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Effect of experimental data accuracy on stochastic reconstruction of complex hydrocarbon mixture

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Introduction

Kinetic models of oil refinery processes require feedstock representation to be developed and used. A molecular reconstruction is a group of methods that use available petroleum cut properties to estimate its composition.

Molecular reconstruction methods usually yield composition estimation no matter what analytical data was used. And, while the precision of the experimental values is known, that estimation's accuracy is not. Sometimes it isn't clear whether the estimated composition is reasonable or just randomly chosen numbers that do not contradict the experimental data.

Effect of the experimental data

In this study, the stochastic reconstruction method and molecule building sequence for vacuum distillates from [1] was used to demonstrate the effects of experimental data and its accuracy.

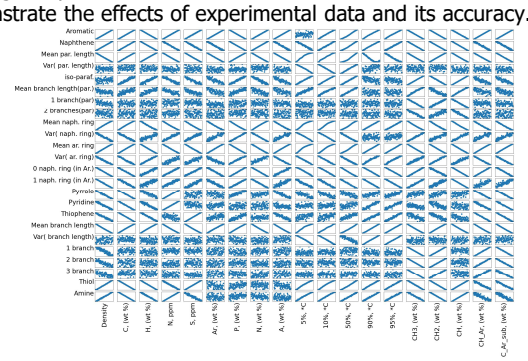

Fig. 1 Dependences of properties upon model parameters

Mixture properties were tracked during model parameter changing in a wide range (Fig.1). Notably, some graphs show a clear monotonous pattern, while other similar to noise. Monotonousness of those dependencies is crucial for parameter estimation, as long as allows one-to-one correspondence between parameter and properties to be established. Indeed, when all parameter values correspond to the same properties value, finding parameters based on that properties is ambiguous.

To avoid ambiguity, the monotonousness hypotheses were tested with the Spearman correlation coefficient. The significances of the calculated coefficients were determined with $\alpha = 0.05$ and Holm-Bonferroni correction being used for multiple hypothesis testing (Fig.2).

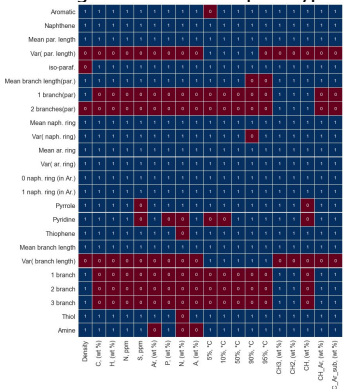

Fig. 2 Significance of Spearman correlation coefficient with $\alpha = 0.05$

Effect of the experimental data accuracy

Fig.2 shows which parameters can not be derived from given properties.

Besides the properties themselves, it's very useful to consider the accuracy of the method used to determine those properties. Indeed, the uncertainty of property values will transfer to the uncertainty of parameter, which may lead to indistinguishable value for the parameter.

Ratios between the span of calculated properties and reproducibility were calculated in order to distinguish analytical data which can contribute the most to different parameters (Fig.3).

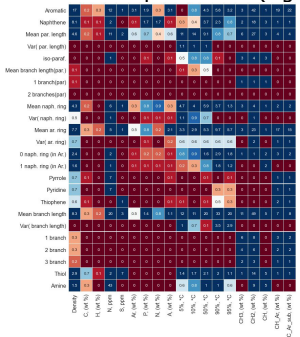

Fig. 3 Effect of different analysis on parameters in scale of reproducibility

The higher the number in Fig.3 the bigger impact this analysis may have on the given parameter.

Discussion

Fig.3 shows that the accuracy of experimental data strongly influences the usefulness of this information for reconstruction. Experimental data with low precision may be useless for the stochastic reconstruction approach.

For example, the accuracy of the carbon and hydrogen content analysis is taken from ASTM D5291-10, with that precision almost any set of model parameters will not contradict the experimental data. Thus, this data is redundant, but carbon and hydrogen content itself may be useful for various parameters if the accuracy increase, as stated in Fig.2.

Some model parameters are identified solely on one type of analytical data. For example, information concerning the variance of chain length in paraffins and cyclic molecule branches can be derived only from distillation curve data. Isomer distribution cannot be identified without NMR data (in a given data array).

The parameter-property relation may be classified into 3 groups:
1. Independent. Changing parameters won't change the mixture property. Those relations are useless for parameter identification.
2. Dependent and "low" precision. Most of the parameter values correspond to the same property value, thus providing little information.
3. Dependent and "high" precision. Wide range of parameters correspond to the wide range of property. Most valuable data for the parameter identification.

Reference:

[1] **Deriving the Molecular Composition of Vacuum Distillates by Integrating Statistical Modeling and Detailed Hydrocarbon Characterization**
Anton Alvarez-Majmutov, Rafal Gieleciak, and Jinwen Chen
Energy & Fuels **2015** *29* (12), 7931-7940
DOI: 10.1021/acs.energyfuels.5b02082