PROCEEDINGS OF THE 30th European Symposium on Computer Aided Process Engineering
(ESCAPE30), May 24-27, 2020, Milano, Italy

Coproduction of ethylene and propylene based on ethane and propane feedstocks

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Abstract

In this work, we develop a mathematical model to make decisions about the optimal scheme and operating conditions of an olefin plant. We formulate a superstructure that includes ethane and propane steam cracking, propane dehydrogenation and olefins metathesis process for the co-production of ethylene and propylene. Furthermore, considering the relevance of the separation scheme, the state equipment network (SEN) representation is considered and rigorous equations to model distillation columns (MESH) are formulated. This model is implemented in GAMS to maximize the project net present value (NPV). Numerical results show that the combination of ethane steam cracking and olefin metathesis is the most profitable configuration under the price scenario considered in this work.

Keywords: olefin production, superstructure optimization, propane dehydrogenation, metathesis, steam cracking

1. Introduction

The shale gas revolution has led to a high availability of natural gas liquids (NGLs), which are excellent feedstocks for chemical industries. In particular, there are economic advantages of using NGLs for olefin production instead of naphtha feedstock (Siirola, 2014). Thus, there is a general trend to turn reactive furnaces to work with ethane for ethylene production, even in countries that do not have shale gas exploitation, since they can import ethane at competitive prices (U.S. Energy Information Administration, 2019). This feedstock switch has also promoted a propylene yield reduction since propylene selectivity from naphtha is higher than from ethane. In addition, propylene demand continues rising mainly due to polypropylene consumption (Baker, 2018). The combination of both facts encouraged the development of on purpose technologies for propylene production (Lavrenov, Saifulina, Buluchevskii, & Bogdanets, 2015).

There are numerous process alternatives to produce propylene from both, petrochemical raw material and chemical intermediates, such as methanol into olefins, methanol into propylene, olefin metathesis, propane dehydrogenation, and deep catalytic cracking. Among these alternatives, both propane dehydrogenation and olefin metathesis are particularly interesting technologies since either could be used with ethane steam cracking to produce ethylene and propylene more efficiently.

To the best of our knowledge, an optimal design of a plant producing ethylene and propylene that includes propane dehydrogenation and metathesis of olefins as process alternatives has not been studied in the literature. In addition, numerous papers that address optimal plant designs use short-cut models in distillation columns (Chen & Grossmann, 2017). While these approaches allow simplifying the optimization model, unfortunately, they are much less accurate in comparison to rigorous mass balances, equilibrium, summation and heat (MESH) equations, and consequently, may provide only rough estimations that directly affect economic indicators.

In this work, we formulate a superstructure to determine the optimal scheme of an olefin plant. Raw materials include both ethane and propane, and the superstructure embeds steam cracking furnaces, propane dehydrogenation, and metathesis as potential technologies. Furthermore, taking into account the relevance of the separation scheme, the state equipment network (SEN) representation (Chen & Grossmann, 2017), and rigorous equations (MESH) to model distillation columns are formulated. Numerical results show that the optimal scheme includes a combination of ethane steam cracking and olefin metathesis.

2. Process description

The present work addresses the optimal design of a plant producing ethylene and propylene at a rate of 500 kt/year for each olefin. Figure 1 shows the plant sections, where the different alternatives for the reactive pathways are presented. The raw materials are ethane and propane, and the entire process can be represented through three different sections: alkane conversion, separation train, metathesis section.

2.1. Alkane conversion

2.1.1. Ethane conversion

The commercial technology to produce ethylene from ethane feedstock is steam cracking. We should note that the reactor capacity for ethylene production is not fixed. This olefin is required to satisfy market demand, but it could also be transformed into propylene in the plant. Thus, discrete decisions are related to the number of furnaces included in the optimal design.

2.1.2. Propane conversion

We consider three different reaction pathways for handling propane feedstock, which are: steam cracking of propane, Pt-based propane dehydrogenation (Pt-PDH), and Cr-based propane dehydrogenation (Cr-PDH).

Steam cracking of propane mainly produces ethylene. It employs complex furnaces operating at high temperatures, as in steam pyrolysis of ethane. There are also discrete decisions associated to propane production furnaces in the plant.

Pt-PDH is a commercial process, developed by UOP Oleflex, with a 36 % propane conversion per pass, and an 85 % propylene selectivity (Maddah, 2018).

Cr-PDH is another propane dehydrogenation technology, commercialized as Catofin Process, which has a 40 % propane conversion per pass, and its selectivity towards propylene is around 88 % (Maddah, 2018).

2.2. Separation train

Since the output streams from ethane and propane processing reactors have roughly the same chemical species, both streams can be mixed and processed through the same separation train to purify the olefin products. Thus, this strategy comprises process intensification.

The separation train consists of a quench tower to reduce the temperature reactor output stream, a series of compression stages, an acid gas removal unit to eliminate carbon dioxide and hydrogen sulfide, a dehydration process, a reactor for acetylene hydrogenation, a cold box for hydrogen separation, and a sequence of distillation columns to perform the final product purification.

In the representation of Fig. 1, the "main separation" block includes demethanizer, deethanizer, and depropanizer columns, and acetylene reactor; their interconnections are modeled with discrete variables. C2 and C3 splitters purify the main products, ethylene, and propylene, respectively, and the separated ethane and propane are recycled to "Alkane conversion" section. The debuthanizer column produces a butene stream that can be either sold or fed to the "Metathesis section". In addition, pyrolysis gasoline is obtained from debutanizer column bottom, but for the sake of clarity in Fig. 1, this product is omitted.

2.3. Metathesis section

An alternative process to produce propylene is the metathesis of ethylene and butenes. The propylene selectivity is about 95 %, and the butenes per-pass conversion is over 60 % (Ondrey, 2004). This technology employs a mixture of WO_3/SiO_2 and MgO as a catalyst for the metathesis and isomerization reactions.

A hydrogenation unit is used to eliminate diene and enyne compounds from the butene mixture. Then, the resulting stream is fed to an isomerization reactor to increase the composition of trans-2-butene. Next, ethylene and butene streams are fed to a fixed bed catalytic reactor where the metathesis reaction takes place. The output of this reactor is a mixture of ethylene, propylene, butenes and C_5^+ components. This mixture is treated in a series of distillation columns for propylene purification, which also involves discrete decisions regarding the separation scheme. From this set of columns, three output streams are obtained. First, the ethylene stream can be recycled or mixed with ethylene product stream. Second, the propylene stream is mixed with propylene product stream. Finally, the C_4^+ stream is sent to the debuthanizer column in the separation train section. Thus, in "Propylene purification" block (Fig. 1), there are also discrete decisions regarding the separation sequence.

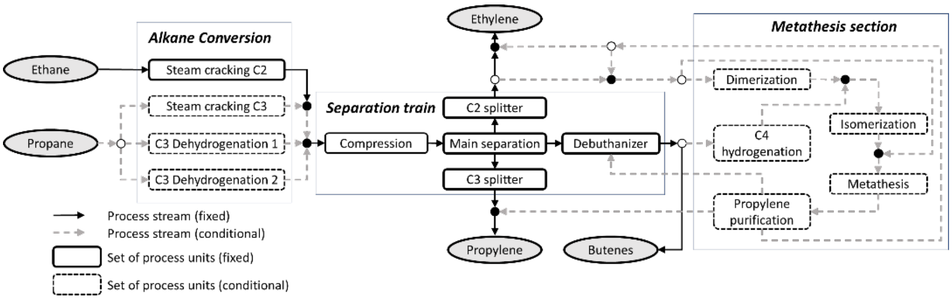

Figure 1: Plant sections for ethylene-propylene co-production

3. Mathematical modeling

We formulate process unit models within the superstructure representation and streams are defined by the connection between two units. The problem complexity of finding the optimal scheme increases with the number of units and tasks considered in the superstructure. In order to tackle this issue, Yeomans and Grossmann (Yeomans & Grossmann, 1999) have proposed the state equipment network (SEN) representation, which allows addressing the problem systematically. In addition, this representation allows presetting the number of columns, avoiding nonexistent process units in the superstructure. Consequently, the number of flow and size variables forced to be zero is reduced, as well as the potential issues regarding numerical singularities. In SEN, the fed and produced states of equipment units depend on potential tasks that can be performed in each unit. In this work, the tasks assignment is based on the location of the separation cut for the distillation column.

Figure 2a shows the state equipment network for the main separation block (see Fig. 1). In this work, states are characterized by their composition. After compression, the reactor output stream is sent to the main separation block which includes the columns: demethanizer, deethanizer and depropanizer separating the stream in component groups. The identified component groups are: H_2 (hydrogen), C_1 (methane); C_2 (ethane and ethylene); C_2^a (ethane, ethylene, and acetylene); C_3 (species with 3 carbon atoms), and C_4^+ (species with 4 or more carbon atoms). Therefore, the discrete decisions associated with the separation scheme focus on task assignments in the demethanizer, deethanizer and depropanizer (based on the separation cuts). In addition, the acetylene hydrogenation is an important process in this section that also has discrete tasks associated. In this work, only front-end configurations were considered for acetylene hydrogenation unit since they are more energy-efficient (Zimmermann & Walzl, 2009). Consequently, H_2, C_1 and C_2 species must be in the acetylene reactor feed stream. Propylene purification (in metathesis section) also includes discrete decisions associated with column separation tasks, as Fig. 2b shows. In this case, the mixture to be processed is composed of ethylene (Et), propylene (Pr), and species with 4 or more carbon atoms (C_4^+).

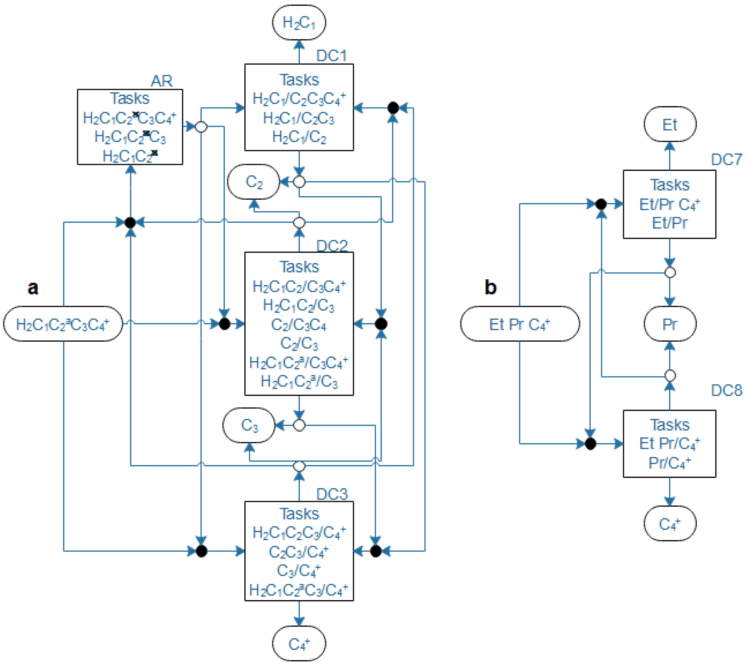

Figure 2: States equipment network. a) main separation train. b) propylene purification in the metathesis section. DC1: demethanizer. DC2: deethanizer. DC3: depropanizer. DC7: Deethylenizer. DC8: Depropylenizer. ●: mixer. ○: splitter

The corresponding disjunctions for the STN representation are as follows:

$$\bigvee_{t\in Ta_u}\left[\begin{array}{c} W_{u,t} \\ \left.\begin{array}{c} F_{s,u',c}=F_{u',u,c} \\ T_{s,u'}=T_{u,u'} \\ P_{s,u'}=T_{u,u'} \\ H_{s,u'}=T_{u,u'} \end{array}\right\} \begin{array}{c} c\in C \\ s\in SI_{u',u,t} \\ u'\in UI_u \end{array} \\ \left.\begin{array}{c} F_{u,s,c}=F_{u,u',c} \\ T_{u,s}=T_{u,u'} \\ P_{u,s}=P_{u,u'} \\ H_{u,s}=H_{u,u'} \end{array}\right\} \begin{array}{c} c\in C \\ s\in SO_{u,u',t} \\ u'\in UO_u \end{array} \end{array}\right] u\in\{DC1, DC2, DC3, AR, DC7, DC8\}$$

where $W_{u,t}$ is the Boolean variable that is true if the task t is performed in unit u, and false otherwise; $F_{s,u',c}$ is the molar flow from state s to u' of the chemical compound c; $T_{s,u'}$, $P_{s,u'}$ and $H_{s,u'}$ are the temperature, pressure and enthalpy flow from state s to u', respectively; C is the set of chemical species; Ta_u is the set of tasks that can be performed in unit u; $SI_{u',u,t}$ is the state that is fed through mixer u' and processed in unit u when the task t is selected; $SO_{u,u',t}$ is the state that is delivered through splitter u and produced in unit u' when the task t is selected; UI_u and UO_u are the sets of input mixer and output splitter corresponding to unit u, respectively.

In the superstructure, we include different reactor types, heat exchangers, flash, pumps, compressors, mixers, splitters, and distillation columns. Each type of process unit has equations to describe its physical behavior and to calculate its costs when applicable. We formulate a Generalized Disjunctive Programming mode (Vecchietti & Grossmann, 2000); thus, the presence of each unit is associated with Boolean variables as follows

$$\begin{bmatrix} Y_u \\ h(x)\le 0 \\ Ax\le b \end{bmatrix} \veebar \begin{bmatrix} \neg Y_u \\ Bx=0 \end{bmatrix}$$

where Y_u is the Boolean variable that is true if the unit u is present, and false otherwise; and the continuous variables x include material flows, operating temperature and pressure, enthalpy flows, unit internal variables, and unit capital cost. To solve the problem, we used the logic-based outer approximation algorithm (Turkay & Grossmann, 1996), in which the problem is decomposed into reduced NLP subproblems and the master MILP problem. In this way, NLP subproblems only include the nonlinear equations related to the disjunction active terms, avoiding potential issues regarding singularities. The master MILP is formulated based on the outer approximation with equality relaxation and augmented penalty approach (Viswanathan & Grossmann, 1990).

4. Case study

USA data prices reported in the literature (Boulamanti & Moya, 2017) were considered for the present case of study. Due to the active exploitation of shale gas resources in this country, ethane feedstock (146 EUR/t) is quite more economical than propane (394 EUR/t). When we solve the problem with the logic-based approach in GAMS 24.2.3, we found the optimal solution after solving three NLP subproblems and two Master problems, as Table 1 shows. The resulting Master MILP problems have 140 binary variables. Table 2 shows the most important economic indicators for the optimal scheme.

Numerical results indicate that the optimal scheme includes four steam cracking furnaces to produce ethylene from ethane in the alkane conversion section. Neither furnaces for propane steam cracking nor propane dehydrogenation technologies were selected. That means, propane feedstock was not employed in the optimal design. Instead, ethane feedstock is used to produce more ethylene for its further conversion in propylene through the metathesis process, whose section is included in the plant. Regarding the separation scheme, Table 3 shows the tasks assigned for each equipment unit. It is observed that a deethanizer first configuration was selected in the optimal solution scheme.

Table 1: Summary of iterations with the logic-based outer approximation algorithm

Iteration/subproblem	Objective	CPU time (s)	Constraints	Continuos vars.
NLP 1 (CONOPT)	1526	74	38847	38783
Master MILP 1 (Cplex)	2006	3921	71699	86919
NLP 2 (CONOPT)	2040	784	37681	37233
Master MILP 2 (Cplex)	1475	59075	115362	132362
NLP 3 (CONOPT)	2037	1104	37764	37316

Table 2: Economic indicators for the optimal solution

Net present value (MM$)	2040	Revenues (MM$/year)	1229
Investment (MM$)	1142	- Ethylene (MM$/year)	569
Net income (MM$/year)	564	- Propylene (MM$/year)	603
		- By-products (MM$/year)	57

Table 3: Selected tasks for equipment in the optimal scheme

Equipment	DC1	DC2	DC3	AR	DC7	DC8
Task	C_1/C_2	$C_1C_2^a/C_3\ C_4$	C_3/C_4	$C_1C_2^x$	Et/Pr	Et Pr/C_4

5. Conclusions

This work addresses the optimal design of an olefin plant producing ethylene and propylene. The optimal plant design includes four ethane steam cracking furnaces, and no propane feedstock is employed. The selected reactive pathway to produce propylene was the metathesis of olefins and the optimal configuration includes the deethanizer column as the first separation step.

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