Brazilian Journal of Chemical Engineering (2021) 38:705–717
https://doi.org/10.1007/s43153-021-00145-y

REVIEW

Application of linear and nonlinear mathematical programming to retrofit hydrogen networks

Patrícia R. da Silva[1] · **Marcelo E. Aragão**[2] · **Jorge O. Trierweiler**[1] · **Luciane F. Trierweiler**[1]

Received: 30 April 2020 / Revised: 2 August 2021 / Accepted: 18 August 2021 / Published online: 26 August 2021

Abstract

Hydrogen network management has economic appeal due to its importance in oil refineries. It has become genuinely relevant due to the restrictions of sulfur content in fuels, which need hydrogen to be removed. Mathematical programming can be used as a tool for optimizing hydrogen networks, and the efficient management of hydrogen within the refineries can be achieved through a material balance of the units that make up the hydrogen network. In this work, an optimization model Mixed-Integer Linear Programming (MILP) and Mixed-Integer Nonlinear Programming (MINLP) for hydrogen networks was applied to minimize the operating costs. The optimization model was developed in GAMS, and it was validated using a literature case study and a real case study from a Brazilian Refinery. The operation cost was reduced by 10% and 19.6% with MILP and 9.7% and 31.5% with MINLP, for example 1 and 2, respectively. Comparing the results, both achieve significant savings in operating costs. The MILP model, which is easier to solve, has proved to be an efficient tool for optimizing hydrogen networks. However, optimization via MINLP, although not guaranteeing the optimal solution, resulted in lower operating and capital costs. The design of the optimized hydrogen networks was also detailed, and other extra restrictions were imposed on the problem.

Keywords Hydrogen network · Mathematical programming · Optimization · Hydrogen management

List of symbols

$FH2I_i$	Flow rate of hydrogen sources
$FH2I_i$, max $FH2I_i$, min	Maximum and minimum flow rate of hydrogen sources
$FIJ_{i,j}$	Flow from source to consumer
$FIK_{i,k}$	Flow from source to purifier
FIW_i	Flow from source to waste (fuel system)
FJ_j	Total consumer flow
$FKJ_{k,j}$	Flow from purifier to consumer
$FJJ_{j,j'}$	Flow from consumer j to consumer j’
YJ_j	Consumer purity
YI_i	Source purity
YK_k	Purifier purity
YP_j	Purge purity of consumer
FP_j	Total purge consumer flow
FJW_j	Flow from consumer to waste (fuel system)
$FJK_{j,k}$	Flow from consumer to purifier
$FPur_{max,k}$	Maximum capacity of purifier
FKW_k	Flow from purifier to waste (fuel system)
$FKW_{rec,\ k}$	Purge flow from purifier to waste (fuel system)
YKW_k	Purity of purge flow from purifier
rec_k	Purifier recovery
$C_{operating}$	Operating cost
$CH2I$, C_i	Total and hydrogen production cost
$CH2K$, C_k	Total and purification cost
$CH2C$, $C_{eletric}$	Total and electricity cost
$CH2F$, C_{fuel}	Cost of burning purge as fuel
t	Annual operating time

✉ Patrícia R. da Silva
rodriguess.patricia@outlook.com.br

[1] Group of Intensification, Modeling, Simulation, Control, and Optimization of Processes, Chemical Engineering Department, Federal University of Rio Grande do Sul (UFRGS), R. Eng. Luiz Englert, s/n, Campus Central, Porto Alegre, RS, Brazil

[2] Food and Chemistry School, Federal University of Rio Grande (FURG), R. Barão do Cahy, 125, Cidade Alta, Santo Antônio da Patrulha, RS, Brazil

FK	Total purifier flow
FW	Total waste flow (fuel system)
y	Hydrogen fraction in the purge flow
$\Delta H^{\circ}_{H2}, \Delta H^{\circ}_{CH4}$	Combustion heat of hydrogen and methane
FC	Total flow that compressor needs
$\overline{Cp}$	Heat capacity
T	Temperature
η	Compressor efficiency
P_{out}	Outlet pressure
P_{in}	Inlet pressure
γ	Cp/Cv ratio
ρ_o	Density in initial condition
ρ	Density
$C_{capital}$	Capital cost
$C_{new\ PSA}$	Cost of new purifier
C_{piping}	Cost of new pipelines
$C_{new\ compressor}$	Cost of new compressor
Af	Annualized factor
c, d	Parameters of piping cost
z_h	Binary variable from new pipeline
$F_{newpipe}$	Total flow in new lines
ϑ	Superficial gas velocity
L	Distance
a, b	Parameters of new purifier cost
z_{kn}	Binary variable from new purifier
$FK_{new\ k}$	Purification flow in the new purifier
e, f	Parameters of new compressor cost
z_c	Binary of new compressor
FC_{new}	Total flow in new compressor
z	Binary associated with flow
$FIC_{i,c}$	Flow from source to compressor
$FCJ_{c,j}$	Flow from compressor to consumer
YC_c	Purity in compressor
$FJC_{j,c}$	Flow from consumer to compressor
$FCK_{c.k}$	Flow from compressor to purifier
$FKC_{k,c}$	Flow from purifier to compressor
FC_c	Total compressor flow
FCW_c	Purge flow from compressor to waste (fuel system)

Introduction

The growth in the use of hydrogen in oil refineries can be justified by increasing environmental restrictions on sulfur content. The Brazilian National Petroleum Agency (ANP) regulates activities that integrate oil, natural gas, and biofuels industries, so it must establish rules and supervise the different areas of activity such as exploration, refining, and processing, including parameters such as sulfur content. The regulations issued by ANP have been gradually decreasing the sulfur content in diesel and gasoline. There are several processes capable of treating oil fractions to reduce the amount of sulfur. It usually occurs in hydrotreatment units (HDT), which use hydrogen to remove sulfur and other impurities. Hydrogen in refineries can be obtained mainly in hydrogen generation units (UGH), which use catalytic reform reactions for their production. Besides, catalytic cracking also provides hydrogen as a sub product.

Therefore, hydrogen has been an essential raw material in refineries, so it must be used efficiently. Usually, the amount produced is higher than that used in hydrotreating, which leads to the burning of this excess. On the other hand, limiting hydrogen production can make HDT's inefficient and inoperative. Therefore, the efficient management of hydrogen within a refinery is fundamental both in economic and safety terms (Borges 2009; Cruz 2010; Figueiredo 2013). Thus, the management of hydrogen networks has a vital appeal and, when done efficiently, generates a production with minimal hydrogen clearance and with satisfactory financial returns.

Process integration, in the context of mass integration, can be used to manage hydrogen networks. Through material balance in the involved steps (sources, consumers, and purifiers of hydrogen), it is possible to manage hydrogen through network optimization efficiently. Optimization is one of the most potent tools in process integration, based on selecting the 'best' solution by choosing an objective function (for example, operating cost) that must be minimized or maximized. The objective function can be subject to several restrictions that include material and energy balances, process modeling equations, and thermodynamic requirements (El-Halwagi 2006).

In general, this methodology can be divided into two categories: (i) segmentation methods (pinch) and (ii) mathematical programming approaches based on network design. The focus of this work is the mathematical programming approach. The mathematical programming based on the superstructure presents advantages concerning the pinch, such as, for example, considering many limitations/restrictions and variables when searching for solutions in the optimization problem. The methodology of mathematical programming is: (i) the development of the superstructure (which units are involved and classification as sources and consumers, in addition to the existing compressors and purifiers), (ii) the formulation of the mathematical model capable of representing it (choice of the objective function to be minimized or maximized through restrictions) and (iii) the resolution of the optimization problem (Jia 2010; Pinheiro 2012).

Thus, this paper approach is based on evaluating different optimization strategies for hydrogen network management through mathematical programming. For this, two formulations were developed, Mixed Integer Linear Programming (MILP) and Mixed Integer Nonlinear Programming (MINLP), capable of representing hydrogen networks. The modeling has been fully described, and the objective is to compare the results obtained in terms of savings in operating costs and the network designs obtained. Two case studies were used to validate the formulations developed, an example from the literature, and a real case study with project data from a Brazilian oil refinery.

Literature review

The optimization need in the hydrogen network in refineries was recognized in the 1990s, and since then, many methodologies have emerged. They are mainly segmentation methods (pinch) and mathematical programming approaches based on the design of networks. Mathematical programming offers advantages when compared to pinch, as already mentioned, as it is more flexible, and the network synthesis takes place automatically as a result of the problem. In the pinch approach, it would be necessary to use another technique to evaluate the process synthesis. Besides, it is possible to consider numerous restrictions in mathematical programming, such as pressure limits, equipment capacity, and investments with new equipment. For this reason, the vast majority of works about hydrogen network management are done using mathematical programming (Jia 2010).

Mathematical programming problems can be elaborated considering several factors, i.e., different objective functions, pressure restrictions, and equipment capacity limitations. This information characterizes the developed problem. Therefore, they can generally be formulated as a linear programming (LP) problem, mixed-integer linear programming (MILP), nonlinear programming (NLP), or mixed-integer nonlinear programming (MINLP). MINLP problems are more challenging to solve because they combine the NLP and MILP models and their characteristics, including nonlinearity. However, they result in more realistic networks and include several additional restrictions. The use of MILP, due to the fact of linearity, facilitates the resolution of the optimization problem, as they are easier to converge to a global solution, since all subproblems, for fixed binaries, are solved linearly for global optimization. Most of the work on hydrogen network management via mathematical programming uses MINLP models, as can be seen below. For the resolution of this formulation, there are different algorithms found in GAMS solvers or even use linearization techniques to facilitate the resolution of MINLP, as McCormick (Gams 2020; Petric 2014).

Hallale and Liu (2001) developed a mathematical model (NLP) to reduce hydrogen consumption. The model considered pressure restrictions, existing compressors, and strategy for installing a purifier. The objective function was to minimize the total cost, including capital and operating costs. Liao et al. (2010) developed a model using an existing hydrogen network with a purifier. The objective function was the total annual cost, and the model was solved in GAMS using DICOPT. The total annual cost decreased by 22.6%, and the new compressor and PSA were incorporated.

In Kumar et al. (2010), mathematical models were developed based on pressure restrictions, sources, consumers, purity, and total operating cost. For this, two case studies were carried out that compared the types of programming. For case study A, the NLP and MINLP model were used, and for case study B, the LP, NLP and MILP were used, and the objective function was minimizing the total annual cost. The MINLP model reduced operating costs by 21.9% in comparison to the NLP model for case A. In case B, the network obtained by the NLP model was more realistic than MILP. So mixed-integer linear and nonlinear programming models are considerably better than linear (LP) because they provide the less complicated and more realistic refinery system, and MINLP can include complexities such as compressors, purity constraints, and pressure constraints.

Sardashti Birjandi et al. (2014) developed a methodology for the global optimization of a hydrogen network based on a problem solved simultaneously by MINLP and NLP. A combination of the bound contraction procedure and linearization technique of McCormick for nonlinear models were used for global optimization. Global optimization strategy reduced operating costs, saved the investment cost, and increased the profit.

Matijašević and Petric (2016) presented a methodology for integrating the hydrogen network in a local refinery case study. The superstructure was modeled using a nonlinear mathematical model whose objective function was to minimize total operating costs. The problem was solved with the GAMS software. Network design flows of hydrogen with two units to purify hydrogen proved to be an optimal solution for this case study.

Jagannath et al. (2018) used a MINLP model to reduce the total annual cost focus in nonconvex problems to global optimality. The nonlinearity is due to the bilinear terms and the pressures that vary in the compressors, so the nonlinearity is bilinear, linear fractional, and posynomial terms. The linear fractional and posynomial terms were eliminated by heuristically assigning suction and discharge pressures for the newly retrofitted compressors. Bilinear terms in MINLP were solved to global optimality using a specific tailor-made global optimization algorithm to be solved to ϵ-global optimality. For that, a bivariate partitioning scheme using incremental cost formulation was utilized for the convexification of the bilinear term.

As mentioned, most of the bibliography is about MINLP formulations, and there is no direct comparison between MILP and MINLP models, their characteristics and advantages. This work aims to apply optimization for the retrofit existing hydrogen networks, comparing models developed via linear (MILP) and nonlinear mathematical programming (MINLP). The objective is to minimize the operating cost, with the possibility of installing new pipelines and equipment, such as compressors and purification units. Additional restrictions may also be imposed on the objective function, such as limiting the installation of new equipment or investment costs. The results obtained in case studies are evaluated with other critical economic parameters such as investment cost and payback time.

Mathematical model formulation

The hydrogen network presents a set of sources i ∈ hydrogen sources (HS), a set of consumers j ∈ hydrogen consumers (HC), a set of purifiers k ∈ hydrogen purifiers ($HP = OHP \cup NHP$), considering the existing purifiers, OHU, and the new purifiers, NHP and a set of compressors c ∈ hydrogen compressors $HCP = OHCP \cup NHCP$), considering the existing compressors $OHCP$ and new compressors $NHCP$ For each source is given the maximum and minimum flow rate, the hydrogen composition, and the outlet pressure. For each consumer is given the inlet flowrate demand, pressure, and composition, the outlet purge flow, pressure, and composition. For each purifier is given the maximum flow capacity, the composition of purified flow and purge flow, the pressure of purification, and the hydrogen recovery. A fuel system is also considered in which waste streams can be burned and used as fuel for the process. For the existing networks, they are also given the existing lines (unit connections), the distance between the units if informed, and the existing compressors and purifiers. Also, it is necessary to know the capacity of the compressors.

The optimization problem is to minimize the operating costs due to hydrogen production and purification, electricity, and economy provided by the streams used as fuel for the process. The optimization problem is subject to the material balances and process operating constraints. For the retrofit case, process modifications are allowed to reduce the total operating costs (the objective function), despite the investment costs due to the installation of new pipelines, compressors, and possibly new purifiers.

Some considerations were made to simplify the model. The flow is considered to be only a binary mixture of hydrogen and methane, and compressors are associated with each possible connection individually in the MILP problem. Therefore, it is not allowed to merge flows before the compressor units, which would result in an unknown inlet hydrogen composition. Hence, a nonlinear material balance would be necessary. The partial pressure of the hydrogen and the flow are constant at the entrance and exit of the consuming units. In the MINLP problem, compressors are like units, so pressure and purity are variable in the process.

MILP model

The hydrogen network can be represented using the diagram presented in Fig. 1. Hydrogen sources with specific purity supply hydrogen to the consumer units ($FIJ_{i,j}$), for purification ($FIK_{i,k}$), or for burning if they are in excess (FIW_i). Consuming units can send hydrogen between them $\left(FJJ_{j,j'}\right)$, or purify to achieve the desired purity ($FJK_{j,k}$) or even send for burning (FJW_j). The hydrogen purification unit provides consumers with pure hydrogen ($FKJ_{k,j}$) and the excess can be burned (FKW_k). The amount not purified in PSA according to its capacity is also sent for burning ($FKWrec_k$).

The mathematical problem proposed in this article is detailed below, which includes material balances in sources, consumers, and purifiers, besides calculations of operating and capital costs. All variables are shown in the List of Symbols. To consider the capital cost, it is necessary to use binary variables, representing the installation or not of a new pipeline, compressor, or purifier. For this, it was necessary to use constraint modeling, through propositions and logical disjunctions.

Material balance in sources:

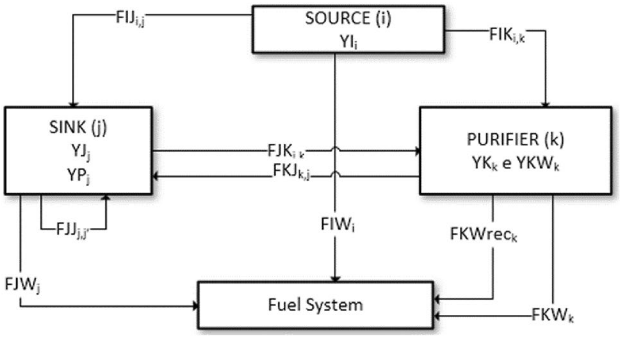

Fig. 1 Scheme developed for the mathematical modeling of the MILP problem

$$FH2I_i = \left(\sum_{j \in HC} FIJ_{i,j} + \sum_{k \in HP} FIK_{i,k} + FIW_i \right) \forall i \in HS \tag{1}$$

$$FH2I_{i,min} \leq FH2I_i \leq FH2I_{i,max} \forall i \in HS \tag{2}$$

Material balance in consumers:

$$FJ_j = \sum\nolimits_{i \in HS} FIJ_{i,j} + \sum\nolimits_{k \in HP} FKJ_{k,j} + \sum\nolimits_{j \in HC} FJJ_{j,j'} \forall j \in HC \tag{3}$$

$$\begin{aligned} FJ_j * YJ_j = \sum\nolimits_{i \in HS} FIJ_{i,j} * YI_i + \sum\nolimits_{k \in HP} FKJ_{k,j} * YK_k \\ + \sum\nolimits_{j \in HC} FJJ_{j,j'} * YP_j \forall j \in HC \end{aligned} \tag{4}$$

$$FP_j = FJW_j + \sum\nolimits_{k \in HP} FJK_{j,k} + \sum\nolimits_{j \in HC} FJJ_{j,j'} \forall j \in HC \tag{5}$$

Material balance in purifiers:

$$\begin{aligned} &\sum\nolimits_{j \in HC} FJK_{j,k} + \sum\nolimits_{i \in HS} FIK_{i,k} \\ &= \sum\nolimits_{j \in HC} FKJ_{k,j} + FKW_k + FKW_{rec,k} \forall k \in HP \end{aligned} \tag{6}$$

$$\begin{aligned} &\sum\nolimits_{j \in HP} FJK_{j,k} * YP_j + \sum\nolimits_{i \in HS} FIK_{i,k} * YI_i \\ &= \sum\nolimits_{j \in HP} FKJ_{k,j} * YK_k + FKW_k * YK_k \\ &+ FKW_{rec,k} * YKW_k \forall k \in HP \end{aligned} \tag{7}$$

$$\sum\nolimits_{j \in HP} FJK_{j,k} + \sum\nolimits_{i \in HS} FIK_{i,k} \leq \sum\nolimits_{k} FPur_{max,k} \forall k \in HP \tag{8}$$

$$\begin{aligned} &\left(\sum\nolimits_{i \in HS} FIK_{i,k} * YI_i + \sum\nolimits_{j \in HP} FJK_{j,k} * YP_j \right) * \left(1 - rec_k\right) \\ &= FKW_{rec} * YKW_k \forall k \in HP \end{aligned} \tag{9}$$

$$\sum\nolimits_{j \in HP} FJK_{j,k} + \sum\nolimits_{i \in HS} FIK_{i,k} = FK_k \forall k \in HP \tag{10}$$

For the operating cost, it is necessary to calculate the cost of hydrogen, cost of fuel, cost of electricity and cost of purifying.

$$C_{operating} = (CH2I + CH2K + CH2C - CH2F) * t \tag{11}$$

Cost of hydrogen from sources:

$$CH2I = \sum\nolimits_{i \in HS} FH2I_i * C_i \tag{12}$$

Cost of fuel:

$$CH2F = C_{fuel} * FW * \left(y * \Delta H^{\circ}{}_{H2} + (1 - y) * \Delta H^{\circ}{}_{CH4} \right) \tag{13}$$

Cost of electricity:

$$CH2C = FC * \mathrm{w} * C_{eletric} \tag{14}$$

where

$$w = (\bar{C}_P * T/\eta) * \left(\left(\frac{P_{out}}{P_{in}} \right)^{\frac{\gamma-1}{\gamma}} - 1 \right) * (\rho_o/\rho) \tag{15}$$

Cost of purifying:

$$CH2K = \sum\nolimits_{k \in HP} FK_k * C_k \tag{16}$$

For the capital cost, it is necessary to calculate the cost of a new compressor, new pipelines, and new purifier unit.

$$C_{capital} = \left(C_{newPSA} + C_{newpiping} + C_{newcompressor} \right) * A_f \tag{17}$$

For new PSA unit:

$$C_{newPSA} = a * \sum\nolimits_{k \in NHP} z_{kn} + \mathrm{b} * \left(\sum_{k \in NHP} FK_{newk} \right) \tag{18}$$

For new pipeline:

$$C_{newpiping} = \left(c * z_h + d * D^2 \right) * L \tag{19}$$

where

$$D^2 = (4 * F_{newpipe}/\pi * \vartheta) * \left(\frac{T}{T_0} \right) * \left(\frac{P_0}{P} \right) \tag{20}$$

For new compressors:

$$C_{newcompressor} = e * z_c + f * FC_{new} * w \tag{21}$$

The parameters related to the capital cost are shown in Table 1. The units of the variables related to the parameters are also in the table.

It was necessary to create a binary variable representing the flow rate (z); that is, if there is a flow in a given connection shown in the scheme, the variable z assumes the value of 1. Also, other binaries were created, representing the need for a new compressor (z_c) (Eq. 22), the need for a new pipeline (z_h) (Eq. 23) and the need for a purification unit (z_{kn})(Eq. 24).

$$\begin{cases} z \geq z_c \\ 1 - u_c \geq z_c \\ u_{deltaP} \geq z_c \end{cases} \tag{22}$$

$$\begin{cases} z_h \leq z \\ z_h \leq 1 - u_h \end{cases} \tag{23}$$

Table 1 Capital costs parameters (Hallale and Liu 2001)

Cost of new compressors [k$]	$e = 115$ $f = 1.91$ W in [kW]
Cost of piping [$]	$c = 3.2$ $d = 11.42$ D^2 [in^2] and L [m]
Cost of new PSA[k$]	$a = 503.8$ $b = 347.4$ F in [MMscfd]

$$\begin{cases} FK_k \geq \varepsilon * z_{kn} \\ FK_k \leq (FPur_{max,k}) * z_{kn} \end{cases} \forall k \in NHP \tag{24}$$

For a compressor to be installed, there must be flow, no compressor previously installed, and a pressure difference that justifies the installation. For a new pipeline to be installed, it is enough that there are flow and no previous pipeline in that connection. For a new PSA to be installed, it is enough that there is flow from some connection that has PSA as its origin or destination.

The objective function chosen for the optimization of hydrogen networks is the minimization of the operating cost, which includes the cost of hydrogen from the sources, the cost of purification, the cost of electricity from the use of compressors, and the cost of burning the excess (Eq. 11). The new equipment, pipelines, compressors, and PSA are accounted for in the capital cost (Eq. 17). The total annual cost is the sum of the operating cost and capital cost penalized with the annualization factor.

The MILP model formulated in this work is described by the Eqs. 1–24. The proposed model has the advantage of being a linear model, for which very robust solvers can be used. However, the main disadvantage is that a compressor is associated with each possible connection individually to avoid nonlinear material balances to identify the composition of the current being compacted. In this case, the streams cannot be mixed to use the same compressor, and the resulting network may end up with more compressor units than an alternative NLP model, in which the streams can mix.

MINLP model

In the nonlinear model, the process variables listed above are used. However, also the variables of the compressors are now considered, which in the MINLP structure are part of the hydrogen network as a unit, as shown in the diagram below (Fig. 2).

The Eqs. 25–36 that describe the MINLP model are below; also, the Eqs. 11–21 are used (equations about operating cost and capital cost). The operating and capital costs are calculated in the same way as in the linear problem, as well as the logical flow restrictions. It is worth mentioning that the binaries involving the compressors in the connections are included here, and the same occurs with the binary variables associated with new pipelines. The binary variables associated with the new compressors are not part of this model, as here they are considered as units of the network.

Material balance in sources:

$$FH2I_i = \left(\sum_{j\in HC} FIJ_{i,j} + \sum_{k\in HP} FIK_{i,k} + FIW_i + \sum_{c\in HCP} FIC_{i,c} \right) \forall i \in HS \tag{25}$$

$$FH2I_{i,min} \leq FH2I_i \leq FH2I_{i,max} \forall i \in HS \tag{26}$$

Material Balance in consumers:

$$\begin{aligned} FJ_j = & \sum\nolimits_{i\in HS} FIJ_{i,j} + \sum\nolimits_{k\in HP} FKJ_{k,j} + \sum\nolimits_{j\in HC} FJJ_{j,j'} \\ & + \sum\nolimits_{c\in HCP} FCJ_{c,j} \forall j \in HC \end{aligned} \tag{27}$$

$$\begin{aligned} FJ_j * YJ_j = & \sum\nolimits_{i\in HS} FIJ_{i,j} * YI_i + \sum\nolimits_{k\in HP} FKJ_{k,j} * YK_k \\ & + \sum\nolimits_{j\in HC} FJJ_{j,j'} * YP_j \\ & + \sum\nolimits_{c\in HCP} FCJ_{c,j} * YC_c \forall j \in HC \end{aligned} \tag{28}$$

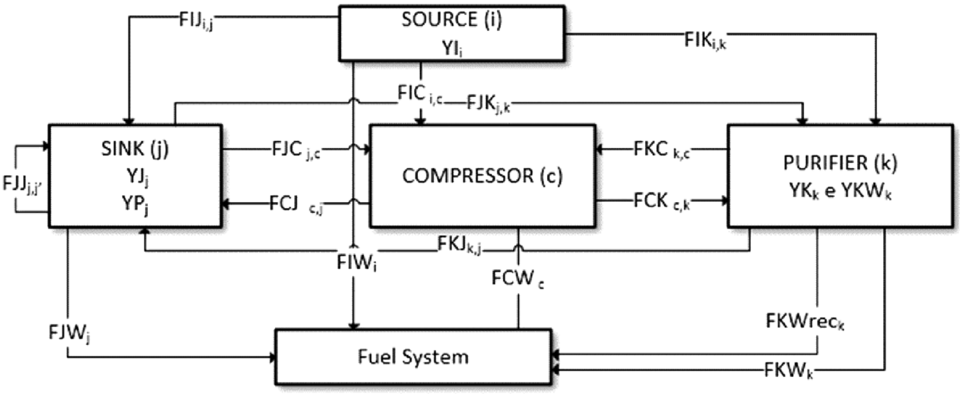

Fig. 2 Scheme developed for the mathematical modeling of the MINLP problem

$$FP_j = FJW_j + \sum\nolimits_{k \in HP} FJK_{j,k} + \sum\nolimits_{j \in HC} FJJ_{j,j'} + \sum\nolimits_{c \in HCP} FJC_{j,c} \forall j \in HC \tag{29}$$

Material balance in purifiers:

$$\sum\nolimits_{j \in HC} FJK_{j,k} + \sum\nolimits_{i \in HS} FIK_{i,k} + \sum\nolimits_{c \in HCP} FCK_{c.k} = \sum\nolimits_{j \in HC} FKJ_{k,j} + FKW_k + FKW_{rec,k} + \sum\nolimits_{c \in HCP} FKC_{k,c} \forall k \in HP \tag{30}$$

$$\sum\nolimits_{j \in HP} FJK_{j,k} * YP_j + \sum\nolimits_{c \in HCP} FCK_{c.k} * YC_c + \sum\nolimits_{i \in HS} FIK_{i,k} * YI_i = \sum\nolimits_{j \in HP} FKJ_{k,j} * YK_k + \sum\nolimits_{c \in HCP} FKC_{k,c} * YK_k + FKW_k * YK_k + FKW_{rec,k} * YKW_k \forall k \in HP \tag{31}$$

$$\sum\nolimits_{j \in HP} FJK_{j,k} + \sum\nolimits_{i \in HS} FIK_{i,k} + \sum\nolimits_{c \in HCP} FCK_{c,k} \le FPur_{max,k} \forall k \in HP \tag{32}$$

In this work, no other different initializations were addressed, but an alternative that provided satisfactory results is the initialization with the linear problem result for the nonlinear model. This subject was addressed in another article, using the MILP and MINLP models with different case studies (Silva et al. 2020).

Results and discussion

The MILP and MINLP optimization problems were validated using an adapted example of a hydrogen network found in the literature, from Liao et al. (2010), and another using a real example of a Brazilian refinery. The entire formulation was implemented in the modeling system GAMS on a 3.6 GHz Intel® Core ™ I7 CPU. The solvers used in MILP and MINLP are CPLEX and DICOPT, respectively. Other solvers have been tested and will be discussed in the examples below.

$$\left(\sum\nolimits_{i \in HS} FIK_{i,k} * YI_i + \sum\nolimits_{j \in HP} FJK_{j,k} * YP_j + \sum\nolimits_{c \in HCP} FCK_{c.k} * YC_c) * (1 - rec_k) = FKW_{rec} * YKW_k \right) \forall k \in HP \tag{33}$$

Material balance in compressors:

$$FC_c = \sum_{c \in HCP} FIC_{i,c} + \sum\nolimits_{c \in HCP} FJC_{j,c} + \sum\nolimits_{c \in HCP} FKC_{k,c} \forall c \in HCP \tag{34}$$

$$\sum_{c \in HCP} FIC_{i,c} + \sum\nolimits_{c \in HCP} FJC_{j,c} + \sum\nolimits_{c \in HCP} FKC_{k,c} = \sum\nolimits_{c \in HCP} FCJ_{c,j} + \sum\nolimits_{c \in HCP} FCK_{c.k} + FCW_c \forall c \in HCP \tag{35}$$

$$FC_c * YC_c = \sum_{c \in HCP} FIC_{i,c} * YI_i + \sum\nolimits_{c \in HCP} FJC_{j,c} * YP_j \sum\nolimits_{c \in HCP} + FKC_{k,c} * YK_k \forall c \in HCP \tag{36}$$

The methodology developed in this article is summarized in Fig. 3. To compare the optimization through the linear and nonlinear models, the cost of the original network was first calculated. The procedure performed was: (i) the flows are fixed according to the current network (base case), including the binary. So, the problem is solved, and the actual cost is accounted. The variables were then released, including lower and upper bounds, and the problem was optimized using the MILP and MINLP model. In the MILP formulation, additional restrictions on the objective function have also been tested, such as limiting the installation of a new PSA or not yet allowing any investment. The same procedure was performed in both examples and the results are discussed in the next section.

Example 1

The hydrogen network is composed of five sources, two hydrogen plants (H_2 plant1 and H_2 plant2), a catalytic reforming unit (CCR), a semi regenerated catalytic reformer (SCR), and a fertilizer plant (FER). In addition, there are six consumer units (HC—hydrogen cracker, WHT—wax oil

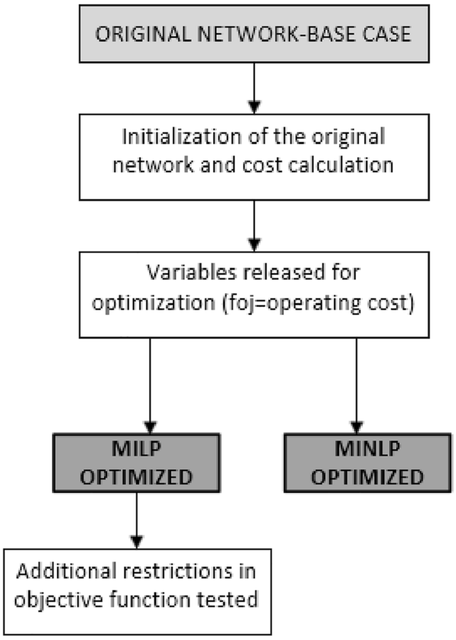

Fig. 3 Methodology used to optimize hydrogen networks

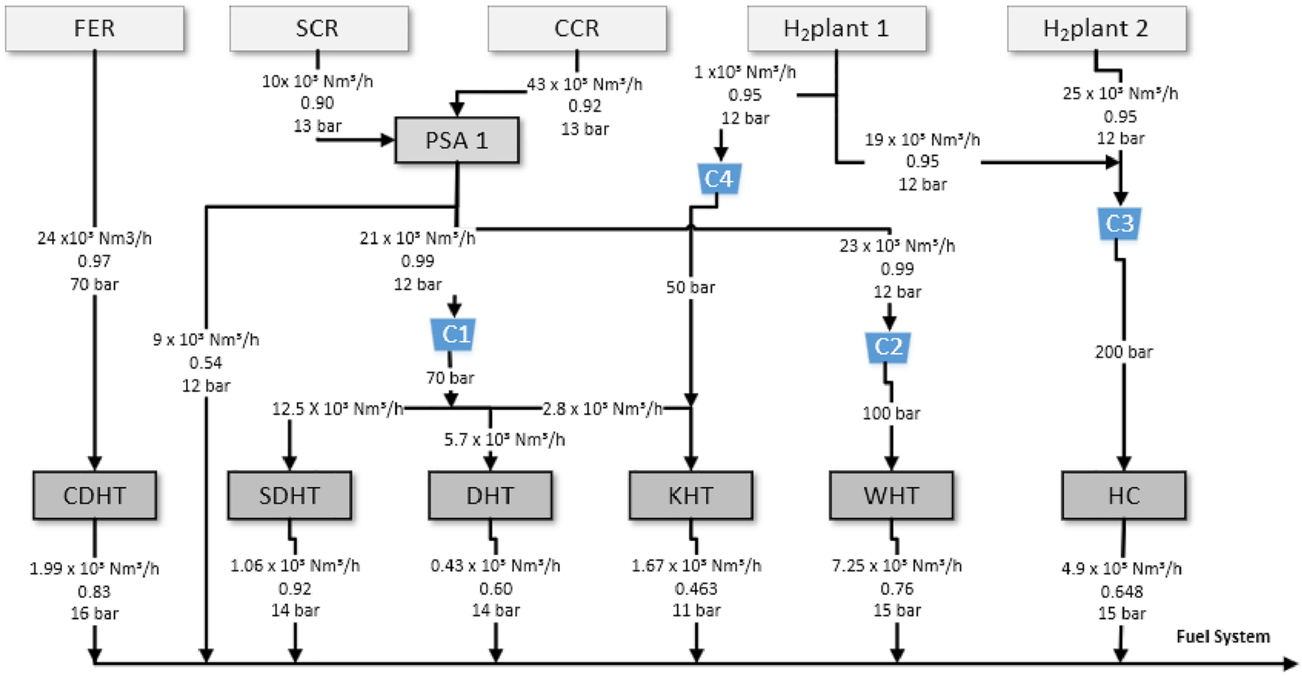

Fig. 4 Existing hydrogen network— Adapted from Liao et al. (2010)

hydrotreater, KHT—kerosene hydrotreater, DHT—diesel hydrotreater, SDHT—straight run diesel hydrotreater, and CDHT—catalytic diesel hydrotreater), and one purification unit (PSA). Also, there are four compressors. The MILP model included 1180 single equations, 505 single variables, and 362 discrete variables. The MINLP present 1297 single equations, 731 single variables, and 444 discrete variables. The network is shown in Fig. 4 and the parameters used are shown in Tables 2 and 3.

For the case study, the retrofit of the existing network was considered to minimize the operational cost. First, the original network (base case) operating cost was calculated using the same model developed following the parameters listed. This was done by setting the flow values according to the original network. Using the equations described in "MILP model" and the parameters listed in Tables 2 and 3, the original network (base case) cost is 71.428 million $/year. The Hydrogen Network BASE CASE (HN- BASE CASE) corresponds to the existing basic topology, that is, the values obtained from operating costs are the current costs in which the refinery is operating, used as a base case for later comparison with the networks obtained through optimization.

After that, using the optimization initialization strategies, the MILP problem was solved. As it is a case of a retrofit, it was possible to increase the efficiency of the hydrogen network through the installation of new equipment, computed in the capital cost. The economy saving is obtained by the operating cost reduction compared to the original solution. However, there is also an investment cost associated with non-existing equipment and pipelines. Another economic indicator, the turnaround time, was also used to evaluate the optimized network. The payback time is defined as the annualized cost of capital divided by the savings obtained.

Table 2 Operating costs parameters (Hallale and Liu 2001; Liao et al. 2010)

Hydrogen cost	C_i	0.08 $/Nm^3
Hydrogen cost –FER	C_i	0.066 $/Nm^3
Electricity cost	$C_{eletric}$	0.03 $/kWh
Purification cost	C_k	0.0011 $/Nm^3
Fuel cost	C_{fuel}	2.5 $/ MMBtu

Table 3 Parameters used to optimize the available network

Parameters	
Waste pressure	6 bar
Temperature	300 K
Pressure	12 bar
$\overline{Cp}$	30 J/mol.K
ΔH°_{H2}	286 kJ/mol
ΔH°_{CH4}	891 kJ/mol
Standard conditions	$T_0 = 288.7$ K $P_0 = 1$ bar
Annual operation time (t)	8760 h
Annualization factor (A_f)	0.5

Then, the hydrogen network was optimized based on the minimum operating cost. It resulted in a savings of almost 7.4 million. The proposed new network design includes one new PSA, nine new compressors, and eighteen new lines, which generates a total investment of 20.6 million. The payback is 33 months. It is the result obtained through the MILP optimization problem and will be called HN1-MILP OPTIMIZED.

A new optimization was made, not allowing the installation of a new PSA. This proposed new network presented savings of 7.1 million. However, the total investment is 1.4 million, which includes nine new pipelines and five new compressors. The payback time is 2.3 months. This optimized network is HN2-MILP OPTIMIZED and its design is shown in Fig. 5. It is worth noting that hydrogen plants were not necessary. As the existing compressors 3 and 4 in the original network were not used in the proposed design and 5 new compressors are needed, they will be reused. With that, it would be necessary to install only 3 new compressors, which reduces the total investment cost to 1.13 million.

To compare the results obtained through different models, the original network was also optimized through a nonlinear mathematical programming model (MINLP). About solvers, the best solution was found with DICOPT, comparing with SBB, and solver BARON was unable to find a solution. As a result, savings of 6.9 million were obtained compared to the HN-BASE CASE network. As in the nonlinear model, it is possible to mix flows in the compressors, and this makes the investment cost less. The optimized network only required the installation of 10 new lines. There is no installation of PSA, and the four existing compressors were used. Thus, the total investment is 0.51 million, with a payback of less than one month. This optimization result from the MINLP is called HN3-MINLP OPTIMIZED. This optimized network is represented in Fig. 6. Table 4 summarized the obtained results.

Compared to the original network (HN-BASE CASE), the MILP result was reduced by 10.4% (HN1), 10% (HN2), and MINLP by 9.7% the operating cost (HN3). Comparing the models, the MILP model reduced the operating cost by 0.8% from the result of the nonlinear model. However, the investment cost is much higher. The payback of the HN3 network is approximately 1 month, and the HN2 network is 2 months. In this example, the cost of operation was very close between linear and nonlinear formulation. The lowest cost of capital was obtained in the HN3 network. However, the result obtained through MINLP is not a global optimum, which allows for improving the solution. It shows that the MILP model is good enough and capable of providing significant results to manage hydrogen networks. As the MINLP model is relatively more challenging to implement; it contains many nonlinearities such as pressure and purity varying in the compressors, making convergence difficult. Also, proper and adequate initialization is necessary to converge and facilitate the achievement of the optimal global.

The original article of this case study, from Liao et al. (2010), was based on hydrogen network optimization minimizing the total annual cost (TAC). For this, two conditions were tested, allowing or prohibiting recycle of off-gases in the hydrogen system via recovery. In this case, the retrofit achieved a 22.8% reduction in TAC. The

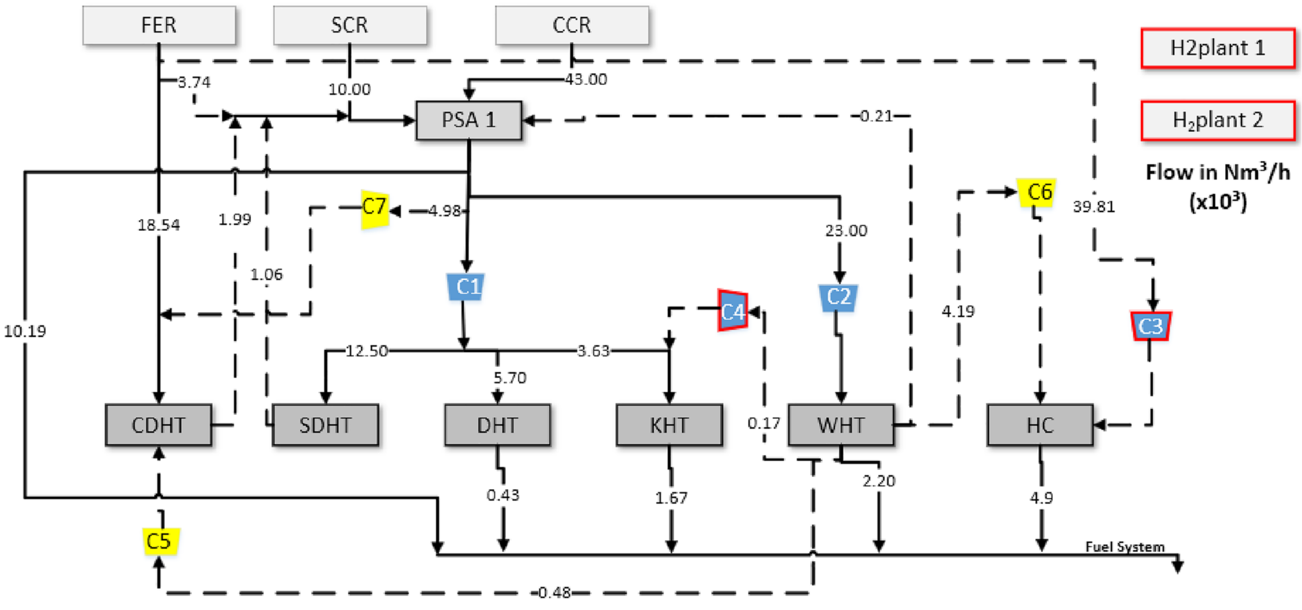

Fig. 5 Optimized network HN2-MILP OPTIMIZED

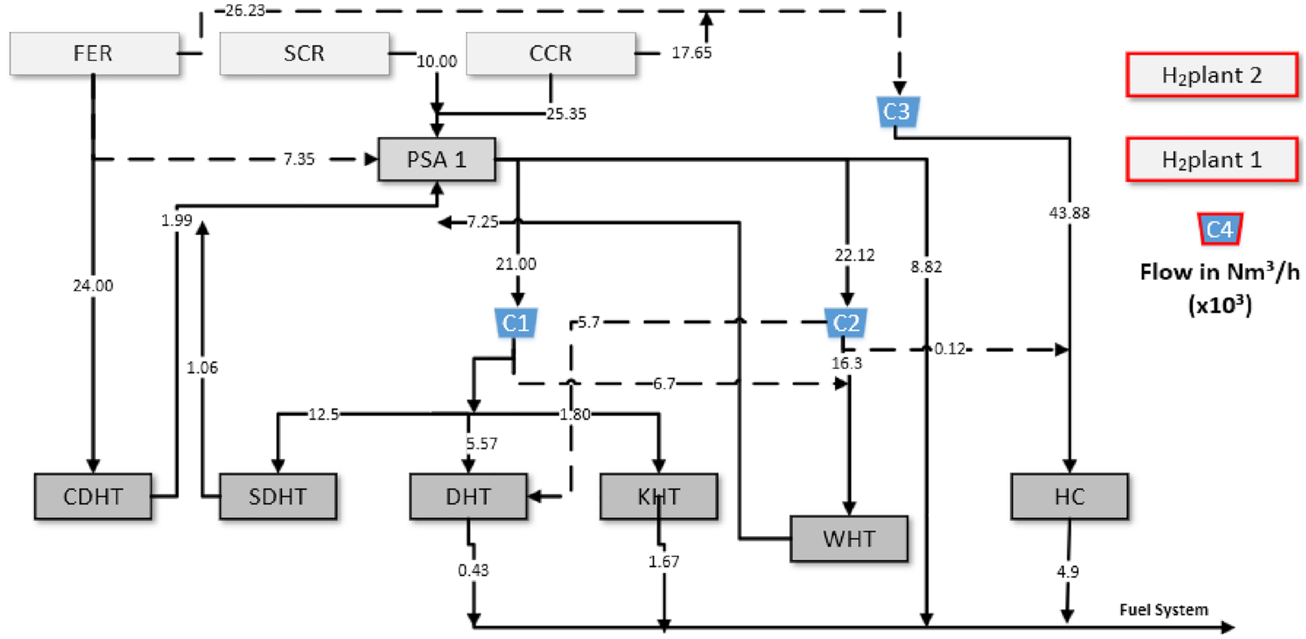

Fig. 6 Optimized network HN3-MINLP OPTIMIZED

Table 4 Results of minimizing operating cost for example 1

	HN-BASE CASE	HN1-MILP OPTIMIZED	HN2-MILP OPTIMIZED	HN3-MINLP OPTIMIZED
	[$\times 10^6$ \$/year]			
CH2I (Hydrogen)	82.554	71.779	73.038	71.589
CH2F (Fuel)	11.992	8.925	9.538	7.956
CH2C (Compressor)	0.354	0.297	0.223	0.392
CH2P (Purification)	0.511	0.857	0.578	0.500
Operating cost	**71.428**	**64.009**	**64.301**	**64.526**
CH2CN (New compressor)	–	1.050	0.497	–
CH2PN (New purification)	–	8.690	–	–
CH2PIPE (New pipeline)	–	0.388	0.069	0.253
Annualized capital cost	–	10.131	0.567	0.253

The results in [bold] are the most important values

direct comparison between the results of this article and the original cannot be made because the objective function is different, and some parameters were not informed. But through the MILP and MINLP formulation of this article, it was possible to achieve around 10% reduction in operating cost with meager investment cost.

Example 2

The MILP and MINLP optimization problems were also validated using a real example of a Brazilian refinery. As the data is confidential, flowrates, pressures, and purities will not be reported in Fig. 7 and the results. The network consists of two hydrogen generation units (UGH I and UGH II), two purification units (PSA I and PSA II), and 3 consumption units, two hydrotreatment units (HDT I and HDT II), and one hydrodesulfurization (HDS), as shown in Fig. 7. The MILP model included 524 single equations, 226 single variables, and 158 discrete variables. The MINLP presents 764 single equations, 383 single variables, and 249 discrete variables.

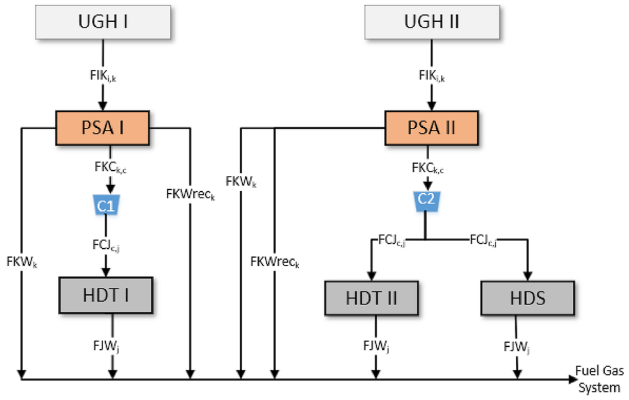

Fig. 7 Existing hydrogen network in a Brazilian Refinery

The retrofit of this real existing network was considered to minimize the operational cost. For that, first, the operation cost of the original network was calculated, fixing the values of flowrates and the existing topology (binary variables-indicating compressors, lines, and purifiers). The operating cost is 40.624 million $/year. The Hydrogen Network BASE CASE (HN- BASE CASE) corresponds to the existing basic topology, that is, the values obtained from operating costs are the current costs in which the refinery is operating (project data), used as a base case for later comparison with the networks obtained through optimization.

To optimize the network via the MILP linear formulation, the variables were released (considered only lower and upper limits), including the binary ones that indicate characteristics of the network topology. It results in an optimal solution of $32.444 million per year. It presents an associated annualized capital cost of approximately $6 million/year, including 12 new lines, 4 new compressors, and a new PSA. This optimal solution will be called HN4 -MILP OPTIMIZED.

As the original network already has two purification units and the cost associated with a new PSA installation is high (around 80% of the capital cost), a new restriction was added to the objective function, forbidding its installation. Thus, in the new optimal solution, the operating cost is $ 32.444 million per year, with an annualized capital cost of $ 0.393 million per year. This solution requires the installation of 3 new compressors and 7 new lines. As one of the existing compressors was not used in the optimal solution by optimization, it can be used in place of one of the new, so only 2 new compressors are installed, and the capital cost reduces by 15% ($ 0.36 million /year). This result, obtained through the MILP optimization problem, will be called HN5 -MILP OPTIMIZED (Fig. 8).

Another test that can be performed, limiting the cost of investment, that is, not allowing the installation of any new equipment. The optimal solution found has an operating cost of 33.903 million $/year. As there is no change in the original network, the cost reduction implies fewer hydrogen imports. This optimal solution results in around 20% less hydrogen coming from each source, which means that less excess hydrogen is burned.

To compare the results obtained through different models, the original network was also optimized through a nonlinear mathematical programming model (MINLP). About solvers, the best solution was found with DICOPT, comparing with SBB and BARON. As a result, the operating cost is around 15% less, and 12.8 million savings were obtained compared to the HN-BASE CASE network. In the nonlinear model, it is possible to mix flows in the compressors, and this makes the investment cost less. The optimized network only required the installation of 1 new compressor and 6 new pipelines. Thus, the annualized capital cost is 0.211 million per year. This optimization result from the MINLP is called HN6-MINLP OPTIMIZED, and it is represented in Fig. 9.

Table 5 summarizes the obtained results. It is essential to highlight that other solvers were tested for the MINLP model, such as The Baron and SBB, but the best value achieved was using DICOPT. The solution obtained is an integer solution.

Fig. 8 Optimized network HN5-MINLP OPTIMIZED

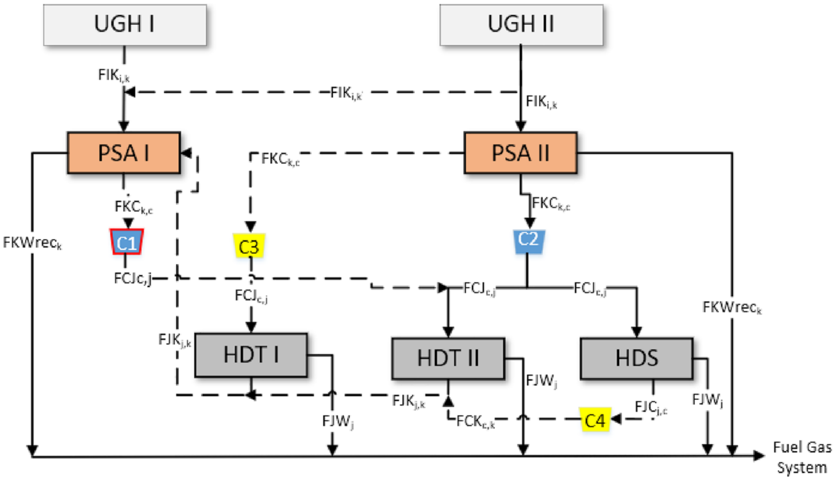

Fig. 9 Optimized network HN6-MINLP OPTIMIZED

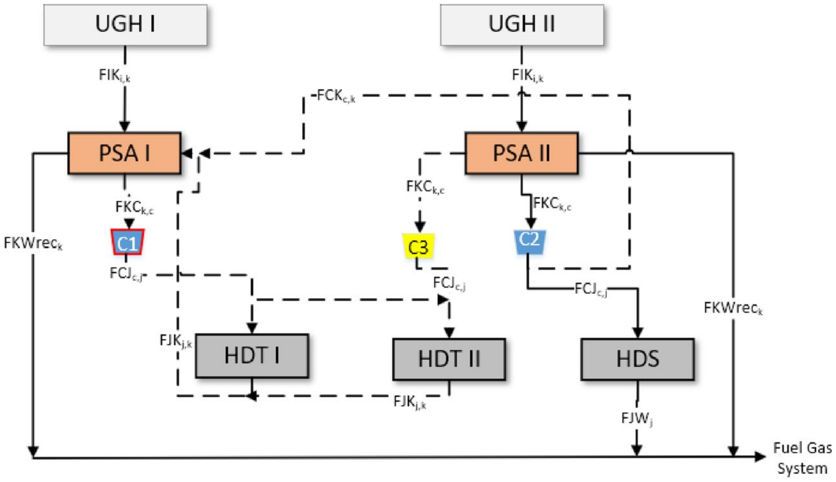

Table 5 Results of minimizing operating cost for example 2

	HN-BASE CASE	HN4-MILP OPTIMIZED	HN5-MILP OPTIMIZED	HN6-MINLP OPTIMIZED
	[$\times 10^6$ $/year]			
CH2I (Hydrogen)	72.896	54.639	54.919	57.911
CH2F (Fuel)	33.494	23.186	23.243	31.387
CH2C (Compressor)	0.076	0.068	0.069	0.074
CH2P (Purification)	1.145	0.922	0.920	1.228
Operating cost	**40.624**	**32.444**	**32.666**	**27.825**
CH2CN (New compressor)	–	0.388	0.277	0.179
CH2PN (New purification)	–	4.668	–	–
CH2PIPE (New pipeline)	–	0.892	0.059	0.032
Annualized capital cost	–	5.948	0.336	0.211

The results in [bold] are the most important values

Compared to the original network (HN-BASE CASE), the MILP result was reduced by 20.1% (HN4) and 19.6% (HN5). Through the MINLP formulation, the operating cost decreased by 31.5% (HN6), the highest value achieved. Comparing the models, the MINLP model reduced the operating cost by 14.8% from the result of the linear model. Besides, the investment cost is also lower (37% comparing HN5 and HN6). Optimization via MILP (HN5) guarantees significant savings of 7.958 million per year. However, in this case, the MINLP formulation proved to be the best option in terms of savings for the retrofit of the hydrogen network, even if it did not guarantee that the solution is the global minimum.

Conclusions

In this work, a MILP model was proposed to optimize hydrogen networks. In addition, a nonlinear model was also proposed to compare its results. Both models are based on superstructures that include sources, consumers, purification units, and compressors. The proposed models were validated using an existing adapted hydrogen network found in the literature and a real case from a Brazilian Refinery. The goal of minimizing operational cost has been achieved. Different restrictions were explored, as done in this article, for example, limiting investments and different designs were obtained.

The result obtained through the MILP model was satisfactory, with a 10% reduction in operating costs in example 1 and 19.6% in example 2. It is an optimization problem that is easier to solve and has proved to be an efficient way of solving along with initialization strategies.

The MINLP model also satisfies the needs of the retrofit case and has shown the best results, but the nonlinearity problems are more difficult to converge and requires initialization strategies to facilitate resolution. Although it did not guarantee the overall optimal, in example 2 it provided a lower operating cost than the optimal solution via MILP, and in example 1 the results were similar between MILP and MINLP. It is worth mentioning that the MINLP model uses a superstructure different from MILP, as the compressors are seen as a unit. The resolution time for nonlinear problems is also longer, which can be challenging when this type of mathematical programming is extended to the multi-scenario formulation necessary to capture uncertainties in a real industrial application.

Therefore, the linear formulation presented satisfactory results and has its advantages of use, but the MINLP formulation guaranteed lower operational cost combined with the lower cost of capital, besides providing more realistic designs. It is important to evaluate the use of formulations to ensure that one is working with a robust model capable of meeting the needs of each process.

References

Birjandi S, Reza M, Shahraki F, Birjandi MS, Nobandegani MS (2014) Application of global optimization strategies to refinery hydrogen network. Int J Hydrogen Energy 39(27):14503–14511. https://doi.org/10.1016/j.ijhydene.2014.07.047

Borges JL (2009) Diagrama de Fontes de Hidrogênio. Universidade Federal do Rio de Janeiro, Rio de Janeiro

Cruz FE (2010) Produção de Hidrogênio Em Refinarias de Petróleo: Avaliação Exergética e Custo de Produção. Escola Politécnica da Universidade de São Paulo, Paulo

El-Halwagi MM (2006) Process integration, 1st edn. Elsevier, Amsterdam

Figueiredo EAH (2013) Aplicação Do Diagrama de Fontes de Hidrogênio Em Refinarias de Petróleo. Universidade Federal do Rio de Janeiro, Rio de Janeiro

Gams (2020) GAMS–documentation. GAMS Development Corporation. https://www.gams.com/33/docs/gams.pdf. Accessed May 2020

Hallale N, Liu F (2001) Refinery hydrogen management for clean fuels production. Adv Environ Res 6(1):81–98

Jagannath A et al (2018) Retrofit design of hydrogen network in refineries: mathematical model and global optimization. Ind Eng Chem Res 57(14):4996–5023

Jia N (2010) Refinary hydrogen network optimization with improved hydroprocesso modelling. University of Manchester, Manchester

Kumar A, Gautami G, Khanam S (2010) Hydrogen distribution in the refinery using mathematical modeling. Energy 35(9):3763–3772. https://doi.org/10.1016/j.energy.2010.05.025

Liao Z, Wang J, Yang Y, Rong G (2010) Integrating purifiers in refinery hydrogen networks: a retrofit case study. J Clean Prod 18(3):233–241

Matijašević L, Petric M (2016) Integration of hydrogen systems in petroleum refinery. Chem Biochem Eng Quart J 30(3): 291–304. http://silverstripe.fkit.hr/cabeq/assets/Uploads/2-3.pdf

Petric M (2014) Integracija Sustava Vodika u Procesima Prerade Nafte. Sveučilište U Zagrebu Fakultet, Zagreb

Pinheiro SFM (2012) Gestão Da Rede de Hidrogénio Da Refinaria de Matosinhos. Instituto Superior de Engenharia do Porto, Porto

Silva PR, Aragão ME, Trierweiler JO, Trierweiler LF (2020) MILP for solving and initialization of MINLP problems applied to retrofitting and synthesis of hydrogen networks. Processes 8:1102