

Structural Startability of Reaction Pathways with Petri Net Analysis

Rozália Lakner

Alba Regia Technical Faculty

Óbuda University

Székesfehérvár, Hungary

lakner.rozalia@amk.uni-obuda.hu

Abstract – The systematic exploration of candidate reaction pathways has theoretical and practical significance to understand the mechanism of a complex chemical and biochemical reaction and potentially improve its yield. Therefore, many works deal with issues related to the synthesis of reaction pathways for a given mechanism. One of the most effective method for reaction pathway synthesis is the P-graph algorithm, which is applicable to generate the feasible solution structures for complex reactions, including the catalytic and enzyme-catalytic reactions. As this method produce the possible structures based on dynamic equilibrium state, it is very important to investigate whether these states can be reached from the initial state of the system, i.e., whether the reaction pathway is structurally startable. The present work suggests Petri net analysis methods for the structural startability examinations.

Keywords – reaction pathway, structural startability, Petri net analysis, P-graph (process-graph).

I. INTRODUCTION

The reaction mechanism serves as an accurate model for prediction of the behavior of the reaction and its control. The determination of the proper reaction mechanism is, therefore, a key point both in chemistry and industrial applications.

Chemical reactions often composed of individual sub-steps, so called elementary reactions. The network demonstrating the connections of the elementary reactions of the overall reaction is conventionally described as reaction pathway that is the basis for the reaction mechanism. Different pathways of a reaction may have different properties in terms of energy requirements, yield, and geometrical structure of final products.

There are experimental tools to determine the reaction mechanism, such as recognition of the appearance of reaction intermediates, where a set of hypothetical elementary reactions can be determined from the available intermediates. Besides that, there are graph-theoretic methods serving as effective tools for determination of the structure of reaction pathways, based on the elementary reactions. These methods generate the set of stoichiometrically feasible reaction pathways, that contains all possible alternatives, at the same time included unworkable ones. For practical reason, before the selection of the proper solution or solutions, it is useful to prune the unrealizable ones. Since startability is crucial for accomplishing a reaction pathway, the violation of startability is an obvious reason for the elimination. This paper presents different methods for recognizing if a reaction pathway is structurally startable or not. To do so, Petri net theory is used, based on stoichiometrically feasible solution structures generated by P-graph framework.

P-graph has been first applied for reaction pathway synthesis by Fan and Friedler [1] in 1997 utilizing Process Network Synthesis (PNS) algorithms originally developed for

chemical engineering process synthesis on a rigorous axiomatic basis and P-graph representation [2]. In 2001 Fan et al. [3] highlighted the specialties of reaction pathway synthesis among process synthesis problems and established new axiomatic system tailored for reaction pathway synthesis problems of catalytic reactions, as well as the algorithms tailored for reaction pathway synthesis.

Petri net is a modeling language that has both graphical and mathematical formalism for the description of concurrent, asynchronous, distributed systems [4]. In the last half-century, different extensions for Petri nets, e.g., colored, timed, hierarchical were developed and several successful applications have been done on a wide range of domains. These methods support both the modeling and the analysis of systems in different fields of application including process engineering, manufacturing systems and computer sciences [5].

Recently Petri net served as a promising modeling and analysis tool of reaction mechanism, which have successfully been applied to systems biology of metabolic and signal transduction pathways in modeling both discrete and continuous processes. Angeli et al. [6] investigated the conditions for persistence of chemical species in reaction systems based on Petri net theory. This property plays an important role in the ecosystems, where preserving non-zero populations of all the species which are present at the initial time is crucial.

The similarities between P-graphs and Petri nets mainly based on the similar structures, namely both have strict formal mathematical definitions and graph-representation, also. The unique feature of the P-graph framework due to the strict mathematical basis can generate all combinatorially feasible solution structures of a given problem, moreover, determine the optimal structure for predefined objective function. In contrast, the usage of Petri nets is to determine the behavior and the properties of a system given by a predefined structure [7].

In the present work Petri net analysis methodologies was applied for the determination of structural startability, based on the stoichiometrically feasible reaction pathways generated by P-graph algorithms. The proposed methods have been demonstrated by the well-known hydrogenation of ethylene to ethane on biactive-site platinum catalysts [8].

II. PETRI NET METHODOLOGIES FOR DETERMINING THE STRUCTURAL STARTABILITY

To determine structural startability of a stoichiometrically feasible reaction pathway it must be examined whether all the elementary reactions operate from the given initially available species. These properties can be investigated based on the simulation and analysis of the Petri net, corresponds to the stoichiometrically feasible reaction pathway.

A. Formal definition of Petri nets

A Petri net [4, 5] formally can be described by a quadruple in the form $PN = \langle P, T, E, w \rangle$, where P is the finite set of the places, and T is the finite set of the transitions, with $P \cap T \neq \emptyset$ and $P \cap T = \emptyset$. Petri net is also called place/transition net, where places act as passive elements, e.g., states, conditions, chemical species, and transitions represent the active elements, e.g., events, actions, chemical reaction steps. $E \subseteq (P \cup T) \times (T \cup P)$ defines the edges from places to transitions and vice versa, and the weight function of the edges (w) is a mapping from E to $\mathbb{N}^+$.

The preset of a transition $t \in T$ is the set of its input places (i.e. the places connected directly to t with arcs) denoted by $\bullet t = \{p \in P \mid w(p, t) > 0\}$, while its postset is the set of its output places (i.e. the places connected directly from t with arcs): $t \bullet = \{p \in P \mid w(t, p) > 0\}$.

The interpretations of preset and postset of a place are analogous.

A marking M of a Petri net is a mapping from P to $\mathbb{N}$, where $M(p)$ denotes the state of $p \in P$ defining with the number of tokens in place p . So, the state of the Petri net can be represented by a $|P|$ -dimensional marking vector M , and M_0 denotes the initial marking representing the initial state of the system, respectively.

The transitions can consume tokens from, and can produce tokens to their input and output places according to w .

Petri nets can be described as bipartite graphs, where places are indicated by circles and transitions by rectangles. The places and transitions are connected by weighted directed arcs representing the weight functions.

For the illustration of the formal definition of Petri nets, the reaction of nitrous oxide (N_2O) and carbon monoxide (CO) in the presence of rhodium catalyst (the active site is denoted by ℓ) to form dinitrogen (N_2) and carbon dioxide (CO_2) is introduced. [8] The elementary reactions are summarized in Table I.

TABLE I. ELEMENTARY REACTIONS OF THE SIMPLE EXAMPLE

	Elementary reaction
e_1	$N_2O + \ell \rightarrow N_2Ol$
e_2	$CO + \ell \rightarrow CO\ell$
e_3	$N_2Ol \rightarrow N_2 + Ol$
e_4	$CO\ell + Ol \rightarrow CO_2 + 2\ell$

Note that only forward steps are included in the illustration, i.e., the elementary reactions are irreversible. In contrast, for reversible elementary reactions both forward and reverse steps must be included in the set of elementary reactions. The overall reaction is $N_2O + CO \rightarrow N_2 + CO_2$.

The formal definition of Petri nets represents the reaction of nitrous oxide and carbon monoxide in the presence of rhodium catalyst to form dinitrogen and carbon dioxide is as follows:

$$P = \{N_2O, CO, \ell, N_2Ol, CO\ell, Ol, N_2, CO_2\}$$

$$T = \{e_1, e_2, e_3, e_4\}$$

$$E = \{(N_2O, e_1), (\ell, e_1), (e_1, N_2Ol), (CO, e_2), (\ell, e_2), (e_2, CO\ell),$$

$$(N_2Ol, e_3), (e_3, N_2), (e_3, Ol), (CO\ell, e_4), (Ol, e_4), (e_4, CO_2), (e_4, \ell)\}$$

$$w((e_4, \ell)) = 2, \text{ otherwise } w = 1$$

$$M_0 = [1, 1, 2, 0, 0, 0, 0, 0].$$

The graph representation of the example is illustrated in Fig. 1(a). The Petri net figures are depicted by Petri net modeling tool Snoopy [9].

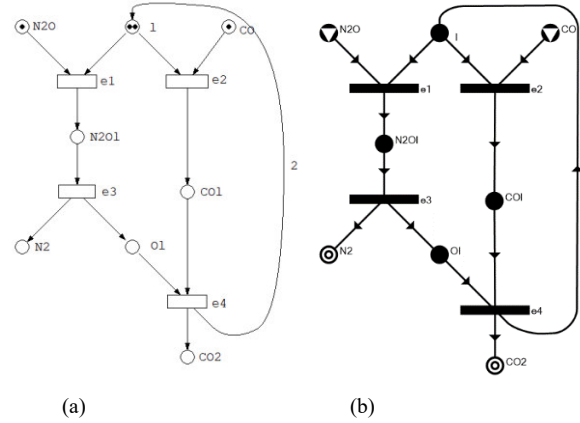


Fig. 1: Petri net representation with the initial marking (a) and P-graph representation (b) of the simple example.

The similarities between P-graphs and Petri nets are mainly comes from their structure, i.e., both are represented by bipartite directed graphs. The P-graph representation of the reaction pathway of the reaction nitrous oxide and carbon monoxide to form dinitrogen and carbon dioxide example is illustrated in Fig. 1(b), where the reaction pathway was determined by the help of P-graph Studio [10].

Both P-graphs and Petri nets are for complex systems. The major difference is that P-graphs are primarily for synthesis and Petri nets are primarily for simulation and analysis.

P-graph framework has effective algorithms to synthesize process systems to be constructed from potential building blocks, computes both the optimal structure and the optimal parameter values, but not used for examining the dynamics of the system. On contrary, Petri nets are tools for simulation and analysis of the dynamic behavior of complex systems. They are used for examining the operation of preliminarily defined model, but not support the synthesizing of the structure.

B. Simulation and analysis of Petri nets

In state M of a Petri net the transition t is enabled, in other word fireable, if all of its input places contain at least the required numbers of tokens defined by the weight function, i.e., $\forall p \in \bullet t: M(p) \geq w(p, t)$. When a transition t is firing, a defined number of tokens are consumed from its input places and produced to its output places, so the state of the net changes producing new marking M' according to: $\forall p \in \bullet t: M'(p) = M(p) - w(p, t) + w(t, p)$. The simulation of these two basic rules of enabling and firing transitions presents the dynamic behavior of a Petri net. Note that the execution of a Petri net is nondeterministic, i.e., when multiple transitions are enabled at the same time, any one of them may fire, and different transition sequences may lead to different states from the same initial state.

Petri nets serve for system analysis, too, where different system properties can be investigated, e.g., reachability, boundedness, reversibility, liveness, deadlock. Most of these properties can be examined with the help of reachability graph that contains all the possible states of the Petri net, constructed by all the sequences of the firing transitions from the initial state M_0 .

The reachability graph of the simple example in Fig. 1(a) generated with Petri net analysis tool Charlie [11] can be seen in Fig. 2. The states of the Petri net are represented by graph nodes including the initial state as top node, and the graph edges are labeled with the identifier of the transitions.

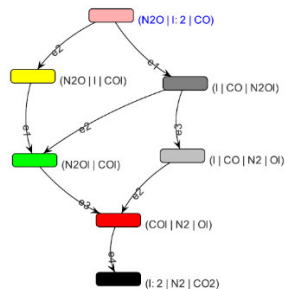


Fig. 2: The reachability graph of the simple example

The reachability graph serves information about system properties, such as

- **Reachability** - The state M is reachable, when there is a sequence of fireable transitions from the initial state to M . If M can be found as a node of the reachability graph, then M is reachable, otherwise not.
- L_1 **liveness** - The Petri net is L_1 live when every transition fires at least once in some firing sequence from the initial state. If every transition can be found as arc label of the reachability graph, the Petri net is L_1 live, otherwise it is dead.
- **Liveness** - The Petri net is live when every transition can fire from any reachable states.
- **Deadlock** - A reachable marking of the Petri net, where none of the transitions can fire. All deadlocks constitute leaves in the reachability graph, as node (l , N_2 , CO_2) indicates in Fig. 2.

The properties of the Petri nets can be marking-dependent, or in other words behavioral, depending on both the structure and the initial state of the Petri net, and can be structural, independent of the initial marking. The behavioral properties, e.g., reachability, liveness, deadlock, can be investigated based on the reachability graph containing the state space of Petri net constructed from the initial state M_0 . The main drawback of these investigations is their exhaustive characteristic, as the reachability graph can be very large, and both the time and the space requirement grow exponentially in the number of places. Therefore, this type of analysis is computationally hard.

Structural analysis enables the investigation of some properties without constructing the reachability graph. Most of the structural properties, e.g., place and transition invariant, siphon and trap analysis, can be easily determined by means of algebraic techniques.

As siphons and traps [12, 13] play essential role, and used extensively for the analysis of the reachability, liveness and

deadlock of Petri nets, their main characteristics and properties are summarized as follows.

A siphon is a non-empty set of places $S \subseteq P$ whose presets are also postsets: $\bullet S \subseteq S^\bullet$, i.e., every transition having an output place in S has an input place in S , too. An important property of the siphon S is, that if it once insufficiently marked, it will never be marked again, and consequently, all transitions having arcs from the places in S become dead. As a result, if a Petri net contains a blank siphon, liveness cannot be obtained. So, a Petri net without siphons is live, while if the system is in a deadlock, it must contain insufficiently marked siphon.

A trap is a non-empty set of places $\tau \subseteq P$, however its postsets are also presets: $\tau^\bullet \subseteq \bullet \tau$, i.e., every transition having an input place in τ has an output place in τ . An essential property of the trap τ , that if it catches tokens, then it keeps at least one of them, i.e., if once a trap has any token, it remains marked. Firing of the transitions can move tokens but cannot remove all the tokens from the trap. Consequently, from the definitions of siphon and trap, if a siphon contains a marked trap, it will never become blank.

The union of two siphons is a siphon, and a siphon is minimal if it does not contain any other siphon. The same goes for traps, too.

The Petri net in Fig. 1 (a) contains 4 minimal siphons and 3 minimal traps as summarized in Table II.

TABLE II. THE MINIMAL SIPHONS AND TRAPS OF PETRI NET

Minimal siphons	Minimal traps
$S_1 : \{ N_2O \}$	$\tau_1 : \{ N_2 \}$
$S_2 : \{ CO \}$	$\tau_2 : \{ CO_2 \}$
$S_3 : \{ N_2O, O, l \}$	$\tau_3 : \{ N_2O, O, CO, l \}$
$S_4 : \{ CO, l \}$	

In case of Petri net, that defines reaction pathway, siphons can represent both the starting reactants and the cyclic structures producing species by consuming themselves; moreover, traps can represent both the products and the cyclic structures consuming species produced by themselves.

C. Determining the structural startability of reaction pathways with Petri nets

For the investigation of structural startability of stoichiometrically feasible reaction pathways, Petri net simulation and analysis was used for the predefined reaction pathway constructed with P-graph framework [14]. The elements of the reaction pathway represented by Petri net are as follows: the transitions correspond to the elementary reaction steps, and the places correspond to the species. So, the investigation of the structural startability of stoichiometrically feasible reaction pathway is as follows:

- an elementary reaction step e_i is structurally startable, if all the chemical or active species consumed by e_i are available, i.e., the transition corresponds to the elementary reaction step e_i is fireable
- a chemical or active species is available, if it is either an initially available species, or it produced by a structurally startable elementary reaction, i.e., the place correspond to the species is marked in the initial state or becomes marked after the firing of a fireable transition

- a reaction pathway is structurally startable, if all its elementary reaction steps are structurally startable, i.e., all transitions are fireable.

According to these basic statements, for determination of structural startability, it must be examined, whether every elementary reaction step operates from the given initially available species, i.e., all the transitions become fireable at least once from the given initial state. This examination corresponds to the determination of liveness, deadlock, and reachability analysis of the Petri net model of the reaction pathway.

III. CASE STUDY

The proposed methods for determining the structural startability of stoichiometrically feasible reaction pathways are illustrated with the example of ethylene hydrogenation. The elementary reactions of the example [8] are summarized as Table III.

TABLE III. ELEMENTARY REACTIONS OF ETHYLENE HYDROGENATION [8]

	Elementary reaction
S ₁₁	$H_2 + 2 l_1 \leftrightarrow 2 Hl_1$
S ₁₂	$H_2 + 2 l_2 \leftrightarrow 2 Hl_2$
S ₁₃	$C_2H_4 + 2 l_1 \leftrightarrow l_1 C_2H_4 l_1$
S ₁₄	$l_1 C_2H_4 l_1 + Hl_1 \leftrightarrow C_2H_5 l_1 + 2 l_1$
S ₁₅	$l_1 C_2H_4 l_1 + Hl_2 \leftrightarrow C_2H_5 l_1 + l_1 + l_2$
S ₁₆	$C_2H_5 l_1 + Hl_1 \leftrightarrow C_2H_6 + 2 l_1$
S ₁₇	$C_2H_5 l_1 + Hl_2 \leftrightarrow C_2H_6 + l_1 + l_2$

The eight stoichiometrically feasible reaction pathways of the problem as far as it is given by Fan et al. [15] are demonstrated in Table IV. Note that all these solutions fulfill the axioms of the combinatorially feasible reaction pathways in P-graph framework [2] and the balances of the species in all elementary reactions of the reaction pathway and for the overall reaction of the problem $C_2H_4 + H_2 = C_2H_6$.

TABLE IV. STOICHIOMETRICALLY FEASIBLE REACTION PATHWAYS OF ETHYLENE HYDROGENATION

	Reaction pathway
RP ₁ :	$S_{11} + S_{12} + 2S_{13} + 2S_{15} + 2S_{16}$
RP ₂ :	$S_{11} + S_{12} + 2S_{13} + 2S_{14} + 2S_{17}$
RP ₃ :	$S_{11} + S_{13} + S_{14} + S_{16}$
RP ₄ :	$S_{11} + S_{13} + 2S_{14} + S_{15}(\text{reverse}) + S_{17}$
RP ₅ :	$S_{11} + S_{13} + S_{15} + 2S_{16} + S_{17}(\text{reverse})$
RP ₆ :	$S_{12} + S_{13} + S_{14}(\text{reverse}) + 2S_{15} + S_{16}$
RP ₇ :	$S_{12} + S_{13} + S_{15} + S_{17}$
RP ₈ :	$S_{12} + S_{13} + S_{14} + S_{16}(\text{reverse}) + 2S_{17}$

A. Structural startability determined by Petri net analysis

The structural startability of a stoichiometrically feasible reaction pathway can be investigated based on the simulation by Petri nets as follows. If all the transitions can fire at least once from the given initial state, the reaction pathway is structurally startable, otherwise not. The firing of every transition in a stoichiometrically feasible reaction pathway ensure, that the places correspond to the final products become available, i.e., states contain the final products reachable from the initial state. The hardness of this investigation lays on the situation, when two or more transitions are applicable at the same time, i.e., in case of concurrent system, when the next state depends on the selection from the fireable transitions.

For investigating all the possible states, the reachability graph of the Petri net from a predefined initial state is

generated. In this case the observation of the structural startability of reaction pathway is as follows: if all the transitions appear on the reachability graph as arc-label, the system is structurally startable, otherwise not.

The Petri net with the initial state and the resulted reachability graph of the investigated reaction pathway RP₆: $S_{12} + S_{13} + S_{14}(\text{reverse}) + 2S_{15} + S_{16}$ is shown in Fig. 3.

For defining the initial state, unbounded amounts of starting reactants are supposed, that is implemented by so called test arcs from place H_2 to transition S_{12} , and from place C_2H_4 to transition S_{13} . The role of the test arcs is the initialization of their output transitions, while tokens in H_2 and C_2H_4 remain unchanged. The initial tokens of places l_1 and l_2 representing the two catalysts in the system was set to 4 and 2, respectively, ensuring the firing of their output transitions S_{13} , S_{14} and S_{12} .

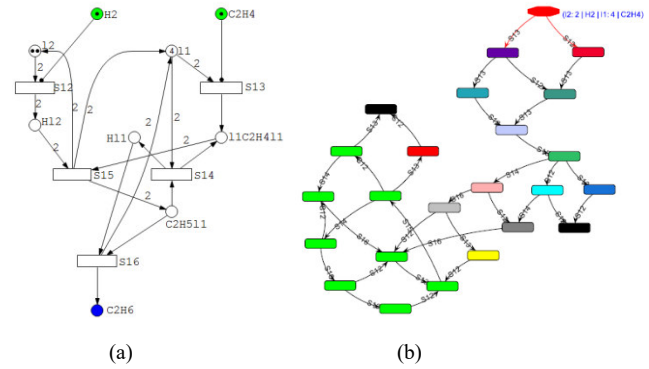


Fig. 3: The Petri net (a) and the reachability graph (b) of stoichiometrically feasible reaction pathway RP₆.

The reachability graph in Fig. 3(b) shows that all the elementary reactions represented by transitions of the Petri net appear on the reachability graph as arc-label. This observation verify that the reaction pathway is structurally startable.

In case of stoichiometrically feasible reaction pathway RP₅: $S_{11} + S_{13} + S_{15} + 2S_{16} + S_{17}(\text{reverse})$ only two elementary reactions, S_{11} and S_{13} can be found on the reachability tree, as can be seen on Fig. 4(b). It means that there are elementary reactions that are not startable, and because of this, the reaction pathway is not structurally startable.

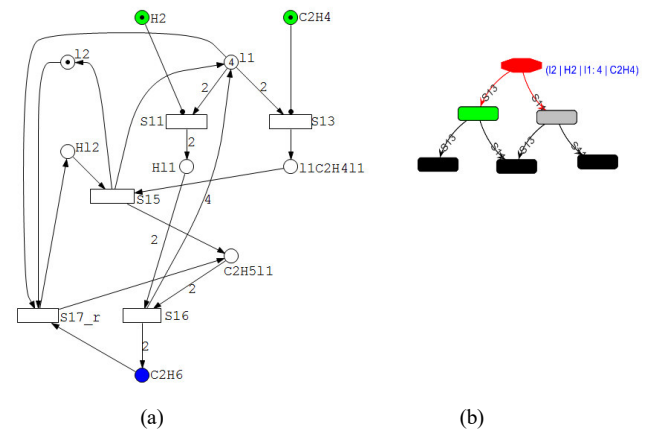


Fig. 4: The Petri net (a) and the reachability graph (b) of stoichiometrically feasible reaction pathway RP₅.

Another method to determine the structural startability of reaction pathway is the siphon and trap analysis of Petri nets. The resulted minimal siphons of RP₅ and RP₆ reaction

pathways are shown in Fig. 5. and Fig. 7., respectively. The places of the siphons and the postset transitions of them are denoted by filled circles and rectangles, respectively.

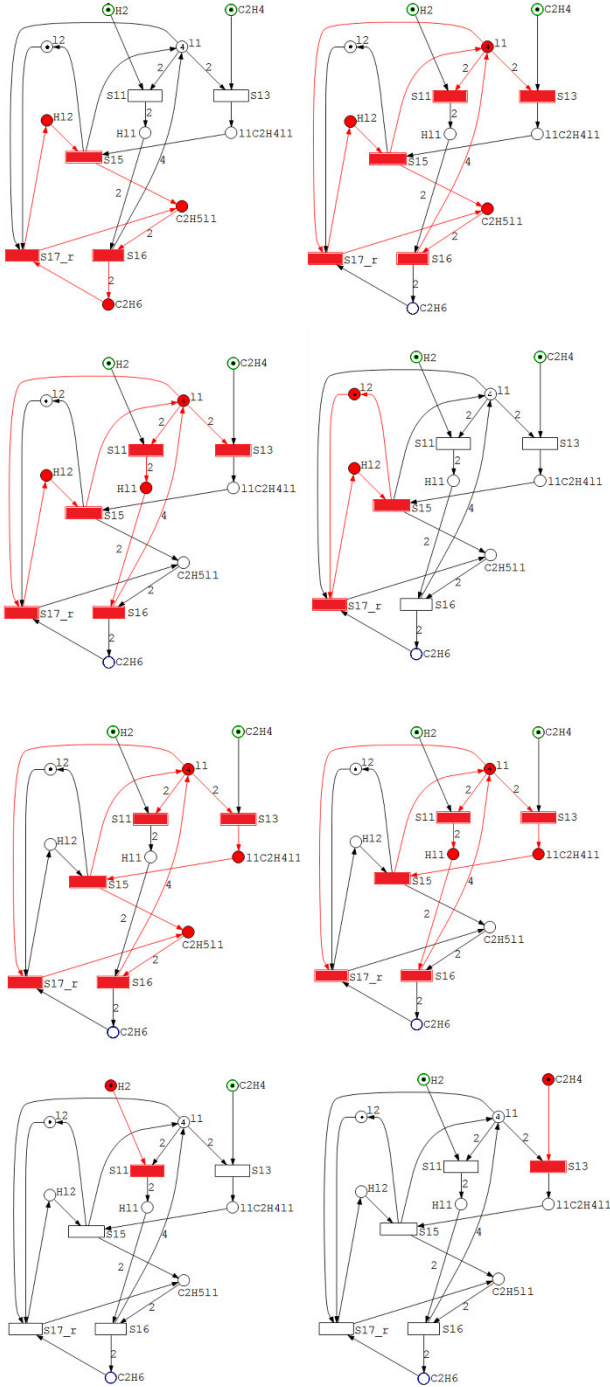


Fig. 5: Minimal siphons of stoichiometrically feasible independent pathway RP_5 .

The necessary condition to avoid deadlock is, that every siphon must contain appropriate number of tokens, i.e., every siphon must have properly marked place(s) for firing almost one transition. In the initial state of reaction pathway RP_5 : $S_{11} + S_{13} + S_{15} + 2S_{16} + S_{17}(\text{reverse})$, where the marked places are H_2 , C_2H_4 , ℓ_1 and ℓ_2 , as can be seen on Fig. 4(a), siphon $S_1 = \{H\ell_2, C_2H_5\ell_1, C_2H_6\}$ is empty. As a result of this, all transitions in postset of siphon S_1 , namely S_{15} , S_{16} and $S_{17}(\text{reverse})$ are dead, therefore these elementary reaction steps are not

structurally startable, so the reaction pathway is not structurally startable.

For ensuring the necessary condition of deadlock-free in siphon S_1 , at least one of the places of it, i.e., $H\ell_2$ or $C_2H_5\ell_1$ or C_2H_6 , must be marked in the initial state. From a modified initial state, where H_2 , C_2H_4 , ℓ_1 , ℓ_2 and C_2H_6 are the initially available species, the resulted reachability graph of reaction pathway RP_5 can be seen in Fig. 6. As all the elementary reactions can be find as arc label, the reaction pathway is structurally startable.

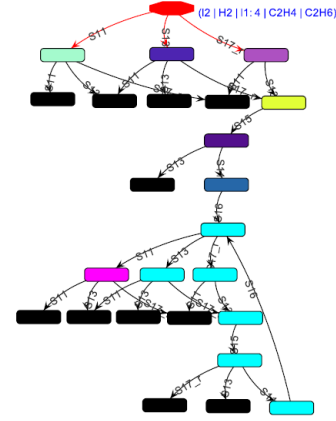


Fig. 6: The reachability graph of RP_5 from initial state marked H_2 , C_2H_4 , ℓ_1 , ℓ_2 and C_2H_6 .

The stoichiometrically feasible independent pathway RP_5 : $S_{11} + S_{13} + S_{15} + 2S_{16} + S_{17}(\text{reverse})$ contains 8 minimal siphons and 4 minimal traps as summarized in Table V.

TABLE V. THE MINIMAL SIPHONS AND TRAPS OF RP_5 REACTION PATHWAY

Minimal siphons	Minimal traps
$S_1 : \{H\ell_2, C_2H_5\ell_1, C_2H_6\}$	$\tau_1 : \{\ell_1, H\ell_2, \ell_1 C_2H_4\ell_1, H\ell_1\}$
$S_2 : \{\ell_1, H\ell_2, C_2H_5\ell_1\}$	$\tau_2 : \{\ell_2, H\ell_2\}$
$S_3 : \{\ell_1, H\ell_1, H\ell_2\}$	$\tau_3 : \{\ell_1, \ell_1 C_2H_4\ell_1, C_2H_5\ell_1, H\ell_1\}$
$S_4 : \{\ell_1, H\ell_2\}$	$\tau_4 : \{C_2H_5\ell_1, C_2H_6\}$
$S_5 : \{\ell_1, C_2H_5\ell_1, \ell_1 C_2H_4\ell_1\}$	
$S_6 : \{\ell_1, H\ell_1, \ell_1 C_2H_4\ell_1\}$	
$S_7 : \{H_2\}$	
$S_8 : \{C_2H_4\}$	

In case of reaction pathway RP_6 : $S_{12} + S_{13} + S_{14}(\text{reverse}) + 2S_{15} + S_{16}$, when the marked places of the initial state are H_2 , C_2H_4 , ℓ_1 and ℓ_2 , as can be seen on Fig. 3(a), all the siphons are marked, so the necessary condition of the deadlock-free is fulfilled. The reaction pathway is structurally startable.

The stoichiometrically feasible independent pathway RP_6 : $S_{12} + S_{13} + S_{14}(\text{reverse}) + 2S_{15} + S_{16}$ contains 5 minimal siphons (see Fig. 7.) and 3 minimal traps as summarized in Table VI.

TABLE VI. THE MINIMAL SIPHONS AND TRAPS OF RP_6 REACTION PATHWAY

Minimal siphons	Minimal traps
$S_1 : \{\ell_2, H\ell_2\}$	$\tau_1 : \{\ell_2, H\ell_2\}$
$S_2 : \{\ell_1, \ell_1 C_2H_4\ell_1, C_2H_5\ell_1\}$	$\tau_2 : \{\ell_1, \ell_1 C_2H_4\ell_1\}$
$S_3 : \{\ell_1, \ell_1 C_2H_4\ell_1, H\ell_1\}$	$\tau_3 : \{C_2H_6\}$
$S_4 : \{H_2\}$	
$S_5 : \{C_2H_4\}$	

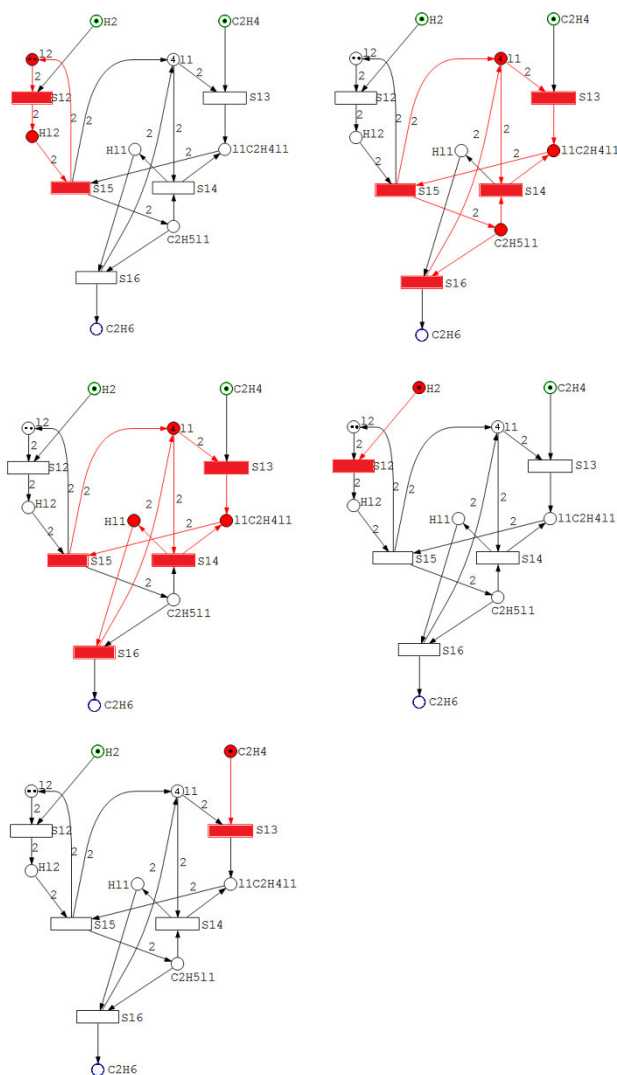


Fig. 7: Minimal siphons of stoichiometrically feasible independent pathway RP_6 .

The places in siphon S_4 and S_5 represent the starting reactants. Therefore, these siphons remain marked until the starting reactants are available. Siphons S_1 , S_2 and S_3 contain minimal traps τ_1 , τ_2 and τ_3 , respectively. As all these siphons are marked in the initial state, therefore according to the property of traps, they remain marked in any state. From the initial state where places H_2 , C_2H_4 , l_1 and l_2 are available, all the transitions can fire at least once (it means that every elementary reaction step operates), so the reaction pathway is structurally startable.

IV. CONCLUSIONS

P-graph framework can generate stoichiometrically feasible reaction pathways. The startability of these pathways can be tested by Petri net analysis. The reachability graph

analysis of Petri nets is theoretically capable of determining the startability of reaction pathway, but as this method is started with the generation of reachability graph, it is practically limited to small problems due to the computational effort growing exponentially according to the number of elementary reactions to be considered.

Contrarily structural startability examinations on siphon-trap analysis of Petri nets can effectively check the startability of reaction pathways. Moreover, the siphon-trap analysis helps identifying those initial states may potentially lead to a startable stoichiometrically feasible pathway.

All the major steps of the above proposed methods have been illustrated by case studies.

V. REFERENCES

- [1] Fan, L. T.; Friedler, F. Reaction Pathway Analysis by a Network Synthesis Technique. AIChE Annual Meeting 1997, Los Angeles, CA, U.S.A., November 16-21.
- [2] Friedler, F.; Tarjan, K.; Huang, Y.; Fan, L. Graph-theoretic approach to process synthesis: axioms and theorems. Chemical Engineering Science 1992, 47, 1973-1988.
- [3] Fan, L. T.; Bertok, B.; Friedler, F.; Shafie, S. Mechanisms of Ammonia-Synthesis Reaction Revisited with the Aid of a Novel Graph-Theoretic Method for Determining Candidate Mechanisms in Deriving the Rate Law of a Catalytic Reaction. Hungarian Journal of Industrial Chemistry 2001, 29, 71-80.
- [4] Petri, C. A. Kommunikation mit Automaten ; Rheinisch-Westfälisches Institut für Instrumentelle Mathematik an der Universität Bonn: Bonn, Germany, 1963.
- [5] Peterson, J. L. Petri Net Theory and the Modeling of Systems ; Prentice Hall: New Jersey, 1981.
- [6] Angeli, D.; De Leenheer, P.; Sontag, E. D. A Petri net approach to the study of persistence in chemical reaction networks. Mathematical Biosciences 2007, 201, 598-618.
- [7] Lakner R., Friedler F., Bertók B.: Synthesis and Analysis of Process Networks by Joint Application of P-graphs and Petri Nets. Lecture Notes in Artificial Intelligence, 10258 : Zaragoza 2017. 309-329.
- [8] Davis, M. E., Davis, R. J., Eds. Fundamentals of Chemical Reaction Engineering ; Mc-Graw - Hill: New York, 2003.
- [9] Heiner, M.; Herajy, M.; Liu, F.; Rohr, C.; Schwarick, M. Snoopy - a unifying Petri net tool. Proc. Petri nets 2012, LNCS 2012, 7347, 398-407.
- [10] Software P-graph Studio: <http://p-graph.org/downloads>
- [11] Heiner, M.; Schwarick, M.; Wegener, J. Charlie - an extensible Petri net analysis tool. Proc. Petri nets 2015, LNCS 2015, 9115, 200-211.
- [12] Murata, T. Petri Nets: properties, analysis and applications. Proc IEEE 1989, 77, 541-80.
- [13] Hideki, Y. On the Structure of Siphons of Petri Nets (Logics, Algebras and Languages in Computer Science). RIMS Kokyuroku 2014, 1915, 132-141.
- [14] Lakner R., Bertok B., Friedler F.: Synthesis of Startable Reaction Pathways. Chemical Engineering Transactions, 70, 2018, 1129-1134.
- [15] Fan, L. T.; Yu-Chuan, L.; Shafie, S.; Bertok, B.; Friedler, F. Exhaustive Identification of Feasible Pathways of the Reaction Catalyzed by a Catalyst with Multiactive Sites via a Highly Effective Graph-Theoretic Algorithm: Application to Ethylene Hydrogenation. Ind.Eng. Chem. Res. 2012, 51, 2548-2552.