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Molecular Management of Gasoline Streams

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A novel methodology is developed to characterise gasoline streams with molecular details. The method comprises the enhancements of both representation matrix construction and transformation methodology of bulk properties into molecular composition on the basis of MTHS (molecular type homologous series) framework (Aye, 2005). More detailed description of molecular structures is introduced into the MTHS framework. By introducing statistical distribution and applying extensive bulk properties, the method abandons the sample matrices database which demands a large amount of stream information from different refining processes. A case study illustrates the good accuracy of the methodology.

1. Introduction

The refining industry today has to comply with higher product quality specifications and more stringent environmental regulations, with more emphasis on the molecular composition of refining products. The inherent disadvantages of the bulk property based reaction models prevent the refining processes simulation and optimisation for different feedstocks. Simon (2001) pointed out that "molecular management" is crucial to refineries' survival. Therefore, the aim of this work is to develop a methodology to characterise a petroleum fraction in the form of detailed molecule composition.

Most endeavors on the molecular modeling of a petroleum fraction contain two basic problems. One is what can be used to represent petroleum streams because of the astronomical number of hydrocarbons and hydrocarbons with heteroatoms. The other is how molecular information is obtained since streams with similar bulk properties could have significantly different molecular compositions. To overcome these problems, two kinds of methods have been developed: deterministic and stochastic methodology.

The idea behind the stochastic methodology is that any molecule in a petroleum feedstock can be viewed as a collection of molecular attributes (Klein, M., 2005). Neurock et al. (1994) developed a Monte Carlo construction technique. Campbell (1998) developed the overall steps to transform indirect analytical information into a molecular representation. Recent works was carried by Hudebine et al. (2004). Although stochastic method was fairly accurate, it is impractical for application in detailed kinetic modeling with the computational power available today.

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The deterministic methodology is significantly faster than the stochastic methods by predefining a molecular library instead of generating a new one. Jabr et al (1992) attempted to characterize petroleum naphtha by dividing it into five cuts with unified boiling ranges. Albahri (2005) treated the distillate profile as the source of an infinite number of experimental data for estimating the composition of any desired number of components. But as the key factor of the representation accuracy, number of candidate molecules is hard to decide. Hudebine et al. (2007) developed a methodology based on Shannon's entropy criterion which is too insensitive to molecules with similar physical properties, and similarly the candidate molecules are not easy to decide.
MTHS proposed by Peng (1999) incorporates both molecular type and carbon number. The combination provides efficient determination of the reactivity and the properties of a petroleum fraction. Based on MTHS, Zhang (1999) developed an approach to transfer bulk properties into molecular composition. To include the structural influence on properties, Aye (2005) extended MTHS to consider isomers, and enhanced the transformation method by generating sample streams database to take the processing history into account. However, some inherent limitations of the framework reduce the accuracy and applicability. In this work, an improved MTHS framework is developed in order to address the shortcomings of the previous approaches.

2. A novel methodology for molecular management of gasoline streams

The proposed characterisation framework for gasoline streams comprises of two sections corresponding to the two basic problems: the determination of predefined molecules library based on MTHS matrix and the transformation of the easily obtained global bulk properties into molecular composition based on an optimisation programme.

2.1 A new MTHS representation matrix

Table 1 illustrates the new MTHS representation matrix for gasoline streams, where the rows stand for carbon numbers and the columns for homologous series, with sulphur, nitrogen and oxygenate contents. The molecules with the same homologous series and carbon number are lumped into one entry of the matrix as they have similar properties. The elements defined in the matrix represent the molar/weight/volume percent of either a single molecule or a lump of all possible structural molecular isomers.
The limitations of the analytical techniques and the knowledge on refinery process chemistry determine what molecular types and homologous series are incorporated in the matrix. Aye (2005) tried to catch the structural contribution on properties by assuming thermodynamic equilibrium for calculating the internal distribution between isomers, which varies with the measured distribution of each refining process as Table 2 shows. Instead of using a fixed internal distribution, the new MTHS matrix lumps isoparaffins into three homologous series: monmethyls, dimethyls, and trimethyls isoparaffins, and lumps olefins into two series: normal and branched olefins. The main reason for constructing the new homologous series is based on the observations that the two key properties of gasoline streams – ON (Octane number) and RVP (Reid Vapour Pressure) are similar for isomers within each new homologous series, and molecules belonging to MP, DP and TP take the majority of the isoparaffins concentration. Although the physical properties for olefin isomers do not differ significantly, chemistry

patterns are different (Lappas, 1999). Regarding naphthenes and aromatics, there are small variations in the physical properties of isomers and the detailed information on isomers might not be available. In summary, each entry is a lump of isomers with same homologous series and carbon number. The internal distribution of isomers within each entry may be different for different refining processes.

Table 1 New MTHS representation matrix for gasoline streams

Sulphur Content (wt%) =	Nitrogen Content (wt%)=			Oxygenates content (wt%)=			
	NP	MP	DP	TP	NO	BO	N	A
C4								
C5								
C6								
C7								
C8								
C9								
C10								
C11								
C12								

NP, MP, DP, TP: Normal, Monomethyl-, Dimethyl-, Trimethyl-, NO, BO: Normal, Branched Olefins, N: Naphthenes, A: Aromatics

Table 2 Typical Measured Isomer Distribution (wt%) for i-Octane (Ghosh, P., 2006)

Stream Type	Monomethyls	Dimethyls	Trimethyls
Alkylates	0	18.5	81.5
Reformates	68.9	31.1	0

2.2 A new transformation methodology of bulk properties to molecular composition

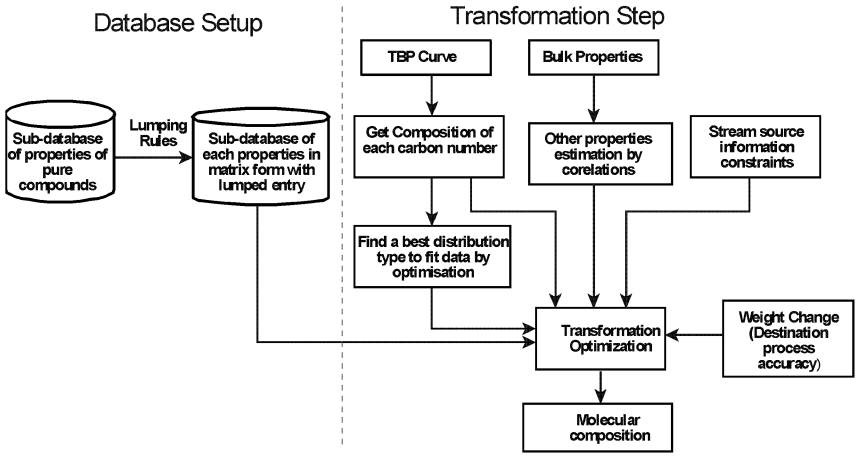

Fig 1 A new MTHS framework for characterisation of petroleum fractions

2.2.1. Assumptions

The proposed methodology is based on two assumptions. One is that the molecular composition within each homologous series follows a statistical distribution on carbon number. Klein (2005) recommends gamma distribution because of its flexibility that the gamma distribution ranges from an exponential distribution to a delta function and can also approximate a normal distribution. The other assumption follows the general belief that the global properties of a petroleum fraction are close to the calculated from pure compounds based on mixing rules. Besides the measured properties such as distillate profile, specific gravity, ON, RVP and etc., other derived bulk properties from correlations are also applied to capture the characterisation of each molecule in a petroleum fraction. Those properties include volume/weight/mole average boiling point, refractive index, waston K, acentric factor, kinetic viscosity (100 °F),critical pressure/temperature/volume/compressibility factor, molecular weight, CH weight ratio, heat of vaporisation (NBP), heat of combustion at 77 °F, isobaric liquid heat capacity (60 °F), isobaric vapor heat capacity (60 °F), liquid thermal conductivity (77 °F), aniline point, cloud point, and surface tension (77 °F). Most correlations are available from API TDB (1970) and Riazi (2005).

2.2.2. Methodology

Figure 1 summarises the new methodology, consisting of two steps, namely database setup and transformation step. The database setup comprises collecting the pure component properties and calculating the properties of each entry.

The transformation step emphasises the transformation of bulk properties into molecular composition by an optimisation programme. Firstly, the bulk properties of gasoline streams such as PIONA, distillate profile etc are analysed. Secondly, based on the distillate profile, an initial guess of molecular composition in the form of MTHS matrix is predicted, and the concentration of each carbon number as well, which would be applied in the optimisation procedure. Thirdly, the global properties outlined above based on correlations are obtained. Fourthly, the process characteristics such as no olefins for streams from catalytic reforming, and the total amount of carbon number four in FCC gasoline stream less than 2-3%, etc are collected as the optimisation boundary conditions. Finally an optimisation program targets on minimizing the objective function as equation 1 shows.

$$Obj = \sum_{T} (w_1 \times TBPdiff)^2 + \sum_{P} (w_2 \times PropDiff)^2 + \sum_{PIONA} (w_3 \times Condiff_{PIONA})^2 + \sum_{C} (w_4 \times Condiff_{carbon})^2 + \sum_{I} (w_5 \times DistrDiff_{I})^2 \quad (1)$$

Where T is the index of the points from the distillation profile, and P is the index of physical properties excluding distillate profile and PIONA composition, and C is the index of volume fraction of each carbon number, $PIONA$ indicates the index of PIONA composition, and finally I is the index of homologous series. w_i is the weighting factor on the difference depending on the accuracy of retrieved data. The objective function is taken as the sum of the square of the percentage errors between the measured and calculated properties. An optimisation subprogram is implicitly included since the optimal distribution parameter values would be determined simultaneously when the optimal molecular composition is found.

3. Case study

To illustrate the capability and accuracy of the proposed methodology, the molecular composition of a feedstock for catalytic reforming from Ancheyta (2000) is predicted first, and then by applying Ancheyta's kinetic models, the product molecular composition and its corresponding bulk properties are determined sequentially, which is compared with those results from the experimental data.

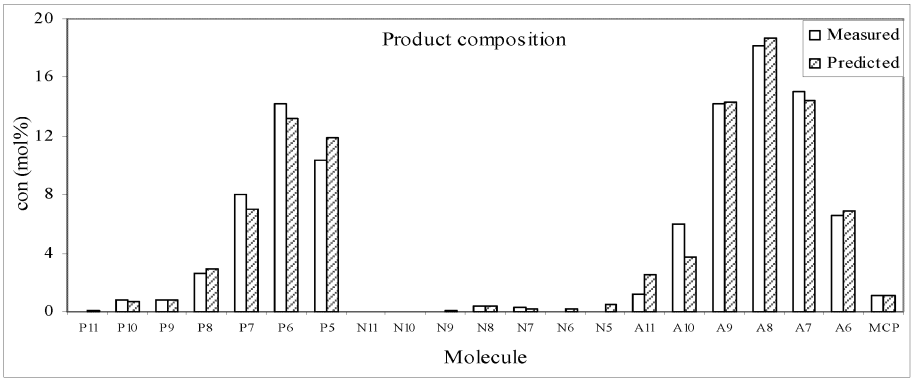

Fig 2 Comparison of the product molecular composition

Figure 2 gives a view of the agreement between the molecular compositions of the measured product and the predicted based on the predicted feedstock. Table 3 compares bulk properties between the measured and predicted feedstock, as well as the product. For the feedstock, the most deviations between the measured and predicted are less than 1% except benzene volume percentage. Regarding the product, it sees a bigger deviation, especially 10 vol% of distillate profile, while as the two key properties of gasoline streams, ON and RVP see small gaps. In summary, the methodology is capable of not only predicting the molecular composition of feedstock, but also providing necessary molecular information for kinetic models.

Table 3 Comparison of the bulk properties between the measured and predicted

	Feedstock		Product	
Properties	Measured*	Predicted	Measured*	Predicted
SG	0.74	0.74	0.79	0.79
RVP(psi)	3.11	3.10	4.32	4.61
RON	62.98	63.15	97.38	97.45
MON	58.95	58.63	86.84	87.00
Benzene (vol%)	0.48	0.64	4.59	4.82
Distillate Profile(^{o}F)				
10	133.60	133.57	121.82	96.54
30	206.99	206.99	183.68	175.95
70	287.01	287.02	287.00	282.48
90	328.08	329.08	328.09	324.87
95	347.15	347.15	347.15	347.48

*The measured properties are calculated from the measured feedstock/product molecular composition based on mixing rules.

4. Conclusions

A new methodology has been developed for molecular management of gasoline streams. Composition of any desirable gasoline streams can be characterised quickly without too much experimental effort. The method revolutionised the MTHS framework on both representation matrix for gasoline streams and transformation approach by introducing statistical distribution and extensive properties. One of the main advantages of this method over others is that the method not only focus on minimizing the difference of properties between the global and calculated, but also take the distribution between molecules into account, which efficiently deal with the problem that Albahri and Hudebine met. The case study has demonstrated the effectiveness and accuracy of the approach for gasoline streams, and refining process simulation based on kinetic models, which is promising for refining optimisation.

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