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CONCURRENT REACTOR ENGINEERING, SEPARATION ENHANCEMENT AND PROCESS INTENSIFICATION; COMPREHENSIVE UNICAT¹ APPROACH FOR OXIDATIVE COUPLING OF METHANE (OCM)

INŻYNIERIA ZBIEŻNA APARATU REAKCYJNEGO I DOSKONALENIE ORAZ INTENSYFIKACJA PROCESU ODDZIELANIA; KOMPLEKSOWE PODEJŚCIE GRUPY UNICAT¹ DO OKSYDACYJNEGO SPRZĘŻENIA METANU (OCM)

Abstract

For more than three decades Oxidative Coupling of Methane (OCM) process has been investigated as an attractive alternative for cracking technologies for ethylene production and exploiting the huge resources of natural gas. Developing a suitable catalyst and analyzing proper reactor feeding policy, reviewing and deploying the efficient methods in separation and purification of the undesired and desired products, possible energy saving and process intensification in each section, each has been the subject of many researches in the past. In this paper, these aspects will be addressed simultaneously in a general overview of the main research activities performed in the chair of process dynamics and operation at Berlin Institute of Technology under the context of Unifying Concepts in Catalysis (UniCat) project. Moreover, a cost estimation of the industrial scale OCM process guiding the analysis method to address the potentials and disadvantages of each OCM scenario structure, highlighted the possible process intensifications potentials in case of energy and equipment.

Keywords: concurrent engineering, reactor engineering, process synthesis, Oxidative Coupling of Methane (OCM), mini-plant scale experimentation

Streszczenie

Proces oksydacyjnego sprzężenia metanu (OCM) był przez ponad trzy dekady rozpatrywany jako atrakcyjna alternatywa dla błyskawicznych technologii wytwarzania etylenu oraz eksploatacji ogromnych zasobów gazu naturalnego. Przedmiotem licznych badań prowadzonych w przeszłości były: opracowywanie właściwego katalizatora i analizowanie odpowiednich metod napędzania aparatu reakcyjnego, poznanie i stosowanie skutecznych metod oddzielania i oczyszczania produktów pożądaných i niepożądanych, możliwości oszczędzania energii i intensyfikacji procesu na każdym z jego etapów. W artykule niniejszym aspekty te będą omawiane jednocześnie w ramach ogólnego przeglądu najważniejszych działań badawczych podejmowanych w Katedrze Dynamiki Działań Procesowych Berlińskiego Instytutu Technologicznego w kontekście projektu UniCat (ujednoczone koncepcje katalizy). Wyciągnięto wnioski konceptualne i podjęto decyzje z wykorzystaniem danych doświadczalnych dostarczonych przez mini-aparaturę grupy UniCat. Ponadto szacowany koszt procesu oksydacyjnego sprzężenia metanu w skali przemysłowej, odnoszącego metodę analizy do zalet i wad każdego ze scenariuszy OCM, uwydatnił możliwość intensyfikacji procesu w zakresie energii oraz aparatury.

Keywords: inżynieria zbieżna, inżynieria aparatu reakcyjnego, synteza procesowa, oksydacyjne sprzężenie metanu (OCM), eksperymenty w skali mini-aparatury

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1. Introduction

Oxidative coupling of methane (OCM) is again attracting attentions after a gap of relatively inactive research period in this area [1]. This process has been proposed to upgrade the huge resource of natural gas and substitute the oil based technologies for producing ethylene as the most demanded chemical intermediate. The OCM process consists of three main sections namely reaction section, carbon dioxide removal section and ethylene separation and purification section as shown in Fig. 1.

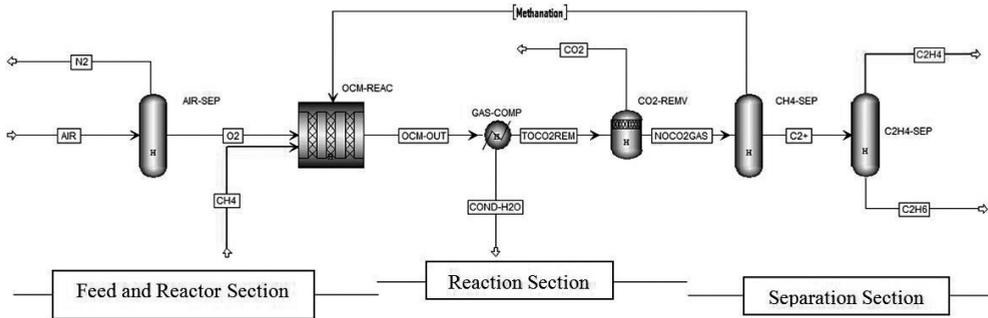


Fig. 1. The structure of the OCM process

Rys. 1. Struktura procesu OCM

In the reaction section, methane reacts with oxygen, in order to produce ethylene. In the carbon dioxide separation section, CO_2 can be removed using different separation methods and the rest of the gas is introduced to demethanizer where methane and other light gas species such as hydrogen and carbon monoxide are separated from ethylene and ethane. Later these two last components are separated from each other and pure ethylene is achieved as a final product.

The structure of the classical OCM process is compatible with the principals of conceptual design heuristics where carbon dioxide is removed as soon as possible to avoid its undesired and challenging presence in the next steps. Moreover, the costly operations such as cryogenic distillations under high pressure only are applied on limited amount of gas flow rate and the potential of the already available high pressure gas streams leaving the CO_2 removal section can be partially exploited in the cryogenic distillations.

So far OCM process has not been commercialized to produce the ethylene as the final product, but some alternative structures have been proposed to improve the efficiency of the direct oxidative coupling of methane even if it means that ethylene cannot be achieved as the final product. On the other hand, most of the challenges and the operating costs are imposed due to the difficulties of separating ethylene. This can be concluded by cost analysis of the industrial scale OCM process in terms of the cost of equipment pieces and operations in different OCM process sections as shown in Table 1.

These data are the cost estimation of an industrial scale OCM process for 240 000 Ton Ethylene/year capacity and the air separation costs has been excluded here

Equipment and operating cost items in OCM process sections

OCM Section	Equipment Cost in Million Euro	OCM Section	Relative Utility and Energy Cost
OCM reactor	24.4	OCM reactor	3%
Gas compression	30.9	CO ₂ removal	43.3%
CO ₂ removal	11.9	Ethylene separation	53.7%
Ethylene separation	8.7	OCM process	100%

As can be seen here, ethylene separation is a very costly operation. Therefore, in some alternative process structures such as ARCO process or OXCO process it has been proposed to convert the ethylene to an easily separable component like Ethylbenzene [2] or fuels [3, 4] and reduce the cost of separation for the integrated OCM-fuel production process. The structures of two typical alternatives in this category are shown in Fig. 2.

In this figure, it can be seen that the process structure is completely similar to the classical OCM process except in the separation section where a chemical reaction extracts ethylene and produce an easily separable product such as Oligomer or Ethylbenzene.

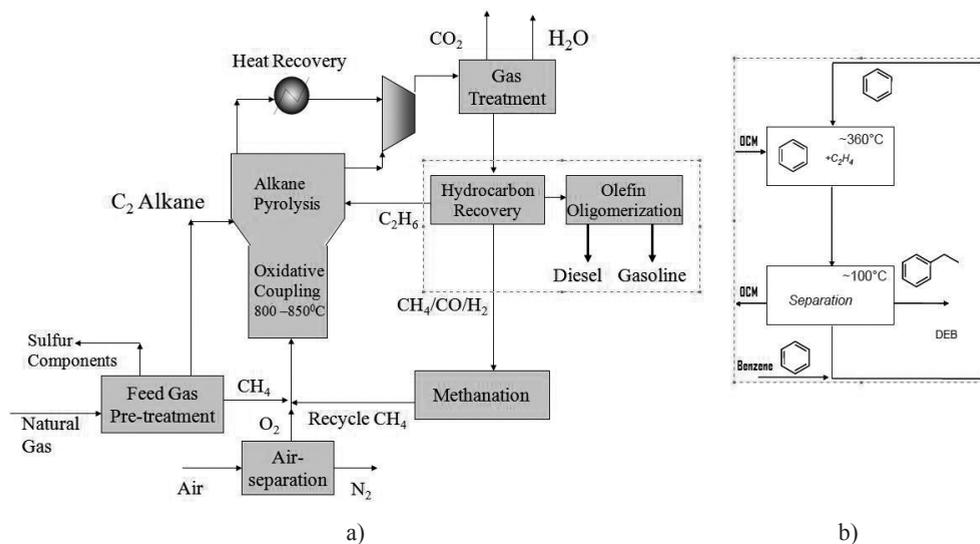


Fig. 2. The alternative process structures for improving the performance of separation section:
a) Oligomerization and fuel production, b) Ethylbenzene production

Rys. 2. Alternatywne struktury procesowe dla podniesienia wydajności etapu oddzielania:
a) Oligomeryzacja i wytwarzanie paliwa, b) Wywarzanie etylobenzenu

Here in this paper, it will be tried to improve the performance of the classical OCM process while targeting ethylene as the final product. To do this, different parameters have to be exploited in their proper level in different sections of the OCM process. An efficient way to analyze all these factors and design them properly in regard to their interactive effects with other parameters is to follow a concurrent engineering path. Normally for developing a chemical process, the catalyst, reactor section, separation section and heat and integration are developed in a hierarchical order [5]. However, in a concurrent engineering approach, the effect of each local parameter (parameters in each section) in the context of the whole process performance is the design driven factor for process synthesis. Such an approach has been applied in a mini-plant scale experimental facility for OCM process in Berlin institute of technology as a part of UniCat research project. Furthermore, the economy of the industrial scale OCM process using different alternative unit operations was also analyzed simultaneously.

In this context, first, the reactor section and carbon dioxide separation section are analyzed individually and in each section, different alternatives are reviewed. The conceptual and operational conclusions made based on the analysis performance indicators in each section are reevaluated in the context of whole process performance.

2. Reactor section

In the reactor section, variety of reactor concepts and catalysts were investigated. In general, the following aspects are the main design concerns in reactor engineering of the OCM process.

1. The high exothermic reaction.
2. Low ethylene yield achieved with low methane conversion and selectivity.

In the catalyst level, UniCat group not only has screened out most of the catalysts suggested for the OCM process [6] and reviewed the whole literature on OCM catalysts, but also developed the stable and efficient catalyst $\text{Mn}/\text{Na}_2\text{WO}_4/\text{SiO}_2$ as well as a catalyst preparation method [7]. The reported results in this manuscript are all based on this catalyst ($\text{Mn}/\text{Na}_2\text{WO}_4/\text{SiO}_2$) except it mentioned other. In the reactor section of the UniCat mini-plant, fixed bed reactor, membrane reactor and a fluidized bed reactor were analyzed experimentally. Beside reporting a typical observed experimental behavior of these reactor concepts, their performance are also conceptually interpreted in the wider context of process evaluation.

2.1. Fixed bed reactor

Fixed bed reactor as a standard reactor from small scale for kinetic development up to large scale for industrial application has been widely investigated for OCM process. However, in all scales, severe hot spot formation over shadows the performance of the fixed bed reactor for the OCM process. For instance, even in the small OCM test reactor, hot spots more than 150°C can be formed which reduce the desired products yield drastically. Even using considerable amount of nitrogen as diluent gas, typical experimental results obtained from mini-plant show that more than 100°C with low C_2 yield up to 14% is achieved. Severe hot spot formation is one of the main aspects makes the fixed bed reactor unattractive for OCM application, while fluidized bed reactor concept which is well known for its almost isothermal operation becomes attractive on this aspect.

2.2. Fluidized bed reactor

Fluidized bed reactor has been investigated for OCM reactions often because of its capability to address the hot spots formation [8] even in an industrial scale application [3].

In the UniCat mini-plant, a fluidized bed reactor made of quartz glass with an internal diameter of 40 mm was used under the reaction temperature of 750–850°C. An electrical tube furnace and a multipoint thermocouple in 10 points along the reactor supplies the heat and measures the temperature respectively. Outlet gas composition was analyzed by on-line infra-red gas analyzer and time to time with an offline gas chromatograph. The whole system was automatically controlled using process Siemens-7 system as shown in Fig. 3 and the value of all parameters and performance indicators were recorded on-line.

In Fig. 3a, the picture of the heating zone of the reactor, catalyst bed and the multipoint thermocouple are shown. Fig. 3b shows how the reactor set-up is controlled and the reactor performance indicators are monitored continually.

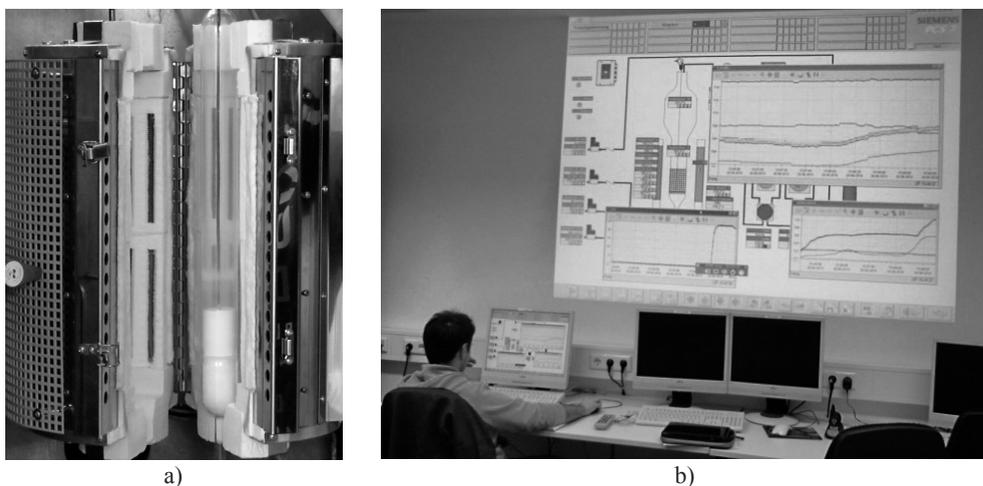


Fig. 3. The picture of: a) reactor set-up; b) the control room and recording the parameters

Rys. 3. a) Układ aparatu reakcyjnego b) pokój aparatury z zapisem parametrów

Typical performance of the fluidized bed shows that almost an isothermal performance with less than 20°C temperature gradient along the reactor is achievable while a typical selectivity toward C₂ production is equal to the selectivity toward carbon dioxide production. Moreover, depending on the catalyst type, the ethylene to ethane production ratio are varied. Furthermore, proper choosing the operating reaction temperature not only affects the amounts of desired products yield, but also the selectivity and methane conversion which are extremely important on the performance of the separation sections. Fig. 4 enables to simultaneously consider such an effect on different performance indicators.

Therefore, parallel to cost-benefit analysis performed based on the amount of the reactant consumption-Ethylene production in the reactor section, the consequences of achieving these levels of performance indicators on the whole process performance should be also analyzed.

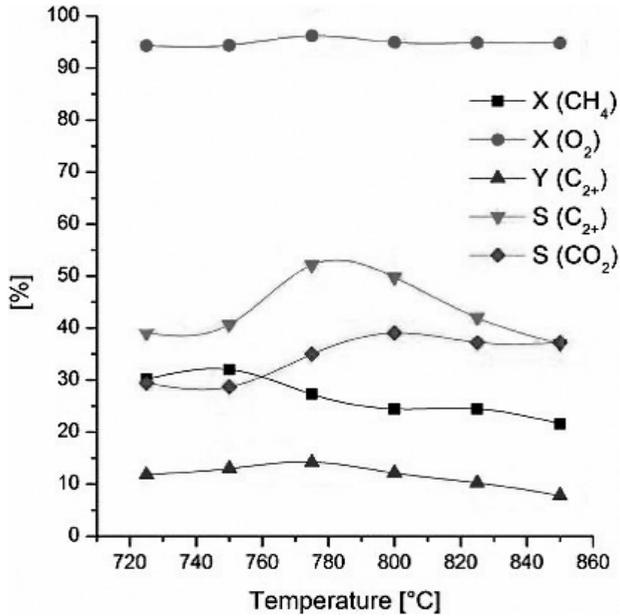


Fig. 4. Simultaneous analysis of conversion, yield and selectivity for OCM reactants and products for La₂O₃/CaO catalyst

Rys. 4. Symultaniczna analiza konwersji, wydajności i selektywności dla substratów reakcji i produktów OCM z katalizatorem La₂O₃/CaO

2.3. Membrane reactor

Packed bed membrane reactor is the most selective reactor concept investigated in UniCat mini-plant facility. A commercial alpha-alumina ceramic membrane with 200 nm pore-size on the membrane layer was modified using silica-sol method as well as other modifications methods. After reaching the required permeability, the membrane reactor performance was investigated under variety of operating conditions. Typically the membrane reactor showed 10-15 percent higher selectivity in comparison to the fluidized bed and fixed bed reactor for similar operating conditions. Moreover, the hot spot formation is not as severe as fixed bed reactor but observing up to 30–80°C hot spot formation is not unusual in membrane reactor.

2.4. Fluidized bed membrane reactor

In order to exploit the advantages of membrane reactor to achieve a selective performance and simultaneously address the hot spot formation, a fluidized membrane reactor concept was simulated for OCM reactions promising a considerable improvement in terms of selectivity and operating aspects. The simulation was performed using Computational Fluid Dynamics model and the concentration profiles of the components were analyzed along the reactor in order to improve the design of fluidized bed membrane reactor. Such typical concentration profiles are shown in Fig. 5.

In this configuration, methane and nitrogen as diluents gas enter from the bottom of the reactor and oxygen enters from the top via the membrane and is dosed along the catalytic fluidized bed area. As can be seen in Fig. 5, the permeability of the membrane and activity of the catalyst impose the oxygen concentration distribution inside the fluidization zone. The number of membranes and their distances will also play a role on the selectivity and conversion of the reactor.

2.5. Take away from reviewing the reactor section

According to the investigation of different reactor concepts, fixed bed reactor suffers from severe hot spot formation and its co-feeding policy does not enable achieving high selectivity and yield of desired products. In this case air can be used as a source of oxygen and also diluting agent to coup with the hot spot formation. However, nitrogen will impose lots of cost on the separation sections by increasing the size of equipment and also difficulties of removing it from desired products. This is the reason why normally an air separation unit produces pure oxygen for the OCM process. Membrane reactor is the most selective reactor concept in which mostly pure oxygen stream is introduced to the catalytic bed via a porous inorganic membrane. Fluidized bed reactor provides an almost isothermal performance but not so much selective one.

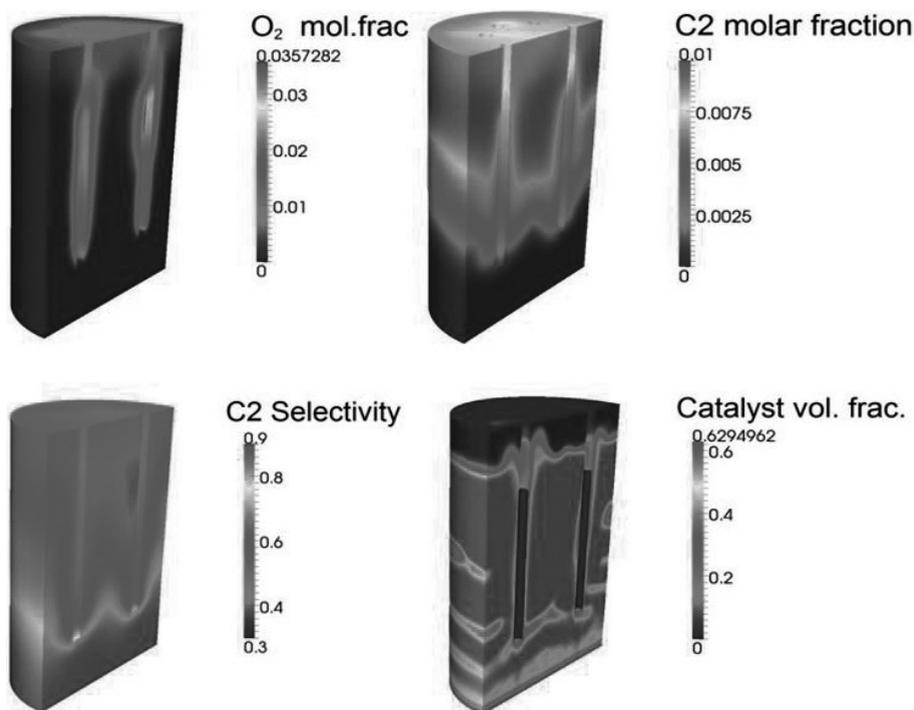


Fig. 5. Typical concentration profiles along the fluidized bed membrane reactor [9]

Rys. 5. Typowe wykresy stężenia w membranowym aparacie reakcyjnym złoża upłynnionego [9]

3. Down stream unit operations for separation and purification

Due to huge amount of carbon dioxide produced in unselective OCM reactor, sometimes up to 25% of the gas stream entering the downstream unit operations in OCM process is CO_2 which should be removed as soon as possible in order to reduce the cost of the equipment and avoid the operating difficulties in the separation section. Therefore, in the UniCat mini-plant, right after the reactor, CO_2 is separated from the rest of the gas components using an absorber or combination of absorber and membranes. Fig. 6 shows the mini-plant view of the reactor, absorber and desorption column and their connections.

In the first step, different aqueous amine solutions were used for carbon dioxide removal. Since in this case only carbon dioxide needs to be removed (there is no other sour gas component such as hydrogen sulfide or other sulfur components), the strong amine such as MonoEthanol Amine (MEA) was applied first for this duty in order to reduce the size of the required amine absorber. However, considerable amount of undesired hydrocarbon absorption and especially some level of ethylene lost were observed when MEA was used as absorber. To avoid this problem and also to reduce the huge energy demand for regenerating strong MEA, other types of amines such as MDEA or combination of amine absorber and polymeric membrane for CO_2 removal were investigated showing an improvement in terms of the energy consumption as well as the selectivity. For instance, the energy consumption using combination of amine and membrane separation was reduced up to 40%. Moreover, with the same level of energy consumption and ethylene lost, using MDEA and Piperazine, carbon dioxide removal of 99% was observed in comparison to 90% using MEA.

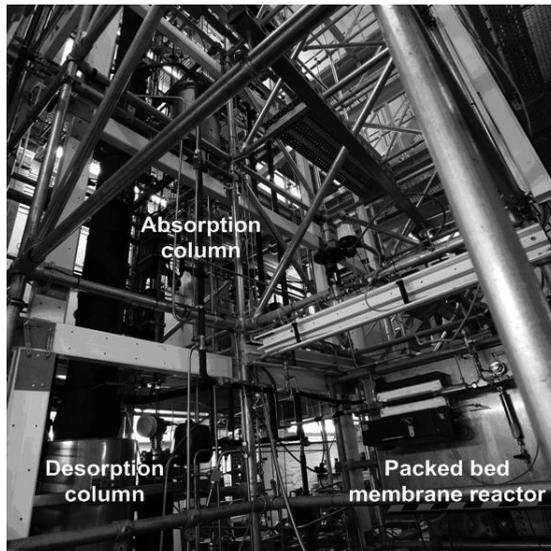


Fig. 6. Picture of the UniCat mini-plant experimental facility showing the OCM membrane reactor and carbon dioxide separation system

Rys. 6. Mini-aparatura doświadczalna projektu UniCat ukazująca membranowy aparat reakcyjny OCM oraz system oddzielania dwutlenku węgla

3.1. Using alternative absorbents and membranes in carbon dioxide removal section

Due to the low energy demand for their regeneration, hyperbranched polymers are promising candidates for high capacity CO_2 absorption. In experimental investigations, the capability of different commercially available hyperbranched polymers for absorbing CO_2 was studied by measuring solubilities of all gaseous components in the solution. The solubility results were measured in the temperature range of 303.15 to 343.15 K. However, due to the viscosity of hyperbranched polymer solution, considerable amount of energy is required for its displacement and circulation. On the other hand, functional end groups of hyperbranched polymers (such as hydroxyl groups) can be properly tailored to meet the specific requirements such as selective carbon dioxide absorption. The preliminary results of testing available hyperbranched polymers show that considerable amounts of the hydrocarbon are also absorbed in these solutions. Therefore, in order to be applicable as an absorbent for OCM process, their design and characteristics have to be improved. Fig. 7 shows the physical absorption behaviors of different gases in the polymer Boltorn U3000 where the temperature almost monotonously affects the absorption performance for all components. These experimental data were used to validate the absorption parameters in the simulation of a packed bed absorber. On the other side, these results also reflect the limitations on improving the selectivity through operating parameters, without improving the characteristics of the hyperbranched polymer itself.

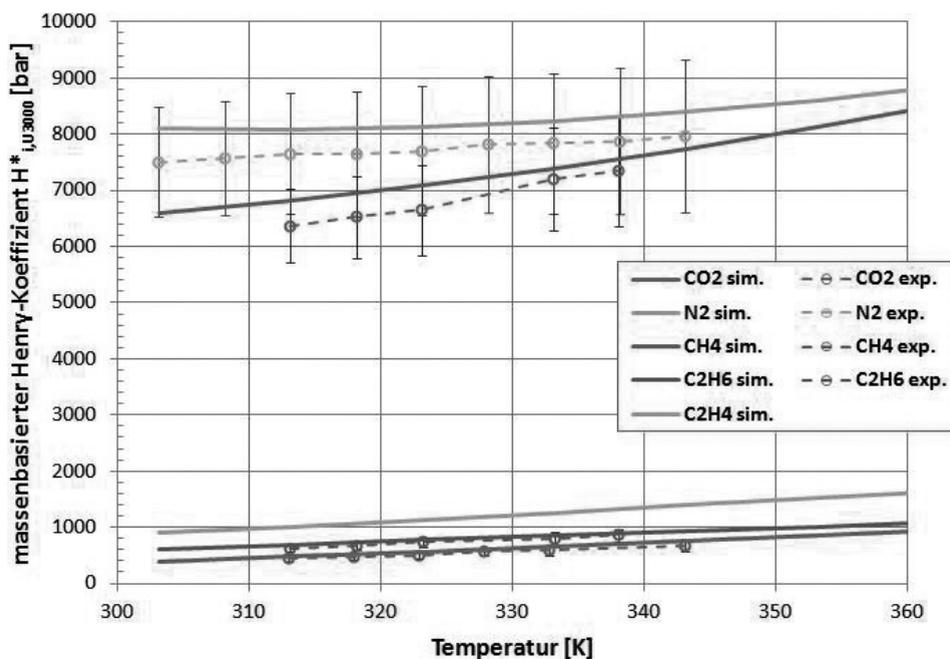


Fig. 7. Mass related Henry's constants for absorption of different components in the hyperbranched polymer Boltorn U3000 (sample supplied by Perstorp)

Rys. 7. Stałe Henry'ego związanie z masą dla absorpcji różnych składników w hiperpolimerze Boltorn U3000 (próbka dostarczona przez Perstorp)

Hereby, methane, ethane and ethylene showed high relative absorption selectivity in comparison to carbon dioxide. For instance ethane and nitrogen showed 17 times less relative absorption potential in comparison to carbon dioxide while methane is less capable to be absorbed by scoring 42 of relative absorption potential. As with any physical absorbent, selectivity strongly depends on partial pressures and therefore, combining this absorption method with another separation method for fine purification of the gas stream can be suggested.

On the other side, using membrane is always an option for separating the gas component due to its low energy demand. In UniCat mini-plant a polyimide membrane was used mostly for preliminarily removing CO₂ from product gas mixture prior to the absorption section. This has been done both experimentally and using simulation model enabling further improving the design and optimization of the dimensions and operating conditions.

The model for membrane unit was validated via experiments and showed that it is difficult to achieve less than 5% loss of C₂H₄ with 50% CO₂ removal or more in a single membrane module. Therefore, a two-stage membrane system was developed and proposed in order to improve the efficiency of the membrane system in which in the first less permeable module, more selective performance is achieved due to high carbon dioxide concentration gradient in the early stage of the separation and in the second stage, a quick removal of carbon dioxide is performed and the permeate stream is recycled back to the first step to increase the performance of the first membrane stage. This system has been modeled using Aspen Custom Modeler® where design parameters in one stage membrane module are feed flow rate, operating pressure and membrane area of the module. In the two stage system, changing the membrane area in different modules as a structural parameter enables to improve the permeability in each module and thereby the selectivity of the whole two stage membrane system. This comes surely with the cost of more complex system and bigger duty of the compressor due to bigger recycled stream.

Pore selectivity of polyimide membrane to separate the CO₂ from the gaseous mixture containing ethylene is because of the fact that carbon dioxide and ethylene both are double bound non-polar molecules favored to interact with the membrane material. Unfortunately also for the hyperbranched polymer, ethylene is the closest competitor in absorption.

3.2. Adsorption as an alternative separation system

According to the known criterion for selecting the separation methods for given feed and operating conditions [10], adsorption is not a prior choice for this OCM gas composition with predefined duty of removing carbon dioxide or ethylene. However, by analyzing the sequence of the required separation systems and the composition of the OCM reactor outlet stream, adsorption can become a promising separation method for OCM process.

The best place for using an adsorber is right after OCM reactor and the best scenario would be to use it instead of demethanizer. Demethanizer imposes huge cost on the classical OCM structure and any effort to substitute it with an efficient unit operation would contribute fundamentally to the whole OCM process economy. On the other hand, using adsorption enables to intensify the process where some part of the carbon dioxide is separated along with light gas components from ethylene and ethane. These two last components will be separated later using a proper separation method and the remaining carbon dioxide can be removed using an absorber or membrane system.

A model based analysis has been performed to analyze the performance of the adsorption system in OCM process. In this simulation, the characteristics of zeolite 4A was used as an adsorbent and detailed modeling of the process enabled to determine the required dimensions of the adsorption system and its performance.

Although using the available sorbents, Pressure Swing Adsorption (PSA) have not shown a promising results for general ethylene-ethane separation tasks in other applications, but achieving high level of purity and recovery for the OCM process in simulation study is encouraging.

In industrial application, the cycle of adsorption, switching, regeneration (with TSA heating or PSA pressure release) and cooling (TSA) will be completed with different time schedule. Beside, a by-pass adsorber is considered in the set of parallel absorber desorber systems in order to guaranty the continual operation of the system. Some ethylene is lost but in general by assuming ideal carbon dioxide separation, ethylene is finally achieved with 99.9% purity and 99.5% recovery.

4. Process scale analysis and process intensification

Beside the best C2 yield, the impact of some other aspects such as C2 selectivity and ethylene/ethane ratio have to be considered on developing the down-stream units. For example, if the best C2 yield is achieved for highly nitrogen diluted feed stream, it will impose extra cost on the down streaming processes due to the bigger equipment size and processing cost. Lower ethylene/ethane ratio can also cause extra cost in cryogenic distillation for separating them in the purification section. In general, following factors have process wide effects:

- The amount of the non-reacted methane,
- The amount of side products especially carbon dioxide,
- Using nitrogen diluents.

Even the type of gas diluents in the reactor, the type of the separation system should be taken into consideration. For instance, by using nitrogen as diluents the chance of losing selectivity in the polyimide membrane separation section becomes higher in comparison to using extra methane and working with lower methane to oxygen ratio in the reactor.

As another example, the duty of demethanizer in OCM process is really high since almost 40% of the gas composition is methane and there is a huge amount of energy needed in demethanizer for such a big scale treatment.

Ethane can be even used in the adsorption as a carrier gas if the adsorption system is preferred for separating the products from the light gas components.

5. Conclusions

A concurrent engineering approach to simultaneously analyze the effects of parameters in the performance of all process sections were technically applied in mini-plant scale OCM process and economically in industrial scale.

Several aspects such as effect of hot spot formation restrict the yield of the reactor and diluents gas for instance was considered to meet this challenge in the reactor section. However, it creates another challenge in the separation section and considering another measure such as higher methane to oxygen ratio in the reactor to tackle the original hot spot formation leads to better performance in some alternative separation parts but it imposes huge operating costs on the others such as demethanizer. The experimental results of the mini-plant facility enabled to investigate these interactive behaviors technically and the model based economic analysis performed on the industrial scale allowed to analyze the consequence of the design and operating decisions in terms of the fixed and operating cost. Using this process synthesis and analysis method enables to shorten the analysis procedure and make it more efficient in comparison to the step wise process synthesis approach.

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