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ETHYLEN PRODUCTION VIA OXIDATIVE COUPLING OF METHANE (OCM) – INVESTIGATION OF ALTERNATIVE SEPARATION PROCESSES

PRODUKCJA ETYLENU METODĄ UTLENIAJĄCEGO ŁĄCZENIA METANU (OCM) – BADANIA ALTERNATYWNEGO PROCESU SEPARACJI

Abstract

One of the most promising opportunities, for the researcher to find alternative methods to ensure the supply with raw materials for the chemical industry, therefore is the activation of methane by oxidative coupling of methane (OCM). With the help of unifying concepts in catalysis technology more benefit for the yield of ethylene production will be expected. The reaction product of the OCM process has to purified and separated. Therefore, data from the literature for the reaction products of oxidative coupling of methane were taken and used to simulate the purification and separation with the commercial tool CHEMCAD. Feasibility study was done to find the most valuable way to reach the aim of the process: most purified ethylene as a product.

Keywords: oxidative coupling of methane, gas separation, membrane process, ethylene production, unifying concepts in catalysis

Streszczenie

Szczególne znaczenie dla naukowców poszukujących alternatywnych metod zagwarantowania surowców dla przemysłu chemicznego ma oksydacyjne sprzężenie metanu (OCM), a zastosowanie połączonych koncepcji w technologii katalizy pozwala oczekiwać zwiększonej produkcji etylenu. Produkt reakcji procesu OCM musi być oczyszczony i oddzielony w różnych procesach. W artykule, na podstawie danych z literatury dotyczących produktów reakcji OCM, przeprowadzono symulację oczyszczania i oddzielania z zastosowaniem komercyjnego programu CHEMCAD. Celem analizy była poszukiwanie optymalnej technologii gwarantującej maksymalną czystość produktu – etylenu.

Słowa kluczowe: utlenianie metanu, rozdzielanie gazu, procesy membranowe, produkcja etylenu, zunifikowane koncepcje w katalizie

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1. Introduction

Catalysis is a strategic area of molecular science of enormous importance because of its implication in many fields in the society, including energy, economy, environmental and life science. Meeting the enormous energy demand of the 21th century is an unsolved problem that catalysis research will play an important role [1]. The oxidative coupling of methane (OCM) is one approach for the direct catalytic conversion of natural gas to more useful chemicals and therefore a challenge of the 21th century [2]. This approach could overcome the lack of energy and resource wasting indirect conversion methods like the Fischer-Tropsch Synthesis and many researchers focus on this process to overcome the poor yield of the OCM by improving catalysis technology.

The German Cluster of Excellence: Unifying Concepts in Catalysis (www.unicat.tu-berlin.de) ensures the applicability of there research results by connecting there research fields like: *Bridging the gap between the in complex catalysis* – a fundamental research area and the field of: *Complex reaction engineering* – by designing and building a mini plant for the OCM process. The integration process design and product preparation with regard to economically and ecologically aspect are the tasks the engineers have to overcome. With the help of modern and new technologies for purification and separation there work is a substantial contribution to reach the goal of a modern sustainable and ecological industry of the 21th century. Therefore the process has to developed and designed with regard to economical and ecological aspects otherwise the process is not preferable.

Therefore a mini plant will be designed and build in modular form to change some parts of the plant easily and evaluate there influence on the hole process in regards to the energy and separation efficiency. In this study a whole process units like the scrubbing unit will be treated as a module. Nevertheless, there is some research work to evaluate such modular design for example by costs and efficiency.

2. Process Overview

2.1. The goal of the investigation

The investigation started with the process is shown in Fig.1. The catalytic conversion of methane to higher hydrocarbons, especially to ethylene is the major goal of the process. This can be realized due to improve the catalysts performance to reach a yield up to 50%. The catalysts developed in the laboratory of the TU Berlin chemists have to be used in a pilot plant. The investigated process is divided into three sections:

1. Reaction section.
2. Purification section.
3. Separation Section.

2.2. The reaction section

The reactor is continuously fed with natural gas and oxygen. The feed gas is preheated to 700 °C and will catalytic partial oxidized at pressure of 0,5 MPa. The Reactor is jacked cooled to operating temperature of 750 ° C. The exothermic reaction heat has to remove

while steam is produced. The desired composition of the reaction product is listed in Table 1. While with a off coming mass flow rate of

$$\dot{M} = 20\,\frac{\text{kg}}{\text{h}} \tag{1}$$

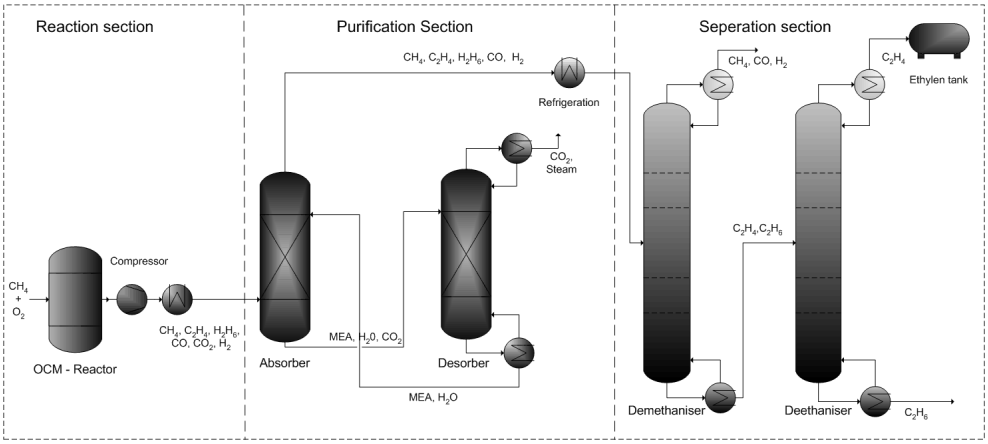

Fig. 1. Flow sheet of the investigated OCM process

Rys. 1. Schemat badanego procesu OCM

Table 1

Reaction composition for pre limited design aspects

OCM reaction products	CH_4	C_2H_4	C_2H_6	CO_2	Purge
	[% mol]	[% mol]	[% mol]	[% mol]	[% mol]
750°C, 0,5 MPa	66	8	2	5	19

The reaction products are compressed in a multi-compaction section to 3,5 MPa and cooled down to 40 °C later on. This stream is fed to the following purification section.

2.3. The purification section

In the following purification step the carbon dioxide has to be removed. This is realized by an amine scrubber and the following sodium hydroxide scrubber. The first scrubber based on an absorption process with 0,1 molar mono ethanolamine solutions (MEA) as detergents. The concentration of carbon dioxide is reduced to 0,15 mol% in this section. The used detergent will be regenerated in the stripper section and recycled to the absorption column. The absorber operating conditions are: 3,5 MPa top pressure, a top temperature of T = 35 °C and T = 65 °C in the bottom. The stripper operates at a pressure of 1 bar and a temperature range of T = 80 °C on top and T = 100 °C in the bottom. In the next following scrubber the carbon dioxide will be removed completely. This sodium hydroxide scrubber

operates at a head pressure of 3,5 MPa and temperatures of T = 35 °C on the head and t = 65 °C in the bottom.

2.4. The product separation section

This section consists of two cryogenic distillation columns. The first one is called the demethaniser and operates at a top pressure of 3,5 MPa and in a temperature range of T = –110 °C on the top and T = –7 °C at the bottom of the column. In this unit the unconsumed methane is separated from the product stream. The product stream consists of ethane and ethylene that is separated in the Deethaniser. The Deethaniser operates with a top pressure of 3,5 MPa and in a temperature range of T = 12 °C in bottom and T = –12 °C in the top of the column.

3. Simulation and first evaluation

For the process design and operation of an integrated down streaming process, a steady state simulation of the purification and separation step where done by using the in build AMIN model. This model describes the chemical absorption of Carbon dioxide and hydrocarbons lighter then C3 by solution of amine [3]. This model solves the chemical reaction equation (2) to (6) simultaneously, with (7) for the chemical reaction constants to calculate the free concentration of carbon dioxide in the liquid phase. The partial pressure of the gas phase components will be calculated by Henry's law constants (8) and free concentration in the liquid phase.

The main considered chemical reaction wit its equilibrium coefficients

$$K_1: \mathrm{RR'NH_2^+} \leftrightarrow \mathrm{H^+ + RR'NH} \tag{2}$$

$$K_2: \mathrm{RR'NCOO + H_2O} \leftrightarrow \mathrm{RR'NH + HCO_3^-} \tag{3}$$

$$K_3: \mathrm{CO_2 + H_2OH} \leftrightarrow \mathrm{HCO_3^- + H^+} \tag{4}$$

$$K_4: \mathrm{HCO_3^-} \leftrightarrow \mathrm{CO_3^{2-} + H^+} \tag{5}$$

$$K_5: \mathrm{H_2O} \leftrightarrow \mathrm{H^+ + OH^-} \tag{6}$$

$$\ln K_i = A_{1i} + \frac{A_{2i}}{T} + \frac{A_{3i}}{T^2} + \frac{A_{4i}}{T^3} + \frac{A_{5i}}{T^4} \text{ with } i = 1...5 \tag{7}$$

The gas liquid solubility coefficient

$$\ln H_j = \frac{B_{1j}}{T} + B_{2j} \cdot \ln T + B_{3j} \cdot T + B_{4j} \tag{8}$$

$$\text{with } j = \mathrm{CH_4, C_2H_4, C_2H_6, CO_2} \text{ etc}$$

3.1. Energy efficiency

The most energy consuming units in this separation process are the demethaniser, the deethaniser and the stripping column where the economic and profitability of the process depend on. The energy consumption of these three units is listed in table 2 to reach a ethylene product stream of

$$\dot{M}_{C_2H_4} = 2 \ \frac{\text{kg}}{\text{h}} \tag{9}$$

Table 2

The most energy consuming units

	Demethaniser	Deethaniser	Stripper
	[kW]	[kW]	[kW]
Reboiler	5,2	22	10
Condenser	6,2	23	9

Beside the compressors and pumps are the demand of energy for the cryogenic distillation and the regeneration of the detergent the largest one and therefore they are of certain interest for the operating costs.

3.2. The column design and the equipment

The numbers of theoretical plates, with the high equivalent to a theoretical plate are the determining point of the column high. Therefore they are of certain interests to evaluate the investment costs. In table 3 the numbers of theoretical plates (NTP) obtained by the simulations. It can be seen that the highest number of theoretical plates used in the ethane/ethylene separation unit. The investment costs are rising with the column high, so with the numbers of theoretical plates. Another aspect is the cooling power to reach temperature below –100 °C of the cryogenic distillation. Therefore large amounts of liquefied nitrogen has to used, the column material has to be resistant against embitterment and deep temperature heat exchangers has to used.

Table 3

The numbers of theoretical plates, calculated with the simulation

	Absorption	Desorption	Demethaniser	Deethaniser
	[-]	[-]	[-]	[-]
Numbers of theoretical Plates	15	15	15	45

4. Process alternatives for the ethylene separation

To improve the profitability is a challenge for the process the following aspects will be considered in the work:

4.1. Absorption

As an alternative for the cryogenic distillation absorption process with aqueous silver nitrate solution can be chosen. This process was developed in the 1990s. The concept based on a membrane process, but was commercialised as a conventional absorption process [4]. The lack of this process is the hydrogen in the feed gas, which can cause precipitation of silver and some more research work is necessary to overcome this problem [5].

4.2. Adsorption

An adsorption process could be an alternative. While for the current adsorbents, separation factors between ethylene and other gases are not high enough to achieve the deep removal of ethylene and relatively high ethylene purity aimed at in this application, further research work can overcome this lack [4].

4.3. Membrane separation

Polymer Membranes are available for ethane/ethylene separation but the lack of the low selectivity has to overcome. There are some promising studies about Silver Polymer electrolyte membranes [6], silicate-1 membrane [7].

5. Conclusion

It was shown that cryogenic state-of-the-art separation process for ethane and ethylene is not economically and not ecologically. Furthermore it was pointed out that the energy consumption of the there units: stripper, demethaniser and deethaniser has to decrease. Therefore some alternatives were mentioned, which have to investigate further more. The most promising possibility seems the separation of methane and ethylene by membranes. Detailed investigation with focus on selectivity and permeability in regarded to the special feed conditions has to be done.

Symbols

A_i	–	ChemCad in build coefficients	[-] … [K^4]
d	–	column diameter	[m]
$HETP$	–	High equivalent to theoretical plate	[m]
K_i	–	Chemical reaction equilibrium constants	
$\dot{M}$	–	mass flow	[kg/s]
NTP	–	numbers of theoretical plates	

P	–	pressure	[Pa]
R, R'	–	alcohol groups	
T	–	tempearture	[°C, K]

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