ENERGY INTEGRATED OXIDATIVE COUPLING WITH STEAM REFORMING FOR ETHYLENE PRODUCTION FROM NATURAL GAS

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Summary

The objective of this process design study was to combine the exothermic oxidative coupling (OCM) and the endothermic steam reforming (SRM) of methane to produce ethylene, ethane and syngas. The overall energy consumption can be minimized by tuning the process conditions of the exothermic and endothermic reactions. The reactor design results in a combination of a multitubular reactor for the oxidative coupling installed inside a fluidized bed reformer. To increase the ethylene yield an additional oxidative dehydrogenation (ODH) reaction section was added to convert the ethane present in the natural gas and formed in the oxidative coupling. The process design shows that the separation section will become rather complex

Keywords

Novel reactor technologies, multiphase and particulate reactors, energy integration, process intensification.

Introduction

The objective of this process design study was to combine the oxidative coupling and the steam reforming of methane to produce ethylene, ethane and syngas. A plant capacity of 240 ktpa natural gas was selected. By combining OCM and SRM in a single reactor, the energy produced by the exothermic OCM can be consumed by the endothermic SRM reactions. Unreacted methane and byproducts from OCM are used as a feed for the steam reforming, thereby increasing methane conversion (see Fig. 1).

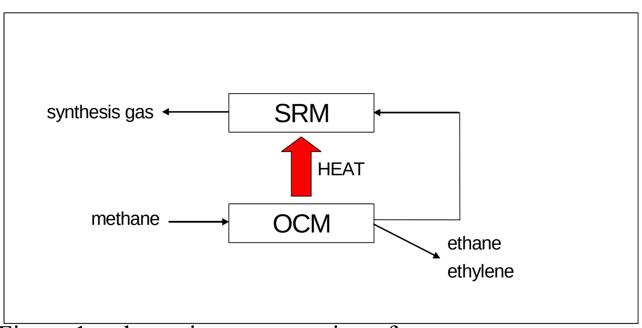

Figure 1: schematic representation of process.

The main reactions of the OCM section are:

$CH_4 + \frac{1}{4}O_2 \rightarrow \frac{1}{2}\, C_2H_6 + \frac{1}{2}H_2O$ $\Delta H = -87$ kJ/mol

$CH_4 + \frac{1}{2}O_2 \rightarrow \frac{1}{2}\, C_2H_4 + H_2O$ $\Delta H = -192$ kJ/mol

and combustion which consumes more oxygen and generates more heat:

$CH_4 + 1\frac{1}{2}O_2 \rightarrow CO + 2H_2O$ $\Delta H = -519$ kJ/mol

$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$ $\Delta H = -802$ kJ/mol

Laboratory tests over a SrO/La_2O_3 catalyst at atmospheric pressure and a temperature of 750-900°C show a CH_4 conversion of 30% per pass and a selectivity to C_2 of 85% with a ethylene/ethane ratio of 1.

In the steam reforming section the reactions are:

$CH_4 + H_2O \rightarrow CO + 3H_2$ $\Delta H = 206$ kJ/mol

$CH_4 + 2H_2O \rightarrow CO_2 + 4H_2$ $\Delta H = 166$ kJ/mol

$CH_4 + CO_2 \rightarrow 2CO + 2H_2$ $\Delta H = 247$ kJ/mol

$CO + H_2O \rightarrow CO_2 + H_2$ $\Delta H4 = -40$ kJ/mol

Steam reforming can be performed conventionally over a nickel catalyst in a packed bed at 750-900°C and 20-30 bar pressure.

The challenge is to combine the exothermic and endothermic reaction systems and to design a heat integrated process with an optimum yield of valuable components.

We assumed that the synthesis gas produced can be used on site, e.g. for methanol production.

Process design

A systematic procedure was applied to design this process from the stage of black box via a conceptual flowsheet, index flowsheet to a PFD with detailed mass and energy balances. During the process the different alternatives and choices were evaluated and documented. The final

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functional block diagram created and for which mass and energy balances have been worked out is rather complex.

The following choices were made (see also Fig. 2):

- In case of ethane containing natural gas, the ethane is separated before the OCM reaction system.
- Split of the outlet stream of the OCM reactor into a recycle for the SRM which contains a.o. unconverted methane, an ethylene product stream and an ethane stream.
- Two ethane streams are combined and are sent to an oxidative dehydrogenation (ODH) unit to increase the ethylene production.
- Streams from the separation units after the OCM and ODH reactor form the feed for the steam reforming.
- Heat from the OCM reaction is used for the SRM, which covers about 40% of the heat needed.

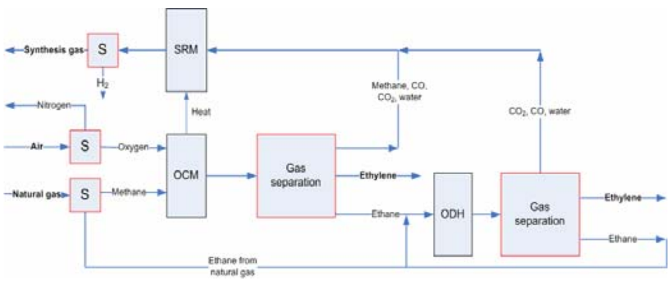

Figure 2: Functional diagram of energy integrated OCM/SRM process.

- Hydrogen from the syngas can be used for additional heating of the SRM reactor
- A 240 ktpa NG plant produces 80 ktpa ethylene and 300 ktpa syngas.

A number of alternatives for lining up and separations have been developed to balance the system at an optimal ethylene and syngas production.

Reactor designs

OCM – Oxidative Coupling of Methane

OCM is performed in both packed bed and tubular membrane reactors. The formation of higher oxidation products can be reduced by keeping the oxygen concentration low with staged feeding of oxygen, e.g. by using membranes. We selected the following configuration as a multitubular unit:

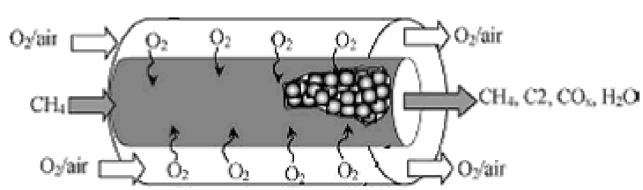

Figure 3: schematic representation of tubular membrane reactor.

Oxygen is fed through a perovskite membrane $SrCo_{0.8}Fe_{0.2}O_{3-\sigma}$. In the optimal design the oxygen was introduced at the tube side and the methane at the shell side. Reaction conditions are 850 °C and 25 bar.

SRM – Steam reformer for methane

A fluidized bed reformer has advantages over a fixed bed reactor: effectiveness factor enhancement by using smaller particles 50-100μm, good mass and heat transfer. Kinetics are known and are used to calculate the bed height.

CO_2 from the OCM to the SRM reactor improves the methane conversion. Operating conditions are set at 850°C and 25 bar. The catalyst chosen is $NiO\text{-}CaO/Al_2O_3$, this catalyst has a high conversion and selectivity of 98.5%.

The OCM system is placed in the SRM fluid bed reactor and efficient heat transfer is created. The detailed reactor design showed that the volume of the OCM reactor takes about 17 % of the SRM reactor volume and the installed heat transfer area is sufficient for a temperature difference of 10 °C.

For the Oxidative dehydrogenation of ethane a fluidized bed reactor has been selected.

Conclusions

The SRM and OCM reactions have been combined in one reactor system to produce syngas and ethylene from natural gas in an energy integrated way.

For the generation of the total process set-up a number of assumptions had to be made. The main technical problem of the process design is the immaturity of the oxidative coupling. Nevertheless, we may conclude that the oxidative coupling with a low yield for ethylene in combination with steam reforming is a promising additional ethylene production alternative. Addition of the dehydrogenation of ethane also increases the yield.

The main economical drawback is the uncertainty in the price of the products and energy consumption of the separations required.

References

Extensive literature searches were done for chemsity, reactor and process design. The design was based on over 100 references.