

## FRactal ANALYSIS OF FUEL MOLECULES IN THE BULK LIQUID PHASE

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### ABSTRACT

The topological structure and boiling point of individual fuel molecules provide sufficient information for determination of their respective fractal dimensionalities in the bulk liquid phase. Molecules considered need to be members of well-defined series such as homologous series. Our fractal analysis yields a time-averaged molecular conformation for each species. The results are used to estimate the flexibility of each species in the bulk liquid phase. The presence of heteroatoms or multiple bonds in the species can produce marked effects which are alluded to in our conclusion. The present analysis elucidates the behavior of molecules in the liquid phase and sheds useful light on the physicochemical properties of many different types of fuel molecules.

Keywords: Fuel Molecules, Fractal Analysis, Molecular Behavior of Hydrocarbons

### INTRODUCTION

Dwindling crude oil supplies and the many uncertainties in world oil markets render it imperative to conserve our oil resources and to utilize them as efficiently as possible. With this in mind, the method introduced here is intended to contribute to the optimal use of fuel molecules. This goal can be accomplished only after the behavior of fuel molecules at the molecular level has been thoroughly elucidated. We show here how it is possible to gain valuable insights into the average conformation of fuel molecules and analyze the factors determining these conformations. In addition, we estimate the flexibility of individual molecules in the bulk liquid phase. All this is achieved by making use of no more than the topological structures of the species under study and their experimentally measured boiling points. Although we focus here on straight-chain hydrocarbon molecules, our methodology can be readily extended to more complex species.

Our approach, originally introduced in 1986 by Rouvray and Pandey [1,2] has recently been employed in the study of species containing heteroatoms [3]. Key to the approach is the description of hydrocarbon and other chains as fractal objects; for a discussion of such objects and appropriate terminology, readers should consult standard texts [4,5]. The fractal dimensionality of each molecular chain can be related to its time-averaged conformation in the bulk liquid phase and then used to estimate the molecular flexibility. A brief mathematical exposition of the salient features of our approach now follows.

## MATHEMATICAL FORMALISM

We adopt as a convenient measure for the shape of molecular chains the mean-squared end-to-end length of the species. A molecule  $M$  will satisfy a proportionality of the general type:

$$r \propto n^q, \quad (1)$$

where  $n$  is the number of atoms in the backbone of the chain, and  $q$  is typically some fractional number. An equivalent formulation in terms of the fractal dimensionality of  $M$  can also be given thus:

$$r \propto m^{1/d_f}, \quad (2)$$

Because the physicochemical properties of molecules are known [6] to depend on their time-averaged conformation in the bulk phase, we may write for some property  $P_i$  of the molecule  $M_i$  the following relationships:

$$P_i \propto r_i \propto m_i^{1/d_{f_i}}. \quad (3)$$

Now, if  $P_i$  is plotted against  $n$ , or some other scalar numerical description such as a topological index [6,7], the plot can be characterized by the proportionality:

$$P_i \propto T_i^{b_i}, \quad (4)$$

where  $T_i$  is the descriptor for  $M_i$  and  $b_i$  is a constant determined from the slope of the curve at  $T_i$ . From relations (3) and (4) we can conclude that:

$$m_i^{1/d_{f_i}} \propto T_i^{b_i} \quad (5)$$

The use of scaling arguments at this point, similar to those adopted by de Gennes [8], yields the final result:

$$\frac{b_1}{b_2} = \frac{d_{f_2}}{d_{f_1}} \quad (6)$$

for two molecules  $M_1$  and  $M_2$  in a given series.

## RESULTS AND DISCUSSION

For simplicity, we choose for the  $P_i$  the boiling points of members of normal alkane species and for  $T_i$  the carbon number in the chain. Relevant plots on linear and logarithmic scales are shown in Figures 1 and 2 respectively. The fractal dimensionalities are obtained from the  $b_1/b_2$  ratios by making use of the logarithmic plot; the actual values can be read off from the plot in Figure 3. Because the fractal dimensionalities provide a measure of the distribution of mass with distance [4,5], they can be used as measures of the time-averaged conformation of the species they characterize. Fractal dimensionalities for chain-like molecules all lie within the range  $1 < d_f \leq 2$ , with unity corresponding to a totally rigid chain. As values of  $d_f$  become progressively greater than unity they reflect the extent of folding up of the chain. Thus, for the  $C_1$ ,  $C_{10}$ ,  $C_{20}$ , and  $C_{30}$  chains, the respective  $d_f$  values are 1.00, 1.18, 1.43 and 1.69.

The  $d_f$  values determined from our analysis can be employed to yield an estimate of the flexibility of each of the species in the bulk liquid phase. Our estimate is given as the product of the number of bonds in the chain,  $n_i-1$ , and the reciprocal of the mean-squared end-to-end length of the chain, i.e.

$$F_i = (n_i-1)/r_i. \quad (7)$$

Values for  $F_i$  can be determined for any chain containing  $n_i$  atoms from our relation (3) above as follows:

$$r_i \propto m_i^{1/d_{fi}} \propto (n_i m_C)^{1/d_{fi}} \quad (8)$$

where  $m_C$  is the mass of the carbon atom ( $C=12$ ). Substitution of appropriate values for the  $C_2$ ,  $C_{10}$ ,  $C_{20}$ , and  $C_{30}$  chains leads to flexibility values of 0.042, 0.156, 0.412 and 0.900 respectively. On this measure of flexibility therefore, the  $C_{30}$  chain is roughly 21.5 times more flexible than the  $C_2$  chain.

Our results are in accord with calculations on long alkane and other chains. Flory and Yoon [9] showed that the average shape of polyethylene chains containing 10 or more bonds may be visualized as ellipsoids. Very recent work by Erman et al. [10] has confirmed this picture and presented estimates of chain stiffness that are in broad agreement with the results presented here. Moreover, the effects of heteroatoms in the chain have been studied by us [3] as have the consequences of introducing multiple bonds into the chain. It is known that both the substitution of atoms heavier than carbon and the introduction of multiple bonds into the chain will result in a loss of flexibility or a stiffening of the chain in general [3]. This is only to be expected from the form of the expression we have used, namely relationship (7), for the computation of the chain flexibilities. Clearly, our analysis sheds much useful light on the interactions occurring at the molecular level in the bulk liquid phase. It is hoped that similar analyses in the future can be adapted for the design and optimization of fuel molecules.

## REFERENCES

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## FIGURES

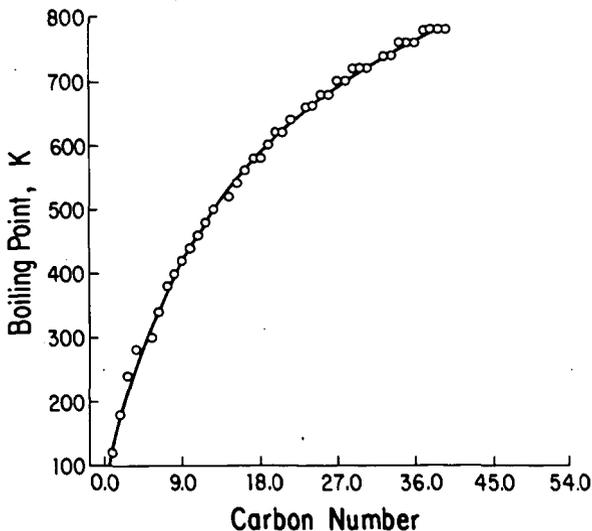


Figure 1. Plot of boiling point against carbon number on linear scales for the first forty normal alkanes.

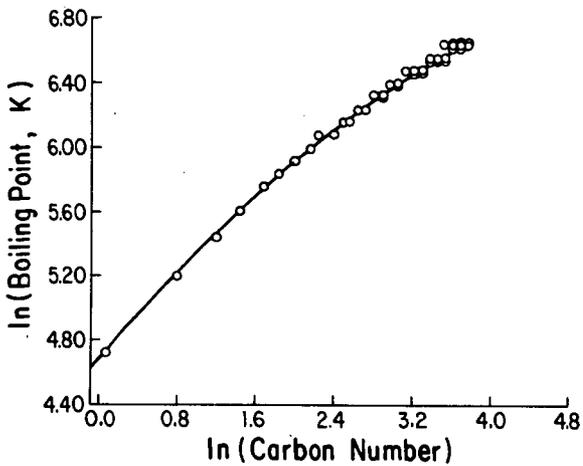


Figure 2. Plot of boiling point against carbon number on logarithmic scales for the first forty normal alkanes.

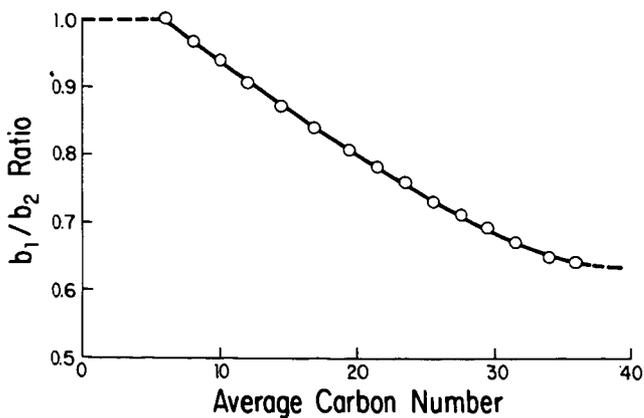


Figure 3. Plot of the  $b_1/b_2$  ratio against carbon number on linear scales for the first forty normal alkanes.