MOLECULAR RECONSTRUCTION OF VACUUM GASOILS

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Introduction

In petroleum refining, both the accurate design and the optimization of conversion processes require the development of reliable kinetic models. In order to account for the differences in reactivity of the various species, more rigorous models containing molecule-based reaction pathways are needed. Such models expect a molecular description of the feed, however. Unfortunately, for petroleum cuts boiling above the naphtha range (gasoil, VGO, residue,), a molecular description can no longer be obtained directly from analyses.

To circumvent this lack of molecular information, a detailed description needs to be obtained from more global analyses. This process of approximating the composition in individual components of a feedstock from overall characterization data of the mixture has lately been referred to as "molecular reconstruction". The idea of these molecular reconstruction algorithms is to generate a discrete set of molecules whose properties mimic the properties of the petroleum cut to be represented.

Liguras and Allen[1] proposed to use a predefined set of key components and to numerically adjust their molar fractions in order to obtain a mixture that closely resembles the input analytical data. Unfortunately, this approach is based on an *a priori* definition of the components, while the adjustment of the mixture composition requires a large amount of analytical data, which are not necessarily available to refiners. To overcome these limitations, Neurock et al.[2] developed a method that was termed "stochastic reconstruction". To arrive at a description on a molecular level, a set of distributions of molecular structural attributes was first defined and then sampled by a Monte Carlo method so as to obtain an equimolar mixture of molecules. When coupled to an optimization loop, the method has been proved able to yield mixtures that closely reproduce the properties of heavy asphalthene fractions[3].

During previous work[4], two different algorithms were developed to generate a complex mixture of molecules from standard petroleum analyses: a stochastic reconstruction technique and a reconstruction method based on information entropy maximization. These algorithms were validated on FCC gasolines and on Light Cycle Oils (LCO)[5]. In the present work, a combination of both approaches will be applied to the molecular reconstruction of vacuum gasoils.

General description of the algorithm

The proposed algorithm consists in two distinct steps. After defining a molecule construction scheme tailored to the specific petroleum cut, a large set of molecules is generated via a stochastic reconstruction method. This generation is iteratively improved until it results in an equimolar mixture whose properties are close to this reference petroleum fraction. This mixture is subsequently used as a starting point and its representativeness is improved by modifying the molar fractions of the various molecules via an information entropy maximization method.

Generation of an initial set of molecules. In the first step, a set of molecules that are typical of the petroleum cut to be represented needs to be created. In this work, a stochastic reconstruction algorithm is used to create a large set of molecules that are assembled from a number of structural attributes (polycyclic cores, rings, chains, substituents,). In order to create a molecule, the type and number of these attributes are selected by randomly sampling a set of parametric distributions of the building blocks via a Monte Carlo method. During the assembly of the selected structural attributes into a molecule, a "construction scheme" and "building rules" are used to avoid the creation of unfeasible or unlikely molecules. The construction scheme is a decision tree that controls the sequence in which the various attributes are sampled. The building rules are constraints that are used to correctly assemble the various building blocks and to discard unlikely molecules based on thermodynamic or likelihood grounds. The molecule construction procedure is repeated N times in order to obtain an equimolar mixture of N molecules. For each molecule, pure compound properties are calculated from their structure, either directly by inspection (e.g. chemical formula, molecular weight, NMR, mass spectra) or numerically by group contribution methods (e.g. density, boiling point). The average properties of the mixture of N molecules are then obtained through mixing rules and compared to the available analytical data of the petroleum cut (elemental analysis, density, molecular weight, mass spectrometry,). The deviation between the experimental and simulated data is then quantified via an objective function. An elitist genetic algorithm finally modifies the parameters of the distributions for the structural attributes to minimize this objective function (Figure 1). By this procedure, the generated set of molecules is successively modified until a mixture is obtained that mimics the properties of the petroleum fraction to be represented.

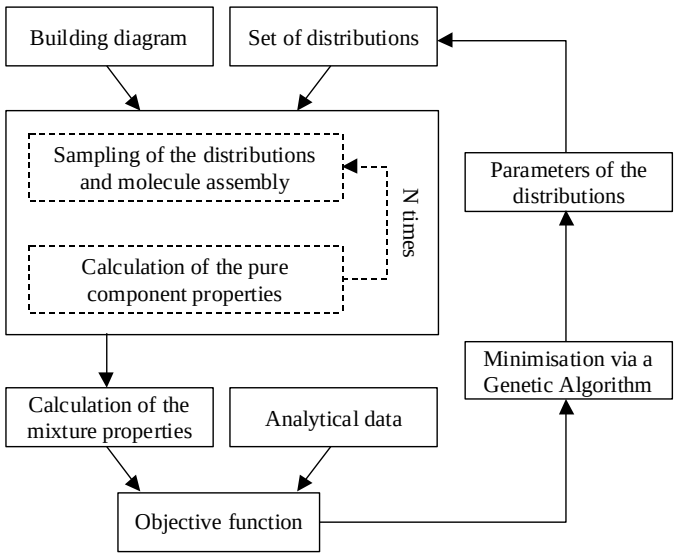

Figure 1. Stochastic reconstruction algorithm.

Enhancement of the molecule-based representation. The initial set of molecules that has been generated by the above described stochastic reconstruction method only yields an average representation of the vacuum gasoil. In order to improve the representativeness of the set of molecules, it is possible to further adjust the molar fractions of these molecules based on the available analytical data. In this work, the adjustment is carried out by maximizing the information entropy. This criterion ensures that, in absence of sufficient information, the distribution of the set of molecules will remain uniform. The introduction of constraints (i.e. analytical data for the petroleum cut to be represented) distorts the uniform distribution of the set in order to match this information. In the current implementation of the algorithm, the only restriction of the method is that the various constraints need to be linear. As

opposed to the stochastic reconstruction technique, the entropy maximization method uses a classical optimization technique. For a more detailed description of the algorithm, the reader is referred to Hudebine et al.[5].

Application to vacuum gasoils

In order to apply the above-described method to the molecular reconstruction of vacuum gasoils, an adapted molecule construction scheme needs to be defined. This requires detailing, on the one hand, the type and distribution of each structural attribute, and the construction scheme and building rules on the other hand.

The choice of the structural attributes and their distributions has been guided by knowledge of the chemical nature of these cuts, although care has been taken to minimize the number of attributes. For vacuum gasoils, the number of polycyclic cores per molecule was limited to one. The corresponding distribution for this attribute must therefore be a histogram with 2 bins: 0 or 1. Analogously, the number of rings in the polycyclic cores was limited to 7. To reduce the number of parameters, the corresponding distribution is considered to be a gamma distribution. Table 1 lists the distributions used to build a vacuum gasoil.

Table 1. Description of the Structural Attributes Used

Structural attribute	Distribution	Values	Param.
1. Number of polycyclic cores	Histogram	0 or 1	1
2. Number of rings	Gamma	0 .. 7	2
3. Presence of aromatic rings	Histogram	0 or 1	1
4. Number of benzenes	Exponential	0 .. 7	1
5. Number of hetero-atomic rings	Histogram	0, 1 or 2	2
6. Number of thiophenes	Histogram	0 or 1	1
7. Number of pyridines	Histogram	0 or 1	1
8. Number of pyrroles	Histogram	0 or 1	1
9. Alkyl chain probability	Histogram	0 or 1	1
10. Sulfide substituent probability	Histogram	0 or 1	1
11. Amine substituent probability	Histogram	0 or 1	1
12. Length of a paraffin chain	Exponential	> 0	1

The construction scheme allows to define the sequence in which the distributions are sampled. For a given molecule, the number of polycyclic cores is first selected. If this number is equal to 0, the molecule is a paraffin. Distribution 12 is then used to determine its length and each carbon atom is tested to define whether a sulfide or amine substituent should be added (distributions 10 and 11). If the number of cores is equal to 1, distribution 2 gives the total number of rings in the core, while distribution 3 indicates whether aromatic rings are present. In the latter case, the number of benzene rings and the number of hetero-atomic rings are given by distributions 4 and 5 respectively, while the number of naphthenic rings is calculated by difference. The type of the hetero-atomic rings is defined by distributions 6, 7 and 8. Once the various elements are assembled into a polycyclic core, each peripheral carbon atom is tested to check whether an alkyl chain should be inserted or not (distribution 9). The length of the alkyl chains is determined by distribution 12. Finally, distributions 10 and 11 are used to add sulfide and amine substituents.

With this molecular construction scheme, the stochastic reconstruction was used to generate an initial set of 5000 molecules that was obtained after minimization of the objective function. The latter contains the differences between the experimental and calculated values for the elemental analysis, the density, the basic nitrogen content, the liquid chromatography S.A.R. distribution and the detailed Fisher[6] mass spectrometry analysis. As can be seen in Table 2, the properties of the initial equimolar mixture of molecules obtained at the end of the stochastic reconstruction step are already close to the corresponding experimental values. Some differences still exist, especially in the simulated distillation curve, which was not included in the objective function, and in the Fisher analysis.

The second step of the algorithm adjusts the molar fractions of the various molecules via an entropy maximization method that minimizes the differences between experimental and calculated values for the simulated distillation curve, the elemental analysis, the basic nitrogen content, the liquid chromatography S.A.R. distribution and the detailed Fisher mass spectrometry analysis. The properties of the resulting final mixture are very close to the corresponding experimental values, indicating that this mixture is a good representation of the actual vacuum gasoil.

Table 2. Comparison of the Properties of the Vacuum Gasoil and of the Corresponding Molecular Set

	Exp.	Initial	Final
Simulated Distillation			
0% (°C)	388	*363*	363
5% (°C)	426	*374*	424
10% (°C)	434	*388*	434
30% (°C)	454	*434*	455
50% (°C)	476	*469*	475
70% (°C)	501	*511*	501
90% (°C)	529	*592*	528
95% (°C)	536	*626*	537
100% (°C)	543	-	568
Elemental analysis			
Carbon (wt%)	87.09	87.04	87.10
Hydrogen (wt%)	12.27	12.33	12.28
Sulfur (wt%)	0.47	0.43	0.49
Nitrogen (wt%)	0.17	0.20	0.13
Density at 15°C (g/ml)	0.9247	0.9294	*0.9246*
Basic nitrogen (wt%)	0.06	0.12	0.04
Liquid chromatography class			
Saturates (wt%)	58.6	59.1	58.6
Aromatics (wt%)	31.6	32.1	31.6
Resins (wt%)	9.8	8.8	9.8
Partial Fisher mass spectrometry			
C_nH_{2n+2} (wt%)	18.0	18.8	18.0
C_nH_{2n} (wt%)	15.2	5.4	15.2
C_nH_{2n-2} (wt%)	29.3	8.6	29.3
C_nH_{2n-4} (wt%)	0.0	7.1	0.0
C_nH_{2n-6} (wt%)	4.6	7.5	4.6

Conclusions

A molecular reconstruction algorithm was developed for vacuum gasoils. The proposed two-step algorithm first generates an initial equimolar set containing a large number of molecules via a stochastic reconstruction method. The representativeness of this mixture is subsequently refined by modifying the molar fractions of the various molecules via an information entropy maximization method. The properties of the resulting set of molecules are very close to vacuum gasoil to be represented, indicating that this mixture can now be used as input to a detailed reaction scheme for hydrocarbon conversion processes.

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