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Reactor network synthesis for isothermal conditions

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ABSTRACT. In the present paper, a computational systematic procedure for isothermal Reactor Network Synthesis (RNS) is presented. A superstructure of ideal CSTR and PFR reactors is proposed and the model is formulated as a constrained Nonlinear Programming (NLP) problem. Complex reactions (series/parallel reactions) are considered. The objective function is based on yield or selectivity, depending on the desired product, subject to different operational conditions. The problem constraints are mass balances in the reactors and in the considered reactor network superstructure. A systematic computational procedure is proposed and a Genetic Algorithm (GA) is developed to obtain the optimal reactor arrangement with the maximum yield or selectivity and minimum reactor volume. Results are as good as or better than those reported in the literature.

Key words: process synthesis, reactor network synthesis, optimization, reactor superstructure, genetic algorithms.

RESUMO. Síntese de redes de reatores para condições isotérmicas. No presente trabalho apresenta-se um procedimento computacional para síntese de redes de reatores (SRR) operando em condições isotérmicas. Uma superestrutura de rede de reatores formada por reatores ideais CSTR e PFR é proposta e o problema apresenta uma formulação de programação não linear (PNL). São consideradas reações complexas (série/paralelas). A função objetivo é baseada no rendimento ou na seletividade em relação ao produto desejado, sujeito a diferentes condições de operação. As restrições ao problema são provenientes dos balanços de massa e da configuração da superestrutura considerada. No procedimento computacional é proposto um Algoritmo Genético (AG) para obtenção do arranjo ótimo de reatores com máximo rendimento ou seletividade com menor volume reacional. Os resultados obtidos são condizentes com os obtidos na literatura.

Palavras-chave: síntese de processos, síntese de redes de reatores, otimização, superestrutura de reatores, algoritmos genéticos.

Introduction

Industrial chemical processes have as their main objective the conversion of raw material into products with economical value. Reactor design directly influences the process design. Well-designed reactors mean well-designed processes (Smith, 2005). As suggested by Linnhoff *et al.* (1982), in the onion diagram, reactor design is the first stage in the process synthesis task.

The synthesis of a reactor network can be formulated as an optimization problem whose variables to be optimized are the volume of the reactors, the type and interconnection between them, the yield or the selectivity of a desired product in the case of complex reaction schemes, involving series/parallel reactions. Due to the great number of solution possibilities and the higher degree of nonlinearity in equations that describe this kind of

system, the problem is complex and of difficult solution. Perhaps because of these difficulties, the number of papers published in this subject is small when compared to other process synthesis areas, such as heat exchanger networks of separation systems with distillation.

Three different groups of methods have been proposed in RNS literature. Hillestad (2004) proposed the first group, that is the most used in the industrial processes and is based on modifications to an existing design and strongly based on heuristics. The second class of methods is based on the optimization of superstructures, and the third one is based on the systematic generation of the process flow sheet or part of it. The latter two can be considered techniques of mathematical programming and make use of computers and other methods to achieve the best process flow sheet.

Superstructure optimization (Lakshmanan and Biegler, 1996) is a class of methods in which a network structure is initially proposed and an optimal sub-network that optimizes a desired variable is derived from the initial network. However, it proves to be very difficult to assure that the proposed initial superstructure contains all the possible networks. On the other hand, the systematic network generation has as its main objective to find branches of good performance for the system. A functional representation is used to model all the reactions and mixing states. It is based on the concentration state space and is known as Attainable Region (AR).

The first published papers on RNS were based on heuristics and graphical techniques, to simple kinetics and reaction mechanisms with a small number of reactants and products. In chemical industrial processes, nevertheless, the reactions always involve a considerable number of reactants, products and reaction paths, and by using only this set of techniques the solution to the problem will remain impossible. Later papers considered superstructures formed by ideal reactors (CSTR and PFR) and their possible combinations to compose the final network when complex reactions are involved.

Simple rules with geometrical interpretation for the synthesis of ideal isothermal reactors configurations for complex reaction schemes were proposed in Chitra and Govind (1985). The model employed considers two tubular reactors with recycle. The recycle ratio was the variable that determined the system optimization.

The AR geometric technique based on the operation vectors and design equations to the CSTR and PFR reactors was proposed by Glasser and Hildebrandt (1987). Only isothermal systems with no volume change in reaction or mixing were examined in the paper.

Achenie and Biegler (1988) presented an approach to convert the synthesis problem formulation in an optimal control formulation, solved using a gradient-based algorithm that employs successive quadratic programming and adjoint variables.

Kokossis and Floudas (1990) presented a systematic approach to the optimization problem in discussion. A superstructure was proposed substituting the PFR reactors by series of CSTR to avoid the differential equations system to be solved when PFR balances are used. The model was formulated as a large-scale Mixed Integer Nonlinear Programming (MINLP) problem.

Balakrishna and Biegler (1992) developed a targeting model based on optimizing flows between different reactions environments formulated as a dynamic optimization problem.

Bikic and Glavic (1996) proposed an algorithm procedure for generating reactor network design considering the basic principles of reaction and mixing. Candidate reactor networks were generated by expanding the solution space into regions where different levels of mixture are required. Yield was the variable to be maximized.

Marcoulaki and Kokossis (1996) presented a method based upon a general system representation in the form of a superstructure network. The superstructure provides the domain of a stochastic optimization, which is achieved using Simulated Annealing.

Cordero *et al.* (1997) combined a Nonlinear Programming (NLP) method with Simulated Annealing for the automatic synthesis and optimization of reactor networks by using a superstructure containing the potential and feasible configurations to achieve the optimal solution.

Jacobs and Jansweijer (2000) proposed a five-step knowledge-based method for the analysis of reactor networks using well-known concepts in chemical engineering to optimize conversion and selectivity.

Pahor *et al.* (2001) presented a superstructure-based MINLP approach to the RNS in an equation-oriented environment comprising isothermal and non-isothermal reaction problems.

Revollar *et al.* (2004) presented an approach to the synthesis and design of integrated processes considering simultaneously economic aspects and controllability. A superstructure is proposed for the task of synthesis, containing a sequence of CSTR. A MINLP model was proposed and both the problems were solved using a Genetic Algorithm (GA).

In the present paper, a computational procedure to the RNS operating in isothermal conditions considering complex reaction schemes is proposed. A superstructure is proposed considering ideal reactors CSTR and PFR and their possible combinations. The optimization model has a formulation of a constrained NLP problem. The objective function depends on the reaction system used and is based on yield maximization or selectivity to a desired product. The problem constraints are the differential and algebraic equations from the mass balances in the considered reactors. The systems of differential equations are solved by using routines available in the IMSL/Fortran library. A GA was developed to the definitions of the optimal reactor arrangement, with

the maximum yield or selectivity and minimum volume of reaction. Three cases are studied and compared with the values published in the literature.

Material and methods

Problem formulation

The problem studied in this paper is how to find the optimum types, arrangement and volume of the ideal reactors CSTR and PFR that maximizes the yield or selectivity of a desired product for a given complex reaction mechanism operating in isothermal conditions with known initial concentrations, reaction rates and feeds with minimum reactors volume.

The subject is treated as an optimization problem and the objective function to be optimized is the yield or selectivity of a desired product, depending on the complex reactions considered. The problem constraints are the mass balances in the superstructure nodes and the design equations of the considered reactors.

Proposed superstructure

The superstructure proposed is very simple, but sufficiently wide to comprise the optimal solution for a large number of problems as the cases studied in this paper. It considers distinct possibilities of the classical CSTR-PFR arrangement. The most used in the literature are composed by a CSTR followed by a PFR, a unique CSTR, a unique PFR, a PFR followed by a CSTR or a CSTR and a PFR operating in parallel. Figure 1 presents the proposed superstructure.

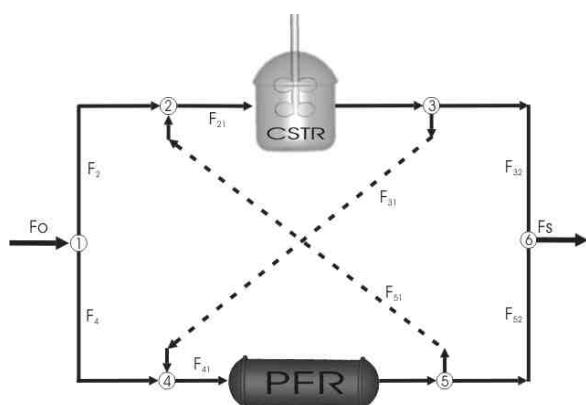


Figure 1. Reactor network superstructure.

The superstructures presented in the literature have at maximum five reactors. Additionally, all the solutions presented to the problem of RNS with the reaction schemes considered in this paper can be

found in the considered superstructure, as will be further demonstrated.

The mathematical formulation is presented below.

Mathematical formulation

The mathematical formulation takes into account the mass balances in the nodes 1 to 6 of the superstructure.

Node 1 represents the superstructure feed. F is the maximum initial feed, and it can be randomly split in two branches, F_2 and F_4 . This can be done as:

$$F_2 = F_0 * RAN1 \quad (1)$$

where $RAN1$, $RAN2$ and $RAN3$ are random numbers between 0 and 1.

$$F_4 = F_0 - F_2 \quad (2)$$

Node 2 is a mixing node, in the CSTR inlet. The inlet flow rate F_{21} , after the mixer, can be formed by the combination of the PFR outlet F_{51} and the branch F_2 :

$$F_{21} = F_2 + F_{51} \quad (3)$$

Node 3 is a splitting node, in the CSTR outlet. The CSTR outlet flow is F_3 , which is equal to F_{21} , and can be randomly split in F_{31} and F_{32} :

$$F_{31} = F_3 * RAN2 \quad (4)$$

$$F_{32} = F_3 - F_{31} \quad (5)$$

Node 4 is a mixing node, in the PFR inlet. The inlet flow rate F_{41} , after the mixer, can be formed by the combination of the CSTR outlet F_{31} and the branch F_4 :

$$F_{41} = F_4 + F_{31} \quad (6)$$

Node 5 is a splitting node, in the PFR outlet. The PFR outlet flow rate is F_5 , which is equal to F_{41} , and can be randomly split in F_{51} and F_{52} :

$$F_{51} = F_5 * RAN3 \quad (7)$$

$$F_{52} = F_5 - F_{51} \quad (8)$$

Node 6 is a splitting node and represents the superstructure outlet. The outlet flow rate F_6 is

given by:

$$F_6 = F_{32} + F_{52} \quad (9)$$

These equations are the superstructure constraints, to be used in the optimization problem.

The other constraints are the design equations of the reactors involved in the superstructure. For the CSTR, the design equation is:

$$\frac{V}{F} = \frac{x}{(-r)} \quad (10)$$

For the PFR, the design equation is:

$$F \frac{dx}{dV} = (-r) \quad (11)$$

where:

V = reactor volume;

F = molar feed flow rate;

x = conversion;

$(-r)$ = reaction rate.

Development

In the present paper, a systematic computational procedure is proposed for the RNS that operate in isothermal conditions, considering complex reaction schemes. A superstructure is proposed considering the ideal reactors CSTR and PFR, comprising its possible combinations. The optimization model has a formulation of a constrained NLP problem. The objective function depends on the reaction system used and is based on the yield maximization or selectivity to a desired product. The problem constraints are the superstructure equations and the differential and algebraic equations from the design of the considered reactors. Routines available in the IMSL/Fortran library are used to solve these systems of equations. A GA was developed to define optimal reactor arrangement, with the maximum yield or selectivity and minimum volume of reaction.

The procedure was computationally implemented in Fortran language, because of the ease in working with the existing calculus routines for the solution of the reactors' algebraic and differential equations systems.

The computational procedure developed is presented in Figure 2. The first step is to define the reaction scheme and the objective function, i.e., the yield maximization or selectivity.

Generally, the objective function is defined as a relation between the desired product flow rate and the reactant feed flow rate in function of the reactor

volume.

A GA is responsible for achieving the optimal variables values, the maximum desired product yield or selectivity, the minimum reactor volume and the desired outlet product flow rate, as well as reactor arrangement according to the superstructure presented in Figure 1. Floating point is the codification used by the GA.

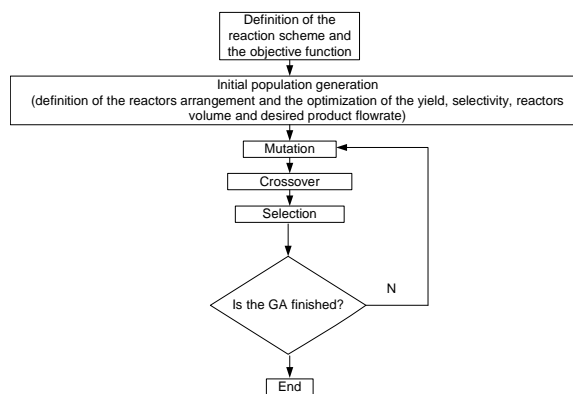


Figure 2. Computational procedure.

Initially, the GA randomly generates a population of candidate concentrations for optimal, according to the Equation (12):

$$X_i^{pop} = (x_{max} - x_{min})(x_i * RAN) \quad (12)$$

In this equation x_{max} and x_{min} represent, respectively, maximum and minimum conversions and RAN represents a random number. The number of individuals generated in the initial population is a previously fixed parameter.

By using Equations (1) to (11), which are the constraints that come from the superstructure presented in Figure 1, a reactor arrangement is considered, as a candidate. With the conversions obtained in Equation (12), the design differential systems of equations from the PFR are solved using the routine IVMRK/DIVMVRK, from the IMSL/Fortran library.

The next GA operator is the mutation. It is responsible for the generation of mutated individuals, represented by X_{mut} , obtained from the Equation (13):

$$X_i^{mut} = X_i^{pop} + \beta x_{max} \quad (13)$$

where β is a random number between 0 and 1.

During the mutation stage, the network configurations can be modified.

The next GA operation is the crossover. In this stage, the mutated individuals are combined

randomly with other individuals. No acquired characteristic is lost, because there is a linear combination among the individuals from the initial population and the mutated individuals, generating a new population, given by the Equation (14):

$$X_i^{cruz} = \theta X_i^{pop} + (1-\theta)X_i^{mut} \quad (14)$$

where θ is a random number between 0 and 1.

The best individuals, i.e., the individuals that present the optimal values to the considered objective function taking into account the problem constraints are selected. The selection is done by the classical procedure of *Ranking*. The individuals are ranked according to their adaptation to the objective function. The most apt individuals are better ranked.

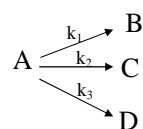
This procedure is repeated until a tolerance is satisfied or until the maximum iteration number is achieved.

Results and discussion

Three kinds of complex reaction schemes were studied: the classical reactions of Trambouze, Van de Vusse and Denbig. The objective functions are distinct, but the priority is the desired product formation in all cases.

Case study 1: Trambouze reaction

This reaction was initially presented in a paper by Trambouze and Piret (1959), and other authors used it in studying the synthesis of reactor networks. It involves four species and it is composed by three parallel reactions:



Reaction rates, feed flow rate and species A concentration are:

$$\begin{aligned} F_0 &= 100 \text{ L min.}^{-1} \text{ (maximum feed flow rate);} \\ C_{A0} &= 1,0 \text{ mol L}^{-1} \text{ (initial concentration of A Pure);} \\ k_1 &= 0,025 \text{ mol (L min.)}^{-1}; \\ k_2 &= 0,2 \text{ min.}^{-1}; \\ k_3 &= 0,41 \text{ L (mol min.)}^{-1}. \end{aligned}$$

The desired product is C. The objective function to be maximized is the selectivity of C, with minimum reactor volume. Selectivity is given by:

$$S_C = \frac{F_C}{F_I} \quad (15)$$

F_C is the desired product outlet flow rate and F_I is the flow rate of undesired products.

The constraints related to the reactor type to the Trambouze reaction are:

To the CSTR:

$$F_A = F_{A0} - V(k_1 C_A^n + k_2 C_A^m + k_3 C_A^p) \quad (16)$$

$$F_B = V(k_1 C_A^n) \quad (17)$$

$$F_C = V(k_2 C_A^m) \quad (18)$$

$$F_D = V(k_3 C_A^p) \quad (19)$$

To the PFR:

$$\frac{dF_A}{dV} = -k_1 C_A^n - k_2 C_A^m - k_3 C_A^p \quad (20)$$

$$\frac{dF_B}{dV} = k_1 C_A^n \quad (21)$$

$$\frac{dF_C}{dV} = k_2 C_A^m \quad (22)$$

$$\frac{dF_D}{dV} = k_3 C_A^p \quad (23)$$

The computational procedure developed is used and the GA found that the maximum yield is obtained when the feed flow rate in the superstructure is directed to the branch formed by a CSTR followed by a PFR. It can be seen because the random number *RAN1* is equal to 1. Results are presented in Table 1 in comparison with other papers results.

Table 1. Results for the Trambouze reaction.

	Paynters and Hashins (1970)	Achenie and Biegler (1986)	Kokossis and Floudas (1990)	Present paper
Objective function value	0.495	0.499	0.500	0.500
Optimal reactor arrangement	CSTR + PFR	CSTR + CSTR	1 - CSTR 2 - CSTR + CSTR 3 - CSTR + PFR with recycle	CSTR + PFR
Reactor volume (L)	$V_{CSTR} = 910.00$ $V_{PFR} = 90.00$	$V_{CSTR} = 722.10$ $V_{PFR} = 9.75$	$1 - V_{CSTR} = 750.325$ $2 - V_{CSTR} = 747.977$ $V_{CSTR} = 1.822$ $3 - V_{CSTR} = 600.637$ $V_{PFR} = 149.276$	$V_{CSTR} = 598.36$ $V_{PFR} = 153.89$

The value of the objective function is the same maximum presented by Kokossis and Floudas (1990), and better than that presented by Paynters and Hashins (1970) and by Achenie and Biegler (1986). The reactor arrangement is the same as obtained by Paynters and Hashins (1970), but with smaller reactor volume (1000 L vs. 752.25 L). The smallest reactor volume, however, is the one obtained by Achenie and Biegler (1996), which corresponds to 731.85 L for two CSTR in series. Kokossis and Floudas (1990) presented three distinct solutions for the problem; a unique CSTR, two CSTR in series, and a CSTR followed by a PFR with recycle, with total reactor volume of 750.325 L, 749.799 L and 749.913 L, respectively.

The solution obtained with the application of the developed GA has a better reactor volume distribution than the other solutions. It is a very important feature in the system balance for industrial operation. It is relatively complicated to operate two continuous reactors in series with such different volumes, as in the second solution proposed by Kokossis and Floudas (1990), where the first reactor has a volume approximately 415 times greater than the second one, and as in the solution presented by Achenie and Biegler (1986), whose first reactor is almost 74 times greater than the second one. This kind of solution has few chances of industrial application.

The Figure 3 shows the convergence frequency as well as the individual evolution for the GA used to solve the problem in the Trambouze reaction. It can be noted that in the fifth iteration, the objective function values are in the range of the optimal solutions.

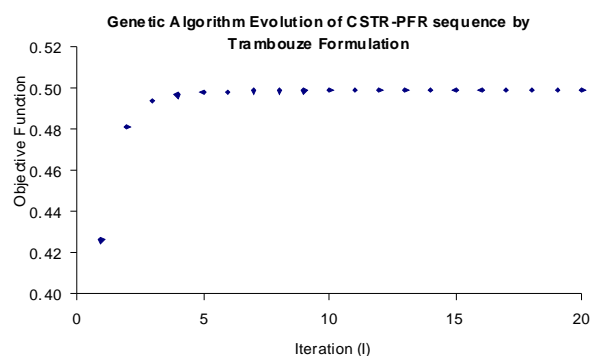
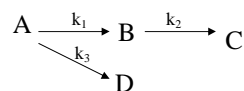


Figure 3. GA evolution of the Trambouze reaction.

Case study 2: Van de Vusse reaction

The second case studied is the reaction of Van de Vusse (1964), composed by a combination of a parallel reaction with two series reactions, also involving four species:



Reaction rates, feed flow rate and feed concentration are:

$$F_0 = 100 \text{ gmol s}^{-1} \text{ (maximum feed flow rate);}$$

$$C_{A0} = 5,8 \text{ mol L}^{-1} \text{ (initial concentration of Pure A);}$$

$$k_1 = 10 \text{ s}^{-1} \text{ (first-order);}$$

$$k_2 = 1,0 \text{ s}^{-1} \text{ (first-order);}$$

$$k_3 = 1,0 \text{ L (mols)}^{-1} \text{ (second-order).}$$

The desired product is the intermediate species B. The objective function to be optimized is the yield (Y) of the desired product.

Reactor constraints to the Van de Vusse reaction are:

To the CSTR:

$$F_A = F_{A0} - V(k_1 C_A^n + k_3 C_A^m) \quad (24)$$

$$F_B = V(k_1 C_A^n - k_2 C_B^p) \quad (25)$$

$$F_C = V(k_2 C_B^p) \quad (26)$$

$$F_D = V(k_3 C_A^m) \quad (27)$$

To the PFR:

$$\frac{dF_A}{dV} = -k_1 C_A^n - k_3 C_A^m \quad (28)$$

$$\frac{dF_B}{dV} = k_1 C_A^n - k_2 C_B^p \quad (29)$$

$$\frac{dF_C}{dV} = k_2 C_B^p \quad (30)$$

$$\frac{dF_D}{dV} = k_3 C_A^m \quad (31)$$

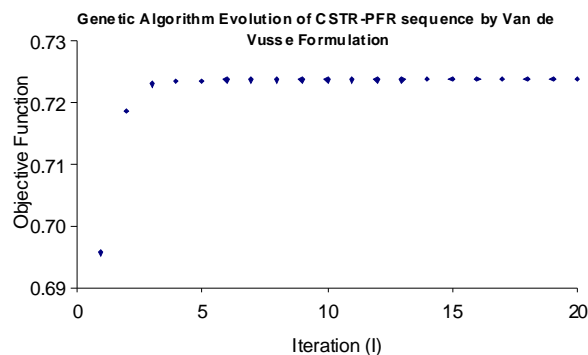
The application of the GA considering the superstructure presented in Figure 1 and the constraints represented by Equations (1) to (11), by optimizing the structure nodes flow rate, the result is similar to the Trambouze reaction. The optimal reactor arrangement is formed by a CSTR followed by a PFR, as presented in Table 2. The value of the objective function is 0.724. A comparison with the results published by other authors is done.

Table 2. Results for the Van de Vusse reaction.

	Chitra and Govind (1981)	Achenie and Biegler (1986)	Kokossis and Floudas (1990a)	Present paper
Objective function value	0.634	0.6372	0.6344	0.724
Yield	3.6772 mol L ⁻¹	3.6956 mol L ⁻¹	3.6796 mol L ⁻¹	4.199 mol L ⁻¹
Reactor arrangement	CSTR + PFR	CSTR + PFR	CSTR + PFR	CSTR + PFR
Reactor volume (L)	V _{CSTR} = 11.21 V _{PFR} = 16.81	V _{CSTR} = 9.562 V _{PFR} = 14.25	V _{CSTR} = 11.382 V _{PFR} = 16.989	V _{CSTR} = 11.35 V _{PFR} = 14.77

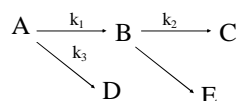
In regards to reactor arrangement, the optimal solution is the same as presented by Chitra and Govind (1985), Achenie and Biegler (1986) and Kokossis and Floudas (1990). The total reactor volumes are 28.02, 23.50 and 28.371 L, respectively. The value obtained with the GA is 26.12 L, better than the values obtained by Chitra and Govind (1985) and Kokossis and Floudas (1990), but greater than the value presented by Achenie and Biegler (1986). The value of the objective function, however, is the best one among all compared results.

Figure 4 shows the convergence frequency and individual evolution for the Van de Vusse reaction, considering the optimal system formed by a CSTR followed by a PFR.

**Figure 4.** Evolution of the GA for the Van de Vusse reaction.

Case study 3: Denbigh reaction

The Denbigh reaction scheme has two reactions in series and two reactions in parallel, involving five distinct species. It is represented by:



with:

$$\begin{aligned}
 F_0 &= 600 \text{ gmol s}^{-1} \text{ (maximum feed flow rate);} \\
 \nu_0 &= 100 \text{ L s}^{-1} \text{ (volumetric feed flow rate);} \\
 C_{A0} &= 6,0 \text{ mol L}^{-1} \text{ (initial concentration of A Pure);}
 \end{aligned}$$

$$\begin{aligned}
 k_1 &= 1 \text{ L (mol s)}^{-1} \text{ (second-order);} \\
 k_2 &= k_3 = 0,6 \text{ s}^{-1} \text{ (first-order);} \\
 k_4 &= 0,1 \text{ L (mol s)}^{-1} \text{ (second-order).}
 \end{aligned}$$

The desired product is *B* and the objective function is the same as presented in the study of the Van de Vusse reaction, i.e., the global yield relative to the desired product.

Constraints are:

CSTR:

$$F_A = F_{A0} - V(k_1 C_A^n + k_3 C_A^m) \quad (32)$$

$$F_B = V(k_1 C_A^n - (k_2 C_B^p + k_4 C_A^q)) \quad (33)$$

$$F_C = V(k_2 C_B^p) \quad (34)$$

$$F_D = V(k_3 C_A^m) \quad (35)$$

$$F_E = V(k_4 C_A^q) \quad (36)$$

PFR:

$$\frac{dF_A}{dV} = -k_1 C_A^n - k_3 C_A^m \quad (37)$$

$$\frac{dF_B}{dV} = k_1 C_A^n - (k_2 C_B^p + k_4 C_A^q) \quad (38)$$

$$\frac{dF_C}{dV} = k_2 C_B^p \quad (39)$$

$$\frac{dF_D}{dV} = k_3 C_A^m \quad (40)$$

$$\frac{dF_E}{dV} = k_4 C_A^q \quad (41)$$

In this case, the algorithm found as the optimal solution is a unique PFR, as opposed to the *Trambouze* and *Van de Vusse* reactions. The maximum feed flow rate is directed to node 4, in the superstructure.

Results for selectivity, yield and reactor arrangement are presented and compared to other papers in Table 3.

Table 3. Results for the Denbigh reaction scheme.

	Achenie and Biegler (1988)	Kokossis and Floudas (1990)	Present paper
Yield	0.2203	0.219	0.22
Selectivity	1.322	1.3168	1.32
Reactor Arrangement	PFR	PFR	PFR
Reactor volume (L)	V _{PFR} = 2.0	V _{PFR} = 20.7061	V _{PFR} = 17.03

The results obtained by the GA are very similar to Achenie and Biegler (1986) and Kokossis and Floudas (1990) for the arrangement (a unique PFR), yield and selectivity, but with a small reactor volume.

Figure 5 shows the convergence frequency to the Denbig reaction, considering the optimal system formed by a unique PFR.

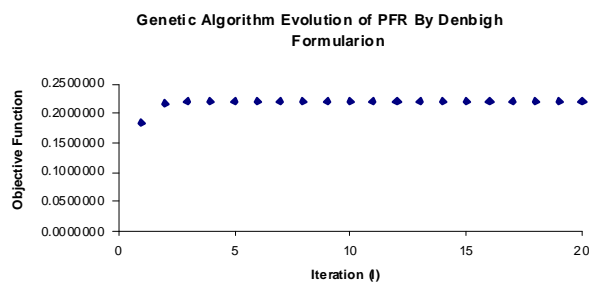


Figure 5. GA evolution for the Denbig reaction.

Conclusion

In the present paper the problem of synthesis and optimization of reactor networks involving classical reaction schemes was studied under isothermal conditions. A simple superstructure formed by a CSTR and a PFR ideal reactor and their possible arrangements was proposed and shown to be very useful. All the cases studied were solved with it. A new computational systematic procedure was proposed to solve this complex NLP optimization problem by using a GA.

The proposed systematic method can handle a variety of objective functions, reaction types and orders, as well as a large number of species. There are no dimensionality problems like in graphical methods or local minima problems as in some deterministic methods. Because of its nature, GA always achieve near global optimum values, avoiding local optima.

Three cases were studied to test the proposed systematic. Results are very coherent with other papers and methods presented in the literature, being as good as or better than the reported ones. Good values for the objective and good reactor arrangement with small volume were obtained for all studied cases.

The use of a GA to solve the problem is an innovation with very good results. In the optimization problem of RNS studied in this paper, the GA had an impressive performance, converging in a few number of iteration. It represents a reliable optimization procedure to avoid local extrema and limitations arising from non-convexities and nonlinearities existing in the complex reaction systems.

Computational effort is small compared to the difficulty degree of the problem.

One can conclude that when compared to the small number of papers presented in the literature, results are compatible and very interesting. The developed procedure in this work can be used as a good alternative for reactor networks design and optimization problem.

The next challenges with this approach are the study of non-isothermal conditions and separation-reactors systems.

Nomenclature

AR – Attainable Region; CSTR – Continuous Stirred Tank Reactor; c – concentration; F – molar feed flow rate; GA – Genetic Algorithms; k – reaction rate; MINLP – Mixed Integer Nonlinear Programming; NLP – Nonlinear Programming; PFR – Plug Flow Reactor; $(-r)$ – reaction rate; RAN – random number; RNS – Reactor Network Synthesis; S – selectivity; v – volumetric feed flow rate; V – reactor volume; Y – yield; x – conversion; β – random number between 0 and 1; θ – random number between 0 and 1.

References

- ACHENIE, L.K.E.; BIEGLER, L.T. Algorithm synthesis of chemical reactor networks using mathematical programming. *Ind. Eng. Chem. Res.*, Washington, D.C., v. 25, n. 1, p. 621-627, 1986.
- ACHENIE, L.K.E.; BIEGLER, L.T. Developing targets for the performance index of a chemical reactor network: isothermal systems. *Ind. Eng. Chem. Res.*, Washington, D.C., v. 27, n. 10, p. 1811-1821, 1988.
- BALAKRISHNA, S.; BIEGLER, L.T. Constructive targeting approaches for the synthesis chemical reactor network. *Ind. Eng. Chem. Res.*, Washington, D.C., v. 31, n. 9, p. 300-312, 1992.
- BIKIC, D.; GLAVIC, P. Innovation designs of reaction networks from reaction and mixing principles. *Comput. Chem. Eng.*, New York, v. 20, Suppl., p. S445-S460, 1996.
- CHITRA, S.P.; GOVIND, R. Synthesis of optimal serial reactor structure for homogeneous reactions. Part 1: isothermal reactors. *AIChE J.*, New York, v. 31, n. 2, p. 177-184, 1985.
- CORDERO, J.C. et al. Synthesis of optimal reactor networks using mathematical programming and simulated annealing. *Comput. Chem. Eng.*, New York, v. 21, Suppl., p. S47-S52, 1997.
- GLASSER, D.; HILDEBRANDT, D. Reactor and process synthesis. *Comput. Chem. Eng.*, New York, v. 21, n. 7, p. 775-783, 1987.
- HILLESTAD, M. A systematic generation of reactor designs. 1: isothermal conditions. *Comput. Chem. Eng.*,

New York, v. 28, n. 1, p. 2717-2726, 2004.

JACOBS, R.; JANSWEIJER, W. A knowledge-based method for the automatic derivation of reactor strategies. *Comput. Chem. Eng.*, New York, v. 24, n. 8, p. 1803-1813, 2000.

KOKOSSIS, A.; FLOUDAS, C. Optimization of complex reactor network. 1: isothermal operation. *Chem. Eng. Sci.*, New York, v. 45, n. 3, p. 595-614, 1990.

LAKSHMANAN, A.; BIEGLER, L.T. Synthesis of optimal chemical reactor systems. *Ind. Eng. Chem. Res.*, Washington, D.C., v. 35, n. 35, p. 1344-1353, 1996.

LINNHOFF, B. *et al.* *A user guide on process integration for the efficient use of energy*. Rugby: The Institute of Chemical Engineers, 1982.

MARCOULAKI, E.; KOKOSSIS, A. Stochastic optimization of complex reaction systems. *Comput. Chem. Eng.*, New York, v. 20, Suppl., p. S231-S236, 1996.

PAHOR, B. *et al.* Synthesis of reactor networks in overall process flowsheets within the multilevel MINLP approach. *Comput. Chem. Eng.*, New York, v. 25, n. 1, p. 765-774, 2001.

PAYNTERS, J.D.; HASHINS, D.E. Determination of optimal reactor type. *Chem. Eng. Sci.*, New York, v. 25, n. 1, p. 1415-1422, 1970.

REVOLLAR, S. *et al.* Algorithmic synthesis and integrated design of chemical reactor systems using genetic algorithms. *In: BIENNIAL WORLD AUTOMATION CONGRESS*, 6., 2004, Oxford. *Proceedings...* Oxford: WAC, 2004. p. 453-458.

SMITH, R. *Chemical process design*. New York: McGraw-Hill, 2005.

TRAMBOUSE, P.J.; PIRET, E.L. Continuous stirred tank reactors: designs for maximum conversions of raw material to desired product: homogeneous reactions. *AIChE J.*, New York, v. 5, p. 384-390, 1959.

VAN DE VUSSE, J.G. Plug-flow type reactor vs. tank reactor. *Chem. Eng. Sci.*, New York, v. 19, n. 1, p. 994-997, 1964.

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