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Process Network Synthesis for Benzaldehyde Production: P-graph Approach

Jean Pimentel Losada[a], Istvan Heckl[b], Botond Bertok[b], Ferenc Friedler[c],
Juan C. Garcia-Ojeda[d], Andres Argoti*[,e]

[a]Department of Chemical and Environmental Engineering, Universidad Nacional de Colombia, Bogotá, Colombia
[b]Department of Computer Science and Systems Technology, University of Pannonia, Veszprém, Egyetem u.10 H-8200, Hungary
[c]Faculty of Information Technology, Pázmány Péter Catholic University, Práter u. 50/A, 1083 Budapest, Hungary
[d]Department of Systems Engineering, Universitaria de Investigación y Desarrollo, Calle 9 No. 23-55, Bucaramanga Colombia
[e]Department of Chemical Engineering, Kansas State University, 1005 Durland Hall, Manhattan, Kansas 66506, USA
argoti@k-state.edu

Benzaldehyde is a chemical of significant importance in a variety of industries, which is mainly manufactured from toluene. In this work, authors develop process flowsheets in terms of profit for the production of benzaldehyde from toluene via process-network synthesis by deploying an algorithmic method based on P-graphs. First, the best reaction combination for the production process in terms of profit is obtained. Second, a set of operating units that can perform the process is identified; the corresponding maximal structure is constructed with the P-graph representations of these operating units. Third, the optimal and near-optimal flowsheets in terms of profit are algorithmically identified from the maximal structure.

1. Introduction

This work explores process-network synthesis (PNS) for producing benzaldehyde from toluene by means of a highly efficient algorithmic method defined in terms of process graphs, or P-graphs (Friedler et al., 1992). PNS in conjunction with the algorithmic method based on P-graphs has proven to be effective in reducing the production costs of chemical processes (Liu et al., 2004), thereby increasing their profitability. In fact, PNS based on the P-graph methodology has also been adopted to solve synthesis problems of combinatorial nature encountered in a variety of fields. Instances of such problems include the optimal design of supply chains (Süle et al., 2011), the routing and scheduling of evacuation schemes in buildings (Garcia-Ojeda et al., 2012) as well as the integration of wastewater systems and energy networks (Kollmann et al., 2014).

Benzaldehyde is the simplest aromatic aldehyde; it is extensively deployed for the production of odorants and flavours in the pharmaceutical, food, and cosmetic industries (Brühne and Wright, 2003). In view of its industrial significance, designing processes that maximise the profit in manufacturing benzaldehyde is of the utmost interest. Currently, benzaldehyde is mainly obtained via two production processes with toluene as the raw material. One process is the hydrolysis of benzal chloride (Opgrande et al., 2003); the other is the partial oxidation of toluene (Brühne and Wright, 2003). The authors aim at generating a set of technically feasible process flowsheets for the production of benzaldehyde from toluene via PNS in light of the P-graph framework. Apparently, the development of such flowsheets by deploying the P-graph methodology has not been performed hitherto. At the outset of flowsheet generation, the identification of the best reaction combination in terms of profit from the set of all the feasible combinations of the reactions involved in the two processes of benzaldehyde production is made. Subsequently, authors select a set of plausible operating units, including reacting and separation units, and construct the process' maximal structure with these operating units represented by P-graphs. The maximal structure contains all the

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feasible combinations of operating units capable of performing the process of concern. In other words, the maximal structure contains all the possible flowsheets capable of producing benzaldehyde from toluene. Finally, optimal and near-optimal flowsheets from the maximal structure, which are ranked according to their profits is algorithmically identified.

2. Process description

Benzaldehyde is industrially obtained from toluene by resorting to two manufacturing routes, the hydrolysis of benzal chloride (Opgrande et al., 2003) and the partial oxidation of toluene (Brühne and Wright, 2003); both of which involve a series of reactions as well as the subsequent recovery and purification of benzaldehyde via distillation. The hydrolysis of benzal chloride consists of two reaction steps. First, liquid toluene reacts with gaseous chlorine at a temperature between 100 ºC and 200 ºC producing benzal chloride (benzylidene chloride). Second, benzal chloride is hydrolyzed in the presence of an acid, or basic, catalyst, thereby yielding benzaldehyde and various by-products (Lipper and Löser, 2003). In this regard, Brühne and Wright (2003) have reported that the yield of benzaldehyde for acid hydrolysis is more than 90 %.

The partial oxidation of toluene involves a single reaction step that can be carried out in gas phase (Downie et al., 1961) or in liquid phase (Kantam and Sreekanth, 2002); benzaldehyde is one of the reaction's products. Gas-phase oxidation is performed by passing a gaseous mixture of toluene and air (oxygen) through a catalyst bed at a temperature between 350 ºC (Gündüz and Akpolat, 1990) and 650 ºC (Brühne and Wright, 2003). The yield of benzaldehyde for gas-phase oxidation has been reported as 20 % (Gündüz and Akpolat, 1990) or as varying from about 40 % to about 60 % (Brühne and Wright, 2003); the latter case is favoured by low conversion rates of toluene (between 10 % and 20 %). Liquid-phase oxidation is usually performed by mixing toluene and air (oxygen) at a temperature ranging from 110 ºC (Borgaonkar et al., 1984) to 170 ºC (Guo et al., 2005) in the presence of a metal-based catalyst and at a pressure that renders the reaction medium liquid. The reaction's selectivity for benzaldehyde ranges from about 30 % (Guo et. al., 2005) to about 73 % (Zhang et al., 2012).

3. Methodology and implementation

The following are the steps for the generation of feasible process flowsheets for the process of under consideration by deploying PNS based on the P-graph methodology. The fundamentals of this approach have been sufficiently discussed in earlier contributions, including its axiomatic basis (Friedler et al., 1992), its rigorous mathematical definition (Friedler et al., 1998) as well as its implementation (Liu et al., 2004).

3.1 Reaction-network synthesis (RNS)

RNS identifies the reaction combination, or network, that maximizes the process' profit from the comprehensive set of feasible networks of the reactions underlying the two routes of benzaldehyde production. The identification is performed by adapting the algorithmic method based on P-graphs originally established for PNS; see, e.g., Fan et al. (2002). For initial exploration, it is assumed that the reactions take place in continuous-stirred tank reactors (CSTRs). In this work, the reaction network that maximizes the process' profit is the partial oxidation of toluene in liquid phase as determined by RNS. Naturally, this reaction constitutes the basis for deploying PNS based on P-graphs.

3.2 Specification of materials

Toluene and air (oxygen) are defined as the process' raw materials. Clearly, benzaldehyde is the process' main product; all other reaction products are considered as by-products, e.g., benzoic acid and water. Intermediate materials are all other materials present in the process that are neither raw materials nor products. In this work, intermediate materials can be mixtures, e.g., a mixture of toluene and water.

3.3 Identification of operating units

In this work, 24 operating units are included in the flowsheet-generation problem to be solved algorithmically with P-graphs; these units have been identified from the set of all the plausible operating units capable of carrying out the process of concern. The following are the 24 operating units with their corresponding designations in the flowsheet-generation problem. One (1) reaction unit (LiqOxidation); fifteen (15) distillation units (D1, D2, D3, D4, D5, D6, D7, D8A, D8B, D8C, D8D, D9A, D9B, D9C, and D10); one (1) liquid-liquid-vapor flash unit (F1); one (1) gas stripping unit (S1); five (5) mixing units, or mixers, (M1, M2_1, M2_2, M2_3, and M2_4); and one (1) auxiliary unit (Feed). For preliminary exploration, the reaction unit and the distillation units are assumed to be a CSTR and tray distillation columns, respectively. Auxiliary unit Feed unit differentiates raw material toluene from the toluene streams exiting mixers M2_1 through M2_4, which are recycled into the process, thereby avoiding the violation of one of the axioms of PNS based on P-graphs. This axiom establishes that no raw material can be produced by any of the operating units (Friedler et al., 1992).

3.4 P-graph representations of operating units

The operating units identified are graphically represented by conventional diagrams as well as by P-graphs. These P-graphs consist of circles and horizontal bars representing the materials and operating units, respectively; the operating units are linked to their concomitant materials with arcs (Liu et al., 2004). Figure 1 illustrates the conventional and P-graph representations for operating unit D8A, a tray distillation column.

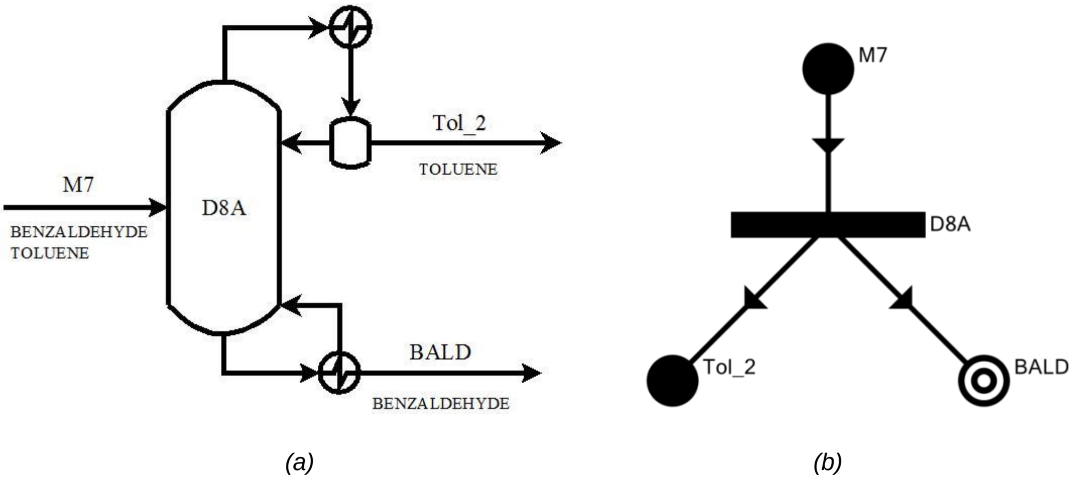

Figure 1: Conventional and P-graph representations of tray distillation column D8A. (a) Conventional diagram; (b) P-graph representation

3.5 Generation of comprehensive flowsheet

Algorithm maximal-structure generation (MSG) constructs the comprehensive flowsheet, i.e., the maximal structure, of the process (Friedler et al., 1993). At the outset, the input structure to the algorithm is obtained by linking the common material nodes of the P-graphs representing the 24 operating units identified. Subsequently, the algorithm eliminates from the input structure the materials and operating units that violate any of the axioms of PNS based on P-graphs (Friedler et al., 1992). The maximal structure comprises all the combinatorially feasible flowsheets capable of yielding benzaldehyde from toluene.

3.6 Generation of optimal and near-optimal flowsheets

Algorithms solution-structure generation (Friedler et al., 1992) or accelerated branch-and-bound (Varga et al., 1995) identify the optimal and near-optimal process flowsheets from the maximal structure. Algorithm solution-structure generation (SSG) yields all the combinatorially feasible flowsheets that satisfy the set of axioms of PNS based on P-graphs. For each of these flowsheets, a suitable objective function is optimized via linear programing (LP) in light of the process' mass-balance constraints. Subsequently, the optimized flowsheets are ranked in terms of the objective function, thereby identifying the optimal and all the near-optimal process flowsheets. Algorithm SSG in conjunction with LP is termed algorithm SSG+LP. In practice, however, only a finite number of the optimal and near-optimal process flowsheets is of interest; thus, they should be obtained and ranked rapidly without generating all other feasible flowsheets. Algorithm accelerated branch-and-bound (ABB) accomplishes these tasks efficiently; such a computational advantage is particularly useful when the number of combinatorially feasible flowsheets generated by algorithm SSG is exceedingly large, thereby rendering their optimization time consuming.

4. Results and discussion

For illustration, the flowsheet-generation problem for the process of concern assumes an annual production of benzaldehyde of 10,000 t with a purity of 99.4 wt %. Moreover, it is assumed that the process is operated continuously for 8,000 h/y. Algorithm MSG has synthesized the process' maximal structure from the input structure constructed by linking the common material nodes of the P-graph representations of the 24 operating units identified. Algorithm MSG has been executed by software PNS Studio (PNS Studio, 2015) on a PC (Intel Core i5, 2.4 GHz, 4GB RAM), thereby generating the maximal structure in less than a second. Upon execution, the algorithm has eliminated mixer M1 as well as its concomitant material streams from the input structure: This operating unit has no contribution in the production of benzaldehyde. Figure 2 depicts the P-graph representation of the maximal structure comprising 23 operating units. In this figure, the process' raw materials, toluene and air, are designated as Toluene_Feed and Air_Feed; the main product, benzaldehyde, is denoted by BALD. Mixer M1 eliminated from the input structure is shown in grey.

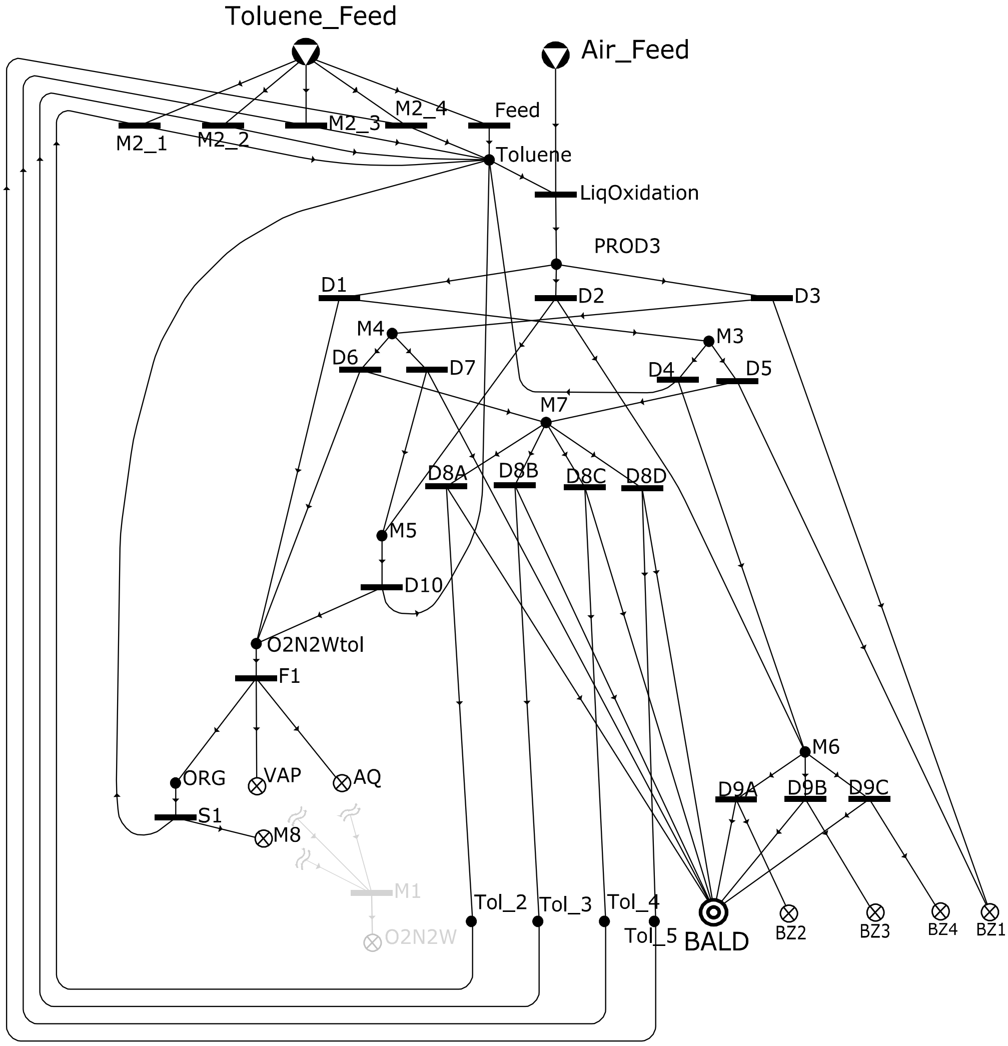

Figure 2: P-graph representation of the maximal structure for the production of benzaldehyde from toluene as generated by algorithm MSG

Algorithms SSG+LP and ABB have identified the optimal and near-optimal process flowsheets from the maximal structure by maximizing the objective function, profit. Herein, profit is defined as the difference between the total process revenue and the total production cost. The former is the proceeds obtained from selling main product benzaldehyde with a purity of 99.4 wt % only; the combined contribution of by-products and intermediate materials to the total process revenue is assumed to be negligible. The latter comprises the total cost of raw material toluene only and the total operating costs, i.e., the cost associated to purchasing, operating, and maintaining the processing units (operating units). The contribution of raw material air to the total production cost is also assumed to be negligible.

Algorithms SSG+LP and ABB have been executed by software PNS Studio (PNS Studio, 2015) on a PC (Intel Core i5, 2.4 GHz, 4GB RAM) with objective function profit, thereby yielding the optimal and near-optimal process flowsheets for the process under consideration; naturally, these flowsheets maximize profit in ranked order. Algorithm SSG+LP has identified 222 solution flowsheets in about 20 s; moreover, algorithm ABB has identified 199 solution flowsheets in approximately 2 s. Both algorithms have identified the same optimal flowsheet as well as the same next four near-optimal flowsheets; all of them are capable of producing 10,000 t/y of benzaldehyde with a purity of 99.4 wt %. The optimal flowsheet contains 8 of the 23 operating units originally comprising the maximal structure, specifically, reactor LiqOxidation; auxiliary unit Feed; mixer M2_1; distillation units D3, D6, and D8A; liquid-liquid-vapour flash unit F1; and gas stripping unit S1. For the optimal flowsheet, the proceeds obtained from selling benzaldehyde with a purity of 99.4 wt % have been computed as 23,000,000 USD/y; moreover, the total production cost has been computed as 22,065,154 USD/y. Consequently, the optimal process flowsheet yields a profit of 934,846 USD/y. For comparison, the profits corresponding to the next four near-optimal flowsheets in descending order are 894,025 USD/y, 801,188 USD/y, 800,206 USD/y, and 799,861 USD/y. Figure 3 shows the P-graph representation of the optimal flowsheet for the process under consideration.

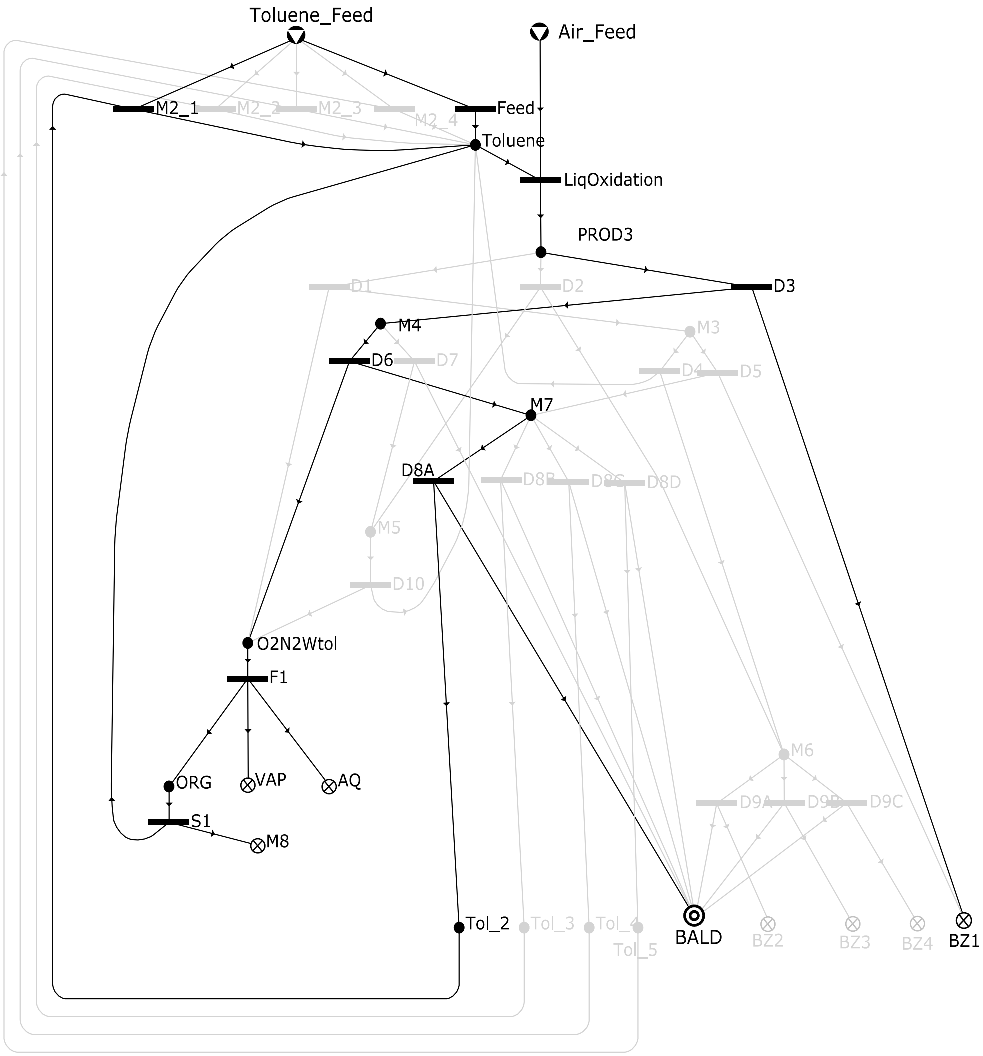

Figure 3: P-graph representation of the optimal flowsheet (shown in black) for the production of benzaldehyde from toluene as identified by algorithms SSG+LP and ABB from the maximal structure

5. Conclusions

Our preliminary exploration has revealed that the algorithmic method based on P-graphs can be successfully applied to the development of process flowsheets for the production of benzaldehyde from toluene in terms of profit via PNS. The partial oxidation of toluene in liquid phase has been identified as the reaction that maximizes the profit of the production process. On the basis of this reaction, a number of operating units capable of performing the process have been identified; algorithm MSG has synthesized the process' maximal structure with the P-graph representations of these operating units. From the maximal structure, algorithms SSG+LP and ABB have identified the optimal and a finite number of near-optimal process flowsheets, which maximize the profit. The generation of the maximal structure and the identification of the optimal and near-optimal flowsheets have been accomplished rapidly and efficiently with modest computational requirements.

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In memoriam, Prof. L. T. Fan (1929-2014)

References

Borgaonkar H.V., Ranvenkar S.R., Chandalla S.B., 1984, Liquid phase oxidation of toluene to benzaldehyde by air, Ind. Eng. Chem. Prod. Res. Dev., 23, 455-458.

Brühne F., Wright E., 2003, Benzaldehyde, Ullmann's Encyclopedia of Industrial Chemistry, Wiley-VCH, Weinheim, Germany, 223-235.

Downie J., Shelstad K. A., Graydon W. F., 1961, Kinetics of the vapor-phase oxidation of toluene over a vanadium catalyst, Can. J. Chem. Eng., 39, 201-204.

Fan L.T., Bertok B., Friedler F., 2002, A graph-theoretic method to identify candidate mechanisms for deriving the rate law of a catalytic reaction, Comput. Chem., 26, 265-292.

Friedler F., Fan L.T., Imreh B., 1998, Process network synthesis: problem definition, Networks, 31, 119-124.

Friedler F., Tarjan K., Huang Y.W., Fan L.T., 1992. Graph-theoretic approach to process synthesis: axioms and theorems, Chem. Eng. Sci., 47, 1973-1988.

Friedler F., Tarjan K., Huang Y.W., Fan L.T., 1993, Graph-theoretic approach to process synthesis: polynomial algorithm for maximal structure generation, Comput. Chem. Eng., 17, 929-942.

Garcia-Ojeda J.C., Bertok B., Friedler F., 2012, Planning evacuation routes with the P-graph framework, Chemical Engineering Transactions, 29, 1531-1536.

Gündüz G., Akpolat O., 1990, Catalytic vapor-phase oxidation of toluene to benzaldehyde, Ind. Eng. Chem. Res., 29, 45-48.

Guo C.-C., Liu Q., Wang X.-T., Hu H.-Y., 2005, Selective liquid phase oxidation of toluene with air, Appl. Catal. Gen., 282, 55-59.

Kantam M., Sreekanth P., 2002, An improved process for selective liquid-phase air oxidation of toluene, Catal. Lett., 81, 223-231.

Kollmann R., Maier S., Shahzad K., Kretschmer F., Neugebauer G., Stoeglehner G., Ertl T., Narodoslawsky M., 2014, Waste water treatment plants as regional energy cells – evaluation of economic and ecologic potentials in Austria, Chemical Engineering Transactions, 39, 607-612.

Lipper K.A, Löser E., 2003, Benzyl Chloride and other Side-Chain Chlorinated Aromatic Hydrocarbons, Ullmann's Encyclopedia of Industrial Chemistry, Wiley-VCH, Weinheim, Germany, 367-381.

Liu J., Fan L.T., Seib P., Friedler F., Bertok B., 2004, Downstream process synthesis for biochemical production of butanol, ethanol, and acetone from grains: generation of optimal and near-optimal flowsheets with conventional operating units, Biotechnol. Prog., 20, 1518-1527.

Opgrande J.L., Brown E., Hesser M., Andrews J., 2003. Benzaldehyde. Kirk-Othmer Encyclopedia of Chemical Technology, John Wiley & Sons, Hoboken, New Jersey, USA, 590-596.

PNS Studio, 2015, Process graphs <www.p-graph.com>, accessed 12.02.2015.

Süle Z., Bertok B., Friedler F., Fan L.T., 2011, Optimal design of supply chains by P-graph framework under uncertainties, Chemical Engineering Transactions, 25, 453-458.

Varga J.B., Friedler F., Fan L.T., 1995, Parallelization of the accelerated branch-and-bound algorithm of process synthesis: application in total flowsheet synthesis, Acta Chimica Slovenica, 42, 15-20.

Zhang G.Q., Zhang X., Lin T., Gong T., Qi M., 2012, Synergetic effect of $FeVO_4$ and α-Fe_2O_3 in Fe–V–O catalysts for liquid phase oxidation of toluene to benzaldehyde, Chin. Chem. Lett., 23, 145-148.