Numerical Reconstruction of residue hydrotreating effluents

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ABSTRACT

Residue hydrotreating enables the conversion of heavy petroleum fractions into more valuable products by removing the impurities, such as S, N and metals, found in this fraction. Residues are composed of very complex molecules and are generally only characterized by their bulk properties. These bulk properties are not detailed enough to develop a reliable kinetic model. To overcome this drawback a complex analytical procedure was employed on the feeds and effluents to obtain a more detailed characterization of residues, with the objective to improve the kinetic modeling of a residue hydrotreating fixed bed reactor with a complex reaction system. Yet, this analytical procedure is very costly and time consuming.

In the present work, a two-step numerical reconstruction algorithm using global analytical data was tested to create a set of molecules whose properties are consistent with the experimental data. A new methodology was proposed with the aim of reducing the experimental analytical procedures to obtain a detailed mixture characterization. In the first step, an equimolar set of molecules is created using a building diagram by assembling structural blocks in a stochastic manner. Three different building diagrams are discussed in this work. In the second step, the mole fractions of the molecules are adjusted by maximizing an information entropy criterion. In the new methodology, an approach called molecular discretization was included to replicate the molecules based in their molar fraction to obtain a new equimolar mixture that more closely resembles the effluent composition. Both methodologies were applied to different points of the same hydrotreating test to evaluate the prediction of the detailed analytical data from global analytical data. With the new methodology, for the best scenario of optimal input data (2nd REM), the average relative error for the complex analytical procedure decreased from 26% to 18% or 12% considering, respectively, the building diagram B or C.

KEY WORDS

HDT effluents, Molecular Reconstruction, Vacuum Residues, Entropy Maximization, Stochastic Algorithm, Molecular Discretization

1 – INTRODUCTION

Petroleum is by far the most commonly used source of energy, however, the debate between using crude oil or alternative energy sources is an important global issue. In 2016, the world's consumption of crude oil reached almost 97 million of barrels per day [5]. Currently crude oil supplies about 40% of the European-28's energy consumption and 94% of its transportation energy [3]. Forecasts made by International Energy Agency (IEA) [10] indicate that the oil demand is expected to grow with the main developing economies, such as China and India.

In petroleum industry, the production of light conventional crude oil is declining, and projected to decline further in the future. At the same time, residual fuel oil demand continues to decrease, while, there demand for motor fuels continues to increase [6]. Consequently, the necessity of processing heavy oils and residue to obtain more valuable cuts like gasoline and other liquid fuels increases.

However, the complexity of petroleum increases rapidly with the boiling point (BP) as a result of the increasing number of atoms in a molecule and the immense number of their possible structural arrangements [2]. Hence, to characterize a vacuum residue (VR) mixture, due to their high number of atoms per molecule, the exact molecular structures present in heavy petroleum fractions can currently not be unveiled, so a different methodology must be followed in order to be able to develop reliable and accurate kinetics models for these fractions. The lack of detail about VR impedes the use of

traditional kinetic models in which the characterization of molecules and reactions is possible, consequently, it is necessary to numerically reconstruct a mixture from partial analytical data, model hypotheses and expert knowledge.

In this work, a two-step reconstruction algorithm, SR-REM method, will be used. The first step, called stochastic reconstruction (SR) step assume that oil mixtures can be described by distributions of structural blocks. The choice of the blocks and the distributions is based on expert knowledge and partial analytical data. The transformation from a set of distributions into a mixture of molecules is obtained by a Monte-Carlo sampling, while a genetic algorithm adjusts the parameters of distributions. The second step, reconstruction by entropy maximization (REM), improves the representativeness of the set of molecules reconstructed by adjusting their molar fractions using Shannon entropy maximization criteria. The generated set of molecules, accomplish by the SR-REM method, can be used after as input for a molecule-based kinetic models to access the molecular information which is not provided by current analytical techniques[6]. With this is possible to overcome the lack of detail information and create an accurate kinetic model to simulate and optimize the refining processes.

1.1 – VACUUM RESIDUE (VR)

A VR is a petroleum fraction that is drawn from the bottom of a vacuum distillation column. As mentioned before, a complete molecular characterization cannot be achieved with the current analytical techniques due to their complexity. In general, VR effluents are characterized by their bulk properties as elemental analysis (EA: C, H, S, N, O, Ni, V), specific gravity, average molecular weight, Conradson carbon (CCR), distillation profile, ^{13}C NMR and SARA analysis. The SARA analysis classifies molecules according to their polarity into saturates, aromatics, resins or asphaltenes. Asphaltenes are the heaviest and most polar fraction of VR, it can contain high concentrations of heteroatoms[11]. Furthermore, asphaltenes are known to be coke precursors and catalyst inhibitors[6]. The saturate fraction is the lightest and least polar fraction mainly constitute by paraffinic and naphthenic compounds. Given the low concentration of metals, these elements were not accounted during the molecular reconstruction due to their low abundance (trace levels).

With the objective of improving the reaction model of an HDT residue simulator of a fixed bed, called *Thermidor,* a more detailed description of the feedstock is required as an input: Thermidor Lumps analysis (TLA). This analysis provides a deeper detail about the mixture providing the elemental analysis for each SARA group in a range of boiling points named lumps: (middle distillates (MDt), vacuum gas oil (VGO) and VR. However, it is very costly and time consuming.

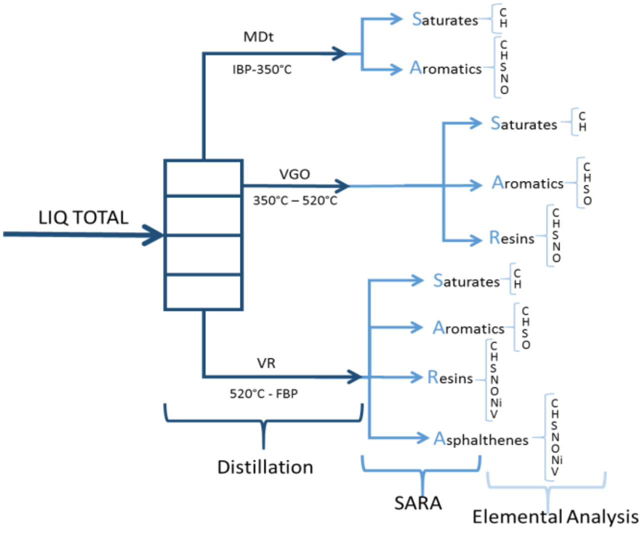

Figure 1: Scheme Thermidor Lumps Analysis (TLA).

1.2 – RESIDUE HYDROTREATING (HDT) PROCESS

In *IFPen* a simulator for the residue HDT fixed bed model was developed. This process allows the hydrotreatment and until 30% of hydroconversion of the charge turning it into more valuable products such as gasoline or gas oil in the presence of a catalyst and of hydrogen at high temperature (350°C-410°C) and high pressure (150-200 bar). The catalyst contains oxides of Mo, Co and Ni, and/or W which is supported in an alumina and/or silica used in their sulfide form.

The process scheme, shown in Figure 2**Error! Reference source not found.**, includes permutable fixed bed guard reactors technology [14] that can be switched in operation (Reactor 1a and 1b) allowing the possibility to isolate temporally one reactor for change out of the guard HDM catalyst, considering the large deactivation of the catalyst by coke deposit and metal poising.

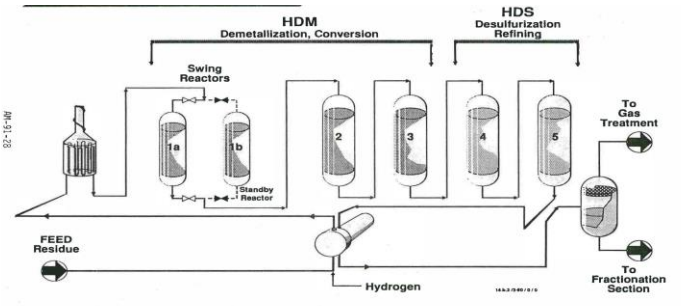

Figure 2: HYVAHL Process flow diagram with PRS [1].

2 – MOLECULAR RECONSTRUCTION

Three different approaches of kinetic models had been developed to establish a reliable kinetic model. The first strategy, lumping approach, was developed in the 50's in which the chemical complexity is reduced by grouping chemical compounds into families called lumps. The kinetics is developed for each. The major drawback of lumping is not being associated to a molecular theory badly estimating the chemical properties of the effluent turning it into a very limited approach. Although, this approach is very simple to apply requiring few analytical details and a reduced calculation time.

However, over the last decades, these industries have been subjected to more stringent regulations and this approach cannot ensure the right prediction of the process performance due to its limitations. So, detailed kinetic approach was developed. It is a complex kinetic model based on a detailed explicit description of the reaction pathways, including its reactants, elementary steps and reactions intermediates, overcoming the disadvantages of the approach by lumping. In any case, it needs high calculation times impeding an industrial process monitoring in real time. Besides that, it is mandatory to know the molecules present in the petroleum cut, for heavy fractions such as VR to measure the complete molecular content is almost unfeasible so, other approach needs to be applied.

An intermediate approach capable to overcome the lack of molecular detail in the lumping approach, and able to reduce the calculation time of the kinetic approach was developed, called molecular approach. This strategy can retain a molecular description by the simplifications made to reconstruct a feed so reaction simulation with a molecular-based description is possible.

At IFPen, in the context of molecular based approaches, the SR-REM has developed. Hudebine [7, 8] proposed to combine the SR with the REM in one method. This two-step molecular reconstruction algorithm can be used to predict missing analytical data or to generate molecular mixtures that can serve as input to detailed kinetic models.

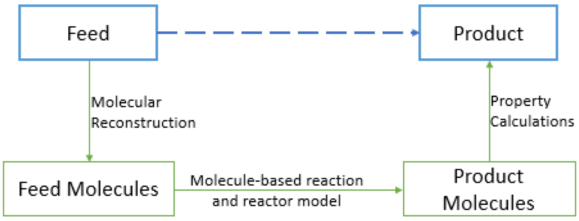

Figure 3: Molecular based approach [12].

2.1 – STOCHASTIC RECONSTRUCTION (SR)

The SR step aims to construct an equimolar set of N molecules representative of a selected petroleum fraction with approximate properties of the mixture to be represented based on a set of probability distribution functions (PDF) for molecules characteristics called attributes as molecules type, length of chains, etc. Molecules are seen as a combination of structure blocks that corresponds to the constituent elements of the molecule (e.g. aromatic cycle, sulfur functions, etc.) characterized by molecular attributes.

The choice of chemical attributes and their PDFs are based on expert knowledge of the chemical nature of the petroleum cut. In practice, each distribution is sampled via a Monte-Carlo procedure to identify the structural attributes of one molecule. The sequence of the PDF sampling steps is oriented by a building diagram, which is defined by the modeler. The BD defines the hierarchic relationship between the PDFs and the order of the sampling steps. During the assemble of structure blocks, chemical rules must be applied in order to avoid the creation of impossible or improbable molecules [12].

The Monte Carlo procedure is a probability simulation technique used to obtain numerical results relying on repeated random sampling. To draw a probability distribution, in a Monte Carlo simulation, a random value is selected for each parameter. The model is calculated based on this random value. The result of the model is recorded, and the process is repeated each time using different randomly-selected values. When the simulation is complete, the large number of results obtained are used to describe the PDF depending how many times the model returned a certain result in the simulation.

Once the molecule has been constructed, its properties are calculated by inspection of the structure, by group contribution methods or by correlations. To obtain a mixture of N molecules, the Monte-Carlo sampling technique must be repeated N times, each molecule has a molar fraction equal to 1/N. The average properties of the mixture are calculated and compared with available analytical data through an objective function. The aim is to minimize it modifying the parameters of the PDFs.

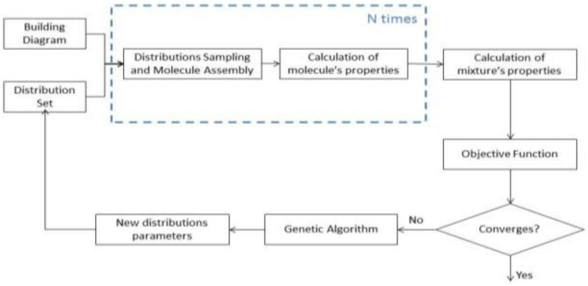

Figure 4: Block diagram of the SR step.

2.2 – RECONSTRUCTION BY ENTROPY MAXIMIZATION (REM)

In the REM a mixture of molecules is not generated, instead the molar fractions of SR pre-existing mixture are modified to achieve a better representation of the fraction. REM method is CPU efficient and provides a very good agreement between simulated and experimental properties.

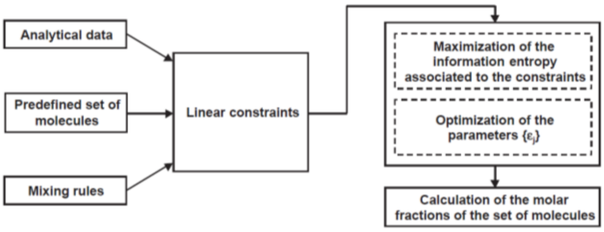

Figure 5: Block diagram of the REM step.

However, the mixture can be very difficult to reconstruct and inconsistent if the initial molecular set is not correct or very different from the feedstock type. The adjustment of the molar fractions to optimize the properties of the mixture is accomplished by using Shannon maximization of entropy criteria:

$$H = -\sum_{i=1}^{N} x_i \ln x_i$$ *Equation 1*

To maximize the function other constrains are added like the molar balance given by Equation 2.

$$\sum_{i=1}^{N} x_i = 1$$ *Equation 2*

And constrains associated to the properties of the library, if they follow a linear law the general property can be calculated by Equation 3.

$$f_j = \sum_{i=1}^{N} f_{i,j}\, x_i \qquad with\ j \in J$$ *Equation 3*

Where, *H* represents the entropy criteria, x_i represents the molar fraction of the molecule *i*, and *N* is the number of molecules in the library. It was demonstrated by Hubedine [9] that the maximization of this criteria ensures in the absence of further data, any molecule is favored over another and that when data is added to the system, the molar fractions are adjusted to obtain the best correspondence between the properties of the mixture and the added information.

It is also known that the analytical constrains can be non-linear and can contain uncertainties therefore the equations must be transformed. In the present work, only linear constrains will be applied, the remain deductions can be found in the work of Hubedine [9].

3 – OBJECTIVES

The objective of this work is therefore the numerical study of molecular reconstruction by SR-REM method, analyzing the performance of such models over hydrotreated effluents using macroscopic analytical data to predict the detailed description of the effluent. Further, this work aims at defining the optimal input analytical data that must be used to assure a correct reproduction of the hydrotreated fractions, while limiting the amount of demanded analysis.

The prediction of the detailed effluent description by numerical reconstruction may be able to avoid exhaustive and costly experimental work to obtain a full TLA description, thereby saving time and money. It may also allow the utilization of existing pilot plant points for kinetic regression, where only partial analysis is available.

4 – DESCRIPTION OF THE ADOPTED METHODOLOGY

The proposed methodology consists in reconstruct one hydrotreated pilot plant point assuring the correct reproduction of the molecular mixture by the SR step. This step takes more time when compared to REM due to its random character, therefore the remaining points of the test were reconstruct using the library of molecules pre-created applying the REM methodology to assure a reasonable calculation time and reproduction. Different ways of obtaining the library of molecules were tested in this work (Figure 6).

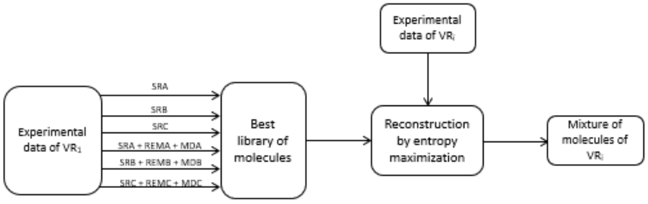

Figure 6: Methodology diagram.

Considering the study made by Luís [13] about the impact of the number of molecules in the performance of the objective function, it was concluded that a mixture of 5000 molecules would assure a good commitment between calculation time and correct reproduction.

The library of molecules was obtained applying two approaches for three different building diagrams. The first approach intents to stochastic reconstruct a VR using the equimolar output mixture as a library of molecules. In Figure 6, this approach is denominated SR followed by the letter of the respective BD. The second approach uses the SR to obtain a mixture of molecules, that is optimized changing the molar fractions of the previous mixture through a REM step, since the REM step of other VR needs as input an equimolar mixture another tool was utilized: molecular discretization (MD) to achieve a new library of molecules. In Figure 6, this approach is called SR+REM+MD followed by the letter of the respective BD.

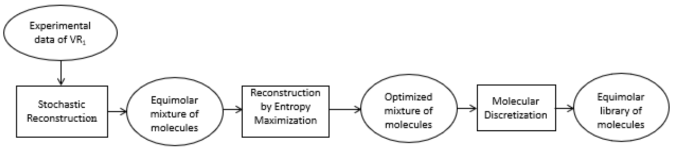

Figure 7: SR + REM + MD approach.

Three building diagrams for VR were used with different quantities of distributions and parameters to evaluate their performance. Residue A version is the BD implemented by Pereira de Oliveira in his thesis [13]. This diagram has 16 distributions and a total of 24 parameters.

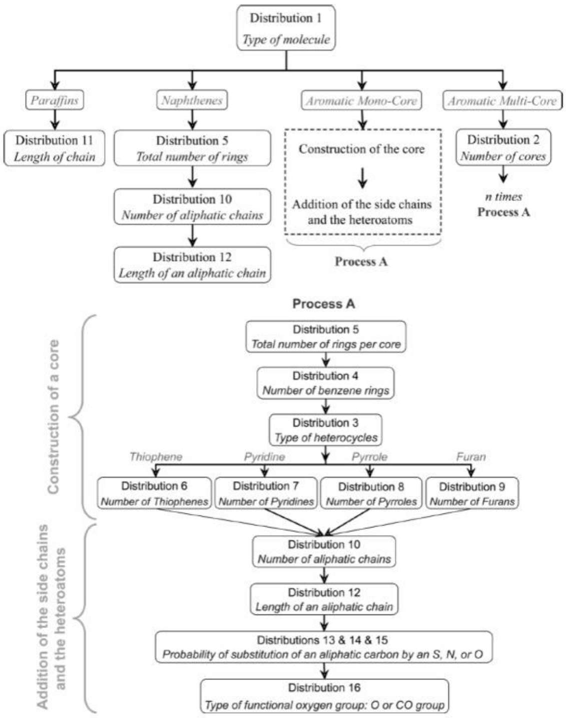

Figure 8: Residue A building diagram version [13].

Residue B BD was developed by Ana Rita Costa during her thesis [4]. The aim is to reduce the number of attributes as well as the number of parameters relatively to the previous one. This modification takes advantage of stochastic nature of the procedure giving it more flexibility. Residue B version can be described by 10 distributions with a total of 17 associated parameters.

A more suitable BD could be developed regarding thermidor lumps mixture property introduction allowing a deeper research about the molecular reconstruction. This new BD is called Residue. Finally, the parameters of the genetic algorithm for the optimization loop must be chosen to explore all the space of solutions to obtain the best set of parameters. In this work, the same parameters proposed by Luís Pereira de Oliveira [13] are applied. In his thesis is demonstrated that this configuration allows to explore well the space of optimization comprising an admissible calculation time.

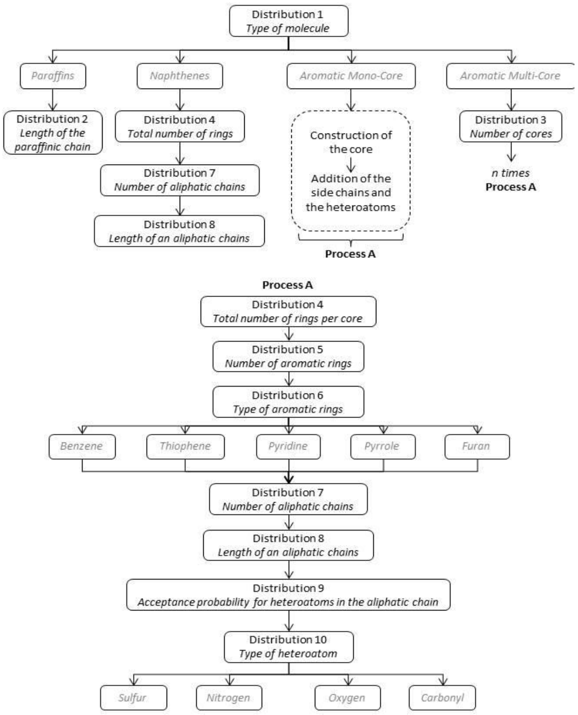

Figure 9: Residue B building diagram version [4].

5 – RESULTS AND DISCUSSION

Concerning a pilot plant scale residue HDT composed with two reactors that allows the testing of several catalysts activity, two experiment points were studied (Table 1).

Table 1: Main characteristics of the points.

	Point 1	Point 2
Density (15°C)	0.968 g/cm^3	0.974 g/cm^3
CCR %wt	10.87%	11.61%
Asphalthenes %wt	3.25%	3.85%
Sulfur %wt	2.48%	2.85%
Nitrogen %wt	0.26%	0.28%
Nickel %wt	13.7 ppm	16.0 ppm
Vanadium %wt	29.0 ppm	37.2 ppm
BP 5% wt	337.5°C	341.1°C
BP 50% wt	561.4°C	568.3°C
BP 95% wt	774.7°C	776.4°C

The errors evaluated are the absolute quadratic error (AQ) and the average of the relative error (AR) calculated by the following equations, respectively:

$$AQ\ Error = \sum_N \left(x_{experimental} - x_{calculated}\right)^2 \qquad \text{Equation 4}$$

$$AR\ Error = \frac{1}{N}\left[\sum_N \left|\frac{x_{experimental} - x_{calculated}}{x_{experimental}}\right|\right] \qquad \text{Equation 5}$$

In which x represents the value and N the number of values in each analysis. In the top of each column of the graphs the value of the relative error is revealed for each BD. When the experimental value is equal to 0 the relative error is not evaluated. Notice that all the experimental values have an associated error relative to the uncertainty of the measures.

5.1 – STEP 1: SR

In SR step the library of molecules was created taking into account as comparison the detailed analytical data necessary to the *Thermidor Simulator:* distillation profile, EA, SARA analysis and TLA. Using all the detailed analyses the objective function (difference between experimental and calculated data) was minimized to fit the experimental data. Therefore, the molecules created by the algorithm should be the most appropriate.

Considering the calculated properties for both BDs, the global analytical data in Table 2 shows some deviations relatively to the experimental values although the algorithm calculates reasonable values. It was expected to find the biggest discrepancies in the heteroatoms, mainly in nitrogen and oxygen since they are present in lower quantities and, the experimental uncertainty in these elements is larger. For the distillation profile, the initial and the final boiling points are not so well adjust as expected. This can be attributed to both the experimental uncertainty and the group contribution method used for the calculation of the boiling points. For the SARA analysis the fit in BD B is almost perfect.

Table 2: Results SR step.

Point 1			Calculated Values	
Experimental Values			BD A	BD B
C	wt%	85.67	85.77	85.74
H	wt%	11.46	11.37	11.27
S	wt%	2.48	2.47	2.60
N	wt%	0.26	0.27	0.26
O	wt%	0.13	0.12	0.13
Saturates	wt%	25.03	25.26	25.11
Aromatics	wt%	46.85	47.79	46.99
Resins	wt%	24.87	24.08	24.51
Asphaltenes	wt%	3.25	2.87	3.39
Initial BP	°C	150.5	148.1	148.1
5% BP	°C	337.4	312.5	286.5
10% BP	°C	378.9	370.3	353.8
20% BP	°C	438.8	445.9	437.9
30% BP	°C	484.9	498.6	491.1
40% BP	°C	524.3	540.6	533.6
50% BP	°C	561.4	576.8	573.1
60% BP	°C	598.1	608.7	610.5
70% BP	°C	640.6	641.8	645.4
80% BP	°C	692.5	673.1	682.0
90% BP	°C	740.4	709.3	717.9
95% BP	°C	774.7	739.5	741.3
Final BP	°C	866.6	801.3	826.1

Regarding the TLA, Figure 11, a more detailed analysis, a perfect adjustment of the carbon content is accomplished with both BDs. Very low relative errors are observed, always below 5% and most of them below 1%. For hydrogen, the same behavior is observed for both BDs: the hydrogen content for the high-boiling polar products is systematically too high, revealing an unsuitable hydrogen distribution as function of the MW. Overall, the lighter lumps have less hydrogen than experimental observed, and, the heavier lumps have more hydrogen than their corresponding experimental value. In TLA of the heteroatoms (Figure 12), sulfur has an increasing experimental profile in function of the MW. However, this is not predicted by any of the BDs and an unsuitable distribution is revealed. Similarly, the fit for nitrogen and oxygen is not good, even considering the experimental uncertainty. Fortunately, for the HDT process, both these elements are less relevant.

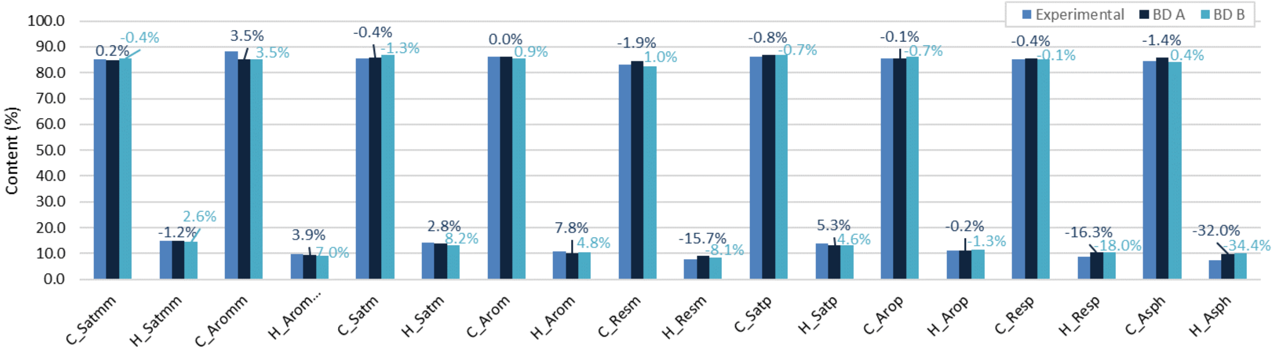

Figure 10: Thermidor lumps results SR for C and H.

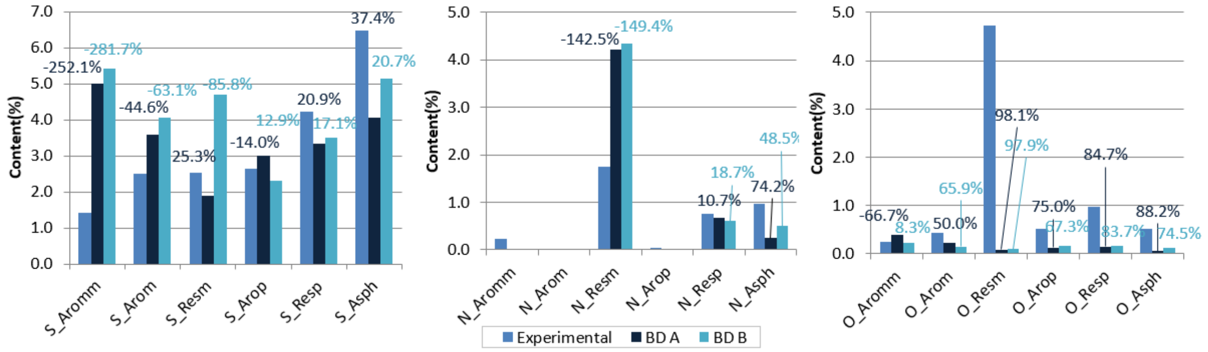

Figure 11: Thermidor lumps results SR for heteroatoms.

For the SR step, BD B demonstrated to be more suitable to the creation of the library of molecules since the errors are lower, even though BD B has a lower number of distributions and parameters, and therefore a lower degree of freedom to adjust the data and create more suited molecules.

5.2 – STEP 2: REM + MD

The objective in this second step is to try to obtain a better library of molecules that the previous one. The REM procedure will generate an optimal mixture of molecules by adjusting the molar fractions of the equimolar mixture given by SR. However, to use this library of molecules for the other points an equimolar mixture is required, to overcome this drawback a procedure called molecular discretization (MD) was applied.

5.2.1 – MOLECULAR DISCRETIZATION (MD)

After the REM of an effluent, each molecule has its own molar fraction, leading to a non-equimolar mixture. The molecular discretization algorithm replicates each molecule n times in order to reobtain an equimolar mixture usable by the REM algorithm to reconstruct other reactor effluents. This procedure was developed by Luís Pereira de Oliveira in his PhD thesis. For deeper understanding of this procedure, the reader is referred to reference [12]. For the replication of the molecules is applied the concept of repeat frequency (fr). The replication of molecules is done knowing that the repeat frequency is directly proportional to the molar fractions, x_i. The repeat frequency is calculated by rounded the value to the nearest integer considering a replication factor, K.

$$fr = ROUND\ (x_i.K) \qquad \textit{Equation 6}$$

The replication factor has two functions: the first one is to impose a maximum number of molecules in the discretized mixture. The second one enables to eliminate the molecules with a molar fraction lower than $1/2K$ since the procedure will round those values to nearest integer (zero). For that reason, the value of K should be as high as possible, otherwise, the MD will eliminate a large number of molecules, consequently degrading the representativeness of the mixture. Meanwhile, a high value for K means a larger number of molecules, increasing the CPU effort and the calculation time. In this work, a value of 10 000 was applied to assure a good trade-off between the representativeness of the obtained mixture, CPU effort and calculation time.

Regarding Table 3, applying the REM to the mixture globally improves the results, as was expected, because this procedure optimizes the mixture by adjusting the molar fractions of the molecules in order to be closer to the experimental data. However, issues are found on the oxygen content due to the mass balance inconsistencies. The application of this new procedure (SR+REM+MD) has as main advantages: the achievement of a proper sulfur profile and a better fitting of the hydrogen distribution, therefore decreasing the TLA error and ensuring a better reproduction of the experimental data (Figure 12 and Figure 13). Therefore, the BD A presents slightly better results mainly for TLA the BD B was considered more appropriated to construct the library of molecules due to the higher stochastic character provided by a lower number of distributions and parameters.

Table 3: Results REM+MD step.

Point 1			Calculated Values	
Experimental Values			BD A	BD B
C	wt%	85.67	85.67	85.60
H	wt%	11.46	11.43	11.36
S	wt%	2.48	2.44	2.46
N	wt%	0.26	0.25	0.27
O	wt%	0.13	0.22	0.30
Saturates	wt%	25.03	25.11	25.43
Aromatics	wt%	46.85	47.20	46.58
Resins	wt%	24.87	24.39	24.82
Asphaltenes	wt%	3.25	3.30	3.17
Initial BP	°C	150.5	153.5	148.1
5% BP	°C	337.4	333.5	153.5
10% BP	°C	378.9	371.2	342.8
20% BP	°C	438.8	439.9	423.1
30% BP	°C	484.9	486.7	472.2
40% BP	°C	524.3	525.5	520.7
50% BP	°C	561.4	562.5	551.3
60% BP	°C	598.1	597.5	587.1
70% BP	°C	640.6	640.1	624.7
80% BP	°C	692.5	691.1	663.1
90% BP	°C	740.4	740.8	730.5
95% BP	°C	774.7	776.0	770.5
Final BP	°C	866.6	801.4	807.5

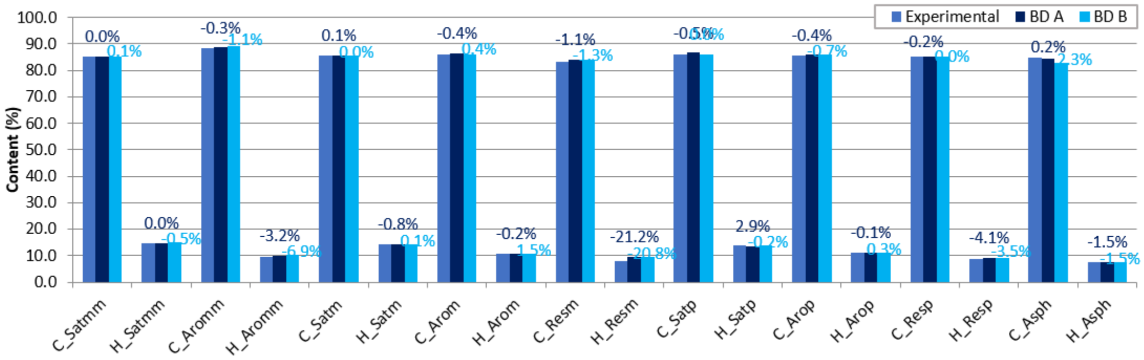

Figure 12: Thermidor Lumps results REM+MD step for hydrocarbons.

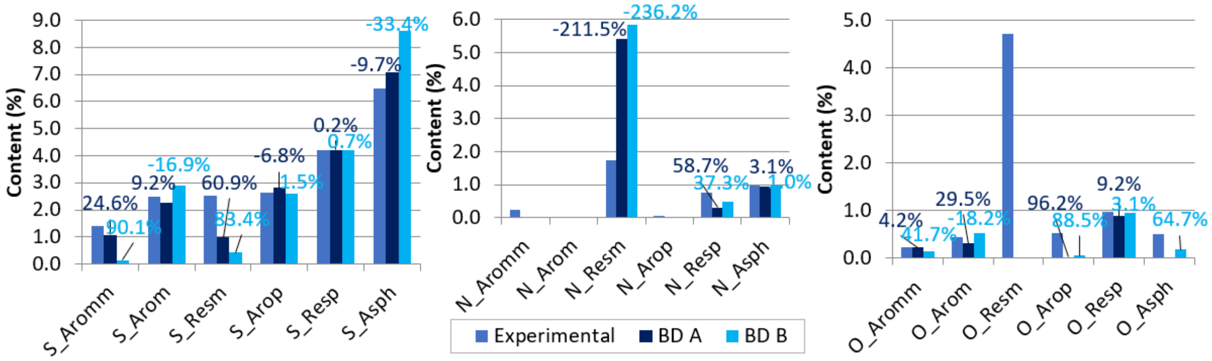

Figure 13: Thermidor Lumps results REM+MD step for heteroatoms.

5.3 – STEP 3: VR_I APPLICATION CASES

Figure 14 illustrates the method proposed to reconstruct the VR_i from the pre-created library of molecules exploring the optimal quantity of analytical data that assures a correct reproduction of the petroleum fraction.

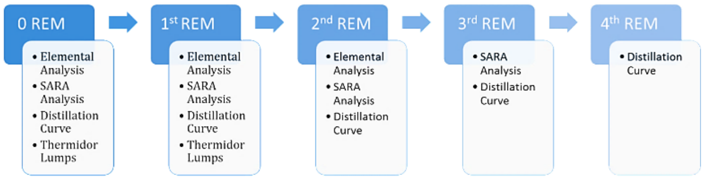

Figure 14: VR_i reconstruction procedure scheme.

Case zero and the first case use all the analytical data that must be given to the simulator. In those two cases, there is no reducing of the analytical work. The most relevant case is the second one (2nd REM) in which the REM is applied taking as input the global analytical data necessary to the simulator to predict the TLA. The third and fourth cases are limiting cases in which a strongly reduced amount of information is given. The third and fourth cases are limiting cases in which a strongly reduced amount of information is given. The results for the 2nd REM case will be discussed considering the BD B seen as the most flexible therefore the most suitable.

In this case, only the global analytical data was considered in order to predict the TLA values. Comparing the results for the global analyses given as input to the algorithm (Table 4), for both methodologies, step 1 and step 1+2, the same results are roughly obtained. Furthermore, the global analytical data given as input adapts the values perfectly to the experimental ones.

Table 4: Results 2nd REM application case BD B.

Point 2			Calculated Values	
Experimental Values			Step 1	Step 1+2
C	wt%	85.31	85.31	85.31
H	wt%	11.36	11.36	11.36
S	wt%	2.85	2.85	2.85
N	wt%	0.28	0.28	0.28
O	wt%	0.2	0.20	0.20
Saturates	wt%	23.89	23.89	23.89
Aromatics	wt%	46.11	46.11	46.11
Resins	wt%	26.15	26.15	26.15
Asphaltenes	wt%	3.85	3.85	3.85
Initial BP	°C	151.0	148.1	148.1
5% BP	°C	341.1	338.3	339.8
10% BP	°C	380.9	381.0	381.0
20% BP	°C	439.2	439.5	439.4
30% BP	°C	487.3	487.5	487.1
40% BP	°C	530.2	530.4	530.1
50% BP	°C	568.3	568.4	568.1
60% BP	°C	606.7	606.8	606.5
70% BP	°C	651.5	651.6	651.3
80% BP	°C	704.3	704.1	703.8
90% BP	°C	746.3	745.9	750
95% BP	°C	776.4	776.3	776.3
Final BP	°C	854.8	826.1	807.4

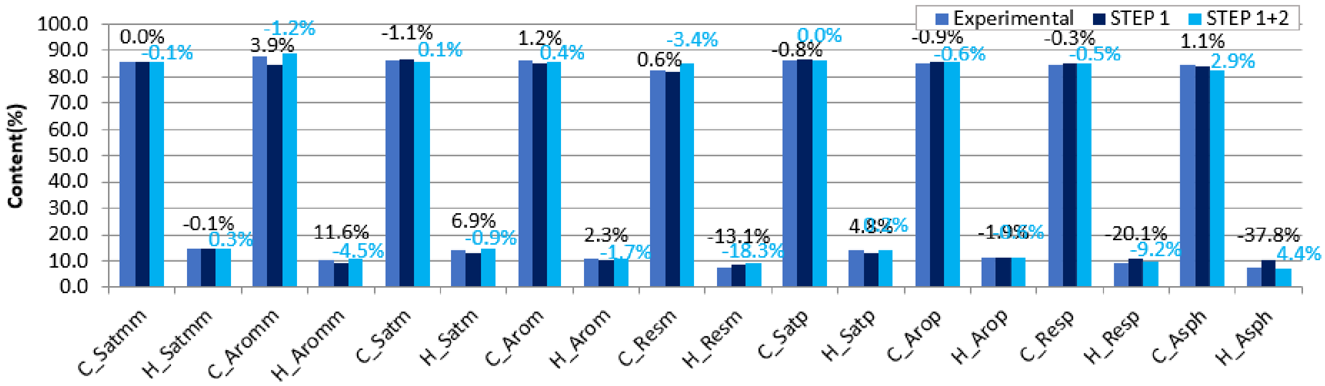

Figure 15: Thermidor Lumps 2ND case results for hydrocarbons.

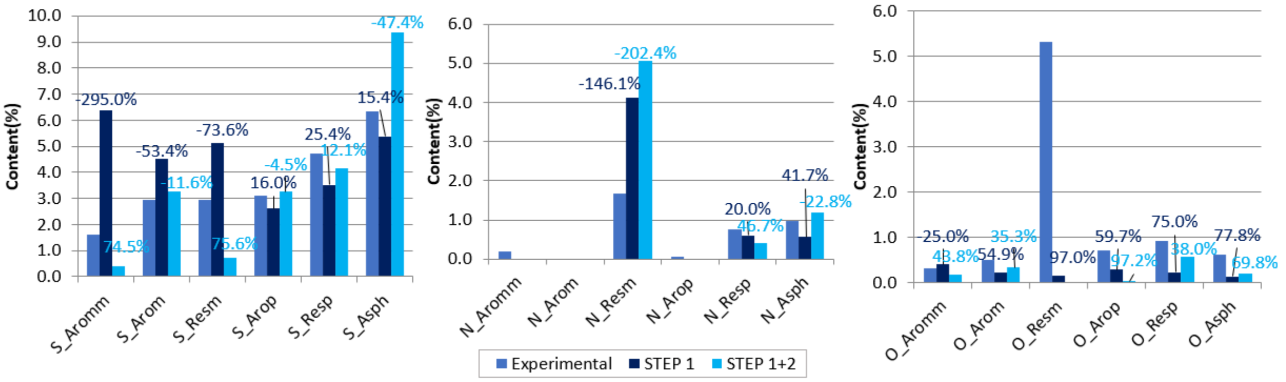

Figure 16: Thermidor Lumps 2ND case results for heteroatoms.

Regarding the prediction of the TLA, (Figure 15 and Figure 16), the best results are obtained using the library of molecules previously fine tune, step 1+2. Since the application point is from the same test, the type of molecules found are similar and the fine tuning done to the library of molecules allows to narrow the calculation of the TLA, presenting best results, consequently the S and H distributions are more accurate that the less restricted library (step 1). This library of molecules, step 1+2, is considered more suitable when the number of input analytical data is reduced. Although, unsuitable distributions were found for the H and S in function of the MW.

To ameliorate the effluent reconstruction, two ways can be taken. The first one was increasing the replication factor increasing the representativeness of the mixture. This method will maintain the same library of molecules by eliminating fewer molecules and keeping the optimal mixture achieved by the REM procedure. The second one was the development of a new BD to construct more suitable molecules. This BD should provide a higher freedom to create distributions in function of the MW. Since changing the replication factor of the MD procedure to delete less molecules will not correct the problems found for the H and S distributions, it was decided to construct a new BD to solve the root of the problem: the construction of the molecules.

5.4 – BUILDING DIAGRAM PROPOSAL

The objective of this BD is to reduce the error associated to TLA. The edification of this scheme is based on the BD B, in which to calculate the cyclohexane rings an equation was used considering the difference between the distribution 4 and 5. To try to improve, the distribution 5 was eliminated and a new parameter specific to the cyclohexane rings was added to the type of rings distribution. Consequently, this new BD called BD C has 9 distributions and the same number of parameters as BD B. It is expected that this alteration gives more flexibility to H distribution and afterward to the addition of the heteroatoms to the chains.

Considering Table 5, the library of molecules constructed by the new BD reveals a better fitting for the global analytical data (SR+REM+MD). Comparing to the BD B, applying the REM step the properties are fine-tuned and the improvements for the EA and the SARA analysis enable an almost perfect fit excepting for the distillation curve in which the BP are successively lower than the experimental value, since the molecules are not heavy enough to achieve the BPs of the mixture. Moreover, the higher weight given to the saturates results in a very low BP for 5%wt (SR step).

As before, due to the inconsistencies in the O mass balance the calculated value is not suitable.

Table 5: Results library of molecules BD C.

Point 1			Calculated Values		
Experimental Values			SR	SR+REM	SR+REM+MD
C	wt%	85.67	85.93	85.63	85.64
H	wt%	11.46	11.38	11.38	11.38
S	wt%	2.48	2.33	2.44	2.43
N	wt%	0.26	0.22	0.24	0.24
O	wt%	0.13	0.14	0.31	0.30
Saturates	wt%	25.03	26.67	25.08	25.22
Aromatics	wt%	46.85	44.95	46.85	46.63
Resins	wt%	24.87	24.26	24.84	24.87
Asphaltenes	wt%	3.25	4.12	3.24	3.28
Initial BP	°C	150.5	148.1	148.1	148.1
5% BP	°C	337.4	220.5	170.8	177.6
10% BP	°C	378.9	272.4	348.1	347.1
20% BP	°C	438.8	344.0	421.5	419.4
30% BP	°C	484.9	396.1	479.5	481.8
40% BP	°C	524.3	447.0	521.9	525
50% BP	°C	561.4	499.1	554.5	553.4
60% BP	°C	598.1	554.9	594.6	592.8
70% BP	°C	640.6	615.9	626.6	617.9
80% BP	°C	692.5	653.0	673.8	673.8
90% BP	°C	740.4	677.7	699.4	699.4
95% BP	°C	774.7	693.6	750.1	750.2
Final BP	°C	866.6	750.2	750.1	750.2

Regarding the TLA, the results are equivalent to the ones found for the BD B given the proximity of schemes but H and S distributions are improved (Figure 17 and Figure 18). Although, the H and S distributions in the asphaltenes are not well optimized. Due to the random character of the procedure a deeper research regarding the distillation profile needs to be study to find a way of improving the TLA without prejudicing the remaining analytical data.

Since the BD C is derived from the BD B the results for the molar fraction distribution are equivalent, so unsuitable molecules have less impact meaning a lower molar fraction, since the results between the SR+REM and SR+REM+MD are similar the replication factor of 10 000 is validated.

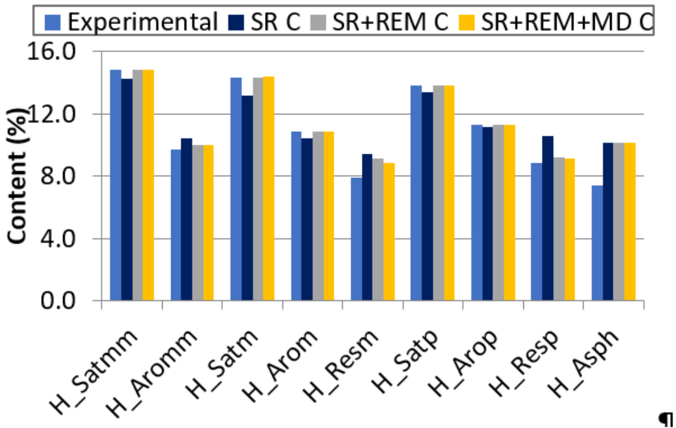

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Figure 17: H distribution BD C.

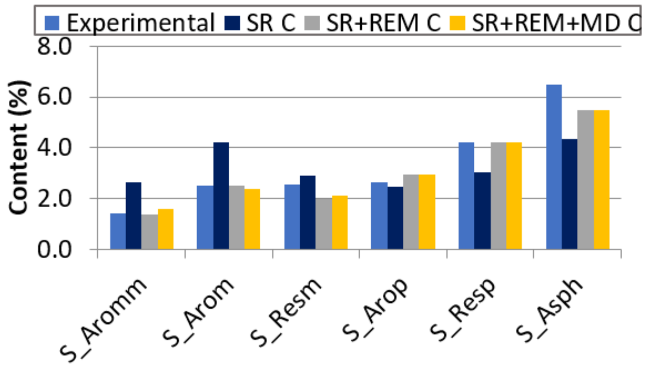

Figure 18: S distribution BD C.

6 – CONCLUSIONS AND PERSPECTIVES

In this work a new methodology to reconstruct the VR was developed considering HDT effluents that consists in applying three different steps: SR, REM and MD; this new methodology seems to be more suitable that other methodologies when less analytical data is provided to the algorithm since the library of molecules is optimized therefore closer to the experimental data. The best BD is the one in which the stochastic character of the procedure is higher, this means the ones with less distributions and parameters, so BD B and BD C, although the BD B presents best results when edifying an equimolar set of molecules (SR step).

Additionally, the TL reconstruction needs to be improved to achieve an AR error lower than 5%, during this work a minimum of 12% was reached for the application case and 8% for the molecules library, these values correspond to the 2nd REM case reducing the experimental work by predicting the TLA, the most costly and time consuming analysis. Considering the MD procedure, the replication factor imposed deletes around 40% for the BD A and around 60% for the BD B and BD C, since this factor is closely related with the loss of representativeness of the mixture the lower the elimination of molecules the closer the mixture is to the optimal given by the REM step. To improve the results a deeper research in the edification of the BD needs to be done to create more suitable molecules and decrease the TLA error to better fit the experimental data increasing the representativeness of the mixture by deleting less molecules.

Finally, it is suggested to study the propagation of errors of the TLA to fully understand the uncertainties of the experimental values. To validate the methodology other points, need to be tested.

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