SIMULATION OF LIGHT PETROLEUM FRACTIONS

Tareq A. Albahri

Chemical Engineering Dept. - Kuwait University
P.O.Box 5969 - Safat 13060, Kuwait
albahri@kuc01.kuniv.edu.kw

Introduction

Petroleum refiners have not traditionally considered their products on a molecular basis but rather they have modeled and marketed their products as volatility fractions (e.g. gasoline, kerosene, and fuel oil). Current simulation procedures resort to pseudo-component approaches which suffer from many limitations. This work focuses on the development of a molecularly explicit characterization model (MECM) that will allow the simulation of the molecular composition of petroleum fractions using a pre-selected set of pure components. Such molecular-level characterization of petroleum fractions will allow us to simulate the physical separation processes and the chemical reaction processes, as well as allow for catalysts such as zeolites to be designed and optimized for processing complex, multicomponent mixtures such as petroleum.

Technical Development

The concept of the proposed model is that the global properties of a petroleum fraction such as the boiling point, specific gravity, vapor pressure, etc. must be equal to those calculated from the pure components contained in that petroleum fraction. When both bulk and pure component properties are available, the composition of the petroleum fraction may be predicted using optimization algorithms as simplified in Figure 1.

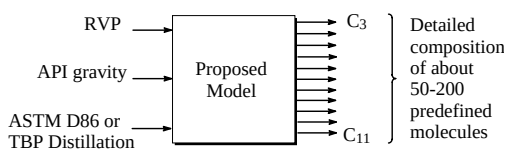

Figure 1. Simplified schematic representation of the proposed model.

Since petroleum fractions contain thousands of molecules the concentration of which is hard or even impossible to measure, it is imperative to simulate such mixtures using a limited set of pure components to avoid prohibitively extensive computation time during kinetic modeling or rigorous phase equilibrium calculations.

The minimum input properties for the model are the true boiling point (TBP), the API gravity, and the Reid vapor pressure (RVP). The internally calculated properties are the molecular weight, the true vapor pressure at 100°F, the specific gravity, the cubic average boiling point (CABP), the mean average boiling point (MeABP), the volumetric average boiling point (VABP), the weight average boiling point (WABP), the molar average boiling point (MABP), the Watson characterization factor (K_w), the refractive index, the carbon to hydrogen ratio (C/H), the kinematic viscosity at 100 and 210°F, the surface tension, the aniline point, the true and pseudo critical temperatures and pressures, the critical compressibility factor, the acentric factor, the freezing point, the heat of vaporization at the normal boiling point, the net heat of combustion at 77°F, the isobaric liquid heat capacity at 60°F, the isobaric vapor heat capacity at 60°F, the liquid thermal conductivity at 77 ºF, and the paraffins, naphthenes, and aromatics content. These properties are calculated for the petroleum fraction using well established methods in the literature or were developed specifically for this project. For example, the molecular weight for the light petroleum fraction is calculated from the boiling point and the specific gravity using the following API recommended equation[1],

$$MW = 42.965\,(T_b^{1.26007}\,S^{4.98308})\,[\exp(2.097.10^{-4}\,T_b - 7.78712\,S + 2.08476.10^{-3}\,T_b\,S)] \qquad (1)$$

Whereas the same is calculated from the pure component composition using the following simple mixing rule,

$$MW=\sum_{i=1}^{n}(MW)_i\,(x)_i \qquad (2)$$

When the pure component properties are not available in databases they can be estimated using group contribution methods available in the literature or others developed specifically for this project.

The difference between the values obtained from equations 1 and 2 for the molecular weight in addition to other equations and mixing rules for the other properties are minimized in the objective function (second line of Equation 3) the purpose of which is to calculate the values of x_i which is the mole fraction of the pure components in the petroleum fraction.

The First line in the objective function represents the sum of errors in the boiling points of the pure components and the corresponding value on the true boiling point (TBP) curve as shown in Figure 2.

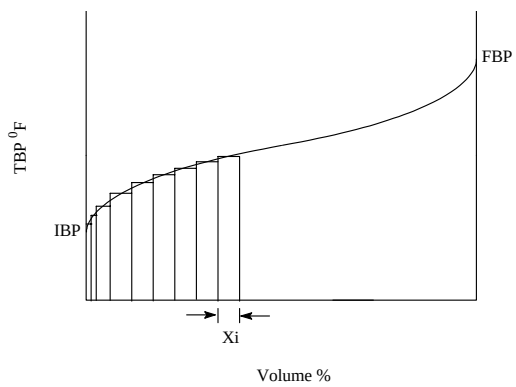

Figure 2. Simulation of a true boiling point (TBP) curve using real components.

The pure component concentrations are determined by minimizing the following objective function,

$$S = \sum_{j=1}^{n}\left((T_{b_j}-T'_{b_j})\times W_o \times 100/T_{b_j}\right)^2 + \sum_{i=1}^{P}\left((Y_i - Y'_i)\times W_i \times 100/Y_i\right)^2 \qquad (3)$$

where i is the index number of the physical property, j is the index number of the molecule, P is the total number of physical properties considered (except boiling point), and n is the total number of molecules. Y_i and Y'_i refer respectively to the actual and predicted property i. T_{bj} and T'_{bi} refer respectively to the boiling point of the pure component *j* and the corresponding value on TBP curve. W_i and W_o are weighting factors and S is the objective function to be minimized.

An optimization algorithm based on the least square method was used to minimize the objective function while calculating the concentration of the pure components. The nonlinear regression algorithm minimizes the sum of the difference between the fuels bulk properties and those estimated from pure components. Using the Microsoft Excel Solver tool and the Generalized Reduced Gradient (GRG2) nonlinear optimization code, convergence was achieved in less than one minute for all cases on a Pentium IV-1.7 GHz PC.

Discussion

The model was tested to simulate the separation process in an industrial naphtha splitter producing light and heavy naphtha from a Hydrocracked naphtha feed according to the validation procedure shown in Figure 3. In one run we used the ASTM D86 distillation data as the input assay for the feed naphtha. In another run we used the detailed hydrocarbon concentrations calculated using the proposed MECM model shown in figures 4 and 5. The MECM model results for the light and heavy naphtha products correlated better with the experimental ASTM D86 distillation data than those using the pseudo-component method incorporated in the HYSYS process simulator.

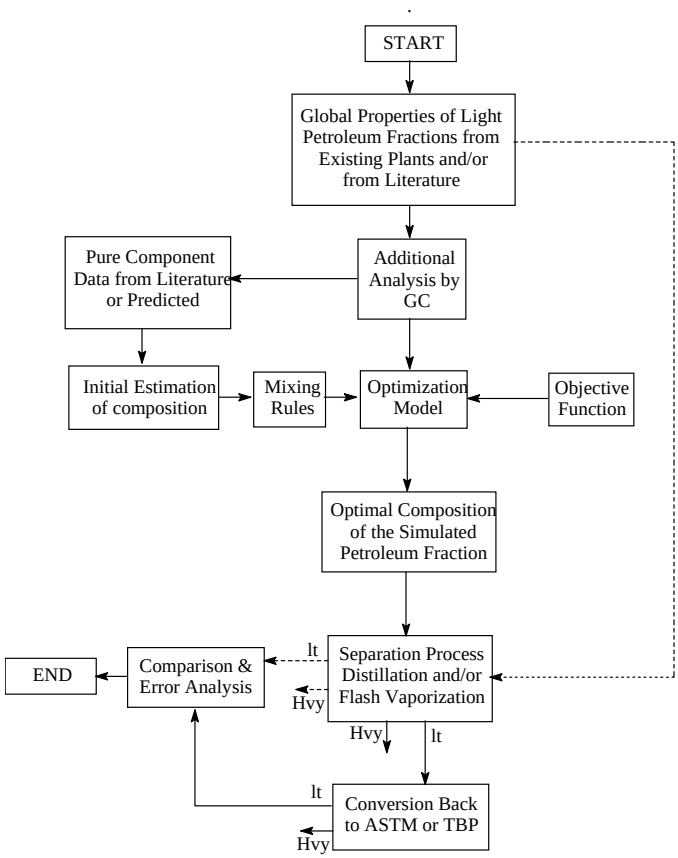

Figure 3. Flow Chart for the methodology used in the proposed model.

The MECM model proves to be a powerful tool for simulating the composition of petroleum fuels. The clear advantage of the method is that the list of pure components used may be tailored to include more or fewer components as needed by the user, to accommodate specific needs, which is an added advantage.

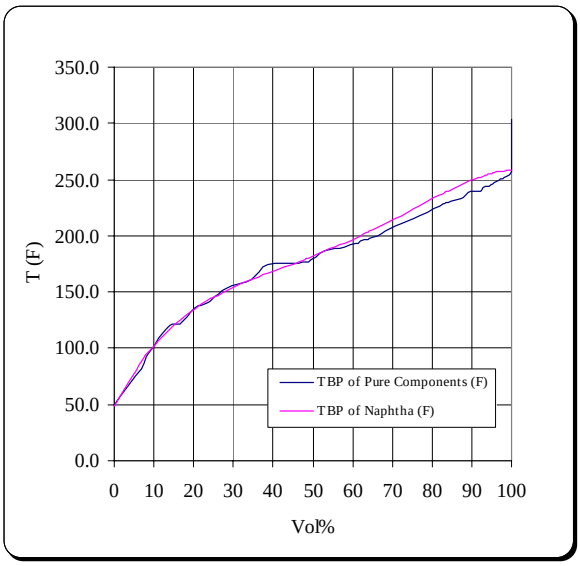

Figure 4. Comparison of Naphtha TBP and Simulated TBP from pure components.

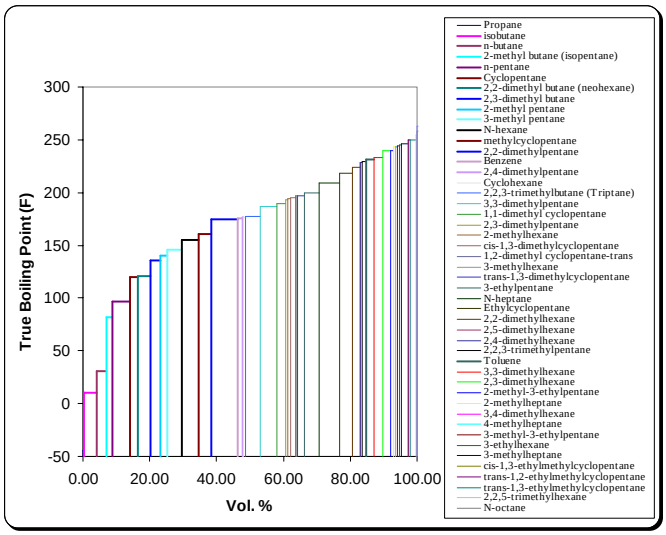

Figure 5. Calculated composition of representative model pure components

This work demonstrates that the complex nature of petroleum fuels may be modeled by a limited set of representative pure components using non-linear-regression optimization models. Considering the difficulty and complexity of accounting for the thousands of compounds in petroleum fuels and the limitations of the pseudo component technique, the proposed method can be an effective alternative.

Acknowledgment

This work was supported by Kuwait University, Research Grant No. EC04/01.

References

[1] Wauquier, J. -P. "Petroleum Refining 1', Editions Technip, Paris, **1995**.