

REFERENCES

- [1] Guy B. Marin, Gregory S. Yablonsky, Denis Constaes, Kinetics of Chemical Reactions: Decoding Complexity, 2nd Ed. 2018, John Wiley & Sons
- [2] John T. Gleaves, Gregory Yablonsky, Xiaolin Zheng, Rebecca Fushimi, Patrick L. Mills, Temporal analysis of products (TAP)—Recent advances in technology for kinetic analysis of multi-component catalysts, J. Mol. Catal.: A, 2010, 315, 108-134
- [3] Denis Constaes, Gregory S. Yablonsky, Guy B. Marin, John T. Gleaves, Multi-zone TAP-reactors theory and application, I: the global transfer matrix equation, Chem. Eng. Sci., 2001, 56, 133-149
- [4] Sergiy O. Shekhtman, Gregory S. Yablonsky, John T. Gleaves, Rebecca Fushimi, “State defining” experiment in chemical kinetics—primary characterization of catalyst activity in a TAP experiment, Chem. Eng. Sci., 2003, 58, 4843-4859
- [5] Gregory S. Yablonsky, Denis Constaes, Sergiy O. Shekhtman, John T. Gleaves, The Y-procedure: How to extract the chemical transformation rate from reaction–diffusion data with no assumption on the kinetic model, Chem. Eng. Sci., 2007, 62, 6754-6767
- [6] Gregory S. Yablonsky, Evgeniy A. Redekop, Denis Constaes, John T. Gleaves, Guy B. Marin, Rate-reactivity model: a new theoretical basis for systematic kinetic characterization of heterogeneous catalysts, Int. J. Chem. Kin., 2016, 48, 304-317
- [7] Raf Roelant, Denis Constaes, Guy B. Marin, TAPFIT manual, 2010

PROCESS SIMULATION AND LIFE CYCLE ASSESSMENT OF STEAM CRACKING PROCESS: EVALUATION OF THE IMPACT OF TECHNOLOGICAL IMPROVEMENTS BASED ON RELEVANT DATA OF THE COMPLETE INTEGRATED FURNACE PLATFORM

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МОДЕЛЮВАННЯ І ОЦІНКА ЖИТТЄВОГО ЦИКЛУ ПРОЦЕСУ ПАРОВОГО КРЕКІНГУ: ВИЗНАЧЕННЯ ВПЛИВУ ТЕХНІЧНИХ МОДИФІКАЦІЙ НА ОСНОВІ РЕЛЕВАНТНИХ ДАНИХ ПРО КРЕКІНГОВУ УСТАНОВКУ

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МОДЕЛИРОВАНИЕ И ОЦЕНКА ЖИЗНЕННОГО ЦИКЛА ПРОЦЕССА ПАРОВОГО КРЕКИНГА: ОПРЕДЕЛЕНИЕ ВЛИЯНИЯ ТЕХНИЧЕСКИХ МОДИФИКАЦИЙ НА ОСНОВЕ РЕЛЕВАНТНЫХ ДАННЫХ О КРЕКИНГОВОЙ УСТАНОВКЕ

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Steam cracking is the most energy-consuming process in the chemical industry and globally uses 8% of the sector's total primary energy. Life cycle assessment of different technical solutions as studied in the IMPROOF project such as high emissivity coatings, 3D reactor designs, advanced coil materials and oxy-fuel combustion with carbon capture have been carried out. The assessment showed that carbon footprint of proposed system can be reduced by up to 25% compared to the base case when oxy-fuel combustion combined with carbon capture and storage is applied.

Keywords: *steam cracking, life cycle assessment, process simulation, global warming, sustainable development*

Паровий крекінг являє собою найбільш енергоємний процес хімічної промисловості і глобально споживає 8% всієї первинної енергії в даній галузі. Проведено оцінювання життєвого циклу різних технічних модифікацій, досліджуваних в рамках проекту IMPROOF, таких як покриття з високою випромінювальною здатністю, трьохвимірною геометрією реактора, вдосконалені матеріали реактора та газокисневе горіння з системою уловлювання та зберігання вуглецю. Оцінка показала, що застосування вищезазначених технологій дозволить знизити вуглецевий слід процесу на 25% при використанні газокисневого горіння з системою уловлювання та зберігання вуглецю.

Ключові слова: *парової крекінг, оцінка життєвого циклу, моделювання процесів, глобальне потепління, сталий розвиток*

Паровой крекинг является наиболее энергоёмким процессом химической промышленности и глобально потребляет 8% всей первичной энергии в данной отрасли. Проведена оценка жизненного цикла различных технических модификаций, изучаемых в рамках проекта IMPROOF, таких как покрытия с высокой излучательной способностью, трёхмерная геометрия реактора, усовершенствованные материалы реактора и газокислородное горение с системой улавливания и хранения углерода. Оценка показала что углеродный след вышеописанной системы может быть снижен на 25% при использовании газокислородного горения с системой улавливания и хранения углерода.

Ключевые слова: *паровой крекинг, оценка жизненного цикла, моделирование процессов, глобальное потепление, устойчивое развитие*

INTRODUCTION

Steam cracking of hydrocarbons is the predominant pathway for the production of base chemicals such as ethylene, propylene and butadiene and globally uses 8% [1] of the sector's total primary energy. The arrangement of a typical steam cracking furnace is shown in Figure 1. Firstly, hydrocarbon feed is heated by flue gas in the convection section, mixed with steam, and further heated to coil inlet temperature (500...700 °C, depending on the feed). The hydrocarbon – steam mixture enters a fired tubular reactor (called radiant coil) and is rapidly heated from 500...700 °C to 750...875 °C for 0.1...0.5 s. During this short reaction time, the feed is converted into high value base chemicals such as ethylene and propylene as well as many by-products such as methane, hydrogen and pyrolysis gasoline. The cracked gas leaving the radiant coil at 750...875 °C is cooled to 550...650 °C within 0.02...0.1 s in transfer line exchanger in order to prevent secondary reactions that reduce process selectivity [2]. The resulting cracked gas, the detailed composition of which depends on feed type, feed quality, radiant coil selectivity and cracking severity, is then further cooled, compressed and separated into the desired products by cryogenic distillation in the so-called cold section of the ethylene plant. Since cracking of hydrocarbons to olefins is highly endothermic, high energy input is required. The high energy demand is met by burning fuel in the furnace. During cracking, coke is deposited on the inner wall of the reactor. The coke inhibits heat transfer and, therefore, reduces radiant efficiency.

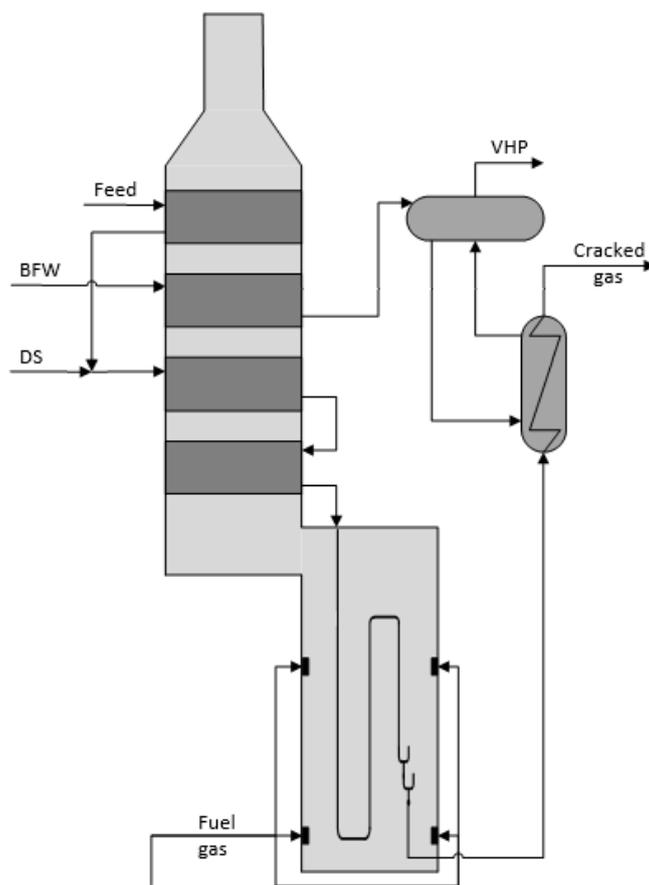


Fig. 1. Typical steam cracking furnace arrangement:
Feed – propane feed, BFW – boiler feed water, DS – dilution steam, VHP – very high pressure steam (105 bar, 315°C)

High heat demand results in considerable large CO₂ emissions, hence, high carbon footprint. Given the ever more demanding environmental regulations, it is also of high priority for producers to develop strategies and methodologies that enable them to significantly reduce these emissions.

Quantifying the impact of such technological improvements is of interest. SimaPro software package is employed to perform comparative cradle-to-gate life cycle assessment (LCA) for cracking products. The raw material and energy datasets are provided by ecoinvent database.

Different technological improvements can be used in order to reduce the CO₂ emissions. Herein, the impact of different technological improvement of steam cracking furnaces is being studied by performing life cycle assessment (LCA) based on simulation data. Different scenarios with technological improvements such as using 3D coil geometry, high emissivity coatings and combination thereof, as well as oxy-fuel case with carbon capture have been studied. The improvements were added to a reference base case, consisting of propane cracking furnace with air firing combustion.

FORMULATION OF PROBLEM

The aim of this study is to evaluate the environmental impact of state of the art steam cracking process and proposed economically viable technical improvements by conducting comparative life cycle assessment focused on carbon footprint based on simulation results validated on industrial data.

RESEARCH ANALYSIS

Since steam cracking products are base chemicals, cradle-to-gate study is being conducted [3]. Therefore, aside from the actual process (steam cracking of propane), cracking effluent separation is also considered. Carbon footprint of other steps of the product value chain, such as petroleum extraction, propane refining and transportation is calculated using inventory data retrieved from the ecoinvent database. A schematic representation of the system boundaries is shown in Figure 2. The impact of feed and natural gas supply has been estimated by using unit processes from the aforementioned ecoinvent database while impacts related to steam cracking process and effluent separation have been obtained from mass balance derived from industrial and simulation data.

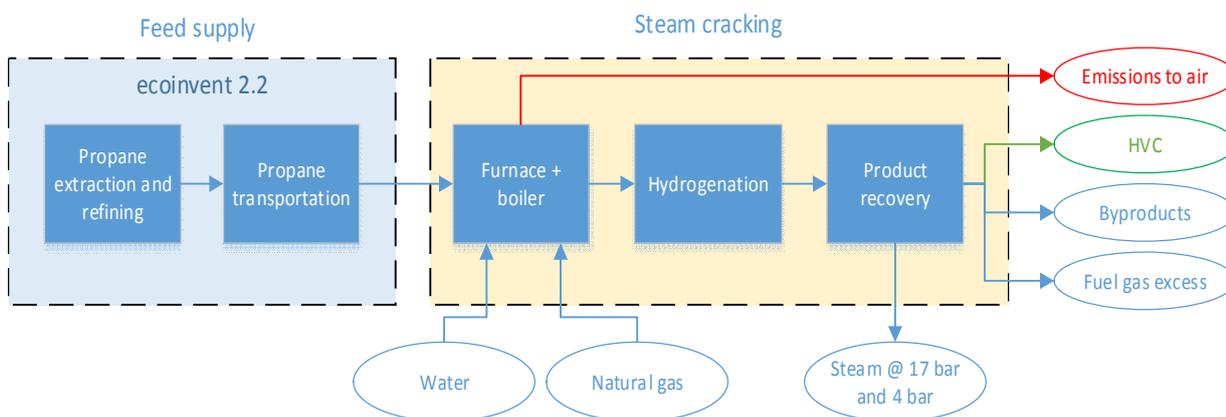


Fig. 2. System boundaries of the study

The steam cracking furnace with reactor coils, radiant box, convection section and TLE has been simulated by using COILSIM1D, a comprehensive steam cracking simulation package [4]. Chemical reactions are simulated with rigorously tested, detailed, single event microkinetic model. The reactant flow is assumed to be of the plug flow type which no radial gradients are assumed, except for the temperature in a very thin film close to the wall in which all resistance to heat transfer is located. Whole furnace simulations have been carried out with thermally coupled models of furnace box, reactor, TLE and convection section. It has been run for whole run length of the furnace with coil pressure drop imposed as limiting factor and all relevant results have been weight-averaged. Flows related to decoking procedure have been obtained from industrial data and assumed to be equal for all studied cases.

Valorisation of cracked gas process mass and energy balance was obtained by rigorous simulation of compression train, fractionation columns and cooling circuits.

FUNCTIONAL UNIT

In steam cracking using the term 'High Value Chemicals' (HVC) as a base unit for accounting product specific process parameters is an industry standard. The following substances are considered to be HVC, according to CEFIC [5]:

- Ethylene;
- Propylene;
- Butadiene contained in the C4 stream;
- Benzene contained in the pyrolysis gasoline stream;
- Hydrogen;
- Acetylene.

Given the aforementioned, the production of 1 metric ton of HVCs has been chosen as a functional unit for life cycle assessment. Material flows have been expressed according to the functional unit ($kg_i / \text{metric ton}_{HVC}$) and therefore, carbon footprint is calculated on the same basis ($kg_{CO_2,eq} / \text{metric ton}_{HVC}$). Three types of reactor coils have been studied. Bare tube coils made of 25/35 Cr Ni alloys are widespread in industry and have been used in this study as a base case. Two types of 3D coil geometries have been studied: finned and helical. Both coils are designed to improve radial mixing and convection inside the coil and therefore intensify heat exchange between the inner tube wall and hydrocarbon/dilution steam flow. The inner tube wall temperature is reduced and, hence, so is the coking rate. The downside of such approach is increased pressure drop which requires higher coil inlet pressure that might impact reaction selectivity. Given the aforementioned, and the high cost of 3D coils, novel geometry has been applied only to the last ~30% of the radiant coil where the highest tube wall temperature and coking rate is observed.

Besides geometry, novel coil material, aluminium-rich alloy, has been studied. The aluminium in the metal alloy substrate forms a thin, inert, stable oxide layer (alumina) on the inner surface that prevents catalytic coke formation, ultimately leading to ~25% reduction in coking rate. This alloy is assumed to be used for whole length of reactor coil.

Since preliminary studies have shown that coils and radiant box modifications alone are not enough to achieve the SPIRE⁴ IMPROOF⁵ project goals⁶, full oxy-fuel combustion with recycle and carbon capture and a storage system is proposed. A sensitivity study based on simulation has been conducted and a recycle ratio of flue gas from the furnace stack back to the burners, co-mingled with the oxygen, that is consistent with publicly available data [6] has been selected to match the flame temperature and convective heat duty of the base, air firing case. Industrial data [6] has been used in order to estimate the energy requirements of the carbon capture and storage (CCS) unit and a unit process for gaseous oxygen manufacture from the ecoinvent database has been chosen to estimate the carbon footprint for oxygen production. The carbon capture and storage system is assumed to absorb 100% of the CO₂ in the furnace flue gas and no other streams, except for electrical power consumption, have been considered. List of cases studied is provided on Table 1.

⁴ Sustainable Process Industry through Resources an Energy Efficiency: URL: <https://www.spire2030.eu/>

⁵ Integrated model guided process optimization of steam cracking furnaces: URL: <https://improof.cerfac.fr/>

⁶ "...to drastically improve the energy efficiency of steam cracking furnaces by at least 20%, and this in a cost effective way, while simultaneously reducing emissions of greenhouse gases and NOX per ton ethylene produced with at least 25%"

Table 1. Studied combinations of improvements

Case	Bare coil	3D coils		Emissive coating	Alumina rich alloy	Oxy-fuel + CCS
		Finned	Helical			
1 (base)	✓					
2 (base_EM)	✓			✓		
3 (ALU)	✓				✓	
4 (FIN)		✓			✓	
5 (FIN_EM)		✓		✓	✓	
6 (HEL)			✓		✓	
7(HEL_EM)			✓	✓	✓	
8 (OXY_CCs)	✓					✓

RESULTS

The results from the LCA study, expressed as % reduction of total greenhouse gases emissions [kg CO₂ eq.] are shown on figure 2. The best results from the air fired scenarios are achieved by combining high emissivity radiant box coating, helical 3D coil geometry and aluminium-rich alloy coils. High emissivity refractory coating reduces the firing rate by increasing radiative heat transfer efficiency and reducing flue gas temperature. The effect of 3D coils and aluminium-rich alloy is attributed mostly to prolonged run length that reduces the amount of CO₂ emissions produced while decoking (non-productive) stage related to a mass unit of high value products. The overall CO₂ footprint reduction is being scaled down by the contribution of upstream (~50% of overall) and by steam consumption by recovery section that is being constant for all the cases.

The best overall result is obtained from full oxy-fuel combustion with CCS despite the additional emissions related to air separation and CCS operation.

CONCLUSIONS

Shifting heat duty from convection section to radiant box alone may yield up to 0.973% reduction of overall HVC carbon footprint. Thus, in order to achieve better results, optimization of whole ethylene plant should be considered. Improvements for the separation stage such as hybrid steam – electric compressors, selectivity oriented upgrades such as ultra-high selectivity coils coupled with novel heat integration arrangement are expected to provide up to 20% reduction in carbon footprint of high value chemicals and therefore should be studied in detail.

Oxy-fuel with CCS has shown potential to achieve project goals and reduce overall HVC impact by 25%; moreover, full oxy-fuel combustion occurs in a nitrogen-free environment, therefore emits only trace amounts of NO_x and provides an opportunity to use CO₂ as a valorised feed. However, the overall footprint is highly sensitive to the assumptions made and needs to be studied in more detail.

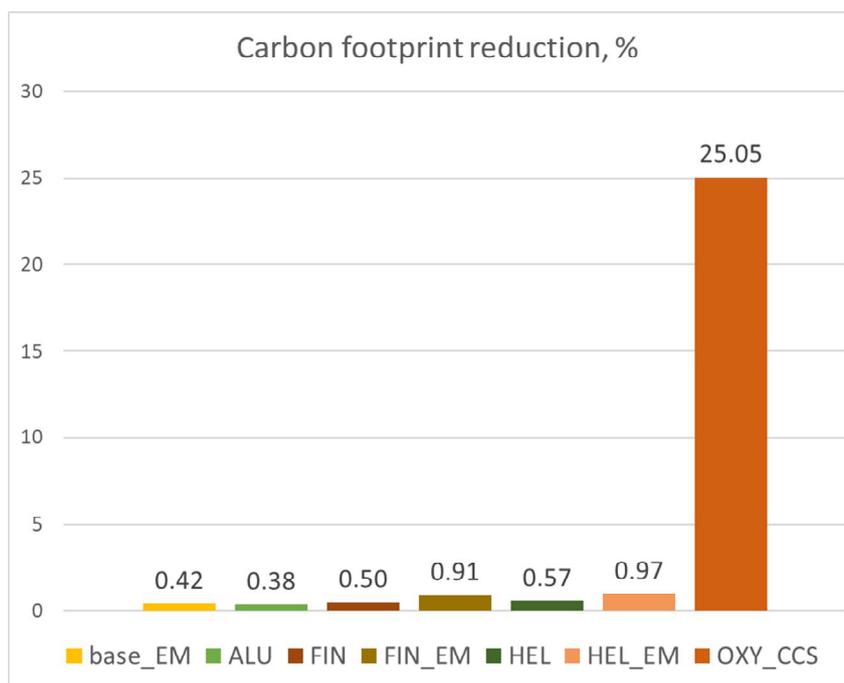


Fig. 2. Life cycle assessment results: relative carbon footprint reduction

REFERENCES

1. Ren, T., Patel, M. K., Blok, K. Steam cracking and methane to olefins: Energy use, CO₂ emissions and production costs. *Energy*. 2008.
2. Zimmermann, H., Walzl, R. Ethylene: Ullmann's Encyclopedia of Industrial Chemistry. Weinheim, Germany, Wiley-VCH Verlag GmbH & Co. KGaA, 2009.
3. WBCSD. Life Cycle Metrics for Chemical Products. 2014. C. 120.
4. Geem, K. M. Van, Reyniers, M. F., Marin, G. B. Challenges of Modeling Steam Cracking of Heavy Feedstocks. *Oil & Gas Science and Technology - Revue de l'IFP*. 2008. Vol. 63, No. 1. C. 79–94.
5. (APPE), A. of P. P. in E., (CEFIC), and the E. C. I. C. Annex to the European Crackers Benchmark Rule Book: The publication of the allocation mechanism for cracking units based on the top10 % benchmark performance value. Background CEFIC 's APPE benchmark for cracking units: 2013. 1–8c.
6. Weikl, M. C., Schmidt, G. Carbon capture in cracking furnaces. *AIChE Paper Number 12c*. 2010. No. 12. C. 21–25.