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P-graph Attainable Region Technique (PART) for Process Synthesis

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Process integration is a technique that allows to plan and design better systems by considering the whole chemical process rather than breaking it down into components. The synthesis of processes using these techniques starts with the reaction to generate the desired product. One of the techniques in reactor design is the attainable region (AR) theory. It involves determining the space of possible products yields from a reaction using geometric techniques. The development of AR approach addresses the limitation of optimization techniques used in chemical reactor design and process synthesis. However, the continuous feasible space of reaction yields lacks a framework for determining which points would be best given certain environmental and economic constraints. In this study, a P-graph approach is used to implement the AR technique to generate optimal and near-optimal reaction pathways. The approach involves determining the combinations of reacting species to produce one unit flow rate of a desired product based on material, energy, and work balance. Using the P-graph approach allows framing the AR technique as a mathematical programming tool by considering the flow rate limits and economic value of the reactants and side products. A case study involving methanol synthesis is used to illustrate the approach.

1. Introduction

Chemical process industries play an important role in meeting the needs of humans for food, energy, and other important commodities. The generation of new products for human consumption is possible through chemical reactions performed in large-scale. The design of chemical reactors is the heart of process synthesis, wherein the main goal is to generate the desired component or chemical (Foo et al., 2005). Different factors such as waste products, energy, and raw material consumption are considered for process synthesis. The creation of a region which includes all possible reaction yields and pathways allows chemical engineers to synthesize a process with optimal yields and minimized environmental impacts. One of the approaches proposed in performing this task is by the construction of the attainable region (AR).

The AR method involves the design of a reactor where all pathways consisting of reaction and mixing phases are generated (Ming et al., 2016). It was originally developed by Horn (1964) and was later established to involve four fundamental properties: it must contain the feed, it is unique, simply connected and exists in a single region, it is convex, and it must contain the reaction and mixing phases only (Feinberg, 2002). The goal of the construction of the AR region is to characterize the kinetic limitation of a given reaction in different reactor configuration. The concept was only applied to continuous-flow stirred-tank reactors (CSTRs) and differential sidestream reactors (DSRs) but was later extended to batch reactors (Ming et al., 2013). AR was applied to reactor design and synthesis of ethanol reforming (Ansari et al., 2020), pyrolysis oil production (Chiwara, et al., 2018), and anaerobic digestion (Abunde Neba et al., 2019). In ethanol reforming application, the approach involves the simultaneous heat, mass, and work balances and the ultimate target is determined in which additional source of energy through the production of H_2 is obtained (Ansari et al., 2020). This approach was developed by Patel et al. (2007) for the synthesis of a process that requires minimal information of heat and Gibbs free energy of formation. The graphical method involved in their study identifies targets based on different physical constraints such as spontaneity of reaction, net negative to zero heat of reaction, and emission

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constraints. It provides all possible reaction pathways based on conservation laws, however, not all points in the AR are optimal for a given process. The generation of optimal and near-optimal reaction pathways is important in process synthesis.

The AR space is constructed with notable points of the interest such as zero CO_2 emissions, and full raw material consumption are identified. However, alternative process pathways can still be generated, where different combinations of chemical components are involved subject to these specifications. Although AR provides the space of all possible reaction pathways, not all pathways are optimal. In this study, the P-graph approach will be used to generate optimal reaction pathways for a given process. Recent applications of P-graph include game-theoretic approach to carbon management (Tan et al., 2021) and sustainability of wastewater treatment network (Aboagye et al., 2021). An extensive review of P-graph applications by Friedler et al. (2019) discussed the wide applications of P-graph in process synthesis and other problems of analogous structure. One of the applications of the P-graph related to reaction pathways is by Lakner et al. (2018) where each reaction is represented by a process node and the components as material nodes. A comprehensive introduction to P-graph methodology can be found in a recently published book (Friedler et al., 2022).

To date, no study has been conducted to use P-graph to represent attainable regions. To address this research gap, the P-graph attainable region technique (PART) is introduced as an approach to generate optimal reaction pathways for a given process based on producing a particular chemical component. The rest of the paper is summarized as follows. Section 2 presents the methodology for constructing the maximal structure of the P-graph for the AR region. Section 3 presents a case study on methanol synthesis. Section 4 presents the conclusions and future works.

2. Methodology

The detailed procedure of PART is as follows:

(S1) The approach is based on representing the system through elemental mole balances, heat balance, and work balance in terms of Gibbs free energy.

(S2) A chemical component is identified as the main product with unit flow rate. This component will be represented using multiple product nodes as elements in the chemical component, which are referred as elemental nodes. The required flow rate demand is based on the number of atoms present for that element in the product component.

(S3) The raw materials used to generate the product component is represented by a process node whose input is a unit input node and the outputs are the elemental constituents of that raw material (e.g., for H_2O the process node produces 2 atoms of H and 1 atom of O connected to the elemental nodes).

(S4) To represent the side products of the process, the same process node is used where the input nodes are the elemental nodes, and the output node is the side product. This step allows to set the constraints for the emissions that may be produced by the system.

(S5) The heat balance for the system can be represented as an intermediate node whose edges have values of the standard heats of formation of each chemical component. The net flow rate of the intermediate node represents the heat of reaction of the system minus the heat of formation of the main product.

(S6) The work balance for the system can be represented as an intermediate node. In this case, the edges are now represented as the Gibbs free energy of formation of the chemical components. The net flow rate of this intermediate node is the Gibbs energy of formation of the system minus the Gibbs free energy of formation of the product node.

(S7) The constraints and optimization objective in the process may be represented by setting certain information in the process nodes. For instance, the constraint for net CO_2 emission may be established by setting the CO_2 side product node to zero flow rate. The objective of maximizing energy generation by H_2 production can be established by setting a price for H_2 product. Minimizing the CO_2 emission may be done by setting a cost for the CO_2-output operating node.

In the next section, a case study is used to illustrate PART as implemented using the online P-graph Studio software (http://p-graph.com/) developed and maintained by a team at the University of Pannonia in Hungary.

3. Case Study: Methanol Synthesis

A case study using the methanol synthesis is used to illustrate the approach, adapted from Patel et al. (2007). The chemical components involved in the formation of 1 mole of methanol (CH_3OH) are CO, H_2, CH_4, H_2O and O_2, all of which are assumed to be in gaseous form. The standard enthalpies and Gibbs free energy of formation for this case is summarized in Table 1. For this example, the operating temperature and pressure are assumed to be constant at 25 ^oC and 1 atm. The methanol synthesis problem can be summarized with the chemical reaction:

$$a\mathrm{CH_4} + b\mathrm{H_2O} + c\mathrm{O_2} + d\mathrm{CO_2} + e\mathrm{H_2} \rightarrow \mathrm{CH_3OH} \quad (1)$$

where the unknowns *a*, *b*, *c*, *d,* and *e* are the molar quantities required to produce 1 mol of methanol. The value of these unknowns can be negative where it will be considered as a side product. The heat of reaction is represented by Eq(2) while the standard Gibbs free energy is shown in Eq(3).

$$\Delta H_{\mathrm{rxn}} = \Delta H_{\mathrm{CH_3}OH} - a\Delta H_{\mathrm{CH_4}} - b\Delta H_{\mathrm{H_2O}} - c\Delta H_{\mathrm{CO_2}} - d\Delta H_{\mathrm{O_2}} - e\Delta H_{\mathrm{H_2}} \quad (2)$$

$$\Delta G_{\mathrm{rxn}} = \Delta G_{\mathrm{CH_3}OH} - a\Delta G_{\mathrm{CH_4}} - b\Delta G_{\mathrm{H_2O}} - c\Delta G_{\mathrm{CO_2}} - d\Delta G_{\mathrm{O_2}} - e\Delta G_{\mathrm{H_2}} \quad (3)$$

Where ΔH_{rxn} and ΔG_{rxn} are the enthalpy and standard Gibbs free energy of the reactions. The component's enthalpy and standard Gibbs free energy are as follows: $\Delta H_{\mathrm{CH_3OH}}$ and $\Delta G_{\mathrm{CH_3OH}}$ for methanol, $\Delta H_{\mathrm{CH_4}}$ and $\Delta G_{\mathrm{CH_4}}$ for methane, $\Delta H_{\mathrm{H_2}O}$ and $\Delta G_{\mathrm{H_2O}}$ for water, ΔH_{CO_2} and ΔG_{CO_2} for carbon dioxide, ΔH_{O_2} and $\Delta G_{\mathrm{O_2}}$ for oxygen, and $\Delta H_{\mathrm{H_2}}$ and $\Delta G_{\mathrm{H_2}}$ for hydrogen.

Table 1: Standard enthalpies and Gibbs free energy of formation of the chemical components

Chemical component	Standard heat of formation (ΔH_f, kJ/mol)	Standard Gibbs free energy of formation (ΔG_f, kJ/mol)
CO_2	−393.51	−394.36
CH_4	−74.52	−50.46
H_2O	−241.818	−228.572
CH_3OH	−200.66	−161.96
H_2	0	0
O_2	0	0

The Maximal Structure Generation (MSG) algorithm of P-graph is used to rigorously assemble system components into an error-free superstructure known as a maximal structure (Friedler et al., 2022). The maximal structure for this case study is shown in Figure 1, generated using the steps presented in Section 2. The methanol product is set to be produced at 1 mol, thus, an elemental balance of 1 mol of C, 4 mol of H and 1 mol of O is set for three product nodes. To obtain a net zero energy requirement for the reaction, the net output of the intermediate nodes for the enthalpy and Gibbs free energy must be equal to $-\Delta H_{CH_3OH}$ and $-\Delta G_{CH_3OH}$ based on Eq(2) and Eq(3). Note that there are two process nodes for each chemical species participating for methanol synthesis – one for the utilization of the component and the other for the generation of the component. To minimize the environmental impact brought by emission of CO_2, an arbitrary value of investment cost to the process node of CO_2 production (CO2_in) can be placed. For the maximal structure in Figure 1, the energy balances are set so that the reaction heat energy and Gibbs free energy can be from net negative to net zero value. The process node for CO_2 generation is set to have an arbitrary proportional investment cost.

The Solution Structure Generation (SSG) algorithm of P-graph is used to enumerate all combinatorially feasible networks (or solution structures), while optimization for a specified objective function is done using the Accelerated Branch-and-Bound (ABB) algorithm (Friedler et al., 2022).The solution structures for the methanol synthesis case study are generated and shown in Figures 2 to 4. 640 structures are generated using the SSG algorithm which represents all configurations for the methanol synthesis. The set of these structures represents the attainable region of the process. Three solution structures are generated using ABB algorithm, two of which does not generate any side products. The ABB algorithm narrows down the possible solution structure based on the constraint presented. The first solution structure shows a synthesis of methanol from methane and oxygen where the reaction proceeds as shown in Eq(4). Here the reaction is exothermic.

$$\mathrm{CH_4} + \frac{1}{2}\mathrm{O_2} \rightarrow \mathrm{CH_3OH} \qquad \Delta H = -126.14\ kJ\ ,\ \Delta G = -111.5\ kJ \quad (4)$$

The solution structure shows that the net energy produced for methanol synthesis is 126.14 kJ per mol of methanol produced. This solution can be verified from the results of Patel et al. (2007) in which hydrogen is circulating around a two-step process consisting of hydrogen combustion and methane conversion. The second solution structure can be summarized in the reaction shown in Eq(5). For this solution structure, the work requirement reduces to zero while a net 14.42 kJ of heat is generated for the synthesis of 1 mol of CH_3OH. In this case, two sources of carbon for methanol can be identified in which 86.1 % of it is produced from methane while 13.9 % of it is generated by CO_2 utilization. This solution structure provides the optimal way for utilizing CO_2 where the Gibbs free energy of the reaction is essentially zero, implying that the reaction is at equilibrium.

$$0.861CH_4 + 0.139CO_2 + 0.222O_2 + 0.278H_2O \rightarrow CH_3OH \qquad \Delta H = -14.42\ kJ\ ,\ \Delta G = 0\ kJ \tag{5}$$

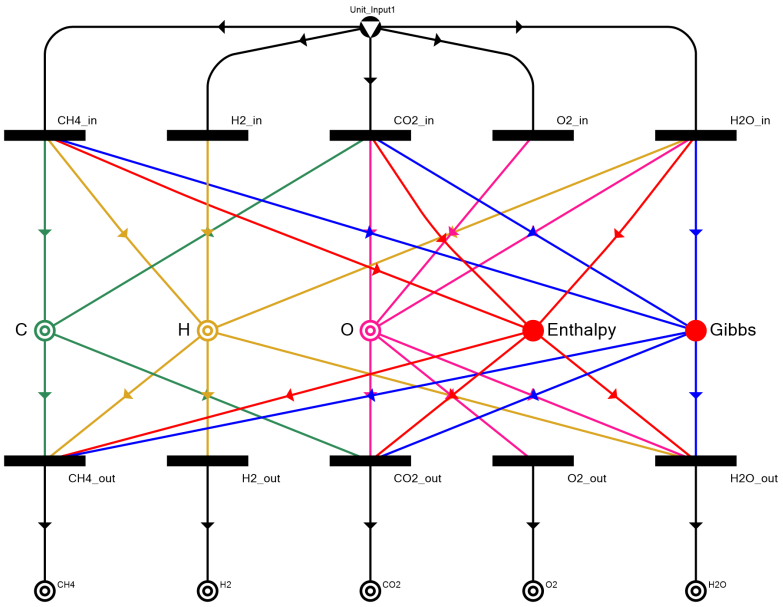

Figure 1: Maximal structure for the synthesis of methanol using five chemical components

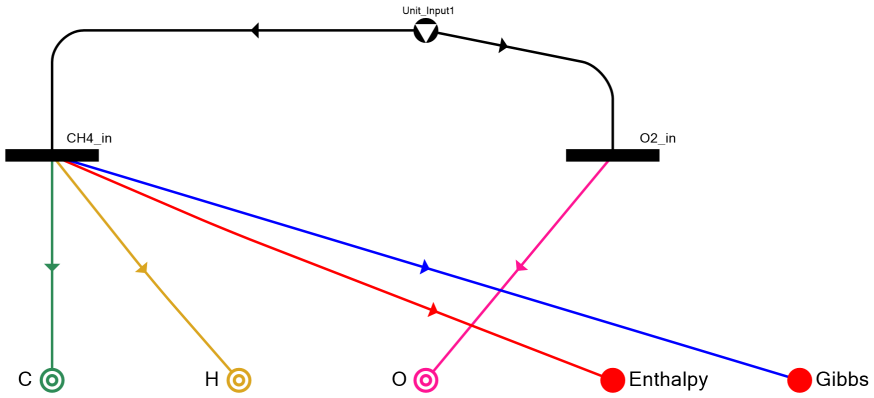

Figure 2: Solution structure 1 for the methanol synthesis case study

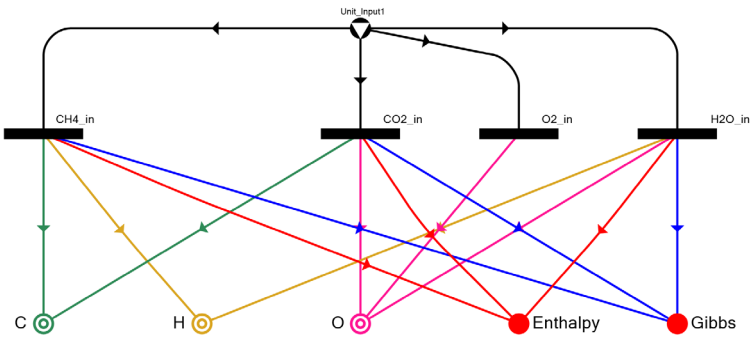

Figure 3: Solution structure 2 for the methanol synthesis case study

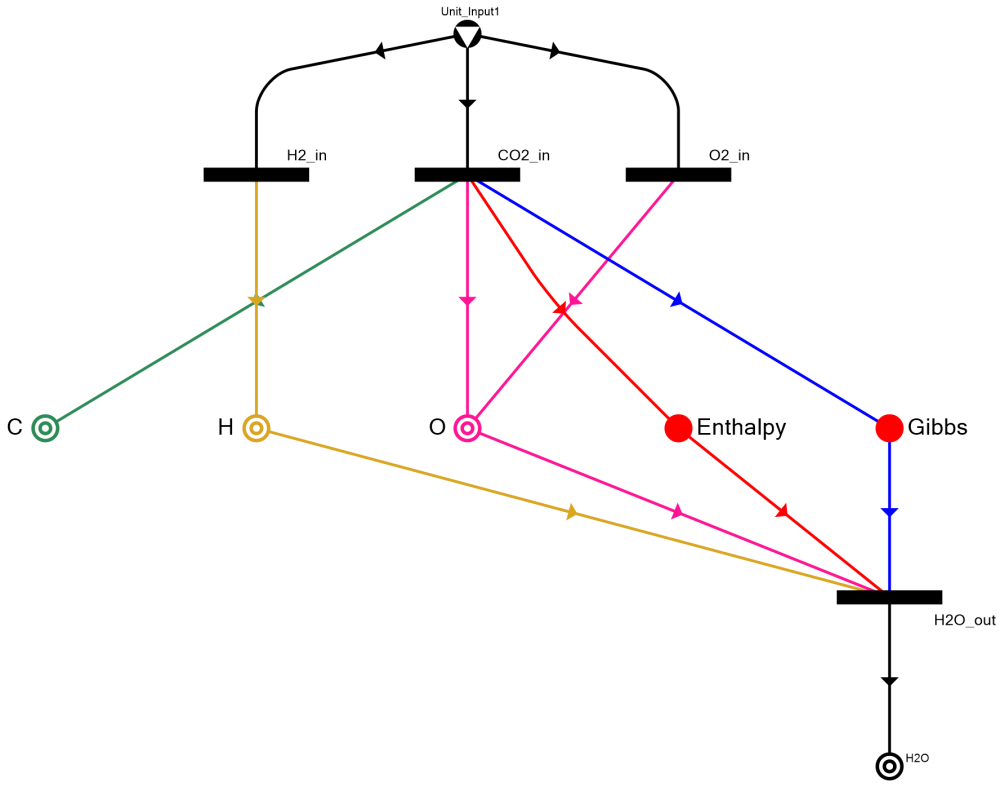

Figure 4: Solution structure 3 for the methanol synthesis case study

The third solution structure for this case study involves water as a by-product of the reaction. In this case, solution structure is based on the following reaction:

$$3.017H_2 + CO_2 + 0.0085O_2 \rightarrow CH_3OH + 1.017H_2O \qquad \Delta H = -53.02\ kJ\ ,\ \Delta G = 0\ kJ \qquad (6)$$

In this case, full utilization of CO_2 is achieved with generation of 53.02 kJ of heat per mol of methanol synthesized. This solution structure can be interpreted where 0.017 mols of H_2 is burned with 0.0085 mols of O_2 then, the heat generated is transferred to the process where CO_2 reacts with H_2 to form methanol. This process is shown in Figure 5. The synthesis of methanol in this solution structure suggests a way to utilize CO_2 to generate valuable products. However, the use of H_2 as a raw material here for both the conversion and energy combustion is not recommended as H_2 is a valuable commodity. Unless the heat generated in this process can be utilized for other purposes, the second solution structure suggests a better approach to utilize CO_2 for methanol synthesis.

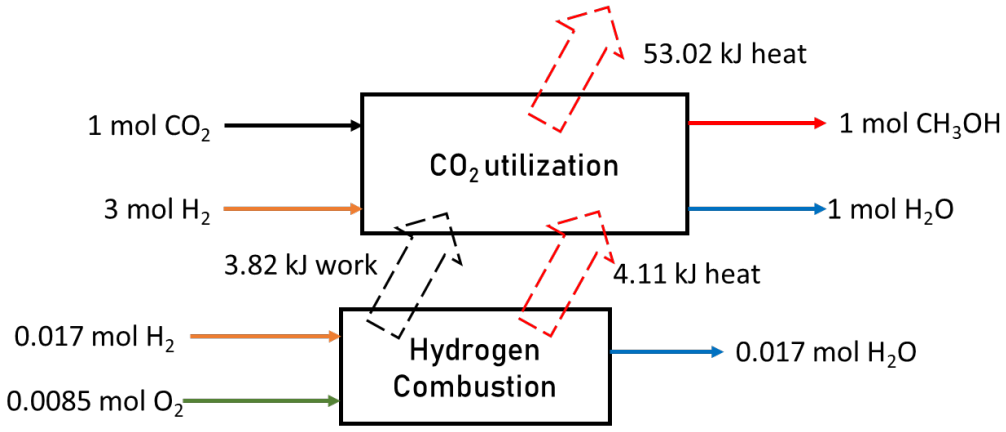

Figure 5: Process configuration for the synthesis of methanol based on solution structure 3

The use of PART in this example enables the generation of specific points in the attainable region of methanol synthesis process. Three solution structures out of the 640 possible configurations are generated where CO_2 is utilized in two of the solution structures. The first one is a direct conversion of methane to methanol, while the second process involves utilization of CO_2 alongside conversion of methane to methanol. Given a supply of hydrogen gas, CO_2 conversion to methanol is also possible without the need for methane input. The P-graph approach provides insights on how to synthesize a process through simultaneous heat, mass, and work balances by providing specific optimal points in the attainable region.

4. Conclusions

The PART approach to process synthesis was developed in this work. The maximal structure represents the network where different chemical components used for the synthesis of one product are represented as process nodes. A simultaneous heat, mass, and work balance is performed. The heat balance is based on the heat of reaction represented by an intermediate node while the work balance is based on Gibbs free energy of the reaction represented by an intermediate node. The main product is represented by several product nodes that represents the elemental composition of the product to perform an elemental balance. Additional constraints based on environmental and economic considerations can be configured in the P-graph model of the attainable region. The case study results show different configuration of possible processes to produce a main product. The attainable region is generated by using the SSG algorithm which can be narrowed down by ABB to generate optimal and near-optimal pathways. The use of P-graph provides insights that conventional graphical approaches to attainable region analysis cannot provide. Future works can include performing simulations of the processes generated using software such as Aspen Plus, consideration of equilibrium and surface-based reaction with catalyst, consideration of factors for generating reactions other than enthalpy and standard Gibbs free energy, and development of tools to manage the complexity of combinatorial nature of PART method.

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