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Superstructure-based Optimization for Assessing Defossilization Pathways in Petrochemical Clusters

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Abstract

The petrochemical industry needs to reduce the use of fossil fuel as carbon feedstock to reduce its CO2 emissions. Several alternative carbon sources (ACSs), such as biomass, CO2 and plastic waste are being proposed to replace fossil carbon. As each of these ACS process routes has its tradeoffs, it is essential to identify the defossilization pathways that will have the most significant impact. In this work, a superstructure-based optimization approach is presented that can be used to assess defossilization pathways in existing petrochemical clusters. The small case study shows that CO_2 is a promising ACS to replace fossil fuel as the main carbon source but requires a large amount of green hydrogen and significant modifications to the existing cluster.

Keywords: superstructure, optimization, petrochemical clusters, carbon transition

1. Introduction

To reach the CO_2 emissions goals set out by the European Commission, the petrochemical industry will have to drastically reduce its usage of fossil-based carbon. With this purpose, alternative carbon sources (ACSs), such as biomass, CO_2, and plastic waste, are being investigated. However, their introduction to existing petrochemical clusters is far from straightforward, as it will require the modification of existing processes or the deployment of entirely new processes. Thereby, potentially affecting other processes in a petrochemical cluster due to the significant number of existing material and energy interconnections. Furthermore, each of these ACS processes has its own tradeoffs and limitations. Therefore, it is vital to identify and assess the defossilization pathways that could provide the most optimal transformation of petrochemical clusters.

PSE tools such as superstructure-based optimization have been used for the synthesis and design of new chemical processes. In this approach, a set of alternative equipment or process options is assessed with respect to an objective function. This approach has been used to design new industrial clusters or optimize the exchange network between processes in existing industrial clusters. Kantor et al. (2020) developed a mixed-integer linear programming model for integrating material and energy in industrial clusters. They

used single objective functions to determine the ideal network configuration. The authors focused on greenfield applications and, therefore, ignored the existing interconnections that are present in today's petrochemical clusters. However, as processes in petrochemical clusters are interconnected by many material and energy flows, altering such connections due to e.g., replacing processes or flows, can have unforeseen consequences. This could, for instance, result in a shift of emissions from one process to another or from inside the cluster to emissions outside the cluster boundaries due to increased demand on energy or carbon-intensive materials.

This work shows a superstructure-based optimization model that explicitly incorporates interconnections existing in an industrial cluster while assessing different processing routes to replace the source of carbon. This model determines the minimal amount of ACS required to completely replace the fossil-based carbon source and the energy required by the cluster.

2. Method

To set up the model, the chemical processes, utility generation units, available feedstocks, and desired products were defined as nodes (see Figure 1). Besides the nodes, the chemical components and the different energy types in the superstructure were defined as follows: CC is the set of all the chemical components, for instance ethylene, propylene, and methyl tert-butyl ether. CU is the set of set of the utility types, for instance, low-pressure steam, cooling water, electricity. Separate layers were introduced for the material and energy connections in the superstructure, allowing different constraints for each layer to close the respective mass and energy balances. The figure shows that in the material layer, the interconnections between the available feedstocks, process, and utility options, and desired products were explicitly defined using transfer blocks to mimic the existing value chains of a cluster as closely as possible. These transfer blocks distribute the flow of mass between the processes.

Based on Figure 1, mass equations were defined. For each node *b* of the material layer, the total mass of component cc into the node equals all the mass flows of component *cc* into the node:

$$mass_{b,cc}^{In} = \sum_{\substack{i \\ i \in \mathbf{B}, b \neq i}} streams_{i,b,cc}^{Mass} \tag{1}$$

Where, $streams_{i,b,cc}^{Mass}$ stands for the mass flowrate from node *i* to node *b*. It was assumed that the process' input and output scales linearly. For each process, a limiting component was selected that scales the other inputs and outputs of each process. Therefore, the mass flow of a component into a component can then be calculated by:

$$mass_{b,cc}^{In} = mass_{p,cc'}^{In} \cdot X_{b,cc}^{MassIN} \tag{2}$$

Where, $mass_{p,cc'}^{In}$ is the mass flow rate into node *p* of the limiting component *cc'* and $X_{b,cc}^{MassIn}$ mass flow in a parameter. Based on the mass flow rate into a process node or utility node, the mass flow out of the process node or utility can be calculated by:

$$mass_{p,cc}^{Out} = mass_{p,cc'}^{In} \cdot X_{p,cc}^{Mass} \tag{3}$$

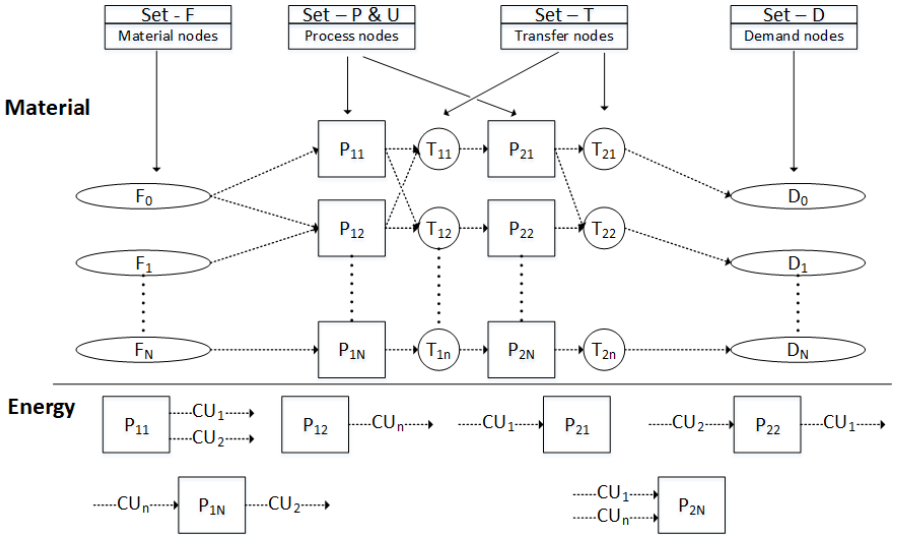

Figure 1

Figure 1: General superstructure representation of the material and energy layers, where F is the set of feed nodes, P is the set of process nodes, U is the set of utility nodes, D is the set of demand nodes, and the set containing all these subsets is B.

Where, $X_{p,cc}^{Mass}$ is the conversion parameter. As there is no reaction in other nodes, the mass flow out is there equal to mass flow in. The mass flowrate between a transfer node *t* and a node *b* can thus be calculated by:

$$streams_{t,b,cc}^{Mass} = mass_{t,cc}^{Out} \cdot y_{t,b} \tag{4}$$

Where, $mass_{t,cc}^{Out}$ is the mass flow rate of component *cc* leaving the transfer node and $y_{t,b}$ is the variable the transfer coefficient that assigns the mass flow rate off each stream leaving the transfer node. For which the following constraint was introduced:

$$\sum_{\substack{b \in B \\ b \neq t}} y_{t,b} = 1 \tag{5}$$

For the other nodes, the mass flow rate between nodes b_1 and b_2 is given by:

$$streams_{b_1,b_2,cc}^{Mass} = mass_{b,cc}^{Out} \cdot S_{b_1,b_2,cc} \tag{6}$$

Where, $S_{b_1,b_2,cc}$ is the separation coefficient, which is a pre-determined parameter based on process simulations that assign the distribution of each component over the outgoing streams. After the definition of the equations of the material layer, the equations for the energy layer were defined. Contrary to the material equations, the available energy connections were not explicitly defined, and the potential connections between nodes can be considered based on the proximity of the other nodes. The energy of type *cu* supplied by a process or utility node $E_{p,cu}^{D}$ is calculated by:

$$E^{D}_{p,cu} = mass^{In}_{p,cc'} \cdot X^{D}_{p,cu} \tag{7}$$

while the energy demanded by a process or utility node is given by:

$$E^{S}_{p,cu} = mass^{In}_{p,cc'} \cdot X^{S}_{p,cu} \tag{8}$$

Where, $X^{D}_{p,cu}$ is the energy demand coefficient of type *cu* and $X^{S}_{p,cu}$is the energy supply coefficient. These coefficients relate the energy supplied and demanded to the mass flow rate of the limiting component entering the process or utility node, thereby linking the material and energy equations. To solve the energy equation, the energy balance needs to close so:

$$\sum_{i \in \mathbf{B}} E^{D}_{i,cu} = \sum_{i \in \mathbf{B}} E^{S}_{i,cu} \tag{9}$$

To ensure, that that the energy leaving a process or utility node does not exceed the energy supplied by the node:

$$\sum_{j \in \mathbf{B}} streams^{Energy}_{i,j,cu} \leq E^{S}_{i,cu} \tag{10}$$

Finally, to determine the flow of energy between nodes,

$$E^{S}_{i,cu} + \sum_{j \in \mathbf{B}} streams^{Energy}_{j,i,cu} = E^{D}_{i,cu} + \sum_{j \in \mathbf{B}} streams^{Energy}_{i,j,cu} \tag{11}$$

In this paper, for the objective function, the flow of the carbon sources was minimized, and the availability of carbon sources was limited to obtain different optimal configurations.

3. Case study

To illustrate the method, we examine the potential of ACS to defosilize the carbon sources used in the production of ethylene, propylene and MTBE in an existing cluster. With this purpose, an in-house model that mimics part of the Port of Rotterdam was used. The model is described in detail in previous work (Tan et al., 2023). From this model, 10 fossil-based processes, five utility processes, processes, 112 chemical components, and six energy components were taken. Four ACS-based processes were added: biomass to isobutylene via an organosolv route, plastic pyrolysis, CO_2 hydrogenation to methanol, and methanol to olefins (MTO).

Based on the locations in the PoR, the 10 processes were assigned to one of three sites. New ACS-based processes were assumed to be located at the same site as the processes they aimed to replace. Furthermore, the material streams can cross the boundaries of each site, while the energy balance would be solved for each site individually. For each process and utility generation node, the assumption was made that the output linearly scales based on the input. These conversion parameters (e.g. $X^{Mass}_{p,cc}$) were used to linearize the processes were derived based on Aspen Plus simulations of each process. Additionally, the minimal production capacity (defined as the minimal mass of product per year) of each process and utility generation process were limited to a 10% deviation from its base

production capacity, while the exiting production capacities in the PoR (e.g., the MTBE process produces 400 kt/y) were set as the upper limit.

For the new ACS-based processes, the production capacity was limited as the vessels involved with these processes are much bigger in size and have a high feedstock demand. Therefore, multiple units of an ACS-based process or combined ACS feedstock (e.g. CO_2 and plastic waste) might be required to replace the current production of a fossil-based product. The petrochemical cluster was required to produce a fixed demand of all the chemicals at the end of each value chain (MTBE, ethylene glycol, and styrene monomer), which was based on the current production levels present in the PoR. Additional demand nodes were added for excess intermediate products (ethylene, propylene, propylene oxide, and tert-butyl alcohol) with no product demand constraint enforced on them. For the energy layer, energy demand and supply nodes were added to each site, representing connections to other processes in the PoR and the electricity grid. These nodes export excess energy from a site and import required energy if the utility processes do not match the demand. The resulting superstructure was implemented as a mixed integer linear programming problem in Pyomo and solved using the Gurobi solver.

4. Results and discussion

The original fossil-based configuration and the optimal configuration of the material layer are shown in Figure 2. The steam that is imported or exported for each configuration is presented in Table 1. The results show that to completely replace the fossil-based naphtha with ACSs, the model selects CO2 as the primary carbon source. This route would require 11 identical CO2 hydrogenation to methanol processes followed by two methanol to olefins plants to replace the fossil-based olefins plant. Therefore, significant modifications to the current cluster are required, requiring a minimum investment of 5.4 billion euros. Furthermore, the CCU route would require 1130 kt/y of green hydrogen.

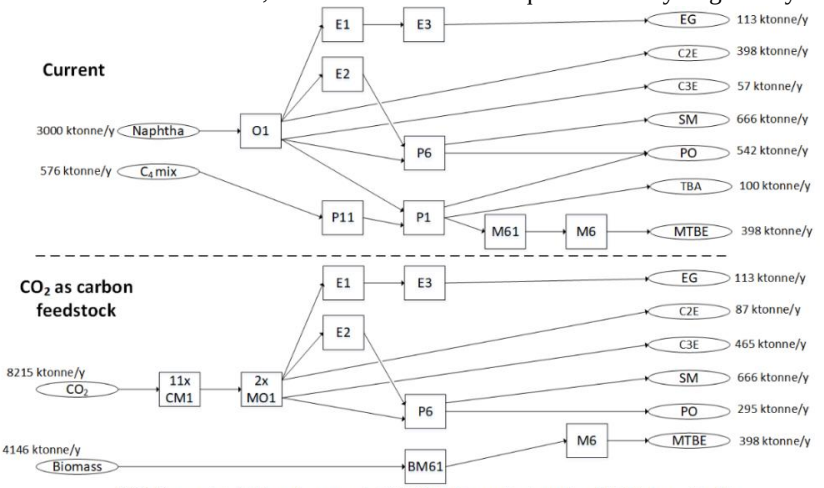

Figure 2: The current fossil-based configuration and the optimal CO_2 based alternative configuration

Table 1: Steam imported or exported for each site of the case study

	Fossil naphtha base case	**CO2 as ACS**
Site 1 [TJ/y]	5,792.5	5,792.5
Site 2 [TJ/y]	5,231.2	143,809.8
Site 3 [TJ/y]	-18,713.5	-24,855.3

To completely remove fossil-based carbon as a feedstock, biomass will be used to produce the isobutylene used for the production of MTBE. This will require the isomerization, PO/TBA, and TBA dehydration processes to be removed from the cluster. As a result, there is an overall lower PO production and TBA is no longer exported from the cluster in comparison to fossil-based route. It can also be concluded that using CO2 as a carbon source will result in a larger fraction of propylene product compared to the conventional. This is a result of the larger fraction of propylene produced by the MTO process. Table 1 shows that for the CCU route, there is a significant increase in the demand for steam at Site 2. This is a result of the biomass to isobutylene route via the organosolv process, which requires a very large number of distillation columns with a significant steam demand. This would result in a rise of steam related CO_2 emissions if natural gas were used as the fuel source to generate the required steam.

5. Conclusion

In this work, a superstructure-based optimization model was developed to assess transformation pathways in petrochemical clusters. The model selected CO2 combined with biomass as ACS to completely replace the fossil-based carbon sources. However, this solution would require significant modifications to the existing cluster, potentially resulting in a non-optimal solution. In the next step, we will include minimizing the changes required to the existing petrochemical cluster (in terms of assets, emissions, lands requirements) as objective in multi-objective optimization. The model will also be extended to include the full representative model of the PoR petrochemical cluster (32 chemical processes) and additional ACS-based processes to evaluate the impacts of defossilization in the PoR.

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