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Optimization approaches to the integrated system of catalytic reforming and isomerization processes in petroleum refinery

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Abstract

In this paper, we deal with the optimization of a cluster comprising two key processes in petroleum refinery: catalytic reforming, and light naphtha isomerization. We propose a novel hybrid methodology which combines direct and indirect approaches. In the direct approach we consider the complete kinetic model and we adopt derivative-free approaches since the analytic expression of the model is not available. In the indirect approach we propose a surrogate modelling based optimization and we apply state-of-the-art solver to retrieve the optimal operating condition and flowsheet configuration of the process. The hybrid method consists of two steps: (i) we compute different good feasible solutions by means of the indirect approach, and (ii) we apply the direct approach using the solutions of the previous step as starting points. Computational experiments for different scenarios are finally discussed.

Keywords: Catalytic reforming; Isomerization; Kinetic models; Surrogate models.

1 Introduction

Catalytic reforming and light naphtha isomerization represent two fundamental processes in petroleum refinery: their target consists in obtaining high octane level gasoline from raw naphtha and maintaining at the same time an acceptable level of benzene in the gasoline. In this paper, we address the optimization of a process network including several reforming reactors, an isomerization reactor, and several separation units. To limit the complexity of the problem, energy is not taken into account. This is a MINLP problem, mixing qualitative and continuous variables. Accurate models, based on kinetics, are available for the reactors. A tempting approach would be to optimize the network using these models. Unfortunately, these models are black box ones, so no derivatives are available, thus preventing the use of state-of the-art global MINLP optimizers. As many optimizations are to be made, a brute-force approach, consisting in making a continuous-variables optimization for each combination of qualitative variables, is expected to be too cpu-intensive.

Several papers have shown the interest of surrogate-based optimization in chemical applications (see surveys [3, 21]): a non exhaustive list includes [4, 25, 26] for flowsheet optimization, [7, 12, 13] for superstructure optimization, [28] for distillation column optimization [23] for polymerization reactor modelling, [27] for sour water stripping plant, and [8] for Fischer-Tropsch synthesis optimization. The common basic idea consists in replacing the first-principle model with a surrogate one and perform the optimization.

For our application, building accurate surrogate models is probably difficult because the dimension of the input space is high (25). So a different two-phase approach has been chosen: surrogate models

are used to replace the accurate kinetics models, but they are kept simple (they are low-degree multi-dimensional polynomials), thus enabling the use of a MINLP optimizer. In a first phase, the process network is optimized with these surrogate models and the MINLP optimizer. But as the surrogate models are not perfectly accurate, the obtained solution cannot be fully trusted. So in a second phase, the network is optimized with the accurate kinetics models, using as initial point the solution of the first phase. In the second phase, the qualitative variables are kept constant, and a derivative-free optimizer is used to determine the continuous variables [5]. In order to maximize the chance of finding the global solution, or at least a (very) good one, several admissible solutions are gathered during the optimization of the first phase. Then in the second phase, several optimizations are made, one for each different combination of qualitative variables. Hence, the novelty of the present paper consists in combining the surrogate optimization approach with a traditional one, in a way that, to our knowledge, has not yet been proposed.

The paper continues as follows. In Section 2, the process network is presented. In Sections 3 and 4 we describe the complete kinetic models and the surrogate ones, respectively. The optimization problem is presented in Section 5. The hybrid approach is detailed in Section 6. Computational results are discussed in Section 7. Finally, conclusions and future work considerations follow in Section 8.

Notation. Given a positive scalar $N \in \mathbb{N}$, we indicate $[N] := \{1, \dots, N\}$.

Table 1: Acronyms.

Acronyms (alphabetical order)	
C_n	molecules with n carbon atoms
C_{n+}	molecules with at least n carbon atoms
CR	Catalytic reforming
DOE	Design of experiments
GDP	Generalized disjunctive programming
LHD	Latin hypercube design
iP	isoalkanes
IS	Isomerization
MBC	Molar balance constraints
MILP	Mixed integer linear problem
MINLP	Mixed integer nonlinear problem
NTC	Network topology constraints
nP	n-alkanes
RON	Research octane number
SQA	Sequential quadratic approximation
WHSV	Weight hourly space velocity

2 Description of the process

The process transforms raw naphtha (mixture of alkanes, cycloalkanes and few aromatics, with 5 to 11 carbon atoms) into hydrogen and high octane gasoline containing mainly isoalkanes and aromatics. By-products are also produced (light hydrocarbons with 1 to 4 carbon atoms).

The main chemical transformations take place in several catalytic reforming reactors [11, 19, 33]. In these reactors, alkanes are hydro-isomerized, dehydrogenated to form isoalkanes and aromatics. Cycloalkanes undergo the same kind of reactions to form aromatics. There is some hydrocracking and hydrogenolysis of alkanes generating light hydrocarbons. Coke is also formed, which tends to reduce the catalytic activity. Typical operating conditions are high temperature (450–500°C), medium level of pressure (3–35 bar) and molar hydrogen-to-hydrocarbon (H_2/HC) ratio between 3 and 8 [1].

However, these reactors produce benzene, whose quantity must be limited. For this, an isomerization reactor [30, 34] is also part of the process: it transforms C_5-C_6 alkanes into isoalkanes. This reactor is operated at lower temperatures, typically in the range 100–150°C.

Low octane molecules are not completely converted into high octane molecules. So part of the reactors products must be recycled and mixed with the incoming naphtha. What should be recycled, and in which quantity is part of the optimization problem. The following subsections describe the chosen process network, and the molecules that are taken into account. Note that energy considerations are out of the scope of this work.

2.1 Process network

A schematic diagram of the process is given in Figure 1. It is based on the process engineers knowledge. The flow to be processed is the naphtha. There are 5 products: hydrogen, two light by-products (FG and LPG), and two valuable products (gasoline and aromatics). The process network is composed of several units:

- the catalytic reforming reactors (their number is to be determined in the optimization phase). They form a block, i.e., the output of one reactor is the input of the next one. As the reactions are globally endothermic, the input flow of the reactors must be heated to the desired temperature. In this study, the corresponding heat exchanges are not taken into account.
- an isomerization reactor
- splitters (flash drums, distillation columns, and aromatics extraction) which split an input flow into 2 or more output flows, with different compositions
- "routers" which divide an input flow into 2 or more output flows, the composition of which is identical to the input composition. There are two kinds of routers: "continuous" ones, for which the total flow of each output flow is a fraction of the total input flow ; "discrete" ones, for which each output flow is either zero or the input flow. The discrete routers are used to model different networks.

  On Figure 1, routers whose state is to be optimized, are given a name : C1 to C3 for 3 continuous routers[1], D1 to D5 for the 5 discrete routers.

  By convention, the state of the routers is equal to 1 (resp. 0) when the input flow goes to the top (resp. bottom) output flow on the figure. For D3, there are 3 output flows. The state values are 1 (top flow), 0 (middle flow), -1 (bottom flow).
- mixers, whose output is the sum of the inputs.

All the lines in the diagram are possible flows joining either the naphtha to the input router, or a unit to another unit, or a unit to a product. All these flows will never be simultaneously present. Their presence or absence is determined by the state of the routers.

The role of the splitters and routers is to make possible the partial recycling of alkanes with 5 to 7 carbon atoms, either to the reforming reactors or to the isomerisation reactor (for the latter, only alkanes with 5 or 6 carbon atoms). Lighter molecules are sent to one of the two light products. Heavier molecules are sent either to the gasoline product or to the aromatics product. What is sent to the products (and which one), or recycled (and how much) is to be determined in the optimization phase.

[1] There is a fourth continuous router. Its role is to adjust the quantity of H_2 at the input of the first reforming reactor. So its state is not an optimization variable.

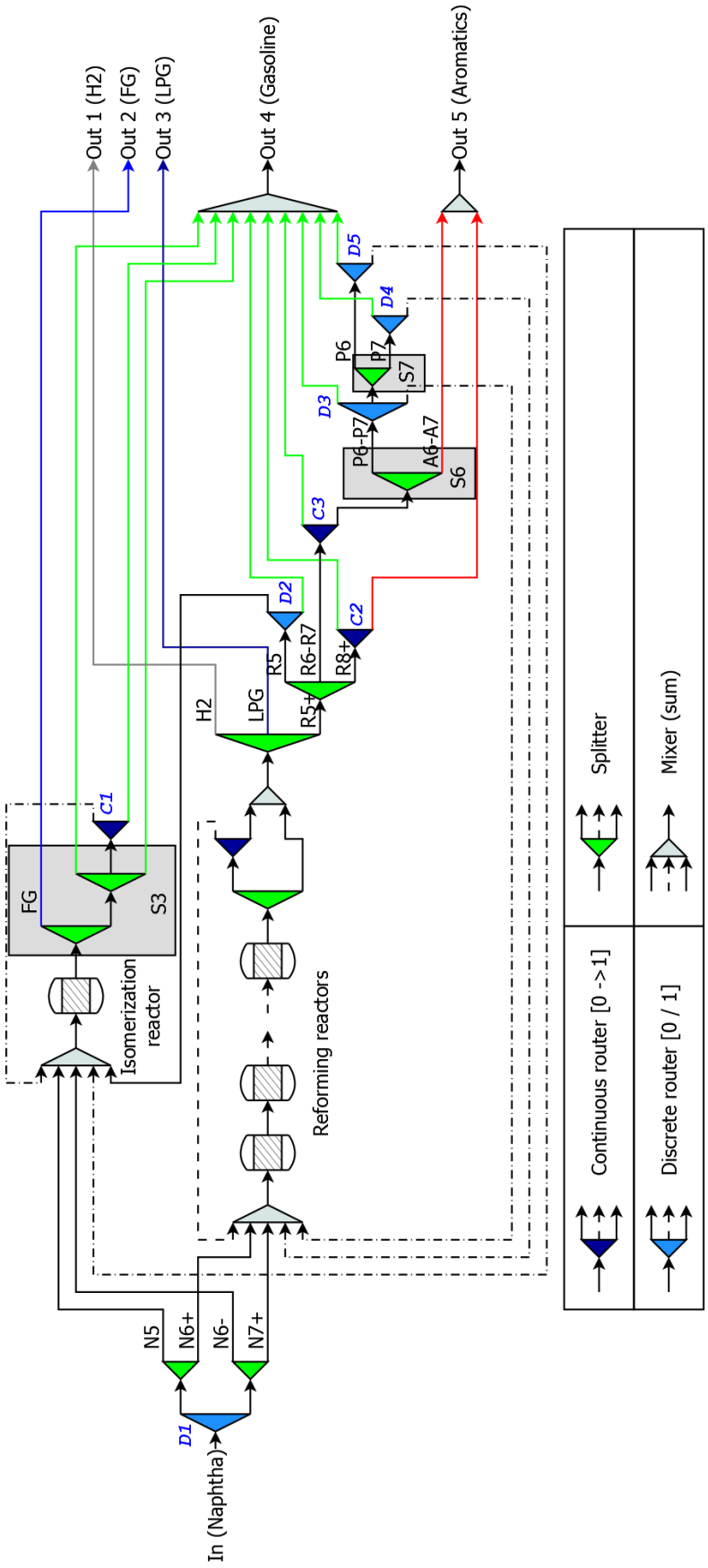


Figure 1: Complete process schema

2.2 Components taken into account

The complete list of components that are taken into account for the process calculation is given in Table 2. They are hydrogen (H_2), light alkanes with 1 to 5 carbon atoms (P_1, P_2, P_3, P_4, P_5), and hydrocarbons with 6 to 11 carbon atoms. These are divided into (the letter i in suffix stands for the number of carbon atoms) linear alkanes (nP_i), isoalkanes (iP_i), cycloalkanes (N_i) and aromatics (A_i). Isoalkanes with 6 to 8 carbon atoms are further divided into mono-branched and double-branched.

Table 2: Compounds of the complete process.

Compounds	
H_2	hydrogen
P_1	methane
P_2	ethane
P_3	propane
P_4	butane
P_5	pentane
$6P_6$	n-hexane
$5P_6$	simple branched alkanes with 6 atoms of carbons
$4P_6$	double branched alkanes with 6 atoms of carbons
N_6	cycloalkanes with 6 atoms of carbons
A_6	benzene
$7P_7$	n-heptane
$6P_7$	simple branched alkanes with 7 atoms of carbons
$5P_7$	double branched alkanes with 7 atoms of carbons
N_7	cycloalkanes with 7 atoms of carbons
A_7	toluene
$8P_8$	n-octane
$7P_8$	simple branched alkanes with 8 atoms of carbons
$6P_8$	double branched alkanes with 8 atoms of carbons
N_8	cycloalkanes with 8 atoms of carbons
A_8	ethyl-benzene + xylenes
nP_9	nonane
iP_9	isononane
N_9	cycloalkanes with 9 atoms of carbons
A_9	aromatics with 9 atoms of carbons
nP_{10}	decane
iP_{10}	isodecane
N_{10}	cycloalkanes with 10 atoms of carbons
A_{10}	aromatics with 10 atoms of carbons
nP_{11+}	hydrocarbons with more than 10 atoms of carbon
iP_{11+}	isotopes with more than 10 atoms of carbon
N_{11+}	cycloalkanes with more than 10 atoms of carbon
A_{11+}	aromatics with more than 10 atoms of carbon

2.3 Models of the units

Chemical reactors

Two different models are used for the catalytic reforming reactors and the isomerization reactor: kinetic models, and surrogate models. The former are precise, but are cpu-demanding in the optimization phase. Moreover they are black-box models for which no derivatives are available; this limits the optimizers

that can be used, especially when considering qualitative variables. The latter are just the opposite: less precise, but their computation is very fast, and their equations are simple. The kinetic models are described in Section 3, and the surrogate models in Section 4.

Splitters

In order to limit the CPU time of the optimization phase, the models of the splitters are very simple: the molar flow of the k-th component in the p-th output, y_p^k is equal to

$$y_p^k = w_p^k \, x^k \tag{1}$$

where w_p^k is a constant (depending on the splitter), and x^k is the molar flow of component k in the input flow. The constants w_p^k are such that

$$\sum_p w_p^k = 1 \quad \text{and} \quad 0 \leq w_p^k \leq 1 \tag{2}$$

for all $k \in [K]$.

Routers

The models of the routers are similar (same notations as above):

$$y_p^k = w_p \, x^k \tag{3}$$

where the w_p are constants (depending on the router), such that:

$$\sum_p w_p = 1 \tag{4}$$

and

$$\begin{array}{ll} 0 \leq w_p \leq 1 & \text{for continuous routers} \\ w_p \in \{0, 1\} & \text{for discrete routers} \end{array}$$

Mixers

The equations of the mixers are

$$y^k = \sum_p x_p^k \tag{5}$$

where y^k is the molar flow of the k-th component in the output flow, and x_p^k is the molar flow of the k-th component in the p-th input.

2.4 Equation solving

The model of the process is composed of the models of the different units, plus the equations expressing the links between units, input flow, and output flows. As flows are recycled, the process flowsheet comprises several loops, which translate into implicit algebraic equations. In the optimization phase, these implicit equations can be handled in two ways : they can be considered as part of the process model (i.e., the optimizer only knows the process as a whole, and ignores these implicit equations) ; or

they can be explicit constraints of the optimization problem. Both alternatives were used, depending on the type of the model: the first one with the kinetics models ; the second one with the surrogate models (see section 6.1).

Depending on the state of the discrete routers, there may be 2 to 4 recycle loops. For each loop the number of unknowns is equal to the number of components (33). To solve the recycle equations, a single fixed-point method is used for the direct approach. All the recycled flows are "cut": the molar flows of all the components in these flows are the unknowns of the fixed-point method. The convergence is fast, in 30 to 80 iterations depending on the configuration of the process.

3 Kinetic models

3.1 Catalytic reforming reactors

The reaction mechanism is based on the components of Table 2, except for mono-branched isoalkanes and double branched isoalkanes that are lumped together (they are denoted iP_i, where i is the number of carbon atoms).

The main reactions transform linear alkanes and cycloalkanes with low RON into isoalkanes and aromatics with high RON. For components with i carbon atoms, they are:

$$\begin{array}{lcl} \mathrm{nP}_i & \rightleftharpoons & \mathrm{iP}_i \\ \mathrm{nP}_i & \rightleftharpoons & \mathrm{N}_i + \mathrm{H}_2 \\ \mathrm{iP}_i & \rightleftharpoons & \mathrm{N}_i + \mathrm{H}_2 \\ \mathrm{N}_i & \rightleftharpoons & \mathrm{A}_i + 3\,\mathrm{H}_2 \end{array}$$

Secondary reactions are hydrocracking and hydrogenolysis of alkanes:

$$\mathrm{P}_i + \mathrm{H}_2 \longrightarrow \mathrm{P}_j + \mathrm{P}_k$$

where P is a linear alkane or an isoalkane, $i = j + k$, and i varies between 4 and 11. For each i, there are several such reactions (the greater i, the greater the number of reactions).

The reactions of hydrocracking of cycloalkanes, dealkylation of cycloalkanes and of aromatics are neglected.

The reactor is assumed to be an adiabatic plug flow reactor, working in steady state. The equations of the model are mass balances for all components, plus an adiabatic energy balance. As the reactor is a plug flow reactor working in steady state, the system of equations is composed of ordinary differential equations (with derivatives taken with respect to a 1-dimensional space variable), see for example [10]. These equations are numerically integrated between the input and the output of the reactor with the LSODE solver [14].

The isoalkanes with 6 to 8 carbon atoms are more detailed in the process than in the reactor (see above). The mono-branched and the double-branched isoalkanes in the reactor input are lumped. Then the reactor is calculated. Finally isoalkanes in the output of the reactor are split with ad hoc correlations.

3.2 Isomerization reactor

The components in the isomerization reactor are a subset of those of Table 2: each component has at most 6 carbon atoms, and there are no cycloalkanes, nor aromatics.

The reaction mechanism is similar to that of the reforming. Only the reactions implying linear alkane or isoalkanes are present. The reactions between 6-carbon alkanes are a little more detailed:

$$\mathrm{nP_6} \overleftrightarrow{} \mathrm{5P_6} \overleftrightarrow{} \mathrm{4P_6}$$

Due to recycle flows in the process, other components may enter the isomerization reactor in small quantities. They are supposed to be inert.

The reactor is also an adiabatic plug flow reactor, working in steady state. So the model is a system of differential equations which is solved with LSODE.

4 Surrogate models

In surrogate modelling approach first we look for mathematical models which are able to reproduce and eventually predict "relatively well" process outputs for a given input configurations.

The surrogate building process is generally composed of four steps [3, 21, 35]: (i) generation of the plan of experiments, (ii) numerical simulation or physical experiments, (iii) model selection and parameters estimation, and (iv) model testing. Once the input/output data couple are obtained via physical experiments or numerical simulations (steps (i)-(ii)), an optimization problem is solved to retrieve the parameters of the models which fit the data (step (iii)). Finally, at step (iv) the performances of the identified model are evaluated with regards to a new data set: if the models does not produce satisfactory results, the procedure restart from step (i) by considering additional input data or from step (iii) by changing for instance the model type.

In our case, a simulator is available for each process. Moreover, we use all the sampling points at once in order to train the surrogate model. We determine a surrogate models for each configuration of involved processes, namely catalytic reforming with 3, 4, and 5 reactors, and isomerization.

In the following, we briefly described the estimation model techniques we adopt, referring the interested reader to the paper [24] for the complete details.

For both the catalytic reforming and the isomerization we have two types of input variables: process variables, such as pressure, temperature, and weight hourly space velocity (WHSV), and composition variables (mass percentages). The process variables represents the effective control parameters in the operating phase of the corresponding process.

In order to generate consistent surrogate models we consider non-negativity constraint for the outputs and molar balance constraints (MBC) for the number of moles of carbon and hydrogen between process inflow and outflow. All compounds but two are modelled in the regression problem to determine the model parameters: MBC for the catalytic reforming and the isomerization processes are enforced in order to retrieve the values of the (two) compounds not modelled in the surrogate models.

For the non-negativity constraints (which should be enforced for all the possible input configurations in the design space) we adopt a two-phase procedure. (i) We solve the regression problem for a given set of finite number of input configurations, and (ii) we address a feasibility problem to identify (if there exists) the input configuration with the maximum violation with regards to the current surrogate model: if such a configuration exists, it is added to the set in phase (i) which is performed again. If the configuration does not exists, we conclude that the current surrogate model is feasible with respect to the non-negativity constraints for all the possible (infinite) input configurations in the design space.

For the catalytic reforming we select as inputs the inverse of the WHSV and the mass fractions of the hydrocarbons listed in Table 3 and as output the mass fractions of the hydrocarbons reported in Table 4. We have selected the inverse of the WHSV (1/WHSV) as the process variable in the surrogate models

instead of WHSV in order to better model the nonlinear behaviours of the processes with respect to the WHSV.

We fit a model with 25 input variables and 33 outputs, obtained by considering 243 naphtha feeds and by varying the process variables (1/WHSV) in the set $\{1/4, 1/3, 1/2, 1\}$.

For the input and output compounds in isomerization see Table 5. For the light naphtha isomerization we adopt the training set described in [24]: we use a set composed of 226 samples generated according to a D-optimal criterion by the statistical software Design Expert 10 [6].

For the surrogate model, we consider the following quadratic model for the reforming

$$\beta_0 + \sum_{i\in[I]} \beta_{1,i} c_i + \sum_{i\in[I]} \sum_{j\in[J]} \beta_{2,ij} c_i p_j, \tag{6}$$

and the following cubic model for the isomerization:

$$\beta_0 + \sum_{i\in[I]} \beta_{1,i} c_i + \sum_{i\in[I]} \sum_{j\in[J]} \beta_{2,ij} c_i p_j + \sum_{i\in[I]} \beta_{3,i} c_i^2 + \sum_{i\in[I]} \sum_{j'\in[J]} \sum_{j''\in[J]} \beta_{4,ij'j''} c_i p_{j'} p_{j''}, \tag{7}$$

where I and J represent the total number of compositions and process variables, respectively. c_i is the i-th composition variable, while p_j is the j-th process variable. From one hand these polynomial models are easy and compact (this is a crucial aspect for the computational side), from the other hand they are able to capture the experimental characteristics of the underlining chemical phenomena. As we will explain in Section 7, the quality of the solutions found via the surrogate models are comparable to the one found by means of the complete model.

The software tool used to numerically simulate the catalytic reforming process is `OSCAR 1.1`, developed and maintained by IFP Energies nouvelles.

5 Optimization problem

The optimization problem consists in maximizing an economic function, with several constraints (they are detailed below). The maximum set of unknowns contains the operating conditions of the isomerization and the reforming reactors (quantity of catalyst, temperature, pressure, molar hydrogen to hydrocarbons input ratio), the number of reforming reactors, and the state of the routers. Preliminary studies showed that there are too many unknowns, making the optimization problem very ill-conditioned (i.e., there are infinite solutions within a very small interval of the economic function). This set of unknowns was reduced by imposing some operating conditions of the reforming reactors (based on the process engineer knowledge): temperature and pressure (the same for all reactors), proportion of catalyst in the different reactors (but the total quantity is to be optimized), hydrogen to hydrocarbons ratio at the input of the first reactor. The hydrogen to hydrocarbons ratio at the input of the isomerization reactor is also fixed.

After this reduction, there remains 7 real unknowns (3 operating conditions in the isomerization reactor, 1 operating condition for the reforming reactors, state of the 3 continuous routers), plus 6 qualitative unknowns (number of reforming reactors, plus the state of the 5 discrete routers). The total number of combinations of qualitative variables is equal to 144, but there are only 72 different process configurations, because depending on the state of one discrete router, two other discrete routers may become inactive.

Economic function

The economic function is an hourly cost taking into account the cost of the flows and of the investment (reactors, catalyst, splitters). The cost of the investment is transformed into an hourly cost by assuming

Table 3: Input compounds of the catalytic reforming process.

Input compounds	
nP_6	hexane
iP_6	isohexane
N_6	cycloalkanes with 6 atoms of carbons
A_6	aromatics with 6 atoms of carbons
nP_7	heptane
iP_7	isoheptane
N_7	cycloalkanes with 7 atoms of carbons
A_7	toluene
nP_8	octane
iP_8	isoctane
N_8	cycloalkanes with 8 atoms of carbons
A_8	ethyl-benzene + xylenes
nP_9	nonane
iP_9	isononane
N_9	cycloalkanes with 9 atoms of carbons
A_9	aromatics with 9 atoms of carbons
nP_{10}	decane
iP_{10}	isodecane
N_{10}	cycloalkanes with 10 atoms of carbons
A_{10}	aromatics with 10 atoms of carbons
nP_{11+}	hydrocarbons with more than 10 atoms of carbon
iP_{11+}	isotopes with more than 10 atoms of carbon
N_{11+}	cycloalkanes with more than 10 atoms of carbon
A_{11+}	aromatics with more than 10 atoms of carbon

it will work for a certain time each year (8000 hours) and that it will be paid off in a certain number of years (5 years for reactors and splitters, 8 years for the catalyst). The hourly cost is simply the initial cost divided by the number of working hours.

The different costs are given in Tables 6 for the flows, 7 and 8 for the different units and catalysts. Only the splitters that may or may not be present (depending on the state of routers) are taken into account. They are marked S3, S6 and S7 on Figure 1.

Constraints

Four constraints must be satisfied: the gasoline RON must be greater than a minimum value. The mass fraction of benzene in gasoline must be smaller than a maximum value. The mass fraction of components with at least 9 carbon atoms in the gasoline flow must be greater than a minimum value. The mass fraction of aromatics in the aromatics flow must be greater to a minimum value (purity constraint).

6 Optimization of the problem

The chosen approach is a hybrid one. It consists in making two successive optimizations. In the first one, the surrogate models of the isomerization reactor and of the reforming reactors are used. As they are simple, the optimization problem can be solved with a state-of-the-art global optimizer. But the accuracy of the surrogate models may not be sufficient, so several solutions are gathered. These solutions are then used as starting points of the optimization with the complete models. In this second phase, a

Table 4: Output compounds of the catalytic reforming process.

Output compounds	
H_2	hydrogen
P_1	methane
P_2	ethane
P_3	propane
P_4	butane
P_5	pentane
$6P_6$	n-hexane
$5P_6$	simple branched alkanes with 6 atoms of carbons
$4P_6$	double branched alkanes with 6 atoms of carbons
N_6	cycloalkanes with 6 atoms of carbons
A_6	benzene
$7P_7$	n-heptane
$6P_7$	simple branched alkanes with 7 atoms of carbons
$5P_7$	double branched alkanes with 7 atoms of carbons
N_7	cycloalkanes with 7 atoms of carbons
A_7	toluene
$8P_8$	n-octane
$7P_8$	simple branched alkanes with 8 atoms of carbons
$6P_8$	double branched alkanes with 8 atoms of carbons
N_8	cycloalkanes with 8 atoms of carbons
A_8	ethyl-benzene + xylenes
nP_9	nonane
iP_9	isononane
N_9	cycloalkanes with 9 atoms of carbons
A_9	aromatics with 9 atoms of carbons
nP_{10}	decane
iP_{10}	isodecane
N_{10}	cycloalkanes with 10 atoms of carbons
A_{10}	aromatics with 10 atoms of carbons
nP_{11+}	hydrocarbons with more than 10 atoms of carbon
iP_{11+}	isotopes with more than 10 atoms of carbon
N_{11+}	cycloalkanes with more than 10 atoms of carbon
A_{11+}	aromatics with more than 10 atoms of carbon

Table 5: Input and output compounds of the isomerization process.

Input compounds	
nP_5	pentane
iP_5	isopentane
nP_6	hexane
$i2P_6$	2-methylpentane
$i3P_6$	3-methylpentane
$i22P_6$	2,2-dimethylhexane
$i23P_6$	2,3-dimethylhexane

Output compounds	
nP_4	butane
iP_4	isobutane
nP_5	pentane
iP_5	isopentane
nP_6	hexane
$i2P_6$	2-methylhexane
$i3P_6$	3-methylhexane
$i22P_6$	2,2-dimethylhexane
$i23P_6$	2,3-dimethylhexane

local optimizer is used. The two following subsections detail each of these optimization phases. The next one summarizes the approach.

Table 6: Costs of the different flows.

flow	\$/ton
naphtha	800
hydrogen	1500
FG	900
LPG	900
gasoline	1000
aromatics	1200

Table 7: Costs of catalyst and reactors.

	unit	reforming	isomerization
catalyst	\$/ton	$2\,10^4$	$2\,10^4$
reactor ($M :=$ mass of catalyst, in tons)	\$	$47\,10^3\,M + 1.3\,10^6$	neglected

Table 8: Costs of splitters. The cost depends on the input flow of each splitter, F (in ton/hour).

	cost (\$)
S3	$7.1\,10^4\,F + 2.5\,10^6$
S6	$4.5\,10^5\,F + 8\,10^6$
S7	$7.1\,10^3\,F + 2.5\,10^5$

6.1 Optimization with the surrogate models

The first step of the hybrid methodology consists in replacing the catalytic reforming and the isomerization processes by their surrogate models developed in Section 4 and solve the corresponding problem.

In particular, for the catalytic reforming we introduce a set of R Boolean variables Z_r ($r \in [R]$) corresponding to the possible process configurations (in our case $R = 3$), such that the following generalized disjunctive programming (GDP) representation holds

$$\begin{aligned} \bigvee_{r\in[R]} \begin{bmatrix} Z_r \\ y^k = f_r(x^k) \quad \forall k \in [K] \end{bmatrix} \\ \Omega(Z_r) = \text{True} \\ Z_r = \{\text{True}, \text{False}\}, \end{aligned} \tag{8}$$

where $f_r(x)$ is the surrogate model for the r-th configuration ($r \in [R]$). In order to obtain a MINLP representation we introduce a set of binary variables $z \in \{0,1\}^R$ and for each number of reactors, we consider the following big-M constraints:

$$\begin{aligned} &y^k \le f_r(x^k) + M_r^k\,(1 - z_r) \text{ and} \\ &y^k \ge f_r(x^k) - M_r^k\,(1 - z_r), \end{aligned} \tag{9}$$

where $M_r^k \in \mathbb{R}_+$ are opportune constants: in particular, in computational experiments we set $M_r^k := 100$ for all $k \in [K]$ and $r \in [R]$: this value is coherent with the order of magnitude of the data. A further constraint must also be considered:

$$\sum_{r\in[R]} z_r = 1. \tag{10}$$

We note that the optimization problem with disjunctive constraints (8) can be directly handled and solved by means of generalized disjunctive programming approaches (GDP) (see [29, 32]). In our current study we restrict ourselves for the sake of simplicity to consider the MINLP reformulation approach, but we intend to analyze the GDP viewpoint in future work.

In order to model the fixed cost associated to the s-th splitter ($s \in [S]$), a binary variable $b_s \in \{0, 1\}$ and a $M_s \in \mathbb{R}_+$ constant are introduced: the corresponding big-M constraint are introduced:

$$\sum_{k \in [K]} x_s^k \leq M_s \, b_s, \tag{11}$$

where x_s^k is the mass inflow for the s-th splitter for the k-th compound. The binary variable b_s controls if the splitter inflow is zero or strictly positive. The fixed cost is then multiplied for the binary variable b_s to be sure it is counted only when the corresponding mass inflow is strictly positive.

We note that, in contrast to the direct approach, the recycles are automatically managed by the model itself (no fixed point iteration is needed), but the optimized model itself determines an equilibrium state which satisfy all the network topology constraints (NTC).

Let f^* be the best solution value found within the time limit, and ε be a positive scalar. In order to obtain "good" starting structures we select the solution whose objective function value obj is such that:

$$obj \geq (1 - \varepsilon) \, f^*, \tag{12}$$

We note that the way we model problem makes guarantees the mass and molar balance constraints are satisfied. The values for the compounds not modelled in the surrogate models are retrieved by implicitly solving the corresponding linear system representing the MBCs. For the other elements of the network, i.e., routers, splitters, and mixers, the MBCs are satisfied by definition (see Section 2.3).

6.2 Optimization with the complete models

The economic function and the constraints of the optimization problem depend on the outputs of the process. As no derivative with respect to the optimization problem unknowns is available, `SQA`, a local, derivative free optimizer was chosen [9, 17, 18]. It can handle general cost functions and non linear inequality constraints (cost function and constraints are assumed to be continuously differentiable). `SQA` stands for Sequential Quadratic Approximation.

As the recycle loops equations are easily solved (see Section 2.4), they are not included in the optimization constraints. They are solved each time the economic function and the constraints are needed. The process as a whole is then considered as a black box.

Preliminary computational experiments were also conducted with two derivative-free optimizers, able to cope with qualitative variables: `NOMAD` [2, 20], and a custom implementation of the `EGO`-based Kriging optimization [16]. But both resulted in quite poor performances. For `NOMAD`, it is necessary to define the neighboors of a set of qualitative variables. This was quite tricky as there many ways to do so. A bad choice was perhaps responsible for the poor performances. For the `EGO`-based Kriging, the cost per iteration grew rapidly, so the optimization had to be stopped before it was finished.

6.3 Summary of the hybrid approach

Let (SP) be the problem of Section 2 with surrogate models and (KP) be the problem of Section 2 with kinetic models. Algorithm 1 shows the pseudo-code of the hybrid methodology.

Algorithm 1 Hybrid approach

Require: problems (SP) and (KP).

compute surrogate models for each output components;
compute L feasible solutions value $\tilde{f}_l$ ($l \in [L]$) for (SP) and let f^* be the optimal solution value;
select the solutions such that the corresponding $\tilde{f}_l$ verifies (12);
cluster $\tilde{f}_l$ according to the value of the qualitative variables (let N be the number of clusters);
for each $n \in [N]$ **do**
    compute the best solution $\hat{f}_n$;
    store the solution x_n^* corresponding to $\hat{f}_n$;
    solve (KP) starting from x_n^* and let g_n^* be the optimal solution value;
end for
$g^* := \max_{n \in [N]} g_n^*$;
return solution corresponding to g^*.

scenario	P isom (bar)	T isom (°C)	RON min	max %wt Bz in gasoline	min %wt C_{9+} in gasoline	min %wt aromatics in aromatics flow
1	21	110	85	0.5%	1%	99%
2	21	110	90	0.5%	1%	99%
3	21	110	95	0.5%	1%	99%
4	opt	opt	85	0.5%	1%	99%
5	opt	opt	90	0.5%	1%	99%
6	opt	opt	95	0.5%	1%	99%

Table 9: optimization scenarios

7 Computational results

Two different feeds and 6 different optimization scenarios are considered. The second feed contains more cycloalkanes than the first one. So it is easier to process, resulting in higher economic functions.

The optimization scenarios differ by the variables that are to be optimized, and by the constraint on the gasoline RON. In the first 3 scenarios, two of the 7 continuous variables are fixed (pressure and temperature of the isomerization reactor), and all of the 6 the qualitative variables are to be optimized. In the last 3 scenarios, all the 7 continuous variables and the 6 qualitative variables are to be optimized. The higher the RON, the more difficult it is to process the feed, resulting in lower economic functions.

The other constraints are the following: maximum mass percentage of benzene in gasoline, minimum mass percentage of C_{9+} in gasoline, minimum mass percentage of aromatics in the aromatics flow.

The different scenarios are summarized in table 9.

7.1 Results of the optimizations with the surrogate models

In the surrogate approach the computational setting is the following. MILPs are solved through `IBM ILOG CPLEX 12.8` [15] with the options `numericalemphasis` and `scaind` activated, since the problems are numerically ill-posed and bad scaled. MINLPs are solved by means of `BARON 18.5.8` [31]. All the codes are implemented in `GAMS 25.1.2` [22] on a Dell machine equipped with Intel(R) Xeon(R) CPU E5-1620 v3 at 3.50 GHz with 4 GB RAM. Parallelization is enabled (up to 2 threads).

Table 10 reports the CPU times for building the surrogate models.

Table 11 reports the time for finding the best solution (sol. time) and the total time (total time). `BARON`

finds the optimal solution in scenario 1, while for scenarios 2–6 BARON is not able to compute the optimal solution within the time limit (3600 sec.): however, a good feasible solution is computed in less than 1800 seconds. Detailed optimal solutions are shown in Tables 12 and 13 for feed 1 and feed 2, respectively (in the reforming column, RX stands for number of reactors).

We set $\varepsilon := 0.05$ for (MSP) and we save the best solutions (up to 50) that BARON have found within 3600 seconds. Table 14 reports the number of solutions found within the time limit: total sol. represents the total number of feasible solutions, while diff. sol. is the number of solutions differing in the values of the qualitative variables.

surrogate model	CPU time
isomerization	4h 15 min
reforming with 3 reactors	6h 29 min
reforming with 4 reactors	5h 12 min
reforming with 5 reactors	5h 29 min

Table 10: CPU times for building the surrogate models.

scenario	feed 1		feed 2	
	sol. time	total time	sol. time	total time
1	20 min	21 min 30s	2 min 8s	47 min 50s
2	5 min 50s	60 min *	14 min 50s	60 min *
3	27 min 10s	60 min *	12 min 50s	60 min *
4	12 min 20s	60 min *	1 min 50s	60 min *
5	10 min 30s	60 min *	11 min 40s	60 min *
6	9 min 10s	60 min *	16 min	60 min *

Table 11: CPU times for optimization with surrogate models per scenario (*time limit is reached).

	discrete routers					cont. routers			isomerization			reforming		objective
	D1	D2	D3	D4	D5	C1	C2	C3	P	T	WHSV	WHSV	RX	function
1	0	0	0	0	0	0.68	0.02	0	20	110	0.8	1.08	5	48.66
2	0	0	0	0	0	1	0.15	0	20	110	0.8	1.08	5	46.71
3	0	0	0	0	0	1	0.49	0	20	110	0.8	1.06	5	41.67
4	0	0	0	0	0	0.68	0.02	0	20	110	0.8	1.08	5	48.66
5	0	0	0	0	0	1	0.15	0	20	110	0.8	1.08	5	46.71
6	0	0	0	0	0	1	0.49	0	20	110	0.8	1.06	5	41.67

Table 12: Solutions for the optimization with surrogate models for feed 1 (1 scenario per line)

	discrete routers					cont. routers			isomerization			reforming		objective
	D1	D2	D3	D4	D5	C1	C2	C3	P	T	WHSV	WHSV	RX	function
1	0	0	1	0	0	0.45	0.01	0	20	110	4.0	1.08	4	55.81
2	0	0	0	0	0	1	0.01	.08	20	110	4.0	1.08	4	55.14
3	0	0	0	0	0	1	0.19	0	20	110	4.0	1.06	5	51.81
4	0	0	1	0	0	0.44	0.01	0	35.83	110	4.0	1.08	4	55.81
5	0	1	0	0	0	1	0.01	.08	36.89	110	4.0	1.08	4	55.12
6	0	1	0	0	0	1	0.19	0	43.09	150	4.0	1.06	5	51.84

Table 13: Solutions for the optimization with surrogate models for feed 2 (1 scenario per line)

	feed 1		feed 2	
	total sol.	diff. sol	total sol.	diff. sol.
1	22	8	50	17
2	16	8	23	17
3	25	15	50	17
4	50	9	50	14
5	20	8	29	18
6	41	10	50	10

Table 14: Number of solutions found by `BARON` (1 scenario per line).

7.2 Results of the optimizations with the complete models

The codes are implemented in a C++ program, and were run on a similar machine as the one used for the optimizations with the surrogate models (the kinetics models of the reactors are available as `Fortran` subroutines, and the `SQA` optimizer can be called through a C interface)

The solutions found by `BARON` with the surrogate models are used as initial points. If several solutions share the same qualitative variables, only the solution with the greatest objective function is kept. The number of different initializations varies between 8 and 18, depending on the scenario and the feed (see Table 14).

The best solutions for each scenario are given in Table 15 for feed 1, and Table 16 for feed 2. A first remark that can be made is that the objective functions at the optimum are significantly different from the one obtained with the surrogate models. This illustrates the trade-off that had to be made when the surrogate models were built: either simplicity enabling the use of state-of-the-art optimizers such as `BARON`; or accuracy at the cost of complexity, either preventing the use of the same optimizers, or increasing significantly the cpu time of the optimizations (and thus reducing the interest of surrogate models).

	discrete routers					cont. routers			isomerization			reforming		objective	cpu
	D1	D2	D3	D4	D5	C1	C2	C3	P	T	WHSV	WHSV	RX	function	(min)
1	0	0	0	1	0	1.00	0.02	0.00	20	110	0.80	1.37	5	45.25	88
2	0	0	0	0	0	1.00	0.18	0.00	20	110	1.77	1.38	5	42.93	33
3	0	0	0	0	0	1.00	0.58	0.00	20	110	2.03	1.52	5	37.57	51
4	0	0	0	1	0	0.99	0.02	0.00	61	110	0.80	1.37	5	45.27	96
5	0	0	0	0	0	1.00	0.17	0.00	61	110	2.30	1.38	5	42.99	66
6	0	0	0	0	0	1.00	0.57	0.00	61	110	2.63	1.52	5	37.62	90

Table 15: Solutions for the optimization with kinetics models for feed 1 (1 scenario per line)

	discrete routers					cont. routers			isomerization			reforming		objective	cpu
	D1	D2	D3	D4	D5	C1	C2	C3	P	T	WHSV	WHSV	RX	function	(min)
1	0	0	1	1	1	0.94	0.01	0.00	20	110	0.80	1.75	5	54.36	78
2	0	0	0	0	0	1.00	0.04	0.00	20	110	1.81	1.73	5	53.51	93
3	0	0	0	0	0	1.00	0.22	0.00	20	110	2.23	1.77	5	50.10	71
4	0	0	0	0	0	0.81	0.01	0.00	60	150	0.80	1.73	5	54.37	162
5	0	0	0	0	0	1.00	0.04	0.00	60	110	2.71	1.73	5	53.58	177
6	0	0	0	0	0	1.00	0.22	0.00	60	110	3.26	1.77	5	50.17	74

Table 16: Solutions for the optimization with kinetics models for feed 2 (1 scenario per line)

With `SQA`, optimizing one scenario implies to make as many local optimizations as there are combinations of qualitative variables, i.e. 72. As the number of test cases was limited (6 scenarios and 2 feeds), and the cost of one process simulation not too high (from 4 to 20 seconds), all these optimizations could be made. The optimization time of one scenario went from a little more than 4 hours, to 15 hours, amounting to a total of approximately 114 hours. This time has to be compared to the $29 = 11 + 18$ hours needed for the hybrid approach. The difference in cpu time is expected to grow rapidly with the complexity of the process (number of units, ...). In the following, these optimizations will be named as the "systematic approach".

With the hydrid approach, the best solution found by the systematic approach could be found 11 times out of the 12 (qualitative and continuous variables). In the remaining one, at least one qualitative variable

is different, but the objective function is very close to the best one (54.37 vs 54.41), making this solution perfectly acceptable (see Figure 2, triangle/cross of point 71 to be compared to cross of point 69).

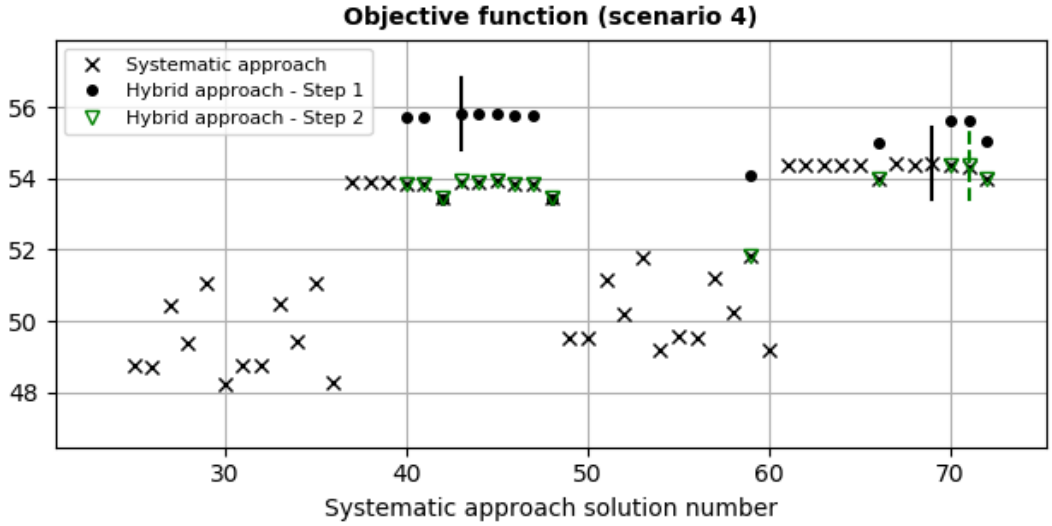


Figure 2: Objective function for some solutions of scenario 4, and second feed. Crosses are some of the solutions of the systematic approach (48 out of 72). The abscissas are an index into the 72 solutions. Full points are all the solutions determined by `BARON` and the surrogate models. Triangles are all the solutions determined by `SQA` and the kinetics models, starting from the solutions of `BARON`. Vertical bars indicate the best solution for each set of solutions.

If the cpu budget is limited, the number of optimizations with SQA can also be limited: first choose the best solution found by `BARON` as starting point of `SQA`, and make the optimization. Then take the second best solution of `BARON` as a new starting point. Continue this way until the cpu budget is attained.

This was tested by taking only the best solution found by `BARON` as starting point of `SQA`. The best solution of the systematic approach is found in only 5 cases out of 12. In the 7 other cases, the qualitative variables are different. The solution found by `SQA`, although not the best, is still good. An example can be found in Figure 2 for scenario 4 and feed 2: the objective function would be equal to 53.92 instead of 54.41 (triangle/cross of point 43 to be compared to cross of point 69). This is a second illustration of the effect of the surrogate model accuracy. To be sure that the hybrid approach finds the best solution (or at least a very close one), we must make several optimizations starting from several feasible solutions found by `BARON`.

8 Conclusions

In this paper, we have presented a hybrid approach for the optimization of a cluster of reforming-isomerization processes. This is a MINLP problem with 6 qualitative variables and 7 continuous variables. An accurate model, based on kinetics, is available for the process. Though it is not too cpu-intensive, it is still too costly to be used for making many optimizations. A two-phase approach has been chosen for the process optimization. In a first phase, a surrogate model is built for the reforming and isomerization reactors. The form of these models is such that it enables the use of state-of-the-art global optimizers, such as `BARON`. But this comes at the cost of accuracy. Then the process is optimized with these models, and the `BARON` optimizer. Several feasible solutions are gathered during this optimization. In a second phase, new optimizations are made with the process kinetics models, and an NLP derivative free optimizer (`SQA`). Depending on the cpu budget, either several feasible solutions or only the best one, are used as starting points of these optimizations. The approoach was tested on 6 scenarios and 2 feeds. To

check the approach, the solutions of the optimization problem were also calculated for these 12 test cases and all combinations of qualitative variables. If several feasible solutions found by `BARON` can be used as starting points, the best solution could be found with the hybrid approach in 11 of the 12 test-cases. In the twelfth one, the objective function was very close to the best one. If only the best solution of `BARON` can be used as a starting point, the best solution is found in 5 cases out of the 12. In the 7 other cases, the found solution is good. The accuracy of the surrogate model is probably not sufficient to guarantee that the best or at least a very good solution can always be found.

For the future, we are interested in testing the hybrid approach to other processes. Based on the above results, we are confident that, compared to the direct approach, it will result in a substantial decrease on the total computational time. This should allow us to address large scale problems (number of units, more splitters, ...), which is our final aim.

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