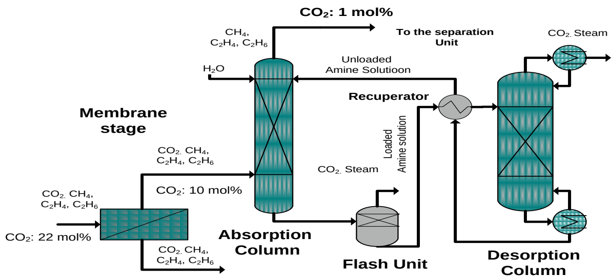

Figure 6: Hybrid Carbon Dioxide Separation Process.

Facing the required purity of the product stream and the lack of an unlimited absorption column, the use of a membrane section for the pre - separation of carbon dioxide was applied successfully. Moreover, carbon dioxide concentrations could be reduced with one and two stage membrane units.

5. Conclusions

The motivating force of this work is to design an alternative process for ethylene production via OCM and that can make the process economically attractive and designed so as to be industrially implemented. Currently, the total project investment, based on total equipment cost (TEC), as well as variable and fixed operating costs, is being evaluated. The feasibility was evaluated in terms of energy savings, CO_2 emission reductions, and costs, in comparison to the separate production of ethylene with conventional OCM technology alone.

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