

# Benchmarking of internal modelling tools using industrial units follow up.

F. Fitas; M.C. Fernandes<sup>a</sup>; T. Sozinho<sup>b</sup>

e-mail: [francisco.fitas@ist.utl.pt](mailto:francisco.fitas@ist.utl.pt)

<sup>a</sup> Instituto Superior Técnico, Universidade de Lisboa, Av. Rovisco Pais, 1049-001 Lisboa, Portugal

<sup>b</sup> IFP Energies Nouvelles, Rond-point de l'échangeur de Solaize, 69360 Solaize, France

AR – Atmospheric Residue;  
 CCR – Conradson Carbon Residue;  
 FCC – Fluid Catalytic Cracking;  
 HDM – Hydrodemetallization  
 HDS- HydrodeSulphurization  
 HSFO – High Sulphur Fuel Oil;  
 IFPEN – IFP Energies Nouvelles;  
 IMO – International Maritime Organization;  
 LHSV – Liquid Hourly Space Velocity;  
 LPG – Liquefied Petroleum Gas;  
 LSFO – Low Sulphur Fuel Oil;  
 MGO – Maritime Gas Oil;  
 NASPH – Normalized Asphaltene content  
 NCCR – Normalized Conradson Carbon Content;  
 NHOS – Normalized Hours On Stream;  
 NM – Normalized Metal content;  
 NMOC – Normalized Metal on Catalyst;  
 NN – Normalized Nitrogen content;  
 NS – Normalized Sulphur Content;  
 NT – Normalized Temperature;  
 PRS – Permutable guard bed Reactor System;  
 RDS – Residue DeSulphurization;  
 SECA – Sulphur Emission Controlled Areas;  
 THERMIDOR – THERmal Monitoring for Isoperformance  
 DeSulphurization of Oil Residues  
 VLSFO – Very Low Sulphur Fuel Oil;  
 VR – Vacuum Residue;  
 WABT – Weighted Average Bed Temperature;

**Abstract**— Heavy residues such as low value atmospheric residue and vacuum residue are often upgraded in order to produce more valuable products such as bunker fuel or even diesel fuel. There are many processes available to purify these residues before their conversion, one of them is the Hyvahl™ process, developed by Axens and IFP Energies Nouvelles. The main goal of this process is the removal of sulphur and metal. In order to predict process performance during a process run, IFP Energies Nouvelles has developed software to simulate fixed-bed reactors called THERMIDOR.

In this work, software results are benchmarked using data from two refineries. The methodology consists in replicating industrial conditions in the simulator, and later comparing output data with industrial records to the model in order to achieve more accurate predictions. This way, it is possible to estimate the reliability of the predictions. Also, in this work, a reactor permutation feature is implemented and tested to improve the result accuracy. Results show that reactor permutation improves overall accuracy of the simulation. Using available input data from industrial records, simulations using the permutation

feature can predict more accurately reactor temperature, permutation frequency and catalyst deactivation in fixed bed hydrotreatment reactors than simulations without reactor permutation. It is also successfully able to accurately predict metal and nitrogen content of the reactor outlets. Improvements could be done on sulphur and asphaltene removal kinetics. Also, the implementation of a dual fixed bed reactor model in the software is suggested.

**Keywords** — Hydrotreatment, Hyvahl™, Fixed-bed reactor, Hydrodesulphurization, Hydrodemetallization.

## I. INTRODUCTION

Crude oil is a blend of hydrocarbons such as olefins, paraffins, aromatics, asphaltenes, among others. It also contains many compounds such as sulphur, nitrogen and metals. Hydrocarbon content in a crude oil depends on the origin of the oil, lighter paraffinic oils can have up to 97%wt of hydrocarbons while bitumen can have only 50%wt, the rest comprising mostly of mineral matter impurities. [1]

In a refinery, crude oil is first desalted, heated and then fed to an atmospheric distillation column. This separates the oil many different fractions, which can be grouped in three categories: light, medium or heavy fractions. Lighter fractions, or cuts, are generally more valuable than medium or heavy cuts. Gas, LPG, gasoline and naphtha are some examples of light distillates from crude oil. Kerosene, diesel fuel, distillate fuel oil are some medium crude oil fractions. Finally, there are also heavy cuts such as lubricating oils, vacuum gas oil and residues that are separated on a vacuum distillation column. [1]

In this study, vacuum residues are the most interesting fraction. These are made mostly of the heaviest and most complex molecules such as asphaltenes, heavy saturates, resins and aromatics. It also contains most of the impurities found on crude oils such as nitrogen, sulphur, metals and oxygen. Due to their compositions, vacuum residues have little value, so they are usually treated and converted into more valuable products such as bunker fuel or diesel. [1]

In recent years, the International Maritime Organization (IMO) has passed legislation to decrease the limit of sulphur allowed on bunker fuel in order to reduce SOx emissions by ships. By 2020, no ship can use fuel with a sulphur content over 0.5% wt. without an effective scrubbing system. In some areas, designated by the IMO as Sulphur Emission Controlled Areas (SECA), the sulphur content in bunker fuels is limited to 0.1% wt. [2,3]

This leads to an increased demand for Very Low Sulphur Fuel Oil (VLSFO), and, to keep up with demand, new hydrotreatment processes are being developed and are being used in refineries worldwide. The lack of a reliable

supply of VLSFO leads most shipping companies to prefer Maritime Gas Oil (MGO) to VLSFO. However, VLSFO demand is expected to increase as refineries adapt existing processes to increase VLSFO production and a steady supply of this fuel can be found in harbours. MGO use in ships is expected to increase as well and an ever increasing number of ships are expected to be retrofitted with onboard scrubbers to remove excess sulphur from High Sulphur Fuel Oil (HSFO) emissions. [4]

So, in order to produce more Low Sulphur Fuel Oil (LSFO), refineries can purchase light low sulphur crude oils to reduce the amount of HSFO produced or they can upgrade residues from heavy high sulphur crude oils to reduce sulphur content. As heavy crude oils are more available, and therefore, cheaper than light crude oils, most refineries are investing in upgrading processes such as hydrotreatment. [5]

Also, from 1986 to 2012, the demand for heavy fuel oils such as residual fuel oil has decreased. In 1986, 12 million barrels per day were consumed worldwide, in 2012, only 8 million were consumed. [6] For the same period, the consumption of lighter fuels such as distillate fuel oil has increased from 13 million barrels per day in 1986 to 26 million in 2012. [7] This also leads to an increasing trend by refineries to upgrade heavy residual fuels into lighter ones.

As vacuum residues have a great amount of impurities, they must be treated before the conversion process. Hydrotreatment is a process where impurities such as sulphur, nitrogen, oxygen and metals are removed. The most common are sulphur, oxygen and nitrogen. These impurities cause corrosion in process equipment, decrease the performance of fuel, increase fuel pollution and poison catalysts downstream. Vacuum residues from heavy crudes are rich in these elements, so they must be upgraded to reduce impurity content. After impurities have been reduced, the residue can be processed into a more valuable product. [1]

The Hyvahl™ process, commercialized by IFPEN, purifies and upgrades a feed of Vacuum Residues (VR) or a mixture of VR/Atmospheric Residues (AR) using a battery of fixed bed reactors. For that, Nickel, Vanadium, Sulphur and Nitrogen contents are reduced, as well as the CCR. This allows for improved feeds to FCC units, which in turn allows a more efficient diesel and low sulphur fuel oil production. Besides improving overall fuel quality, the removal of these poisons increases catalyst lifetime. This allows for longer operations downstream of the Hyvahl™ process and overall increased plant efficiency [8]. Figure 1 shows a generic set-up of the Hyvahl™ process and Table 1 summarizes the operating conditions of the process.

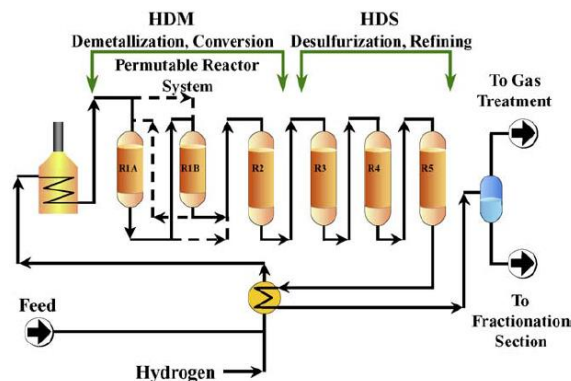


Figure 1 - Generic Hyvahl™ process setup, adapted from [9].

Table 1 - Operating conditions of the Hyvahl process

Operating Conditions	
Temperature (°C)	370-420 [10]
Pressure (bar)	150 to 200 [10]
LHSV(h-1)	2 to 4 [10]
PRS catalyst lifetime (months)	3 to 6 [10]
Feed metal content (ppm)	Preferably 100 to 350 [10]
Overall HDS	90% [10]
Overall HDM	95% [10]

The first part of the process is the Permutable guard-bed Reactor System (PRS). This section reduces metal content through HDM reactions. This protects the downstream reactors by removing a considerable amount of metals and sediments. Otherwise, sedimentation of these materials would cause fouling, plugging and poisoning of downstream catalysts. PRS uses a catalyst that excels in nickel and vanadium removal. It also converts some asphaltenes to lighter hydrocarbons [8,11].

The PRS is composed by two single fixed bed reactors in series, called for example, reactors R1A and R1B. Reactor R1A will receive the fresh feed from the vacuum distillation column, and reactor R1B will receive the effluent from reactor R1A in this run. Due to that, R1A will be referred to as a lead reactor and R1B will be referred to as a lag reactor for now. The setup is represented Figure 2 [8,11].

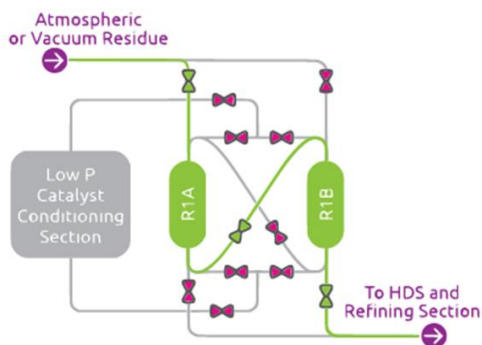


Figure 2 - Initial PRS setup, adapted from [11].

The catalyst loaded in the lead reactor has a shorter lifetime than the catalyst in the lag reactor. This happens due to higher concentrations of metals in the fresh feed than at the entrance of the lag reactor. When reactor R1A must be shut down to replace the catalyst, fresh feed is redirected to R1B, which operates alone during this procedure. Replacing the catalyst in the lead reactor usually takes 15 to 20 days. This is represented in Figure 3 [8,11].

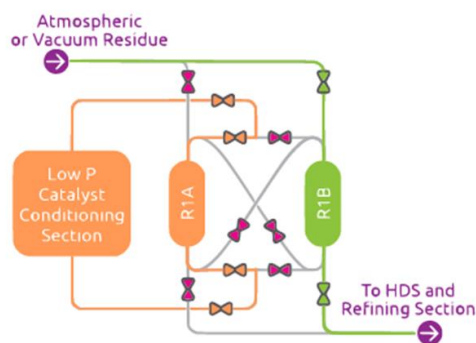


Figure 3 - PRS lead catalyst regeneration, adapted from [11].

After R1A has been loaded with fresh catalyst, the effluent from reactor R1B is fed back to R1A. This means that the reactors have changed roles, now R1B is the lead reactor and R1A is the lag reactor. This is represented in Figure 4 [8,11].

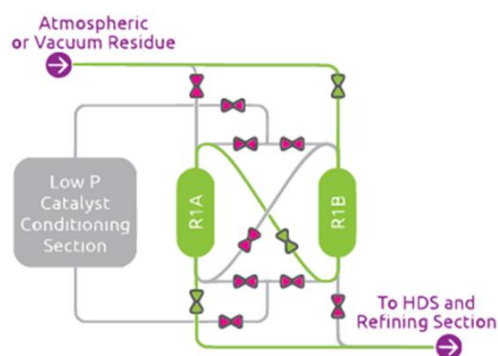


Figure 4 - PRS permutation, adapted from [11].

The PRS system allows for greater cycle times as it decreases the deactivation time of catalysts outside the PRS system. Comparing the process with the PRS system with a similar Residue Desulphurization (RDS) process without the PRS system, the cycle time is 60% longer [8,11].

The second part is the mixed HDM/HDS section is usually made up of one reactor with two catalytic sections with a hydrogen quench in between [11]. The objective of the hydrogen quench is to counter the temperature increase in the reactor due to the heat released by the exothermic reactions [12,13]. The top catalyst is an HDM catalyst to clean any excess metal coming from the PRS section and the bottom section is an HDS section where sulphur removal starts [11]. This section is optional, so it is possible to find refineries using the Hyvahl process without a mixed section. Figure 5 shows a scheme of reactor used in this section.

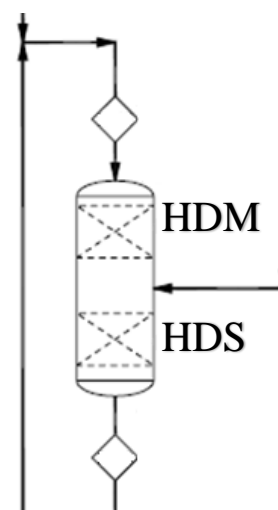


Figure 5 - Dual fixed-bed reactor scheme with inter-bed Hydrogen quench.

The third part is the HDS section. In this section of the catalyst is composed by one or more reactors of the same type of the mixed HDM/HDS section. However, in these, both catalytic sections are loaded with HDS catalyst [11]. The number of reactor of reactors in this section depends on the product specification desired and determines the amount of sulphur removed from the feed. After leaving the HDS section, most of sulphur, metal and a portion of asphaltenes have been removed from the process stream. A significant portion of nitrogen has also been removed at this point [8,11].

## II. THERMIDOR

THERMIDOR is capable of simulating catalyst deactivation in hydrotreatment processes using fixed bed reactors. In order to simulate an entire hydrotreatment unit, THERMIDOR assumes it is a group of plug flow



Case study 1 has two PRS reactors (R1A and R1B), an HDM/HDS reactor (R2) and an HDS reactor (R3). Case study 2 has two PRS reactors (R1A and R1B), an HDM/HDS reactor (R3) and three HDS reactors (R3, R4, R5). As the feed used in case study 2 is the most impure of both, it needs two additional HDS reactors in order to achieve the same product specification. It is also noteworthy that some data had to be excluded for benchmarking purposes for several reasons. On case study 1, on the last permutation of the cycle, the catalyst of the lead reactor was not changed. Instead the lead and lag reactor switched places instantly. As this is not possible to simulate on the current version of THERMIDOR, the final run of case study 1 was excluded from benchmarking purposes. There were also shutdowns during case study 1 cycle. As this is not possible to simulate on THERMIDOR, these time periods were excluded. Case study 2 has no information about the content of the outlets of reactors R3 and R4. Therefore, only the PRS section of case study 2 was used for benchmarking purposes.

#### IV. METHODOLOGY

In this work, THERMIDOR software data is benchmarked with industrial process run data from two case studies. Software performance is evaluated by using industrial data as input for the simulation and comparing its output data with equivalent industrial data. In this way, it is possible to know if THERMIDOR can accurately simulate the Hyvahl™ process.

Input data such as feedstock composition, reactor layout and operating condition during the run are extracted and treated. This data is used as input in order to run a simulation. After that, output data from the simulation such as sulphur and metal contents, as well as reactor temperatures are compared to industrial data. After comparing both data sets, it is possible to conclude if the simulation was accurate or not. If not, it is possible to adjust the software models in order to improve simulation results. Figure 8 shows the work methodology adopted in this work.

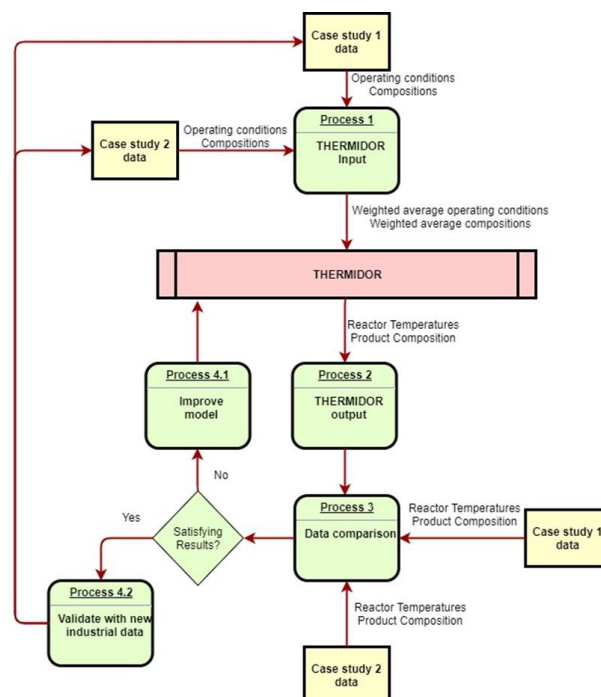


Figure 8 - Work methodology diagram

Refinery data about feedstock composition and operating conditions is not constant as most refineries change their type of feedstock frequently, depending on market conditions. This is problematic as THERMIDOR requires constant input data. In order to turn an industrial variable dataset into constant input data for THERMIDOR, its weighted average is calculated using feed flow rate as a weighting variable. After the industrial data has been adapted to be used as input for the software, it is possible to run a simulation of the industrial run. After that, the output results of the simulation are compared with the industrial records.

Normalization of all data is performed by dividing every variable by the maximum value of itself in the case study considered. For example, in case study 1, all sulphur content values for all reactor are divided by the highest value recorded in case study 1 data base while on case study 2, all sulphur content values for all reactor are divided by the highest value recorded in case study 2 data base.

#### V. RESULTS AND DISCUSSION

In this work, simulations were performed using the conventional fixed bed mode and the permutation mode. The focus of this article is on the benchmarking of the software using the permutation feature.

Figure 9 shows the simulated and industrial temperatures of the PRS system of case study 1 using the permutation feature of THERMIDOR.



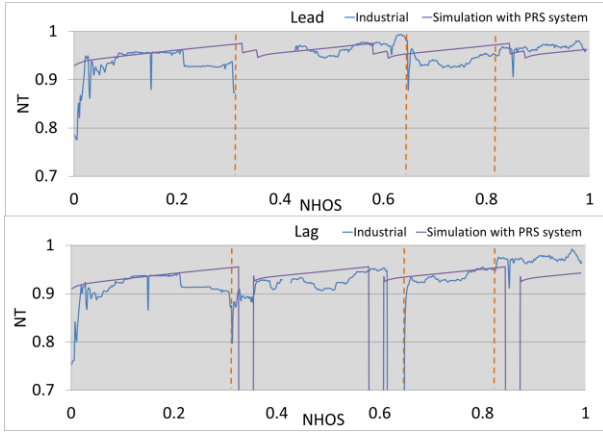


Figure 9 - Permutation simulation temperature and industrial temperature of the PRS system in case study 1

It is possible to verify that simulated temperatures are similar to the industrial record for all runs of the cycle. On Table 3, the difference in permutation time between simulated permutations and industrial permutations is shown.

Table 3 - Permutation time difference between industrial and simulation results of case study 1

Permutation	Permutation normalized time difference
1	0.01
2	-0.03
3	0.02

Considering the length of a cycle, the difference between the start of simulated permutations and the industrial recorded permutation is relatively small. This is validated by case study 2 PRS system simulation, shown in Figure 10. The difference between industrial and simulated permutations is shown in Table 4.

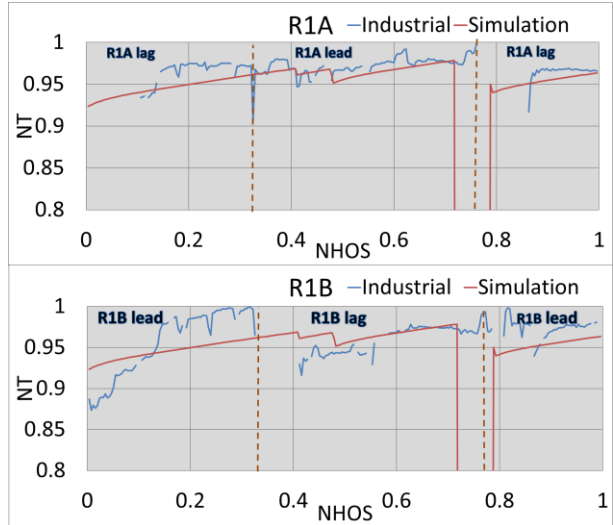


Figure 10 - Permutation simulation temperature and industrial temperature of the PRS system in case study 2.

Table 4 - Permutation time difference between industrial and simulation results of case study 2.

Permutation	Permutation time difference
1	0.03
2	0.02

In this simulation mode, product outlet regulation only occurs in the outlet of the lag reactor of the PRS system, the outlet of the lead is a function of its own temperature that depends on the temperature of the lag reactor. Figure 11 shows the regulated metal content at the outlet of lead and lag reactors of case study 1.

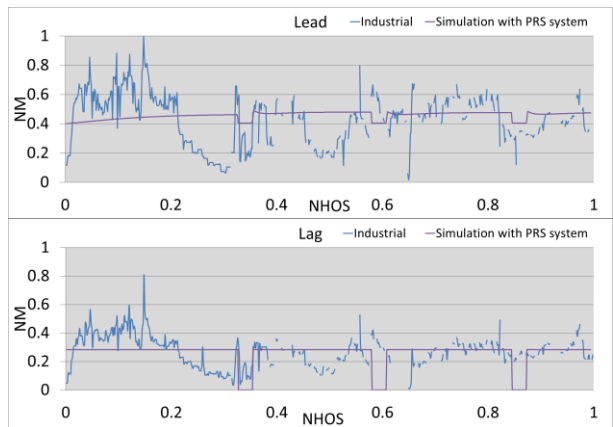


Figure 11 – Industrial and simulated metal content of Lead and Lag reactors of case study 1.

As it is possible to see, the simulated metal outlet of the lead reactor is close to the industrial average metal outlet even if it is only being regulated by the lag reactor. This means that considering the temperature of the lead

reactor as a function of the lag reactor is a valid solution for simulating the PRS system.

Regarding unregulated reactor products, Figure 12 shows the outlet of sulphur, nitrogen CCR content of the lead reactor. Figure 13 shows the outlet of sulphur, nitrogen, asphaltene and CCR content of the lag reactor.

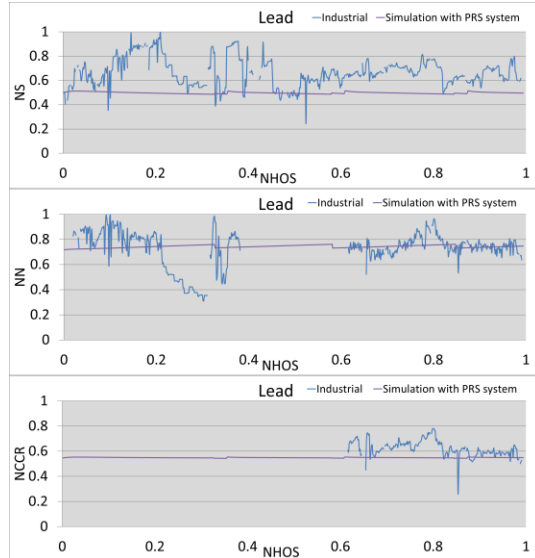


Figure 12 - Simulated and industrial sulphur, nitrogen and CCR content of lead reactor in case study 1.

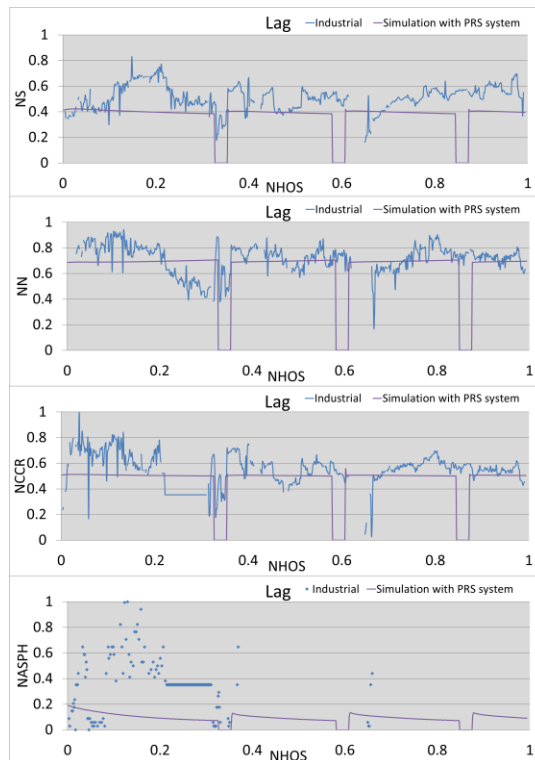


Figure 13 - Simulated and industrial sulphur, nitrogen, asphaltene and CCR content of lag reactor in case study 1.

On both reactors, the simulated sulphur content is lower than the industrial recorded sulphur values. The excessive removal of sulphur on PRS reactors means that there is less sulphur available to be removed by the following simulated reactors. This leads to lower temperatures on downstream reactors that regulate for sulphur as they receive a cleaner feed. Simulated nitrogen and CCR values are similar to industrial values. Asphaltene conversion is excessive, as it can be seen by the asphaltene content at the outlet of the lag reactor.

Regarding the dual bed reactors of case study 1, Figure 14 shows the industrial and simulated temperatures of both sections of reactors R2 and R3 using a conventional simulation and a permutation simulation. Table 5 shows the average temperature difference between conventional and permutation simulation with industrial values.

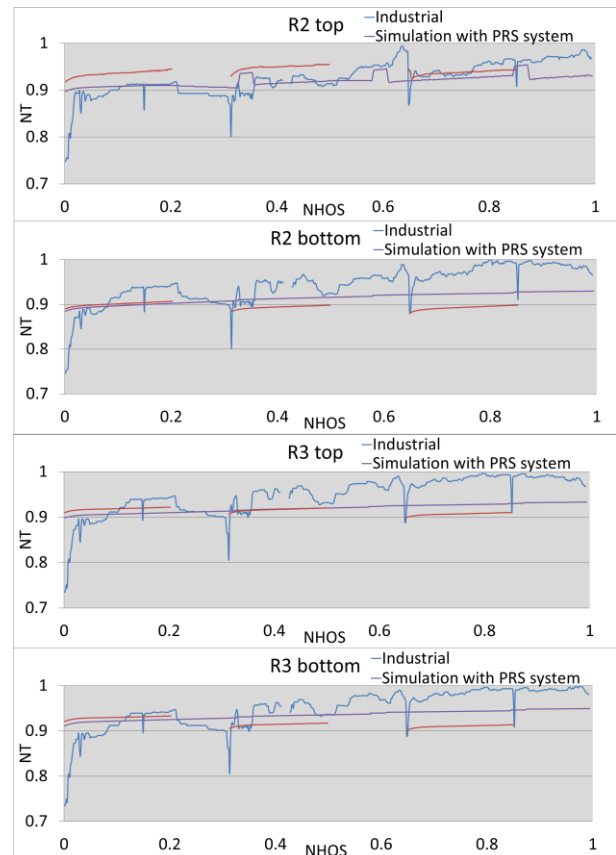


Figure 14 - Simulated and industrial temperatures for top and bottom sections of reactors R2 and R3 of case study 1 using the PRS system (purple) and without using the PRS system (red)

Table 5 - Average temperature difference of conventional and permutation simulations with industrial results

$\Delta T$			
Bed	Run	Conventional	Permutation
R2 Top	1	4%	2%
	2	3%	-1%
	3	0%	-1%
R2 bottom	1	-1%	-1%
	2	-5%	-3%
	3	-8%	-5%
R3 top	1	1%	0%
	2	-3%	-3%
	3	-7%	-5%
R3 bottom	1	2%	2%
	2	-4%	-2%
	3	-7%	-4%

It is possible to verify that permutation simulation results for dual bed reactors are closer to industrial results than conventional simulation results. In a conventional simulation, there is no way to simulate all 3 runs in one simulation. This means that there is no way to save catalyst deactivation values from run 1 to run 2 and from run 2 to run 3. In conventional simulations, all three runs start with fresh catalyst. This lack of deactivation reduces simulated temperatures in order to achieve the same product composition results. It is also possible to see for most conventional simulations that the average temperature error increases with each run.

Figure 15 shows the sulphur, metal, nitrogen and CCR content at the outlet of reactor R2 of case study 1 and Figure 16 shows the sulphur, metal, and nitrogen content at the outlet of reactor R3 of case study 1.

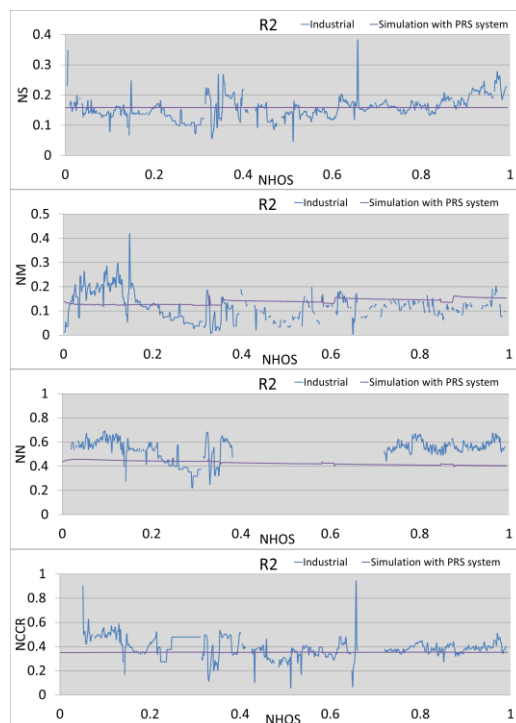


Figure 15 - Simulated and industrial sulphur, nitrogen, asphaltene and CCR content of reactor R2 in case study 1.

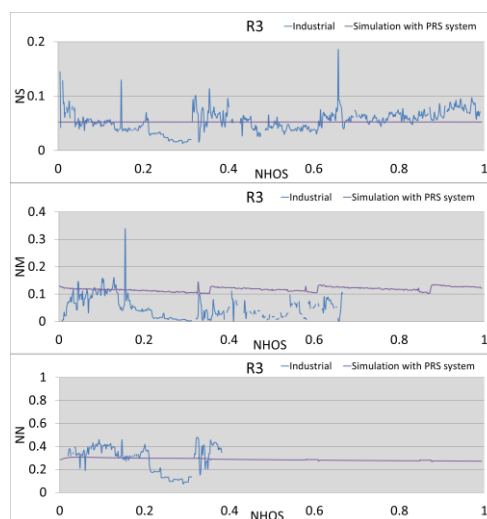


Figure 16 - Simulated and industrial sulphur, nitrogen and CCR content of reactor R3 in case study 1.

It is possible to see that the simulated metal, sulphur, CCR and nitrogen content of reactor R2 outlet are a close match to industrial records. In reactor R3, the simulated sulphur and nitrogen outlet is a close match to the industrial records. Metal content at the outlet of reactor R3 is below the minimum value for reliable readings. This can lead to error in industrial reading and can explain the difference of simulated and industrial metal contents.

There are several differences between the simulated and the industrial process. Firstly, there is no enthalpy balance implemented on the simulator. The temperature is defined



by the selected target and the MOC and COC values of the catalyst. In real life operation, hydrogen quenches are used to control the temperature of the reactor in order to maintain product specification. As seen earlier, the addition of hydrogen quenches without the enthalpy balance causes the temperature to decrease slightly due to an increase of hydrogen in the reactor. With the enthalpy balance, the correct amount of hydrogen could be added before each section in order to get the necessary WABT in order to achieve the set product specification. This way, it would be possible to have more accurate results and predict the correct amount of hydrogen used in every quench of the process.

Second, in the simulator, the catalytic section is isothermal, this means that the temperature at any point of the catalytic bed is the same. This is not true as most reaction occurring in the reactor are exothermic. This means that as the feed progresses through the bed, it reacts and releases heat. This can cause temperature profiles in the catalytic section that are verified in the industrial temperature records. It is also possible to measure the temperature drop caused by the interbed hydrogen quench. These can be seen for one instant of case study 1 cycle in Figure 17.

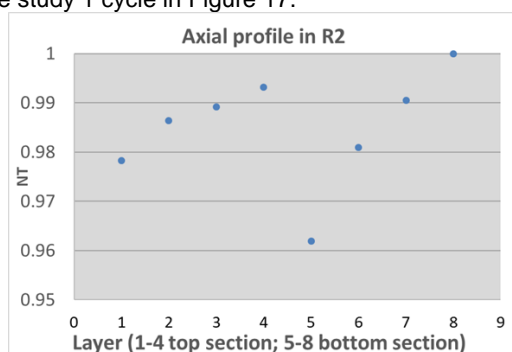


Figure 17 - Daily recorded axial profile of reactor R2 of case study 1.

It is possible to see that the bed is not isothermal and the cooling effect of the hydrogen quench between the beds (4 to 5). Both facts are not accounted for in the simulation and can lead to different results when compared to industrial records. The temperature profile and the quench cooling also change during the cycle. This means that it is possible for a bed to be completely deactivated on the surface of the section and still have good conversion on the bottom. This explains why the bottom layer of a catalytic section is hotter than the top layer after some time. Although the top layer receives more impurities to react, it also deactivates faster, so those impurities will react on the bottom layers and release heat there. This cannot be simulated in the current version of the software. A split of each section in several layers, each with its own temperature, MOC and COC values should be implemented in order to simulate an industrial catalytic section.

Regarding dual bed reactors, in order to be able to simulate the bottom bed, it is necessary to find the right composition target for the top bed through error and trial, as there are no composition measurements between beds. This method may not be the most appropriate to

determine the composition of the feed entering the bottom section. In dual bed reactors where both beds are loaded with the same catalyst, this problem can be solved by considering it as a PRS system that will not permute. In order to this, an average temperature difference between the sections must be provided and the permutation temperature must be set high enough so that it will never be reached by any catalytic section. However, this cannot be done for reactors with two different types of catalysts. For these, correlations in order to determine the right composition between the section should it be implemented in future versions. Also, the temperature in dual-bed reactors with the same catalyst such as reactor R3 in case study 1 is approximately the same in both beds during most of the cycle.

Radial temperature profiles also exist, these indicate the existence of preferential paths of the feedstock through the catalytic section, often caused by distribution problem on the inlet of the reactor. So, it is entirely possible that the centre of the catalytic bed has a different conversion and MOC and COC values than the outer section. These preferential paths can even be caused by deposition of several impurities on specific parts of the bed. These temperature differences are not accounted for in the software and are also a possible explanation for differences between industrial records and simulation results. One way to fix this problem would be the implementation of a 3D radial-diffusive-dispersive plug flow model. However, this would require a significant amount of computation resources. In Figure 18, the maximum radial temperature difference is shown for four different layers of the catalytic section.

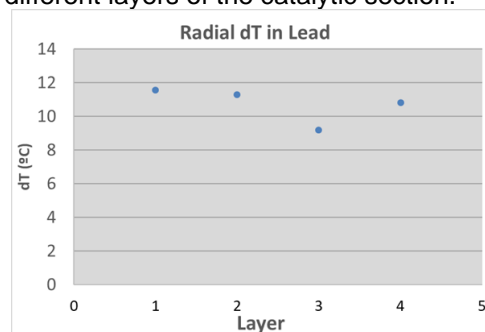


Figure 18 - Daily recorded axial profile of lead reactor of case study 1.

Also, it should be considered that the validity range of normalized temperatures from of 0.88 to 0.94 of case study 1 cycle and time range until 26% of case study 1 cycle or 66% of case study 2 cycle is not appropriate for most of the industrial operation range. It is known that reactor temperatures can reach 420°C in this process [10]. This means that the simulator is often working outside these ranges and extrapolating from its database of correlations. This can lead to inaccurate simulation results. Further kinetics tests should be performed in order to extend the validity range of the model.

## VI. CONCLUSION

It is possible to conclude that the introduction of the permutation feature improves simulation results, especially for the last runs of the cycle, where the catalytic sections are significantly deactivated in real life operation. This happens as catalyst deactivation is well represented in the simulator when the permutation feature is being used and resembles industrial records. The simulated permutation times are also well predicted by the simulator. Permutation differences between the simulator and industrial records are between 1% and 3% of the total length of case study 1 cycle. Considering that a cycle usually has a duration of two years, the error is small.

Overall the reactor can predict sulphur, metal, nitrogen and CCR content of the feed well. Although there are problems with the HDS on the PRS reactors, as there is usually an excessive removal of sulphur, the simulated sulphur compositions at the outlet of the final reactor are accurate. Simulated metal composition is very close to industrial metal composition for all reactors. For all cases where a comparison could be made, simulated CCR and nitrogen values are close to industrial values. Asphaltene is the only component where there are major differences between simulated and industrial values. It is only possible to compare with industrial asphaltene values on the lag reactor. The comparison itself is not enough as there is insufficient data about industrial asphaltene values. However, the software is removing over 90% of the asphaltene in the feed by the time the feedstock exits the last reactor. Usual conversion of asphaltenes in this process is of 15 to 25%[11].

Operation of the PRS system regarding operating temperature and catalyst deactivation is well predicted by the simulator. It is only possible to compare MOC values for case study 1 as case study 2 does not have MOC data available. Also, there are no COC records on both industrial data sets. The difference between simulated and industrial normalized MOC values at the time of permutation is no more than 10%, so the error is relatively small.

As the main goal of the hydrotreatment process is to remove metal, sulphur and nitrogen, the software is overall capable of predicting an industrial hydrotreatment cycle if an average feedstock and product specification is input by the user. A user should be able to predict the outlet composition of sulphur, metal, nitrogen and CCR. He should also have a good prediction of reactor temperatures and permutation times of the PRS reactors. The only major problem is the excessive removal of asphaltene.

## VII. BIBLIOGRAPHY

Speight J. G. *The chemistry and technology of petroleum*. CRC Press; Taylor & Francis, Boca Raton, London, New York, 2014, 1927 p.

Barbier J., Lienemann C.-P., Le Masle A., Chatron-Michaud P., Guichard B., Digne M. New Insights into Resid Desulfurization Processes : Molecular Size Dependence of Catalytic Performances Quantified by Size Exclusion Chromatography-

ICP/MS, *Energy & Fuels*, 2013, **27**, 11, 6567-6574. DOI: 10.1021/ef401540f.

International Maritime Organization. Sulphur oxides (SOx) and Particulate Matter (PM) – Regulation 14. [http://www.imo.org/en/OurWork/Environment/PollutionPrevention/AirPollution/Pages/Sulphur-oxides-\(SOx\)-%E2%80%93Regulation-14.aspx](http://www.imo.org/en/OurWork/Environment/PollutionPrevention/AirPollution/Pages/Sulphur-oxides-(SOx)-%E2%80%93Regulation-14.aspx), consulted on July 2019.

ATKINSON Neil L. O., Petrosyan K. *Oil 2019 - Analysis and Forecasts to 2024*, IEA, The institute of Energy Economics, Japan.

Kressmann, Stephane & Guillaume, Denis & Roy, Magalie & Plain, Cecile. (2004). A New Generation of Hydroconversion and Hydrodesulfurization Catalysts.

World Residual Fuel Oil Consumption. <https://www.indexmundi.com/energy/?product=residual-fuel-oil&graph=consumption>. Consulted on May 2019

World Destillate Fuel Oil Consumption. <https://www.indexmundi.com/energy/?product=fuel-oil&graph=consumption>. Consulted on May 2019

Plain, C. & Benazzi, E. & Guillaume, D.. (2006). Refining: Residue desulphurisation and conversion. 11. 57-58, 60, 62.

Toulhoat H., Hudebine D., Raybaud P., Guillaume D., Kressmann S. THERMIDOR : A new model for combined simulation of operations and optimization of catalysts in residues hydroprocessing units, *Catalysis Today*, 2005, **109**, 1-4, 135-153. DOI: 10.1016/j.cattod.2005.08.023.

Billon A., Morel F., Kim S.D., Ha S.K, Heor H. *Process for hydrotreatment of a heavy hydrocarbon fraction using permutable reactors and introduction of a middle destillate*. Institut Francais du Petrole. USA, Brevet US 6,306,287 B1, 23 octobre 2001.

Axens. HYVAHL™ : *High performance fixed-bed atmospheric and vacuum residue hydrotreating*, 4 p. Internal document, consulted on May 2019

Robinson P.R., Dolbear G.E. Hydrotreating and Hydrocracking : Fundamentals, in *Practical advances in petroleum processing*. Éd. C. S. Hsu, P. R. Robinson. Springer, New York, 2006, 177-218.

Hsu C.S., Robinson P.R., eds. *Practical advances in petroleum processing*. Springer, New York, 2006, 2 vol. (XXVIII-453, XV-411.

Sozinho T., Rebman R. *Dossier de developpement Logiciel*, 14/11/2018, 45 p. Internal document