AUTOTHERMAL REACTOR CONCEPT FOR COMBINED OXIDATIVE COUPLING AND METHANE REFORMING

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A novel autothermal reactor concept has been developed for the simultaneous production of ethylene by oxidative coupling (OCM) and synthesis gas by steam reforming of methane (SRM), supported by a detailed numerical modeling study. The proposed reactor consists of two separate reaction chambers which are thermally coupled. The OCM is carried out in packed bed reverse flow membrane reactor tubes submerged in a fluidized bed where the unconverted methane and by-products, from which the valuable C₂ components have been separated, are reformed together with some additional steam producing synthesis gas and consuming the reaction enthalpy emerged from the exothermic OCM.

Keywords: Chemical Reactors, Reverse Flow, Membranes, Autothermal Operation, Dynamic Simulation, Reaction engineering

1. INTRODUCTION

Bulk chemicals like ethylene with an annual production of 20,000-30,000 metric kilotons in Europe are currently mainly produced from crude oil via a cracking route. With the rapid consumption of the world oil reserves, it is expected that natural gas will more and more become a widely used source of chemicals. The indirect conversion route involves the energy-intensive production of synthesis gas and the consecutive production of higher hydrocarbons via the Fischer-Tropsch process and downstream endothermic steam cracking, resulting in a process with a large methane recycle, a lot of unit operations and reduced energy efficiency. More interesting is the direct conversion of natural gas into ethylene and ethane, which can be achieved by oxidative coupling of methane (OCM), at relatively high temperatures (>750 °C). Despite large efforts from many researchers, the maximum single-pass C₂ yield on the best catalysts is limited to only about 15-20% due to undesired combustion reactions, deteriorating the selectivity to C₂’s. However, if the mixture of by-products from the OCM reactions, typically CO, CO₂, H₂ and H₂O (see Fig. 1), could be shifted and reformed with methane to synthesis gas (SRM), two major advantages can be achieved.

![Overall reaction scheme for combined oxidative coupling and reforming of methane.](image-url)

Fig. 1. Overall reaction scheme for combined oxidative coupling and reforming of methane.
First, the overall methane conversion to valuable products can be increased, producing C\textsubscript{2}’s (reaction 1) and synthesis gas (reaction 3) simultaneously, where the produced synthesis gas can be used for the production of synthetic fuels via the Fischer-Tropsch process. Second, by combining the oxidative coupling and steam and dry reforming of methane an overall autothermal process can be achieved. The challenge is to introduce a reforming catalytic activity in such a way that the reaction rates of the exothermic OCM and the endothermic reforming reactions are balanced to create an autothermal and near isothermal process. This can be either performed on the scale of a single catalyst particle, resulting in the most efficient energy integration possible, or on reactor scale. In this paper it is investigated by a detailed modeling and experimental study whether the OCM and reforming reaction rates can be tuned, resulting in a novel reactor concept for the simultaneous and autothermal production of synthesis gas and higher hydrocarbons.

2. REACTOR CONCEPT

This paper concerns the thermal balancing of the heat released from the exothermic OCM reaction with the endothermic SRM between two different reactor compartments. Both reactions can be performed in several different reactor types, the optimal reactor concept highly depends on the type of process (i.e. exothermicity, reaction kinetics and thermodynamics). In a micro-catalytic fixed bed reactor, the reaction rates of the primary OCM reactions (reaction 1, 2) were determined on a Mn/Na\textsubscript{2}WO\textsubscript{4}/SiO\textsubscript{2} catalyst at 800°C. The overall reaction order \( n \) towards O\textsubscript{2} was determined to be lower for the OCM reaction (\( n=0.4 \)) than for the methane combustion reaction (\( n=1 \)). The lower reaction order towards O\textsubscript{2} results in an increase of the overall C\textsubscript{2} selectivity (as high as 85% at \( p_{\text{O2}} < 5 \text{ kPa} \)) at the expense of a lower CH\textsubscript{4} conversion when the O\textsubscript{2} partial pressure is decreased. In a conventional co-feed fixed bed reactor it is not possible to obtain high C\textsubscript{2} selectivity and a high CH\textsubscript{4} conversion at the same time because of the applied low O\textsubscript{2} concentration.

By using distributive feed of O\textsubscript{2}/air the C\textsubscript{2} selectivity can be enhanced because of the low O\textsubscript{2} concentration while feeding sufficient O\textsubscript{2} along the reactor length to achieve a higher CH\textsubscript{4} conversion than co-feed reactors. The advantageous effect of distributed feed of O\textsubscript{2}/air has been shown with experiments in an isothermal packed bed membrane reactor, where porous Al\textsubscript{2}O\textsubscript{3} membranes were applied to distributively feed air to a diluted CH\textsubscript{4} stream over a Mn/Na\textsubscript{2}WO\textsubscript{4}/SiO\textsubscript{2} catalyst at 800 °C. The total C\textsubscript{2} selectivity increased from 20% to 30% at a CH\textsubscript{4} conversion of approximately 60% (see Fig. 2).

Additionally the reaction heat is released along the entire reactor length, leading to a more uniform temperature profile. Still, unselective gas phase reactions can occur downstream at the reactor outlet, hence the product stream needs to be quenched to low temperature. For this reason the flow direction is periodically reversed so that both product and feed can be at low temperature and recuperative heat exchange between feed and product stream is integrated inside the fixed bed membrane reactor.
In conventional autothermal reverse flow systems where the endo- and exothermic processes are carried out in counter- or cocurrently operated fixed bed heat exchange reactors, stable reactor operation (i.e. cyclic steady state) is difficult to achieve and to maintain because the temperature and concentration fronts of both reactions are traveling at different velocities, requiring complex process control. Next to difficult operability the temperature in the OCM system will increase to very high temperatures at which \( \text{C}_2 \) selectivity decreases to undesired values. Hence efficient cooling is required, which is achieved by immersing the OCM membrane reactor tubes in a fluidized bed reactor in which the reforming of the by-products of the OCM process is performed (see Fig. 3). The excellent mixing properties of the fluidized bed operation ensure a uniform operating temperature, so that the reaction heat produced by the exothermic reactions is efficiently removed. Additionally expensive high temperature (800 °C) gas heat exchangers are not necessary in this process, which can be advantageous from an economical point of view. The feasibility of the reverse flow OCM process is investigated by means of a 1D membrane reactor model, which solves the multi-component mass and energy balances taking into account convection, dispersion and chemical reactions. The influence of distributive feed of \( \text{O}_2/\text{air} \), operating temperature of the fluidized bed and heat transfer coefficients on the overall reactor performance have been investigated. The performance of the SRM fluidized bed reactor, with the OCM product outlet composition (without \( \text{C}_2 \) products) as the inlet composition, is evaluated and the required reaction heat is correlated to the heat produced in the OCM fixed bed membrane reactor to determine effect of parameters on autothermal operation.

With the simulations it has been shown that indeed the exothermic OCM and endothermic SRM can be very efficiently coupled into an overall autothermal reactor and that in the cyclic steady state \( \text{C}_2 \) yields up to 30% at full \( \text{CH}_4 \) conversion can be achieved with a \( \text{CH}_3/\text{O}_2 \) ratio of 2–2.5 and a \( \text{H}_2\text{O}/\text{CH}_4 \) ratio of 3 in the SRM fluidized bed reactor.

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