

## Dynamic simulation applied to refinery hydrogen networks

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### Abstract

*This study analyses the usefulness of process network dynamics simulation for decision-making in refinery hydrogen networks. A theoretical hydrogen network of three desulphurisation plants is modelled, and three case scenarios discussed: baseline, high demand, and low demand.*

*Discussion focuses on how the information from the simulation is interpreted and its usefulness for debottlenecking, scheduling and what-if analysis. Stress is put on dynamics of the system and their consequences in process operation throughout the network. Hydrogen purity is highlighted as the most affected variable, and discussed its network wide effect. In addition, the responses of inflows, outflows and headers are analysed.*

*Although the model used is a simplified representation of the actual processes, the simulation analysis showed potential as decision-making support not provided with steady state models. Further researches based on real case-studies should be conducted to better conclude on the efficient usage of simulation in aiding refinery hydrogen networks operational decisions.*

**Keywords:** network simulation, process dynamics, decision-making.

## 1 INTRODUCTION

Hydrogen (H<sub>2</sub>) is an essential utility in refineries, due to its use as reactant in desulphurisation process

units. Furthermore, environmental regulations limit sulphur content in fuels forcing refineries to produce low sulphur fuels [2, 5, 11-12].

Although less than 10% of the time process units are under transition states, most of the operational deviations, including process safety issues occur then [3]. Hence, simulation of transitions is of key importance in process networks in general and H<sub>2</sub> networks in particular. Interest in the study of transient conditions could minimise the overlooking of process safety. It could lead to unexpected scheduling bottlenecks, for example by delaying on specification products. Other negative effects due to variable H<sub>2</sub> purity could be: high purge rates, reduced catalyst lifecycle and increased rotating machineries malfunction. Simulation can be used for analysis of scenarios, supporting decisions at different levels of operation, aiding in the decision-making process. In fact, increased focus on dynamic modelling and simulation of transition states is seen [1-3, 15]. For instance, in scheduling, process debottlenecking, what-if analysis, flowsheet design, being most of them simulations combined with optimisation [1, 3, 5-8, 10-11, 14-16].

Refinery H<sub>2</sub> networks main components are: gas headers (e.g.: high purity header – HPH -, low purity header – LPH - and fuel gas header – FGH -), hydrotreating plants and their components (e.g.: hydrodesulphurisation plant – HDS -), and H<sub>2</sub> source (e.g.: typically a steam reforming unit). In Figure 1 the arrangement of the network considered in this work is shown. Basically, the network has a H<sub>2</sub> source that serves the consumer plants. However, H<sub>2</sub> should be well in excess to minimise catalyst early decay and suffice compressors safe operation region.

Therefore, reactors outflows are recycled through recycle compressors and consumed gas is fed to comply with units' pressure control. A typical desulphurisation plant is shown in Figure 2.

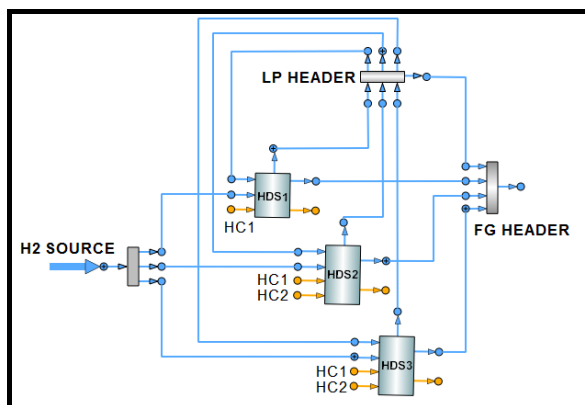


Figure 1: Network topology.

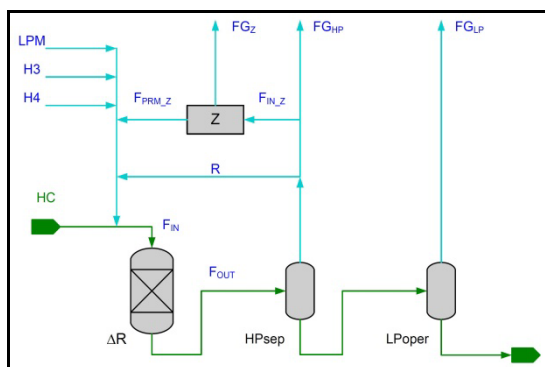


Figure 2: Schematic of a representative hydrotreating unit [5].

This work aims at studying the usefulness of simulation for decision support of refinery hydrogen (H<sub>2</sub>) networks during transition states incorporating simplified process dynamics. This is approached through studying three case scenarios of a representative theoretical network with different process condition transitions. Then discussing which are the main variables and how are they affected. Additionally, the main limitations of this methodology are pointed out, as well as some ideas of future research on this topic.

## 2 METHODOLOGY

### 2.1 NETWORK TOPOLOGY

A hypothetical network flowsheet was modelled (see Figure 1), comprising the components listed in Table 1. These components were modelled using first principles and specific mass and chemical equations

where applicable (i.e.: reactors and separation drums).

Table 1: Network components modelled. \*Components coded within each HDS. \*\*Only in HDS3.

#	Component
1	H <sub>2</sub> source (HP)
1	HP make-up header (HPMU)
1	LPH (Low Purity Header)
1	FGH (Fuel Gas Header)
3	HDS1/2/3
3	Reactor (R1)*
3	HP drum (SHP)*
3	LP drum (SLP)*
3	Amine column (ACL)*
3	Recycle compressor (RC)*
3	Make-up compressor (C MU)*
1	H <sub>2</sub> purification membrane (PERM)**

Flow diagrams of the HDSs modelled are shown in Figure 3.

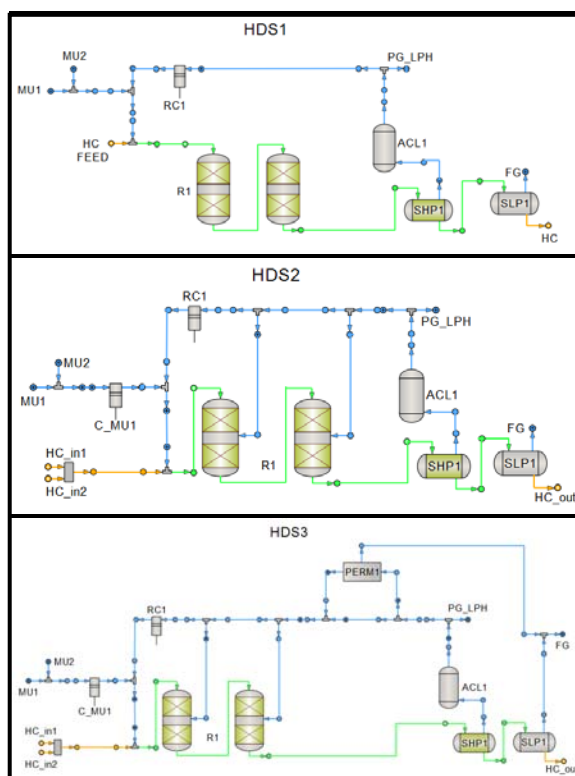


Figure 3: Flow diagram of HDSs 1-3.

### 2.2 MATHEMATICAL MODEL

Equations used are basically mass and gaseous component balances. In fact, both represented with the general form shown in equations 1-2, meaning that input equals output (except in reactors).

$$\Sigma F_{IN} = \Sigma F_{OUT} \quad (1)$$

$$\Sigma(F_{IN} \times y[H_2]_{IN}) = \Sigma(F_{OUT} \times y[H_2]_{OUT}) \quad (2)$$

Where: F is the volumetric flow (IN / OUT of the system), y[H<sub>2</sub>] is the molar fraction of H<sub>2</sub> (IN / OUT of the system)

In reactors, H<sub>2</sub> consumption (H<sub>2CON</sub>) and LIG generation (LIG<sub>GEN</sub>) are calculated proportional to HC (see equations 3-4, where: k<sub>LIGHC</sub> and k<sub>H2HC</sub> are the first order reaction constants). In addition, four terms were considered to account for H<sub>2</sub> consumption and LIG generation with their corresponding effect on mass balances, see equations 5-8. Where: H<sub>2CON</sub> and LIG<sub>GEN</sub> are H<sub>2</sub> consumed and light ends generated through reactions, G is the HC liquid flow (IN / OUT of the system), LIG<sub>MW</sub> is the molecular weight of LIGsand

$$H_{2CON} = k_{H2HC} \times HC_{IN} \quad (3)$$

$$LIG_{GEN} = k_{LIGHC} \times HC_{IN} \quad (4)$$

$$\Sigma F_{IN} - H_{2CON} + LIG_{GEN} = \Sigma F_{OUT} \quad (5)$$

$$\Sigma(F_{IN} \times y[H_2]_{IN}) - H_{2CON} = \Sigma(F_{OUT} \times y[H_2]_{OUT}) \quad (6)$$

$$\Sigma G_{IN} - LIG_{GEN} \times LIG_{MW} = \Sigma G_{OUT} \quad (7)$$

$$\Sigma(F_{IN} \times y[LIG]_{IN}) - LIG_{GEN} \times LIG_{MW} = \Sigma(F_{OUT} \times y[LIG]_{OUT}) \quad (8)$$

Separation drums (HP/LP drums) have specific additional equations (9-10) that represent how they split their mixed gas and liquid inlet (G<sub>IN</sub>) streams into a gas outlet (F<sub>OUT</sub>) and mixed gas and liquid outlet (G<sub>OUT</sub>). The latter containing the gases that remain solubilised from the G<sub>IN</sub>. A solubility constant for: gas in HC and H<sub>2</sub> in HC, should be considered for this behaviour to be useful [6, 13]. In the particular case of LP drums G<sub>OUT</sub> is free of gases.

$$G_{ASL} = k^s_{GHC} \times HC_{IN} \quad (9)$$

$$G_{OUT} \times y[H_2]_{OUT} = k^s_{H2HC} \times HC_{IN} \quad (10)$$

Where k<sup>s</sup><sub>GHC</sub> and k<sup>s</sup><sub>H2HC</sub> are the solubilities of gas and H<sub>2</sub> in HC respectively, HC<sub>IN</sub> is the HC inlet to the drum.

Rather than applying a rigorous model to represent chemical consumption and generation of gases, a simplified empirical first order dynamic is imposed. The same simplification is used to account for solubility dynamics (k<sup>s</sup><sub>H2HC</sub>, k<sup>s</sup><sub>GHC</sub>). Therefore, changes in coefficients k<sup>s</sup><sub>GHC</sub>, k<sup>s</sup><sub>H2HC</sub>, k<sub>H2HC</sub> and k<sub>LIGHC</sub>, are modelled using equation 11 that represents the generic form of them all. Time constants (τ<sub>i</sub>) used were: 0.45 h (τ<sub>R1</sub>) and 0.65 h (τ<sub>SHP</sub>), for reactions and separators respectively. These values were deemed sensible for typical HDS processes reaching steady state after 2 h in reactors and 3 h in separation drums [12-13]. One hour delay is included between reactors and downstream drums to account for fluid hydraulic time.

$$Y(t) + \tau_i \times Y'(t) = k \quad (11)$$

Where: Y is a derivable function of time (t) with value k at t = ∞, and first derivative Y'. Therefore: k<sup>s</sup><sub>GHC</sub>, k<sup>s</sup><sub>H2HC</sub>, k<sub>H2HC</sub> and k<sub>LIGHC</sub> were represented as time dependent coefficients with known steady state values. Transitions were computed applying equation 11 with τ<sub>R1</sub> = 0.45 h, τ<sub>SHP</sub> = 0.65 h.

General statistics of the system from PROSIS® [4] are shown in Figure 3.

GENERAL STATISTICS	
INFO	#
Number of equations:	629
Number of boxes (coupled subsystems of equations):	2
Number of linear boxes:	1
Number of nonlinear boxes:	1
Number of input DATA:	22
Number of input BOUNDARY:	47
Number of output EXPLICIT :	611
Number of output DYNAMIC/DERIVATIVE:	12
Number of output ALGEBRAIC:	6
Size of Jacobian matrix (DYNAMIC+ALGEBRAIC):	18x18
Sparsity factor in Jacobian matrix (% of zeros):	62.962962962962962
Default integration method:	DASSL

Figure 3: General statistics of the system. Source: PROOSIS® [4].

### 2.3 CASES STUDIED

Two state transitions from a baseline case (case1) were simulated: high H<sub>2</sub> demand case (case2) and low H<sub>2</sub> demand case (case3). Process conditions of cases 1-3 are shown in Table 2.

Table 2: Cases process conditions.

	Case 1: Baseline			
	k <sub>H2HC</sub> Nm <sup>3</sup> /m <sup>3</sup>	k <sub>LIGHC</sub> Nm <sup>3</sup> /m <sup>3</sup>	k <sup>s</sup> <sub>GHC</sub> Nm <sup>3</sup> /m <sup>3</sup>	k <sup>s</sup> <sub>H2HC</sub> Nm <sup>3</sup> /m <sup>3</sup>
HDS1	30	1.5	10	6
HDS2	60	5	13	14
HDS3	70	6	14	8
	Case 2: High H <sub>2</sub> demand			
	k <sub>H2HC</sub> Nm <sup>3</sup> /m <sup>3</sup>	k <sub>LIGHC</sub> Nm <sup>3</sup> /m <sup>3</sup>	k <sup>s</sup> <sub>GHC</sub> Nm <sup>3</sup> /m <sup>3</sup>	k <sup>s</sup> <sub>H2HC</sub> Nm <sup>3</sup> /m <sup>3</sup>
HDS1	35	2	11	7
HDS2	60	4.8	13	9
HDS3	75	6	15	9
	Case 3: Low H <sub>2</sub> demand			
	k <sub>H2HC</sub> Nm <sup>3</sup> /m <sup>3</sup>	k <sub>LIGHC</sub> Nm <sup>3</sup> /m <sup>3</sup>	k <sup>s</sup> <sub>GHC</sub> Nm <sup>3</sup> /m <sup>3</sup>	k <sup>s</sup> <sub>H2HC</sub> Nm <sup>3</sup> /m <sup>3</sup>
HDS1	25	1	8	4
HDS2	50	4	10	6
HDS3	63	5	13	8

	HC conditions		
	F <sub>HC</sub>	ρ <sub>HC</sub>	m <sub>wHC</sub>
	m <sup>3</sup> /h	kg/m <sup>3</sup>	kg/kmol
<b>HDS1</b>			
HC1	150	800	150
<b>HDS2</b>			
HC1	130	800	150
HC2	30	850	170
<b>HDS3</b>			
HC1	105	800	150
HC2	45	850	170

Conversely with reaction and solubility coefficients, network flowrates were fixed (i.e.: set as boundaries) and are shown in Table 3. Therefore, system responses were deemed entirely due to HC properties change rather than operating conditions, such as: feed flowrates, gas purge, etc.

Table 3: Fixed process conditions of the cases studied.

Boundary	Units	HDS1	HDS2	HDS3
MU1.F (from LPH)	km <sup>3</sup> /h	3.0	4.0	1.0
RC1.F (recycle)	km <sup>3</sup> /h	70	70	70
PG.F (purge to LPH)	km <sup>3</sup> /h	3.0	5.0	2.0
Q1.F (Quench 1)	m <sup>3</sup> /h		1.0	1.0
Q2.F (Quench 2)	m <sup>3</sup> /h		1.0	1.0
Z.F (PERM inlet)	km <sup>3</sup> /h			9.0
Z.PG (PERM purge)	km <sup>3</sup> /h			2.0

### 2.4 SIMULATION

The simulation experiment consisted in running the network at: baseline conditions first, then case2 and case3. The sequence is shown in Table 4.

Table 4: Simulation sequence

Case	Start time (h)	End time (h)
1	0	3
2	3	8
1	8	14
3	14	20
1	20	24

## 3 RESULTS

### 3.1 Global mass balance

The mass balance of the network was divided into four terms for ease of understanding.

The first term is the H<sub>2</sub> consumption occurring in reactors due to chemical demand of H<sub>2</sub> (see Figure 4).

The second is H<sub>2</sub> from outside being fed to the network (source) and H<sub>2</sub> purged to FG header. This term is shown in Figure 5.

Similarly, two additional terms referring to LIG fed to the network and purged to FG complete the global mass balance. Figures 6-7 show LIG flow rates for the global balance.

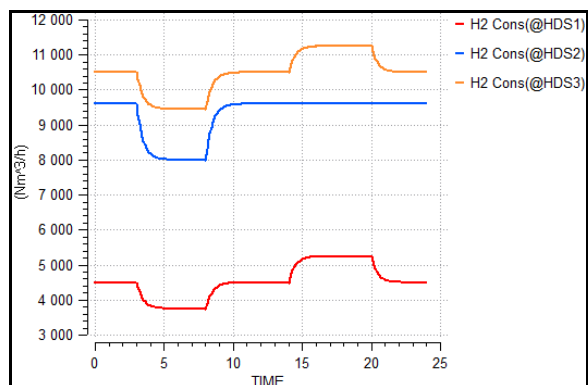


Figure 4: H<sub>2</sub> consumption in reactors.

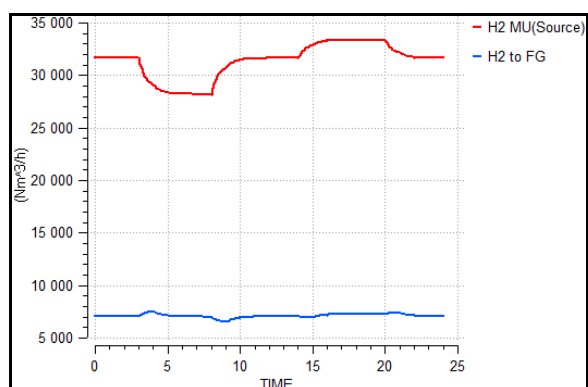


Figure 5: Network H<sub>2</sub> in make-up and purge to FG.

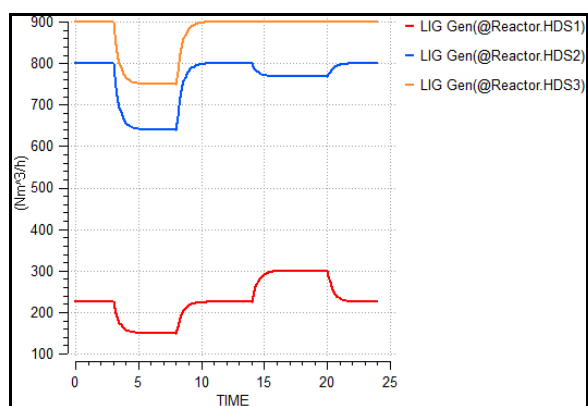


Figure 6: LIG generated in reactors.

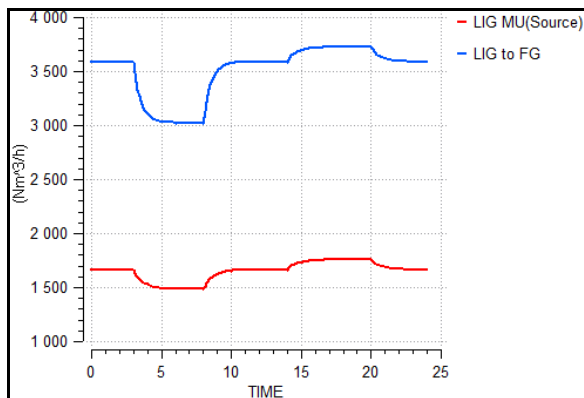


Figure 7: Network LIG in make-up and purge to FG.

### 3.2 Solubility coefficients in separation drums

Gas and H<sub>2</sub> solubility coefficients are shown in Figure 8.

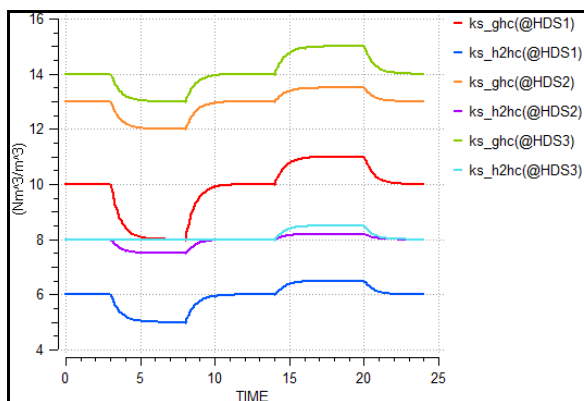


Figure 8: Gas and H<sub>2</sub> solubility in HC at separation drums.

### 3.3 Hydrogen purity

H<sub>2</sub> purity is of key importance in desulphurisation processes, especially to maximise catalyst lifecycle [2, 12-13]. Therefore, is important to control H<sub>2</sub> purity in the network. Figures 9-10 show H<sub>2</sub> purity in the network and its values in reactors.

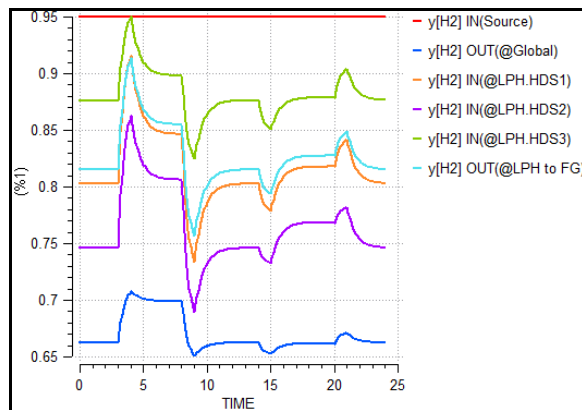


Figure 9: Network H<sub>2</sub> purities. H<sub>2</sub> purities of: source, purge to FG, LPH inflows and outflow.

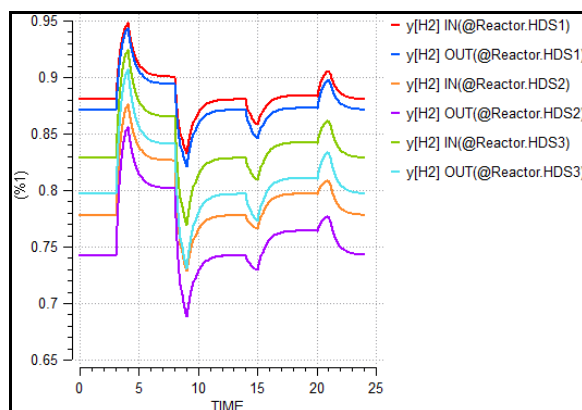


Figure 10: Reactors' H<sub>2</sub> purities.

## 4 DISCUSSION

It is seen how H<sub>2</sub><sub>CON</sub> and LIG<sub>GEN</sub> affect H<sub>2</sub> make-up from the source (Figures 4-5), since the network closes its global mass balance with the make-up gas. Therefore, transitions from case1-2 and case3-2 imply diminutions of make-up flow to the network. The opposite happens with transitions from case2-1 and case1-3. However, H<sub>2</sub> purity (y[H<sub>2</sub>]) within the network changes in the opposite direction (see Figure 9) due to gas and H<sub>2</sub> solubility dependence (k<sup>s</sup><sub>GHC</sub> and k<sup>s</sup><sub>H<sub>2</sub>HC</sub>, equations 9-10), whose changes are seen in Figure 8. In fact, separators hold responsibility for recycle gas composition in each plant, and consequently within the network. Their influence is due to equations 9-10 which determine the separation in terms of composition and flow rates applying the model proposed by Gomez (2016) [6]. The same response is seen in LIGs, although at different rates (see Figures 6-7). An analogous reasoning explains this behaviour.

A similar analysis can be applied to gas headers, from which LPH and FG are of particular interest. This is because, the former works as a gas recycle

sink, receiving plants' LPH purges and providing low purity make-up back into the plants (MU1 inflow and PG\_LPH outflow, see Figure 3). In the LPH the FG purge to the FGH takes care of the pressure control of the header, closing its mass balance against the FGH. Since three inflows to LPH are boundaries (purges to LPH) and three outflows are boundaries as well (MU1 to HDS1-3), LPH outflow to FGH is fixed by the mass balance in  $3000 \text{ Nm}^3/\text{h}$  (expressed in volume in equation 1). In addition, FGH receives plants' purges to FG and from LPH, and again, its pressure control is achieved by purging gas off the network as shown in Figure 11. See Figure 1 for LPH and FGH inflows and outflows diagrams within the network. In overall, LPH gas is a component of actual make-up and FGH outflow is the network's purge, usually to flare header.

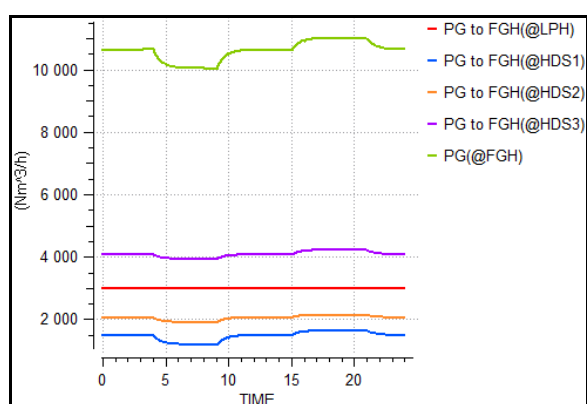


Figure 11: Fuel gas header inflows (PG to FGH) and purge (PG).

$\text{H}_2$  purity in the plants show significant dependence with reactors' specific consumptions (i.e.:  $k_{\text{H}_2\text{HC}}$  and  $k_{\text{LIGHC}}$ ) and their dynamics. In fact, from case1-2 an increment of around 20% is seen for HDS1-2 and around 12% for HDS3 (Figure 10). Smaller variations are shown in the rest of the transitions. Therefore the simulation predicts and presents clearly the dynamics of  $\text{H}_2$  purity in all streams (see Figures 9-10), being this an asset for plant operators, production scheduling team. For instance,  $\text{H}_2$  purity sharp drops and peaks affect negatively scheduling since it may take longer to comply with expected crude processing timetables. Operators will need to smooth down transitions either by feeding lower rates to the units (least likely) or purging more to LPH (most likely). In any case the process will be constrained and will not meet the optimum scheduling unless transition states were known beforehand. In addition, simulation of the network may aid: in debottlenecking (when  $\text{H}_2$  is scarce), or in undertaking what-if analysis, due to its ease of setting different scenarios. For example, purity affects (Figures 9-10): compressors performance and catalysts lifecycle. Therefore, it may be challenging

for compressors to deal with transitions from case1-2 and back. Using the network simulation this will be predicted and operators will be able to act in consequence. In overall, simulation of the network holds potential use as support tool in any decision-making process where prediction of network streams' status is utilised. In this theoretical network is seen that case1-2 and case2-1 transitions lead to the most extreme  $\text{H}_2$  purities. Although their steady states do not show extreme values, in the transitions  $\text{H}_2$  purities reach values that are usually far below minimum required (typical minimum bound: 60%). Therefore, schedulers and operators can anticipate and consider more realistic transition times and how to mitigate their effects. Similar advantages will be seen when studying different scenarios and how the network is likely to respond.

It is important to highlight the limitations of the model and their extent. The results shown rely on the dynamics of the  $\text{H}_2$  consumption and LIG generation in the reactors, and gases solubility in the separation drums (equations 3-4, 9-11). Therefore, a proper and specific determination of:  $k_{\text{H}_2\text{HC}}^s$ ,  $k_{\text{GHC}}^s$ ,  $k_{\text{H}_2\text{HC}}$ ,  $k_{\text{LIGHC}}$ ,  $\tau_i$  would be essential in any actual network case study. In this work only theoretical and sensible values were applied to probe usefulness of the methodology. In addition, the previous parameters are linked to HC composition in actual processes, especially to the sulphur content. This was not modelled.

## 5 CONCLUSIONS

A first principle refinery hydrogen network that considered empirical first order dynamics on:  $\text{H}_2$  consumption, LIG generation, and solubility in separation drums, was modelled. The simulation of the three cases studied showed transient properties along the network that differ significantly from steady states, bringing essential information for operation. In particular the simulation presented an effective analysis of network dynamics in a simplified and empirical-based fashion. The gas purities were the most significantly affected variables with up to 10% difference between transient and steady state responses. This knowledge is useful for: processing schedule development and normal operation. Other potential usage is identified in minimising compressors operation outside their allowed working region.

Further research on real cases of study should be conducted to validate this methodology, and its utility in the decision-making process in actual refinery hydrogen networks.

## Acknowledgements

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