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Dual-membrane reactor for methane oxidative coupling and dry methane reforming: Reactor integration and process intensification

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ABSTRACT

A novel dual-membrane reactor concept was introduced for integrating the oxidative coupling of methane (OCM) and CO_2 methane reforming (dry reforming) reactors. The OCM reactions occur in a conventional porous packed bed membrane reactor structure and a portion of the undesired produced CO_2 and generated heat are transferred through a molten-carbonate perm-selective membrane and consumed in the adjacent dry methane reforming catalytic bed. This integrated reactor provides a very promising thermal performance by controlling the temperature peak to be below 50 °C in reference to the average operating temperature in the OCM section. This was achieved even for the low methane-to-oxygen ratio 2 by introducing 10% CO_2 as the diluent agent and reactant in this integrated reactor structure. This contributed to the improved selective performance of 32% methane conversion and 25% C_2-yield including 21% C_2H_4-yield in the OCM section which also enhances the performance of the downstream units consequently. Around half of the unconverted methane leaving the OCM section was converted to syngas in the DRM section.

The dual-membrane reactor alone can utilize a significant amount of the carbon dioxide generated in the OCM catalytic bed. In combination with adsorption unit in the downstream of the integrated process, 90% of the produced CO_2 can be recovered and further converted to valuable syngas products. The experimental data, obtained from a mini-plant scale experimental facility, were exploited to verify the performance of the OCM reactor and the CO_2 separation section.

1. Introduction

The growing universal demand for ethylene and the rising cost of oil-based feedstock have forced the licensors to diversify the alternative processes and resources used for ethylene production. In this context, oxidative coupling of methane (OCM) is considered to be a promising alternative process mainly because of the potential of natural gas as a relatively economical feedstock. Similarly, the methane reforming process exploits natural gas resources to produce synthesis gas (syngas) which has a very wide range of applications. Each of these two processes still face some challenges which can however, be turned into advantages if they are properly integrated. For instance, an OCM reactor operates optimally in the range of below 50% methane conversion and even under such conditions, more than 40% of the reacted methane is converted into carbon oxides. This unselective methane conversion cannot be improved by simply using a longer reactor, because even smaller portion of the further converted methane will contribute in producing ethylene and ethane (C_2-Products). As a result, the achievable single pass C_2-yield does not reach over 30%. The energy needed for separating more than half of the inlet methane, which remains unconverted in an OCM reactor, is the main source of operating cost in the downstream units of the OCM process. Moreover, due to the highly exothermic nature of the OCM reactions, hot-spots with serious consequences are formed in the fixed bed catalytic reactor structures. It should be mentioned that injecting an inert diluting gas such as nitrogen to overcome the challenge of hot-spot formation will itself increase the costs of downstream units.

Having considered the challenges of the OCM process, it is also reasonable to look at its potentials for being integrated with other processes. For instance, significant portion of the released heat in an OCM reactor can be exploited in an endothermic methane reforming reactor. In order to analyze this aspect in more detail, it should be highlighted that the quality and quantity of the required energy as well as the ratio of the reforming products (H_2/CO) strongly depend on the type and mechanism of reforming. The resulting H_2/CO ratio is a critical factor in determining the subsequent

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application of the produced syngas. In steam methane reforming, this ratio is around 3, which can be adjusted by using the partial oxidation and water-gas shift reactions to provide the required feed specification (H_2 to CO ratio 2) for methanol production. However, when carbon dioxide is used as a reactant for methane reforming (dry reforming methane; DRM), the resulted syngas product has a low H_2/CO ratio close to 1 which can be preferentially exploited to synthesize other valuable hydrocarbon such as dimethyl ether (DME) [1,2]. DRM can be also combined with steam reforming of methane to provide a desired range of final H_2 to CO ratio [3].

Considering the typical range of operating temperature in an OCM reactor (750–850 °C) and up to 20% carbon dioxide content of its outlet gas stream along with the quantity and quality of the required heat for the DRM reaction ($\Delta H^{\circ}_{298\,K} = 247.9\,kJ\ mol^{-1}$), a multi-aspects integration of the highly exothermic OCM and endothermic DRM fits the characteristics of these processes.

In the simplest integrated process structure, some parts of the released heat in the OCM reactor are consumed in the reforming reactor. In the downstream of the integrated process, using an appropriate separation unit such as adsorption allows an efficient separation of the methane and carbon dioxide as the reactants of the DRM. Here in this paper, the focus will be on the reactor section where the procedure for developing a new integrated process usually starts. This procedure ensures evaluation of a wider range of possible integrated process scenarios [4].

The spectrum of the possible integration in the reactor scale ranges from the limited heat integration at one end to full heat and mass integrated reactor design using a dual catalyst [5] at the other end. Nevertheless, the efficiency of these integrated reactor structures determines their potential for implementation in an industrial application. In this regard, still lots of efforts have to be devoted to develop an efficient reactor structure which ensures an efficient thermal-performance and selective conversion in the OCM reaction while maintaining a high level of C_2-yield. As a step forward in this direction and in order to enhance the potential of such integration, the concept and typical performance of a novel dual-membrane reactor for integrating the OCM and DRM are introduced here in this paper. The structure and performance of the distinguished integrated OCM–DRM process scenarios exploiting this dual-membrane reactor are also reviewed.

2. The concept of a dual-membrane reactor for integrating the OCM and DRM

By introducing the capabilities of the two-phase metal-molten carbonate membrane [6], the possibility of using this membrane at high temperature operation has been highlighted [7]. This has motivated us to exploit it for establishing an efficient CO_2-permeation from the OCM reactor into the DRM reactor. In the OCM section, a porous, packed-bed membrane reactor – one of the most recommended reactor concepts for OCM reactions – was implemented in the centre and covered by a molten carbonate membrane to assemble a dual-membrane integrated reactor structure with the adjacent methane-reforming catalytic bed. In this manner, the whole packed-bed OCM membrane reactor is surrounded by a tubular molten carbonate membrane and the resulting structure is implemented inside an outer shell filled with the DRM catalyst. The conceptual schematic representation of this novel reactor is shown in Fig. 1.

In this configuration, the gas stream containing oxygen (e.g. air) is fed into the porous inorganic membrane, for instance an alumina membrane. The membrane acts as a distributor for oxygen. In this manner, oxygen gradually diffuses across the membrane to reach the inner section which is filled with the OCM catalytic bed, where it reacts with methane. Methane and possibly nitrogen or carbon dioxide are injected as the axial feed into this reaction zone. Nitrogen or carbon dioxide is usually used in the experimentation as the inert component to push the gas composition far outside the explosion range. Along the OCM catalytic bed, carbon dioxide is continually produced in competition with C_2-production. Carbon dioxide is gradually adsorbed on the dense molten carbonate membrane and together with a part of the released heat in the OCM section, is transferred into the adjacent reforming section where they are consumed. This mechanism facilitates the endothermic dry methane-reforming reaction which converts methane to syngas using CO_2 as a reactant. The rest of the required energy and reactants for dry methane reforming are supplied respectively via the external wall and the axial inlet feed stream into the reforming section.

Co-current feeding flow in the proposed dual-membrane reactor provides the best thermal and reaction performance.

In order to ensure a safe and efficient operation, pressurizing the oxygen-rich gas stream is recommended to assist in passing it through the membrane especially in a dead-end configuration. Utilizing a proper amount of diluting gas such as nitrogen in the oxygen-rich gas stream also improves the safety of the operation. Other types of diluting gas components such as CO_2can be also used in this section which will directly affect the performance of the DRM section however. In this general concept, even a dense oxygen perm-selective membrane can be used for dosing the oxygen.

3. Feasibility study, mechanisms and experimental observations

In order to evaluate the feasibility of the proposed dual-membrane reactor concept, the governing mechanisms and the experimentally observed performances in different sections of this reactor are reviewed here.

3.1. Molten carbonate membrane

Three concerns might arise regarding the applicability of the proposed dual-membrane reactor for integrating the OCM and DRM reaction zones. The first concern is about the compatibility of the membrane materials with the high operating temperature needed in this application. Lately, using a porous metallic support made by the sintered layer of La–Sr–Co–Fe (LSCF) mixture and infiltrated by Li–Na–K carbonates, the range of operating temperatures for the two-phase metal-carbonate membrane has been extended [8]. For instance, such a membrane has already been used in direct contact with the methane reforming environment from one side and the high-temperature flue gas containing carbon dioxide on the other side [7]. This has ensured the practicality of its operation in a range of up to 900 °C, which is similar to the range of operating temperatures in the integrated OCM–DRM reactor.

A second concern is about the interaction of the molten carbonate material with the OCM product species. The main materials used in the molten carbonate membrane are compatible with the OCM environment because no undesired reaction activity has been reported when ethylene and ethane come to in contact with the molten carbonate materials. Molten carbonate material can not only be in contact with the OCM reaction zone,