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Simplified Modelling and Validation of an Industrial Diesel Hydrodesulfurization Plant

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Abstract: A dynamic reduced model of an industrial diesel hydrodesulfurization plant has been developed and validated against plant data. Its purpose is the prediction of the rate of hydrogen consumption, as well as some other critical variables, as a function of the hydrocarbon feed, so as to be integrated in a decision support system aimed at the operation optimization in real time of the refinery hydrogen network. A model which combines first physical-chemical principles with black box elements is proposed. Model structure and calibration procedure are described, and validation results are presented.

Keywords: hydrodesulfurization, grey-box modelling, parameter estimation, decision support system, process optimization, simulation.

1. INTRODUCTION

Hydrogen is an expensive utility used in many refinery operations that is gaining increasing importance in the economic balance of the refinery. Scenarios where H_2 supply shortage can be a bottleneck in oil processing rates can sometimes occur. In this context, a project oriented towards the optimal management of the real-time operation of a refinery H_2 network is been undertaken in collaboration with the Petronor refinery of the Repsol YPF group (Sarabia et al., 2009), in order to minimize H_2 production by means of fuel gas loses minimization and a better H_2 redistribution.

Within the framework of this project, dynamic models of the hydrogen production and consumption plants must be developed to be used in a decision support system (DSS) managing the H_2 network. One of the most important types of hydrogen consumer plants are hydrodesulfurization units, whose purpose is to remove sulfur and other contaminants from a hydrocarbon stream. Due to the huge size of the problem and the scale it operates, detailed dynamic models of the units are not adequate. So, a simplified model for the dynamic prediction of the hydrogen consumption rate in a diesel hydrodesulfurization reactor is developed with the purpose of computing predictions of the H_2 consumption rate as a function of the hydrocarbon load, integrated in a DSS for the hydrogen redistribution at the network level.

Furthermore, the severity of the operation (mainly reactor temperature) is manipulated by the operator so as to achieve the desired level of desulfurization, being sulfur concentration in the hydrocarbon outlet stream the target of the process. This severity also influences the H_2 consumption rate, as well as contributes to catalyst deactivation, so it could be very useful to be able to operate the reactor at a severity as low as possible, as it would benefit H_2 consumption requirement and also catalyst active life.

Mechanistic mathematical models have mostly been reported to simulate the performance of pilot-plant reactors (Chowdhury et al., 2002), (Froment et al., 1994), (Korsten and Hoffmann, 1996), (Tsamatsoulis and Papayannakos, 1998), being static models. Some authors make an effort to develop a rigorous mathematical model accounting for all the major reactions and simulating the performance of both pilot and industrial scale reactors (Bhaskar et al., 2004), (Bellos, Papayannakos et al., 2005), but only a few are dynamic models (Mederos, Ancheyta et al., 2006).

Regardless of being the reactor the core of the process, a plantwide model must be considered because the way the reactor must be conducted is also the result of many other decisions and constraints on different elements of the plant. Nevertheless, and to the best of our knowledge, a plant-wide reduced model of a diesel hydrodesulfurization process, with the corresponding degrees of freedom and measured variables availability, have not been reported in the literature. Likewise, published industrial tests are limited to short time periods, not considering long periods of time such as months.

In order to obtain a balanced equilibrium between numerical simplicity and accuracy, a grey-box model of the diesel desulfurization plant has been proposed. The grey-box model combines first principles with "pseudo" kinetic parameters that are estimated by means of a neural network. The model can then be used for prediction purposes as it captures the inherent behaviour of the system. Previous contributions to
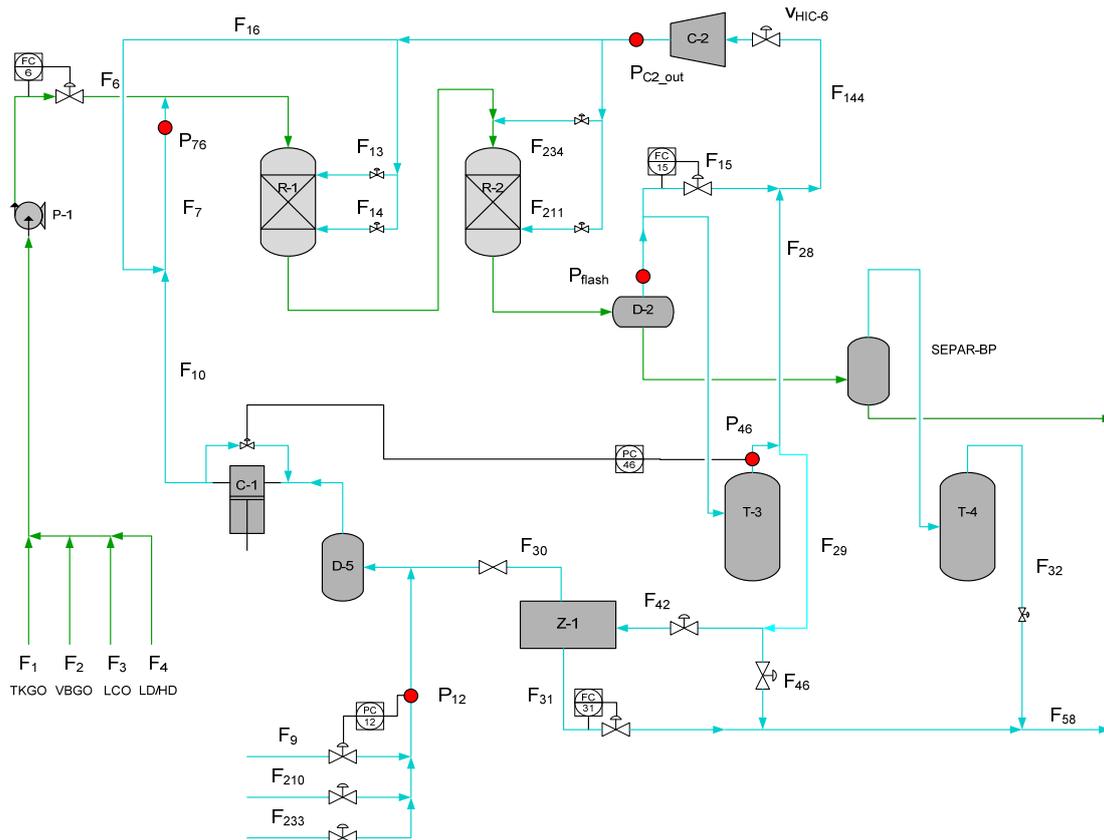
Fig. 1. Hydrodesulfurization plant flow diagram.

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.

The paper is organized as follows: After the introduction, section 2 describes briefly the hydrodesulfurization plant and section 3 provides the basic elements of the model. Section 4 deals with its general structure, simulation and calibration, while validation results are presented in section 5.

2. PROCESS DESCRIPTION

A process flow diagram of a HDS plant is shown in Fig.1. The desulfurization reactions take place in fixed bed catalytic reactors (R1, R2) where a minimum ratio H_2/hydrocarbon must be ensured. The reactors are fed with a blend of fuels of different qualities (F_1, F_2, F_3, F_4). Before entering the reactor, the feed is mixed with the recycled H_2 stream and with a make-up H_2 stream from the network. After being separated in a high pressure separation drum (D2), non reacted H_2 is partially recycled (F_{144}), partially purified and recycled in membranes Z1 (F_{30}), and partially burnt as fuel gas (F_{31}, F_{46}). Reacted sulfur turns into H_2S, which is removed by absorption on an amine solution (T3, T4). Downstream of the high pressure separation drum D2, several distillation columns at lower pressure enable the complete separation of light gases from the desulfurized diesel stream. The stream of light gases from the low pressure separation processes is directed to fuel gas (F_{32}), since hydrogen purity is not high enough for making profitable its recovery.

3. MODEL

According to its purpose, only those units relevant for H_2 consumption are considered in the model. These are the reactors, the high-pressure separator D2, the membranes, and, lumped into a single element, all of the low-pressure separation operations downstream of D2. All these units, as well as the material and momentum balances relating the flow between them, are described below. As temperature is controlled at the reactor inlet, between beds of the catalyst with quenching H_2, and also before the high pressure separator, energy balances have not been considered because they do not influence H_2 consumption and separation remarkably. Considering energy balances can provide an additional idea of the extent of the different reactions that are taking place, but introduces more complexity due to more unknown parameters (reaction and specific heats), so imposing the temperature as a manipulated boundary is close enough to reality.

3.1 Pseudocomponents

The thousands of components actually present in the hydrocarbon feed have been reduced to four named: hydrogen H_2, methane CH_4 (representing the rest of light components different from H_2 in gas streams), sulfur S, and the remaining hydrocarbons HC, with the criterion that these are the key components from the point of view of H_2 consumption and lumping the complex and changing mix of hydrocarbons into a single one.

3.2 Material balances

Material balances for all plant nodes concerning gas streams are considered: total flow rate balance (1), hydrogen flow rate balance (2), and total mass flow rate balance due to the different molecular weight of the light gases that go with hydrogen depending on the particular stream (3).

$$\sum_{i}^{IN} F_i = \sum_{j}^{OUT} F_j \qquad \forall\ node \tag{1}$$

$$\sum_{i}^{IN} (F_i \cdot y_i^{H2}) = y_j^{H2} \cdot \sum_{j}^{OUT} F_j \qquad \forall\ node \tag{2}$$

$$\sum_{i}^{IN} w_i \cdot (F_i / 22.415) = w_j \cdot \sum_{j}^{OUT} (F_j / 22.415) \qquad \forall\ node \tag{3}$$

$$1 = y_i^{H2} + y_i^{CH4} \qquad \forall\ stream\ i \tag{4}$$

$$w_i = a_i + b_i \cdot y_i^{H2} \qquad \forall i \quad after\ separation \tag{5}$$

where F_i refers to the volume flow rate of stream i in normal conditions (Nm^3/h), y_i^{H2} to the hydrogen purity of stream i (%1 mol), and w_i to the molecular weight of stream i (kg/kmol). Linear empirical correlations as (5) relating H$_2$ purity and gas stream molecular weight are used for certain streams after undergoing a separation process, so as to take into account the different composition of impurities mainly due to the pressure of the separation process. All the flowmeters provide flow measurements in normal conditions, so ideal gas equation of state can be considered.

3.3 Momentum balances

Because of its critical role, momentum balance equations must be used to describe the equilibrium of flow and pressures achieved in the closed loop formed between the joint of the liquid and gas feeds upstream the reactor inlet, the reactor, downstream the reactor up to the high-pressure separator, and the line of the high pressure recycle stream driven by the centrifugal compressor C-2. In the remaining of the plant, the model do not come down to this detail. Besides, there are valve openings without signal in the SCADA system. As the rest of the input boundaries concerning flows are linked to flow controllers, infeasibilities will be avoided in predictions by guaranteeing certain experimental relationships between the flows. For example, the inlet and outlet flows to the membranes unit must be within a certain range, obtained from historical experimental data.

The centrifugal compressor C-2 is described by means of the polytropic compression model (6), (7) and the manufacturer characteristic curve (8).

$$H_P = Z_{av} \cdot R \cdot T_S \cdot \left[\left(\frac{P_D}{P_S} \right)^{\frac{n-1}{n}} - 1 \right] / \left(w \cdot \left(\frac{n-1}{n} \right) \right) \tag{6}$$

$$n = (\ln(P_S / P_D)) / (\ln((P_S / P_D)/(T_S / T_D))) \tag{7}$$

$$H_P = a + b \cdot F_S + c \cdot F_S^2 + d \cdot F_S^3 \tag{8}$$

where S, D refers to suction and discharge of the compressor; H_P is the polytropic head (m), P the pressure (Pa), T the temperature (K), R the gas constant, Z the generalized compressibility factor, and F_S the volume flow rate at suction conditions. The polytropic coefficient n can be obtained from measured data (7) and be supposed constant as the polytropic head is not quite sensitive to it, or else be linearly correlated with H$_2$ purity.

Pressure drop in the reactor catalytic beds is described by the Ergun equation (10) for one phase and by the Larkins equation (11) for the two-phase flow, with Chisholm correlation. Pressure drop in lines is obtained by the approximate (9).

$$\Delta P_{(G/L)} = f_T \cdot (L_e / D) \cdot \left(u_S^2 / (2 \cdot g) \right) \tag{9}$$

$$\frac{\Delta P_{(G/L)}}{z_R} = \frac{1 - \varepsilon}{\varepsilon^3} \cdot \left[a + \frac{b \cdot (1 - \varepsilon) \cdot \mu}{d_P \cdot \rho \cdot u_S} \right] \cdot \rho \cdot \frac{u_S^2}{d_P} \tag{10}$$

$$\log(\Delta P_{2f} / (\Delta P_G + \Delta P_L)) = 0.416 / ((\log(\Delta P_L / \Delta P_G)^{1/2})^2 + 0.666) \tag{11}$$

where ΔP_L and ΔP_G refers to pressure drop due to one phase flow of liquid or gas, and ΔP_{2f} to pressure drop due to two phase flow. L_e (m) is the pipe equivalent length, D (m) the diameter, u_S (m/s) the fluid superficial velocity, f_T the friction Fanning factor, and g the gravity constant. The fixed bed reactor is characterized by the void fraction ε ( ), the length z_R (m), and the equivalent particle diameter d_P (m). The fluid density and viscosity are ρ (kg/m^3) and μ (kg m^{-1}s^{-1}).

3.4 Reactor

It is first considered the model describing the mixing of H$_2$ and hydrocarbon feed in a two phase equilibrium. The gas-liquid equilibrium is described according to Riazi (2007). A transport delay is considered between the hydrocarbon feed and gas mixing and the reactor inlet.

$$F_6 + F_{Gin} = L_{Rin} + V_{Rin} \tag{12}$$

$$F_6 x_6^j + F_{Gin} y_{Gin}^j = L_{Rin} x_{Rin}^j + V_{Rin} y_{Rin}^j, j = H_2, CH_4 \tag{13}$$

$$F_6 \cdot x_6^j + F_{Gin} \cdot y_{Gin}^j = L_{Rin} \cdot x_{Rin}^j \qquad j = S \tag{14}$$

$$x_{Rin}^j = \frac{P \cdot \phi_V^j}{\gamma^j \cdot f_L^j} \cdot y_{Rin}^j \qquad j = H_2, CH_4 \tag{15}$$

where Rin refers to reactor inlet, F_6 and F_{Gin} are the mixed hydrocarbon and gas flows (kmol/h), L and V (kmol/h) the liquid and gas flows entering the reactor in equilibrium, and x^j and y^j (%1 mol) the corresponding compositions of component j in the liquid and gas phases.

Regarding the reactor, a full mechanistic model is too complex for the purpose intended of optimization in real time, as well as the lack of available on-line measurements. The complexity is due to the high number of reactions, where H$_2$ is not only consumed in hydrodesulfurization reactions, but also in side reactions: hydrodenitrogenation, hydrodearomatization, hydrocracking, hydrogenation of olefins, etc. as well as to 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; and the fact that usually the rate equations available do not account for the competitive adsorption of other sulfur components, metals or hydrocarbons. Moreover, consideration of these phenomena will increase significantly the number of unknown parameters that should be estimated.

So a grey-box modelling approach, combining the basic global balances with black-box elements to avoid detailed and complex descriptions of intrinsic elements of the process has been adopted. In particular, reactions considered are the removal of sulfur, the consumption of H_2 due to desulfurization, the consumption of H_2 in side reactions, and the generation of light gases. The hydrodesulfurization reaction is modelled as first order with respect to sulfur, and all of the three reactions of zero order with respect to H_2 assuming it is present in sufficient excess in the liquid phase:

$$v_L \cdot \frac{d(c_{Rout}{}^S)}{dt} = L_{Rin} \cdot x_{Rin}{}^S - L_{Rout} \cdot x_{Rout}{}^S - k_S{}^r c_{Rout}{}^S W_{cat} \quad (16)$$

$$v_L \cdot \frac{d(c_{Rout}{}^{H2})}{dt} = L_{Rin} \cdot x_{Rin}{}^{H2} - L_{Rout} \cdot x_{Rout}{}^{H2}$$
$$- \alpha_{H2-S} \cdot k_S{}^r \cdot c_{Rout}{}^S \cdot W_{cat} - k_{H2}{}^r \cdot W_{cat} \quad (17)$$
$$+ k_{H2}{}^{TM} \cdot (y_{Rout}{}^{H2} - y_{Rout}{}^{H2\ eq})$$

$$v_L \cdot \frac{d(c_{Rout}{}^{CH4})}{dt} = L_{Rin} \cdot x_{Rin}{}^{CH4} - L_{Rout} \cdot x_{Rout}{}^{CH4}$$
$$+ k_{lig}{}^r \cdot W_{cat} - k_{CH4}{}^{TM} \cdot (y_{Rout}{}^{CH4\ eq} - y_{Rout}{}^{CH4}) \quad (18)$$

where Rin and $Rout$ refers to reactor inlet and outlet, v_L (m^3) is the liquid holdup in the reactor, L (kmol/h) is the flow of the liquid phase where the reactions take place, c^j (kmol/m^3) is the concentration of component j in the liquid phase, $k_j{}^{TM}$ the mass transfer coefficient between gas and liquid for component j, W_{cat} (kg) the active mass of catalyst –which will decrease in time–, and α_{H2-S} the stoichiometric coefficient relating H_2 consumed in sulfur removal reactions, for which a constant value of 1.5 is supposed. A constant molecular weight w^{HC} has been supposed for HC. The mass transfer coefficients $k_j{}^{TM}$ are assumed high enough so that phases can be considered in equilibrium.

No global mass accumulation is considered. The three kinetic parameters $k_{H2}{}^r$, $k_S{}^r$, $k_{lig}{}^r$ are obtained from a neural network (NN) as a function of the main variables affecting the process: reactor temperature, H_2 partial pressure, and type of hydrocarbon fed (diesel from straight run F_4, light cyclic oil from FCC unit F_3, diesel from visbreaker unit F_2, tank diesel F_1), being the proportions of each flow with respect to the total flow the regressors for the NN. It is known from experience that it is the type of hydrocarbon fed the factor that influence the most the H_2 consumption in the reactor, much more than the quality of the crude oil being processed. Other equations in the reactor refer to the phase equilibria and mass transfer between the gas and the liquid phase:

$$V_{Rin} \cdot y_{Rin}{}^j - V_{Rout} \cdot y_{Rout}{}^j =$$
$$k_j{}^{TM} \cdot (y_{Rout}{}^j - y_{Rout}{}^{j\ eq}), \quad j = H_2, CH_4 \quad (19)$$

$$x_{Rout}{}^j = \frac{P \cdot \phi_V{}^j}{\gamma^j \cdot f_L{}^j} \cdot y_{Rout}{}^{j\ eq} \quad j = H_2, CH_4 \quad (20)$$

3.5 High-pressure separator

It is modelled according to the corresponding mass balances to the gas and liquid phases, and phase equilibrium relationships.

$$\frac{d}{dt}\left(\frac{P_F \cdot v_{VF}}{R \cdot T_F}\right) = \frac{v_{VF}}{R \cdot T_F} \cdot \frac{d}{dt}(P_F) = V_{Rout} + V_V - V_F \quad (21)$$

$$\frac{v_{VF}}{R \cdot T_F} \cdot \frac{d}{dt}(P_F \cdot y_F{}^j) = V_{Rout} \cdot y_{Rout}{}^j$$
$$+ V_V \cdot y_F{}^{j\ eq} - V_F \cdot y_F{}^j \quad j = H_2 \quad (22)$$

$$x_F{}^j = \frac{P_F \cdot \phi_V{}^j}{\gamma^j \cdot f_L{}^j} \cdot y_F{}^{j\ eq} \quad j = H_2, CH_4 \quad (23)$$

$$V_V \cdot y_V{}^j = k_{MT}{}^j \cdot (y_F{}^{j\ eq} - y_F{}^j) \quad j = H_2, CH_4 \quad (24)$$

$$v_{LF} \cdot \rho_L \cdot \frac{d}{dt}(x_F{}^j / w_{LF}) = \frac{\rho_L \cdot F_{Rout}}{w_{Rout}} \cdot x_{Rout}{}^j$$
$$- \frac{\rho_V \cdot F_V}{w_V} \cdot y_F{}^{j\ eq} - \frac{\rho_L \cdot F_{LF}}{w_{LF}} \cdot x_F{}^j, \quad j = H_2, CH_4, S \quad (25)$$

$$F_{LF} = F_{Rout} - F_V, \quad v_{LF} = cte \quad (26)$$

where F refers to the high pressure separator, v_{VF} and v_{LF} (m^3) are the volumes of the gas and liquid phases, V_V (kmol/h) is the flow of gas that undergoes phase change due to forcing function, V_F (kmol/h) the flow of gas that constitutes the drum outlet stream, $k_{MT}{}^j$ (kmol/h) the mass transfer coefficient, F (m^3/h) volume flows, and w_i (kg/kmol). All the liquid densities ρ_L (kg/m^3) are supposed equal; the level of the liquid phase is controlled (26) and F_V (m^3/h) is the volume of the liquid phase corresponding to V_V (kmol/h).

3.6 Membranes

Disregarding mass accumulation, the membranes model can be considered just like another node in the network, with material balances corresponding to (1), (2), (3), (4), and an extra prediction equation (27) obtained by a linear regression of experimental data. So, H_2 purity of the permeate stream is obtained as a function of the H_2 purity in the inlet stream and the ratio of the inlet flow purged to fuel gas.

$$\hat{y}_{PERMT}{}^{H2} = f((F_{PURG}/F_{IN}), \hat{y}_{IN}{}^{H2}) \quad (27)$$

3.7 Low pressure separations

As a result of the low pressure separation processes, the liquid stream from the high pressure separator splits off into a liquid stream containing all the S and HC, and a gas stream containing all the H_2 and CH_4 (light gases). The model also includes a transport delay and two first order lags in series.

$$L_{LF} = F_{SHC} + (F_{BP} / 22.415) \qquad (28)$$

$$(F_{BP} / 22.415) \cdot y_{BP}{}^{H2} = L_{LF} \cdot x_F{}^{H2} \qquad (29)$$

$$(F_{BP} / 22.415) = L_{LF} \cdot x_F{}^{H2} + L_{LF} \cdot x_F{}^{CH4} \qquad (30)$$

$$x_{SHC}{}^{j} = 0 \qquad j = H_2, CH_4 \qquad (31)$$

$$F_{SHC} \cdot x_{SHC}{}^{S} = L_{LF} \cdot x_F{}^{S} \qquad (32)$$

where F_{BP} (m^3/h) refers to the stream composed by all the H$_2$ and light gases coming from the low pressure separation processes and going to fuel gas; that is, F_{32} (Nm^3/h) in Fig 1; and F_{SHC} (kmol/h) refers to the outlet liquid stream.

4. MODEL CALIBRATION

The DAE model comprises 13 differential equations and a total of 492 equations, including 2 nonlinear algebraic loops. Some of the state variables are pressures or correspond to a flow controler with negligible dynamic effects, just with the purpose of numerical decoupling. The model was simulated in the EcosimPro® environment, which uses the DASSL algorithm for integration. The acceleration factor of the model execution speed with respect to real time is about 15000, with an Intel® Core(TM)2 CPU @ 1.86GHz processor, 1.98GB RAM. A sequential approach has been followed for parameter estimation.

First, assuming that the dynamic in the establishment of flows and pressures is negligible compared to the dynamic of compositions, those parameters related to momentum balances have been estimated independently of the rest of the model, since enough measurements of flows and pressures are available. In particular, equivalent lengths of the pipes upstream and downstream the reactor; equivalent length of the recycle pipe; and particle diameter and void fraction of the catalyst bed. The correlation for H$_2$ purity in the permeate stream in membranes was also estimated at this stage.

Secondly, the static inverse problem was solved fixing as inputs the following measured output variables of the system: H$_2$ purity of the recycle stream from the high pressure separator, sulfur concentration of the desulfurized hydrocarbon stream and flow rate of the H$_2$ make-up. In this way, the three kinetic coefficients of the reaction rates can be obtained: $k_S{}^r$, $k_{H2}{}^r$, $k_{lig}{}^r$. Three independent neural networks are then trained in Matlab® with the toolbox NNSYSID 2.0 (Norgaard, 2000). The best results are achieved with recursive NOE models of order one, with architectures of 3 hyperbolic tangent neurons in the hidden layer and 1 linear neuron in the output layer. This enables a first approximate value of the NN parameters.

Finally, the whole set of unknown parameters is estimated, including those directly related to dynamic effects: volumes concerned with transport delays, liquid phase volume in the reactor and in the high pressure separation drum. This is solved in EcosimPro® using a SQP NAG® routine as solver. Large series of historical data, without experimental design, expanding over a month have been used. In this way, sensitivities with respect to dynamic parameters are low due to large time scales compared to sensitivities with respect to parameters which influence the gains of the process. The general structure of the model and the calibration procedure is shown in Fig.2.
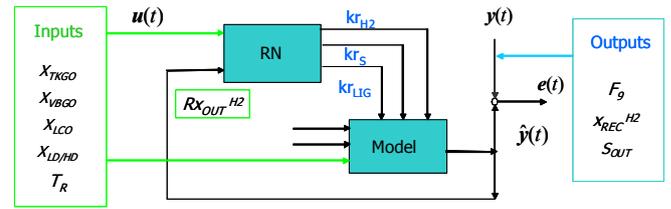
Fig. 2. Structure for dynamic parameter estimation.

5. MODEL VALIDATION

The following figures correspond to model validation for one month of operation, with blue representing model output and green experimental data. For confidentiality reasons, all the variables appear in % of a certain scale.
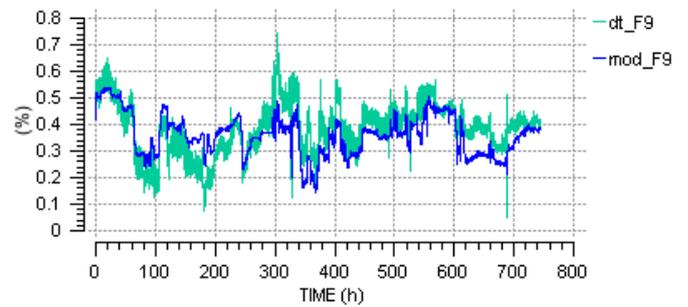
Fig. 3. Make-up H$_2$ from low purity pipe.
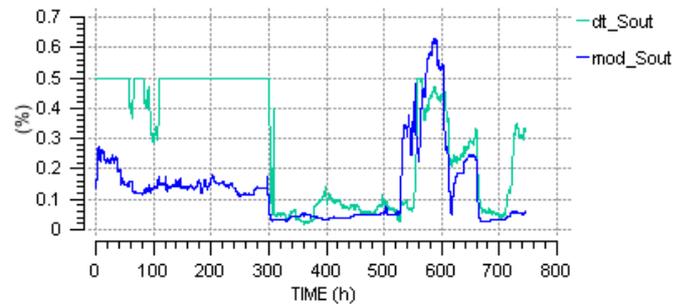
Fig. 4. Sulfur concentration in diesel desulfurized stream (analyser not in operation for 0-300 h).
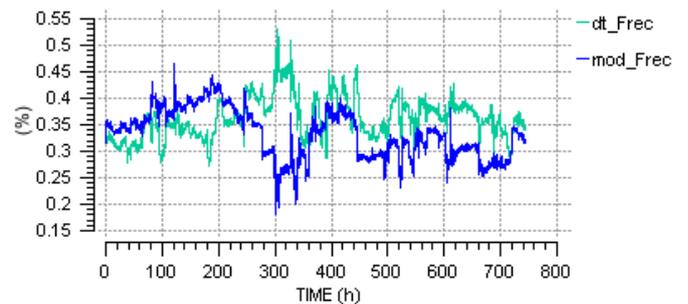
Fig. 5. Flow of the recycle stream from the high pressure separator.
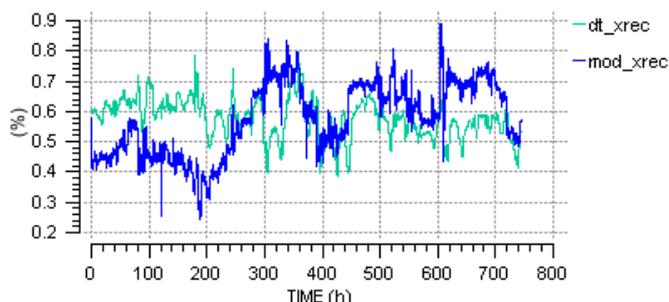
Fig. 6. H_2 purity of the recycle stream from the high pressure separator.

The most interesting output of the model, the flow rate of H_2 make-up, is estimated with less than 10% error, while good results are also obtained for the sulfur concentration in the desulfurized diesel stream. It should be noticed that they have been obtained without a good knowledge of the feedstock sulfur composition and make-up H_2 purity, so that perfect results can never be expected. Similar results have been obtained for other periods of operation.

6. CONCLUSIONS

A dynamic simplified model of a diesel HDS plant has been validated against real data. In spite of the uncertainty in some periods, results are good enough so as to validate the use of this kind of models in a decision support tool.

Despite of the simplicity of the model, predictions for H_2 consumption rate are found to agree well with the experimental data in the range of operating conditions studied, although predictions for sulfur concentration are less accurate. Further work is being done so as to refine some of the hypothesis now considered. In particular, the H_2 purity of the low purity make-up will not be constant and the model of material balances for the whole H_2 network must be included in order to better estimate its value. Moreover, an observer-based estimator will be incorporated to improve the knowledge of another important unknown inlet, the sulfur concentration of the hydrocarbon feed. The assumption of zero-order kinetics for H_2 will be as well reviewed.

Although further improvements should be made before the model can be embedded in a decision support tool, two potencial uses of the model are now possible. The first one is the prediction of the H_2 consumption rate as a function of the hydrocarbon load, so as to take decisions on the rates of production in the H_2 production plants and on the H_2 redistribution at the network level. The second one is the internal plant operation optimization, in particular of the degree of severity in the operation of the reactor (temperature) so as to fulfill the specification of desulfurization being as close as possible to the limit in the most efficient way. This is particularly important, because high temperatures cause an increase in carbon deposition in the catalyst, with the subsequent and undesirable decrease in catalyst activity.

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