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OXIDATIVE COUPLING OF METHANE: A NEW PROCESS CONCEPT FOR THE IMPROVEMENT OF THE DOWNSTREAM PROCESSING BY USING ADSORPTION

OKSYDACYJNE SPRZĘŻENIE METANU: NOWA PROCESOWA KONCEPCJA DOSKONALENIA PÓŹNIEJSZYCH ETAPÓW PRZETWARZANIA ROPY Z ZASTOSOWANIEM ADSORPCJI

Abstract

This paper, inspired by the success of adsorptive air separation in big scale (up to 250 tons/day), looks into the possibility of replacing cryogenic distillation with adsorptive separation, and thus improving the downstream processing of OCM. This results in a new process concept. For this purpose, a plug flow model of fixed-bed adsorber was developed and several separation schemes were investigated via simulation. Among them, the simultaneously separation of ethylene and carbon dioxide using zeolite 4A is found realizable. The results show that by switching from cryogenic distillation to adsorption, separation cost can be significantly reduced.

Keywords: OCM, adsorption, ethylene separation, carbon dioxide removal

Streszczenie

W artykule niniejszym, zainspirowany sukcesem adsorpcyjnego oddzielania powietrza na wielką skalę (do 250 ton dziennie), rozważa się możliwość zastępowania destylacji kriogenicznej oddzieleniem adsorpcyjnym i – co za tym idzie – doskonalenia końcowych etapów procesu OCM. W rezultacie powstaje nowa koncepcja procesowa. W związku z tym opracowano nowy model adsorbera oraz zbadano symulacyjnie kilka schematów oddzielania. Spośród nich za możliwy do zrealizowania uznano symultaniczne oddzielenie etylenu i dwutlenku węgla z zastosowaniem zeolitu 4A. Wyniki eksperymentów udowadniają, że dzięki przejściu od destylacji kriogenicznej do adsorpcji koszt oddzielania może ulec znacznemu ograniczeniu.

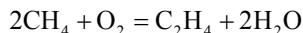
Słowa kluczowe: OCM, adsorpcja, oddzielenie etylenu, usuwanie dwutlenku węgla

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1. Introduction

Oxidative Coupling of Methane (OCM) is a type of chemical reaction for direct conversion of methane to ethylene:



Up to now, ethylene is produced mainly by steam cracking higher hydrocarbons in valuable oil fractions such as naphtha. The long-term reserve exhaustion and short-term price fluctuation of crude oil are motivating ethylene producers to find alternative raw materials. Considering prices in April 2012 of methane (approximately 140 EUR/ton) and ethylene (approximately 1250 EUR/ton), using OCM to convert methane in natural gas, the world's most abundant petrochemical resource, to ethylene, the world's most produced organic compound, is economically attractive with fourfold added value. Nevertheless, no effort to advance this process beyond experimental stage has been successful yet due to the low yield of ethylene per single pass (less than 30% with all reported catalysts). This low yield leads to high cost of product separation, which in turn is a major challenge that renders OCM unprofitable. Therefore, in parallel with catalyst/reactor development, an appropriate measure for separating components of the downstream, in particular ethylene – the desired product, is a key requisite for advancing OCM to commercial level. Reaction product mainly consists of ethylene, ethane, carbon monoxide, carbon dioxide, hydrogen and water, which are popular chemicals and theoretically easy to separate. In spite of that, the big capacities (thanks to low conversion of the reaction step) make the job a big challenge, where the effectiveness of the solution may determine if the whole process is profitable or not. Conventionally, each component in the product requires one separation step. Most proposed separation schemes [1, 2] separate components from the main stream (circulated methane) in the order of easiness and quantity: water, carbon dioxide, ethylene/ethane, carbon monoxide, hydrogen. Since methane is the component in the highest quantity, these arrangements give all steps high duties, consequently high cost, in particular the ethylene separation step, which usually employs cryogenic distillation. Taking suggestion from air separation process, where PSA technique successfully replaces cryogenic distillation at certain scales, the aim of this work is to investigate the adsorption process used for products separation in the downstream of OCM process.

2. State of the art

Ethylene separation by adsorption is not a new idea with patents dated in 1944 [3, 4]. Despite constant efforts since then, effective material and method for light olefin/paraffin separation stay a big challenge.

An adsorbent with high selectivity and capacity for ethylene is the key requirement for successful adsorptive separation. CuCl powder was the earliest candidate with high selectivity [5] but also dropped out early due to low surface area. Synthetic zeolites type A, commercially available in 1954, was the second candidate with more balance between selectivity and capacity. Early experiment on Linde zeolite 4A by Harper et al. showed an

equilibrium selectivity of 1.2 (STP) for ethylene/ethane [6]. Recent study on CECA zeolite 4A gave more details: selectivity is high in Henry's law region but reduce quickly with pressure [7]. Adsorption capacity of ethylene at normal pressure ranges between 2 and 3 mol/kg. The characteristic of zeolite 4A is not good enough for adsorption to compete with cryogenic distillation. Other zeolites were also tried, for example Davison 5A [8, 9] or Faujasite [10, 11], but the results are not notably better. Since commercial physisorptions do not have significant selectivity for olefins over corresponding paraffins, the idea of chemisorptions (like in the case of CuCl) is revived with the π -complexation. By spreading transition metal cations on solid substrates that have high surface area, new sorbents with improved selectivity and capacity were achieved [12–15]. Recently, reports on titanosilicates [16, 17] also show potential of adsorptive ethylene separation. However, another problem arises with these new highly selective sorbents: too strong bonding between sorbate and sorbent let to irreversible adsorption. Therefore, the problem of finding well tailored sorbents for ethylene separation is still not fully resolved.

In parallel with material experts, chemical engineers also tried to devise the best process with available sorbents. Several methods were investigated. Thermal swing adsorption (TSA) using feed or raffinate as purge gas is the oldest and most completely developed. Characterized by low residual loadings and high operating loadings, TSA is generally the process of choice for purification. A critical requirement of this method is the amount of purge gas must be less than feed gas or process will become dilution instead of separation. Long cycle time, which means large bed inventory in bulk separation, is also needed because sorbent temperature changes slowly. These matters limit the application of TSA in bulk separation. It is suggested that TSA at atmospheric pressure is not suitable when feed concentration is more than 1% [18]. Even with high pressure, TSA is not recommended when feed concentration is more than 10% [19]. Pressure swing adsorption (PSA), in some aspect, is contrary to TSA: Characterized by high residual loadings and low operating loadings, it is more suitable than TSA in bulk. Because sorbent particles respond quickly to change in pressure, PSA cycle times are short, lead to smaller bed inventory than TSA. As steps in a PSA cycle are highly coupled, excessive purge is prevented. This guarantee, however, sets a trade-off between product purity and recovery. Study by Rege et al. demonstrates this trade-off in ethylene/ethane separation with zeolite and π -complexation sorbent [20]:

Table 1

PSA performance with zeolite 4A ($P_H = 1 \text{ atm}$, $P_L = 0.1 \text{ atm}$)

Purity [%]	96.33	79.83	73.91	73.19	65.29
Recovery [%]	1.32	7.18	26.71	34.50	45.33
Throughput, g C ₂ H ₄ [h/kg] sorbent	0.109	0.032	0.292	0.160	0.116

PSA performance with $\text{AgNO}_3/\text{SiO}_2$ ($P_H = 1 \text{ atm}$, $P_L = 0.1 \text{ atm}$)

Purity [%]	99.73	91.92	83.86	81.26	85.09
Recovery [%]	8.81	22.46	41.12	41.38	48.73
Throughput, g C_2H_4 [h/kg] sorbent	0.135	0.062	0.058	0.061	0.054

The results show that, with the available sorbents, PSA is far from applicable in ethylene/ethane separation. Another method considered is concentration swing adsorption (cold purge) where regeneration is achieved using additional purge gas [21]. However, the need for extra step of final olefin/purge gas separation negates its attraction. Although researches on adsorption for ethylene separation still continue, the conclusion so far is: “for large-scale production of ethylene and propylene in the olefin plants, distillation will clearly remain to be the process of choice” [22].

3. Concept development

Generally, until a breakthrough of material science, adsorption cannot compete with distillation in large-scale, bulk separation of ethylene and we have to stay with the energy-intensive, costly (both capital and operating cost) cryogenic columns in the near future. The situation is, however, not so dire if ethylene separation is put in particular contexts such as OCM process. The downstream compositions of reactors lead to two important differences in ethylene separation between conventional plant and OCM plant.

In conventional ethylene production plant, the downstream of reactor flows through a series of distillation units: demethanizer, deethanizer, depropanizer, debutanizer, ethylene fractionator... Despite a large number of equipments, utilities cost can be substantially reduced by heat coupling. Since methane is the lightest hydrocarbon, demethanizer works at lowest temperature ($\sim 100^\circ\text{C}$) and highest pressure ($\sim 30 \text{ atm}$). In OCM reaction, there are little hydrocarbons higher than C_2 . Hence, the distillation part essentially consists of only demethanizer and ethylene fractionator. On the other hand, the duty of demethanizer is bigger due to large amount of methane ($> 40\%$ compare to $< 20\%$ in conventional ethylene plant). Simulation shows the heating duties of demethanizer and ethylene fractioner condensers are 1.62 MJ and 2.22 MJ for 1 kg ethylene produced by OCM. Taking into account operating temperature, the operating costs of demethanizer and ethylene fractionator are almost the same and operating cryogenic distillation may costs up to half of ethylene sale. Adsorption, therefore, should not aim at only ethylene/ethane separation but also ethylene/methane separation. Seeing that separating ethane from methane gives no benefit, these two processes can be combined in one equipment.

Unlike steam cracker, OCM reactor produces not only hydrocarbons but also carbon dioxide, carbon monoxide, hydrogen... The second major component, carbon dioxide, must

be separated before cryogenic distillation. When adsorption is used instead, carbon dioxide separation unit can be placed after ethylene separation. In that case, carbon dioxide can be used as purge gas for sorbent regeneration without extra separation unit. As carbon dioxide is adsorbed on zeolite, the regeneration method is displacement-purge. This method is more efficient for less selective sorbate/sorbent system [23] and low selective sorbent like zeolite can be used instead expensive sorbent like $\text{AgNO}_3/\text{SiO}_2$.

Based on the analysis above, a new scheme for OCM plant is proposed:

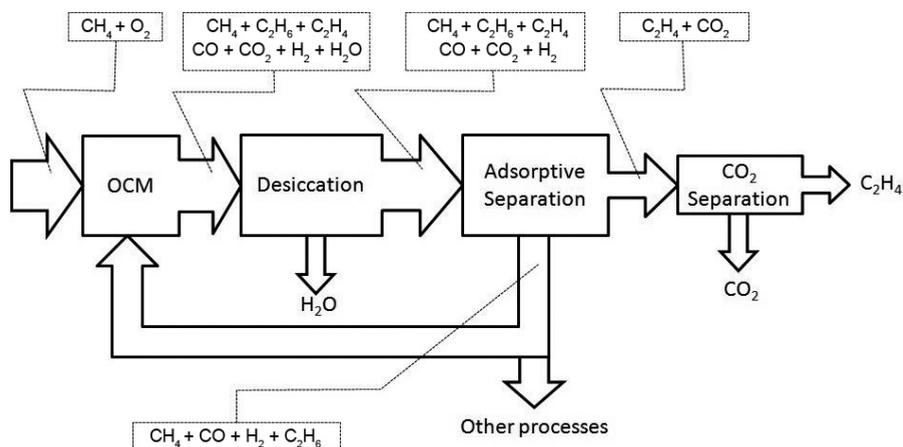


Fig. 1. The proposed scheme for OCM plant

Rys. 1. Proponowany schemat aparatury OCM

4. Simulation

To examine the new process, simulation of fixed-bed adsorber was conducted. Multi-component Langmuir isotherm with parameters from literature [6, 7, 20, 22, 24, 25 and 26] was used:

$$q_i^s = \frac{Q_i b_i p_i}{1 + \sum b_i p_i} \quad (1)$$

$$b_i = \frac{\alpha_i}{\beta_i (2\pi mKT)^{1/2}} e^{\frac{-\Delta H}{RT}} \quad (2)$$

Adsorption rate is approximated by linear driving force:

$$\frac{\partial q_i}{\partial t} = k_i (q_i^s - q_i) \quad (3)$$

$$k_i = k_{i0} e^{\frac{E_A}{RT}} \quad (4)$$

Plug-flow model is used:

$$\frac{\partial c_i}{\partial t} = -\frac{\partial(uc_i)}{\partial x} - \frac{1-\varepsilon}{\varepsilon} \frac{\partial q_i}{\partial t} \quad (5)$$

The model is solved by finite volume method using Matlab.

5. Result and discussion

Adsorption process was simulated with zeolite 4A at atmospheric pressure and temperature ranges between 320 K and 410 K. Void fraction is 0.5 and retention time is 20 s. Feed composition is given in Table 3.

Table 3

Feed composition [%mol]

N ₂	CH ₄	C ₂ H ₆	C ₂ H ₄	CO	CO ₂	H ₂
0.8	41.5	0.4	8.2	2.3	24.9	21.9

Like common TSA processes, the bed is clean after regeneration and cyclic steady state is approached in the first cycle. Each cycle lasts 800 minutes and consists of six steps:

- Step 1: Adsorption. Gas mixture is fed to adsorber in 200 minutes.
- Step 2: Blow. Pure ethylene is fed to adsorber to blow out light components in void space. This step is to increase ethylene purity and last 30 minutes.
- Step 3: Heat up. Adsorber is heated up for 170 minutes.
- Step 4: Desorption. The effluent of step 5 is recirculated in 100 minutes. Recirculation help reduce the amount of purge gas.
- Step 5: Purge. Adsorber is purged in 100 minutes, ethylene is completely desorbed.
- Step 6: Cool down. Adsorber is cooled down by inert gas in 200 minutes. Nitrogen is in simulation but dry air should be used in real plant to reduce cost.

Breakthrough curves of the first two steps are shown in Figs. 2 and 3. Breakthrough curves of the last three steps are shown in Fig. 4.

It can be seen in Fig. 2 that ethylene and methane are completely separated while Fig. 3 shows little impurity of ethane. In desorption step, most of ethylene is desorbed in 200 minutes (Fig. 4). Only effluent in the first 100 minutes flow to next unit, the effluent in the second 100 minutes has low ethylene concentration and will be circulated. Some ethylene is lost in cooling step. The effluent that is fed to carbon dioxide separation unit has composition of 64.9% CO₂ + 35.1% C₂H₄ with 60% flow rate of the original feed. Assuming ideal carbon dioxide separation, ethylene is finally achieved with 99.9% purity and 99.5% recovery.

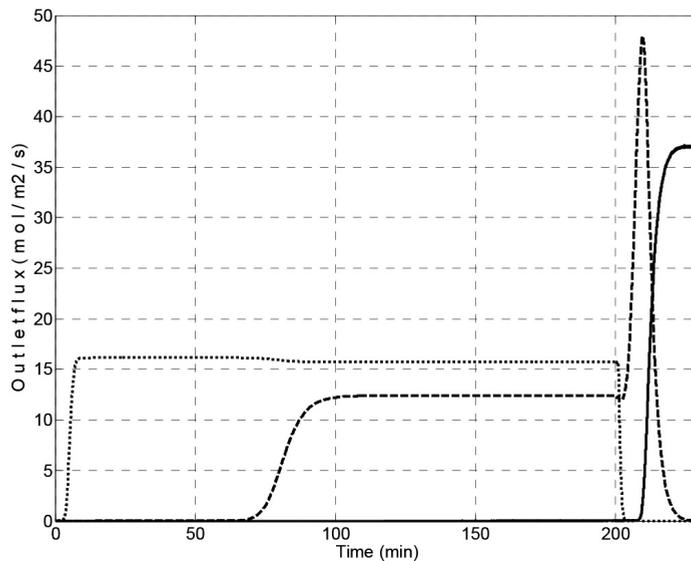


Fig. 2. Breakthrough curves in adsorptions steps of ethylene (solid), carbon dioxide (dash) and methane (dot)

Rys. 2. Przebieg zależności na etapach adsorpcji etylenu (linia ciągła), dwutlenku węgla (linia przerywana) i metanu (linia kropkowana)

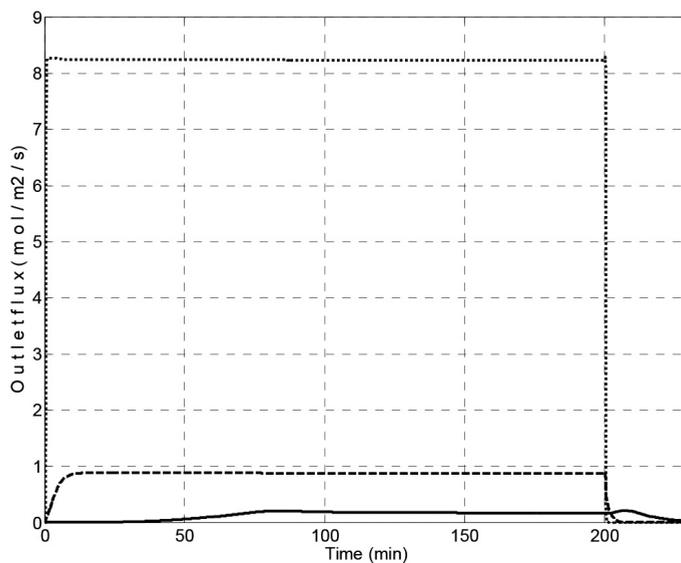


Fig. 3. Breakthrough curves in adsorption steps of ethane (solid), carbon monoxide (dash) and hydrogen (dot)

Rys. 3. Przebieg zależności na etapach adsorpcji etanu (linia ciągła), tlenku węgla (linia przerywana) i wodoru (linia kropkowana)

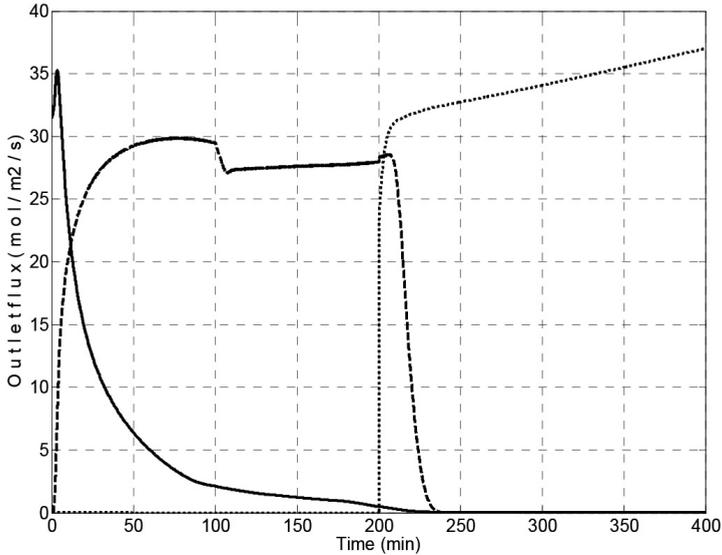


Fig. 4. Breakthrough curves in desorption steps of ethylene (solid), carbon dioxide (dash) and nitrogen (dot)

Rys. 4. Przebieg zależności na etapach desorpcji etylenu (linia ciągła), dwutlenku węgla (linia przerywana) i azotu (linia kropkowana)

6. Conclusions

In ethylene production, light olefin/paraffin separation by adsorption cannot compete with cryogenic distillation due to the lack of appropriate sorbents. Similar situation happens to OCM: it cannot compete with naphtha cracking because the lack of effective catalysts put such a burden on downstream process that traditional solutions like distillation are no longer applicable. However, the combination of two up-to-now uncompetitive processes may lead to a fruitful technology: thermal-concentration swing adsorption can separate ethylene with high purity and recovery, comparable to distillation. Compare to cryogenic distillation, the mild operating conditions of adsorption unit not only reduce utilities cost but also prevent many problems arise with very high pressure and low temperature. Combining with the new proposed scheme, it also makes carbon dioxide absorption easier with lower flow rate and higher concentration. Overall, the new concept can significantly improve OCM process. After simulation, further work on experiment and optimization is in progress.

Symbols

- b – Langmuir coefficient [1/Pa]
- k – adsorption rate coefficient [1/s]
- m – density [kg/m³]

q	–	adsorbed phase concentration [mol/kg]
q^s	–	saturated adsorbed phase concentration [mol/kg]
t	–	time [s]
x	–	axial coordinate [m]
E_A	–	activation energy [J/mol]
K	–	Boltzman constant [J/K]
R	–	gas constant [J/K.mol]
Q	–	maximum adsorbed phase concentration [mol/kg]
T	–	absolute temperature [K]
α	–	sticking probability
β	–	desorption constant [1/s]
ε	–	void fraction
ΔH	–	adsorption heat [J/mol]
i	–	component index (subscript)
OCM	–	Oxidative Coupling of Methan
PSA	–	Pressure Swing Adsorption
STP	–	Standard Temperature and Pressure
TSA	–	Thermal Swing Adsorption

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