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# Grey-box modelling of an industrial hydrodesulphurization process

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## Abstract

This paper deals with the development of reduced models of a hydrodesulphurization plant oriented to computing the dynamic hydrogen consumption rates as a function of the plant load. This is part of a wider project oriented to the optimal management of the hydrogen network in a petrol refinery. The proposed models are of hybrid nature, combining physical-chemical principles with black box elements. The paper describes the structure of the models as well as the procedure of calibration and maintenance with real data from the process.

**Keywords**: Grey-box models, hydrodesulphurization, reduced order modeling, parameter estimation.

## 1. Introduction

Petrol refineries have undertaken profound changes in the last years due to several reasons. Economic pressure has forced to built additional plants were heavy products are converted into lighter and more valuable ones. On the other hand, environmental regulations oblige to commercialize cleaner products, which imply removing most of the sulphur carried on by the hydrocarbons. This operation is performed in several new plants, being the most important the hydrodesulphurization ones (HDS) that eliminate sulphur using hydrogen in the process. As a result, hydrogen is now a key utility in the daily functioning of a modern refinery.

A project with the Petronor refinery of the Repsol-YPF group has been undertaken in order to optimize the operation of the hydrogen supply and consumption network. Since hydrogen is an expensive and sometimes scarce resource, the aim is to adjust as much as possible production to consumption while minimizing purges to fuel gas, needed because even a brief lack of hydrogen will prove highly detrimental to the desulphurization catalyst.

Within the framework of this project, dynamic models of the hydrogen production and consumption units must be developed to be used as key elements in a decision support system managing the $H_2$ network that connects three refineries. Due to the huge size of the problem, and the scale it operates, detailed dynamical models of the units are not adequate. So, a reduced model for the dynamic prediction of hydrogen consumption

rate in a diesel hydrodesulphurization reactor is developed. Dynamic modelling is quite a difficult task, confirmed by industrial experience in this way, although static experimental, proprietary correlations have been extensively used for design and scheduling purposes.

In the paper, a grey-box modelling approach of a desulphurization plant has been considered. The main modelling problems are related to the number of process units in the plant and complexity of the reactions involved.

The grey-box model combines first principles – global mass balances– with "pseudo" kinetic parameters that are estimated on-line by means of a neural network to obtain a balanced equilibrium between numerical simplicity and accuracy. The model can be used then for prediction purposes as it capture the inherent behaviour of the system. Previous contributions to the grey-box modelling area (Georgieva, Meireles, Feyo d'Azevedo, 2003), (Laurent, Boyer, Gatina, 2000), (Chen, Bernard, Bastin, Angelov, 2000) have shown the feasibility of the proposed approach. More specifically, (Korsten and Hoffmann, 1996), (Tsamatsoulis and Papayannakos, 1998) have contributed to the specific field of HDS modelling.

The hydrogen consumption rate is computed depending on the main variables affecting the process: temperature, hydrogen partial pressure, residence time, catalyst activity, some flow set-points and feed composition. For the identification and validation of the model, experimental plant data where gathered covering a wide range in feed quality and operating conditions. The results achieved are accurate enough according to the purpose of the modelling task.

The paper is organised as follows: after the introduction, section 2 describes the specific HDS we have been working on and discuss the modelling problem from the perspective of its final use. Then section 3 explains the grey-box model structure and associated parameters. Finally section 4 gives details of the calibration procedure and presents some results obtained with real process data. The paper ends with some conclusions and references.

## 2. Process description

A schematic of the HDS plant is given in Fig.1., together with the associated instrumentation. The desulphurization reaction at the hydrogen consuming units takes place in catalytic reactors, (R1, R2) where a minimum ratio hydrogen/hydrocarbon must be ensured. The reactor is fed with a blend of fuels of different qualities. After being separated in flashes (D-2), distillation columns and membranes (Z1), hydrogen not reacted is partially recycled and partially burnt as fuel gas. Before entering the reactor, the feed is mixed with the recycled hydrogen stream and with a fresh hydrogen stream from the network piping. The hydrogen is partly solved in the hydrocarbon, being this fraction the only one active in the reactions. Most of the sulphur turns into hydrogen sulphide, which is removed by absorption on an amine solution.

The HDS is operated from a control room being the key loops of the process the temperature and pressure ones in the reactors and the control of the separation in the flash in order to obtain a given hydrogen purity in recirculation. Main decisions on the operation are linked to the flow to the fuel-gas network and the reactor temperature.

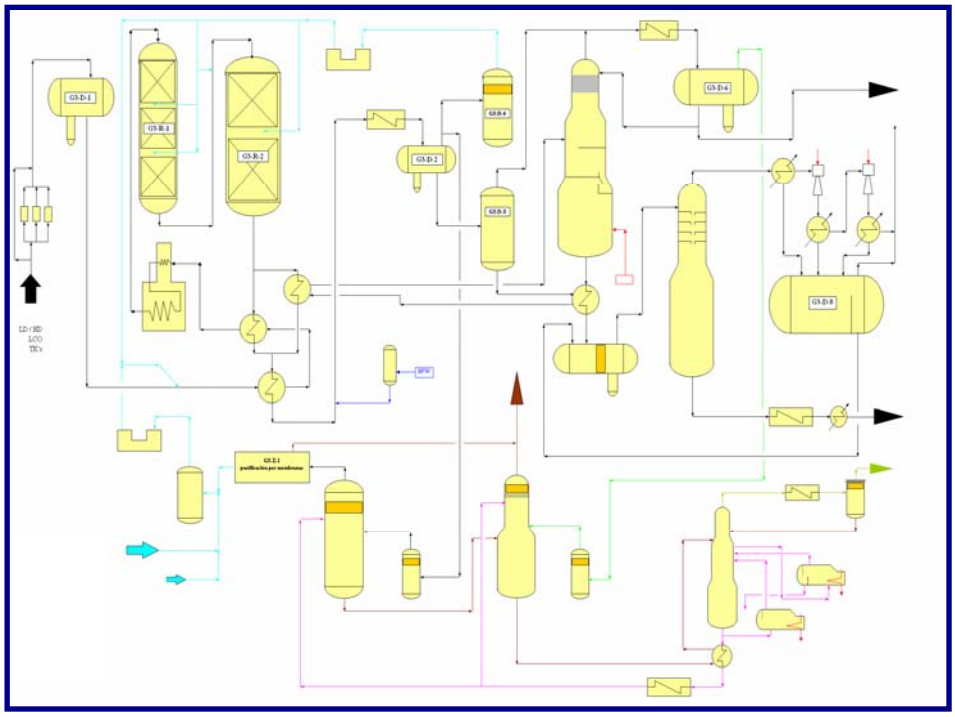

Fig1: HDS process schematic.

The process involves many units to perform its tasks, nevertheless, from the point of view of the intended use of the model, not all of them are relevant. Remembering that the aim is to obtain a dynamic model able to predict the hydrogen consumption, and the associated losses to the fuel-gas network, as a function of the hydrocarbon load, many of the units do not play a significant role, in particular those distillation columns placed on the right hand side of the diagram, devoted to separate final products, assuming that all $H_2$ is recovered in them. As a result only those units related to the hydrogen reaction and separation have been included in the model, basically reactors, flash chambers and membranes..

On the other hand, as the model must be integrated in a wider context for dynamic data reconciliation and optimization decisions, it must be as simple as possible in order to allow for fast computations, while retaining the main process dynamic characteristics. Nevertheless, a direct first-principles models of the process is too complex for this purpose: Most of the models reported in the literature only take into consideration the hydrodesulphurization reactions, but $H_2$ is also consumed in side reactions: hydrodenitrogenation, hydrodearomatization, hydrogenation of olefins, hydrocracking, etc. with unknown compositions and reaction rates. In the same way we can mention the wide range of compounds in the hydrocarbon feed to the reactor, the complex hydrodynamic in a multiphase reactor with trickle-bed flow, the calculation of accurate thermodynamic and transport properties for such complex mixtures, the different stages which take place in series to the reaction: gas-liquid and liquid-solid interphase mass and heat transfer, as well as the fact that usually the rate equations available do not

account for the competitive adsorption of other sulphur components, metals or hydrocarbons (Froment *et al.*, 1994), (Korsten and Hoffmann, 1996), (Cheng *et al.*, 2004). All these factors, and the high number of unknown parameters that must be estimated, make the approach impractical for the optimization aims.

Because of this, the grey-box modelling, combining aggregate global balances with black-box elements to avoid detailed and complex descriptions of intrinsic elements of the process has been adopted.

## 3. Grey-box model.

The proposed model for the estimation of the hydrogen consumption incorporates first principles models of the reactors, flash separation and membranes and a neural network for the estimation of some reaction rates.

Further, in order to simplify the model, the two reactors in series, which are distributed parameter systems, are considered as a single one postulating lumped models for the components in the liquid and gas phases. The components have been reduced to four: hydrogen ($H_2$), methane ($CH_4$), sulphur (S) and the remaining hydrocarbons (HC) using the criteria that these are the key ones from the point of view of hydrogen and grouping the complex and changing mix of hydrocarbons into a single pseudo-component. Global mass balances leads to:

$$\frac{dM}{dt} = W_{IN\_HC} + \sum_j W_{IN\_H2} - W_{OUT} - E$$

$$\frac{d(M \cdot C_{H2})}{dt} = \sum_j (W \cdot C_{H2})_{IN\_H2} - (W \cdot C_{H2})_{OUT} - r_{H2\_S} \cdot C_{H2} \cdot C_S \cdot M - r_{H2\_CH4} \cdot C_{H2} \cdot M - E_{H2}$$

$$\frac{d(M \cdot C_{CH4})}{dt} = \sum_j (W \cdot C_{CH4})_{IN} - (W \cdot C_{CH4})_{OUT} + r_{H2\_CH4} \cdot C_{H2} \cdot M + r_{CH4} \cdot M - E_{CH4}$$

$$\frac{d(M \cdot C_S)}{dt} = (W \cdot C_S)_{IN\_HC} - (W \cdot C_S)_{OUT} - a \cdot r_{H2\_S} \cdot C_{H2} \cdot C_S \cdot M$$

$$E = k(P - P_v(C_{H2}, C_{CH4}))$$

$$\frac{dM_G}{dt} = \sum_j W_{IN\_H2\_G} - W_{OUT\_G} + E$$

$$\frac{d(M_G \cdot C_{H2\_G})}{dt} = \sum_j (W \cdot C_{H2\_G})_{IN\_H2} - (W_{OUT\_G} \cdot C_{H2\_G}) + \mathrm{E_{H2}}$$

$$\frac{d(M_G \cdot C_{CH4\_G})}{dt} = \sum_j (W \cdot C_{CH4\_G})_{IN} - (W_{OUT\_G} \cdot C_{CH4\_G}) + \mathrm{E_{CH4}}$$

$$P(M_G, C_{H2\_G}, C_{CH4\_G})$$

$$W_{OUT\_G} = \mathrm{Re}\, g(P_{SP}, P)$$

where $M$ stands for the mass of liquid in the reactor and $C_i$ refers to the mass concentration of component $I$ in the liquid phase. In parallel, $M_G$ and $C_{i\_G}$ applied to the

mass of gas and composition, while *E* describes the flow of $H_2$ and $CH_4$ from the liquid to the gas phase due to pressure and temperature changes, which is assumed proportional to the differences between gas phase pressure and vapour pressure of these components. Pressure is regulated by a PID manipulating the outflow of gas, in fact, last equation in the previous model is a compressed form for a PID regulator..

In a flash unit the separation is assumed to be driven by:

$$W_{IN\_HC} = W_{OUT\_H2} + W_{OUT\_HC}$$
$$P \cdot y_{H2} = P^{o} \cdot x_{H2}; \quad P \cdot y_{CH4} = P^{o} \cdot x_{CH4}$$

And the membranes, in working and stand by states are described by:

$$F_{IN\_H2} = F_{OUT\_H2} + F_{RCHZ}$$
$$(F \cdot x_{H2})_{IN\_H2} = (F \cdot x_{H2})_{OUT\_H2} + (F \cdot x_{H2})_{RCHZ}$$
$$\frac{F_{RCHZ\_H2}}{F_{IN\_H2}} = f\_out \qquad \frac{n\_memb\_op}{n\_memb}$$
$$(x_{H2})_{OUT\_H2} = (-a \cdot f\_out + b) + (x_{H2})_{IN\_H2}$$

and

$$\frac{F_{OUT\_H2}}{F_{IN\_H2}} = 1$$
$$(x_{H2})_{OUT\_H2} = (x_{H2})_{IN\_H2}$$

The flash and membranes model are static ones, assuming that its dynamic is much faster that the one in the reactors.

The model incorporates four adjustable parameters, in particular the global reaction rates $r_{H2\_CH4}$, $r_{H2\_S}$, $r_{CH4}$, that are computed using a neural network (NN) having as inputs the main variables affecting the process: temperature, hydrogen partial pressure, residence time, catalyst activity and feed composition, according to the schematic of Fig. 2. The NN is a perceptron one incorporating three layers.

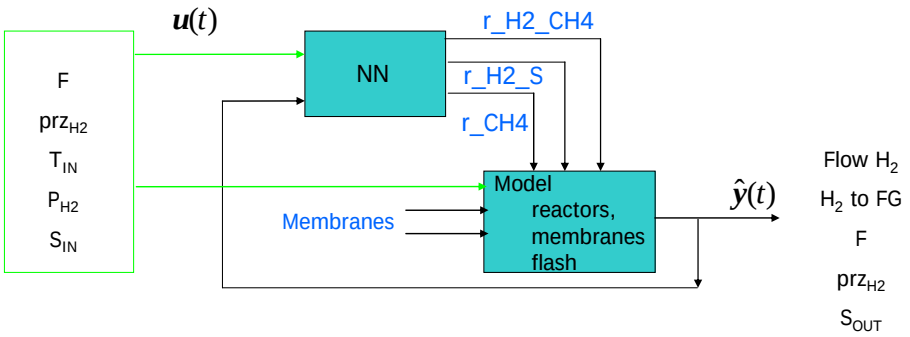


Fig.2 Grey-box HDS model

## 4. Model calibration and experimental results.

The model has been calibrated using and optimization procedure that adjusted the NN weights in order to fit the model output with experimental data. For the calibration, a sequential optimization approach was followed, simulating the model in the

EcosimPro® environment and using a NLP library (NAG®). Results of the calibration are given in Figs. 3 and 4.

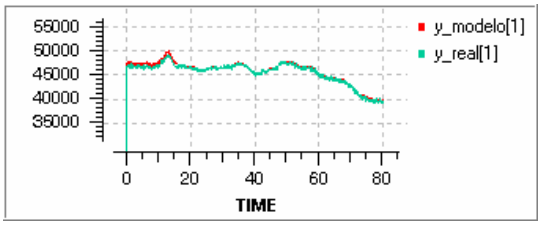


Fig. 3. Outlet hydrogen to fuel gas, comparison between simulated and experimental data.

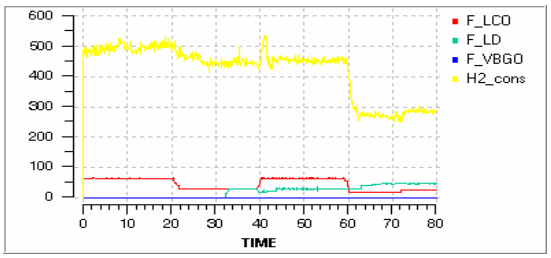


Fig. 4. Flow inlets of hydrocarbon streams treated and hydrogen consumption rate.

## 5. Conclusions

A simplified dynamic model of a HDS has been developed combining fundamental principles and a neural network for inferring H2 consumption rates and Fuel gas losses.

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