

# An *a priori* thermodynamic data analysis based chemical lumping method for the reduction of large and multi-component chemical kinetic mechanisms

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**Abstract**—A chemical species lumping approach for reduction of large hydrocarbons and oxygenated fuels is presented. The methodology is based on an *a priori* analysis of the Gibbs free energy of the isomer species which is then used as main criteria for the evaluation of lumped group. Isomers with similar Gibbs free energy are lumped assuming they present equal concentrations when applied to standard reactor conditions. Unlike several lumping approaches found in literature, no calculation results from the primary mechanism have been employed prior to the application of our chemical lumping strategy.

## I. INTRODUCTION

As reported by Tomlin et. al. [1] due to strong nonlinear nature of chemically reactive systems it is quite tough, in principle, to find *a priori* assumptions for an automatic lumping procedure. It is nevertheless a reasonable aim to explore to what extent chemical reaction schemes can be reduced with thermodynamically driven linear chemical lumping with an acceptable loss of accuracy. The motivation is to maintain the applicability of the lumping approach to automatic mechanism generators, and keep the reduction strategy independent from the detailed mechanism performance under relatively restrictive benchmark reactor conditions whatsoever.

The choice of the kinetic mechanism involved the selection of surrogate fuel components that match both regular Diesel and Rapeseed Methyl Esther (RME) properties. Cetane number and lower heating value have been considered, among other properties, as main targets to be matched by the modelled surrogate fuel mixtures. The detailed reaction mechanism adopted herein presented 807 species and 7807 reactions describing oxidation of *n*-decane,  $\alpha$ -methyl-naphthalene and methyldecanoate. Application of the lumping strategy led to a mechanism size of 463 species and 7600 reactions.

## II. CONSTRUCTION OF THE ISOMERS LUMP GROUP

As a first step the Gibbs free energies of all species of each isomer class within methyldecanoate and *n*-decane mechanism have been assessed and compared to each other. Main constrain considered to decide whether to include or not each isomer in the lumped pseudo-species has been the absolute difference in Gibbs free energy. In other words, isomers which showed very small differences in Gibbs free energy have been selected to be part of the lump group under the assumption that they would present equal concentrations. To

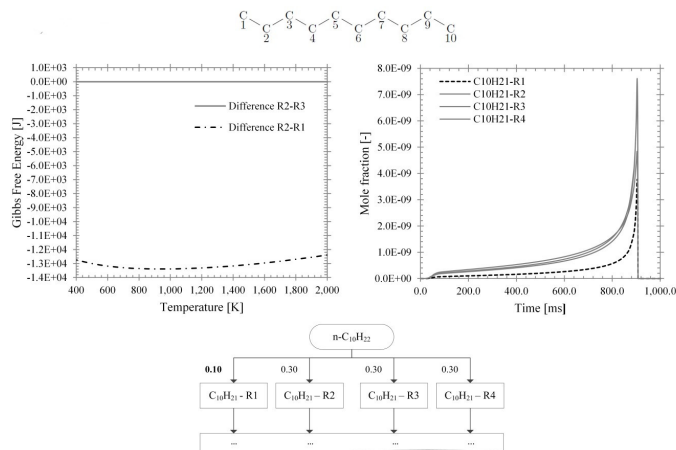


Fig. 1. Schematic verification of the strategy adopted to choose the isomers to include in the lumped groups for *n*-decane

verify until which extend this assumption can be considered valid, several constant volume reactor calculation have been performed and isomers concentrations have been analysed. A representative outcome of the outlined thermo data analysis and its verification is shown in figure 1.

## III. CALCULATION OF LUMPED SPECIES RATE COEFFICIENTS

Once the isomers to be included in the group have been evaluated, a linear lumping approach is applied. All selected isomers lumped to one species are assumed to have equal concentrations. The resulting rate coefficients are weighted by the rates for the lumped isomers and the numbers of reactants and products in the reaction equation. If isomers with slightly different thermodynamic data are lumped these differences have been taken into account in the formulation of the calculated rate coefficients of the backward reactions. In the lumped scheme we describe the total backward reaction as the sum of duplicate reactions with the different backward rate coefficients of the former isomeric species. This approach is similar to that suggested by Ahmed et. al. [2]. When introducing one lumped species the source term for the differential equation is transformed from a single species

$x = j$ , via the isomers  $x = l$  to the lumped species  $x = L$  as follows:

$$\omega_j = \sum_{k=1}^{N_R} \left( \nu_{j,k} \prod_{i=1}^{N_S} (c_i^{\nu'_{i,k}}) k_k \right)$$

$$\omega_l = \sum_{k=1}^{N_R} \left( \nu_{l,k} \prod_{j=1}^{N_L} (c_j^{\nu'_{j,k}}) \prod_{i=1}^{N_S-N_L} c_i^{\nu'_{i,k}} k_k \right)$$

$$\omega_L = \sum_{l=1}^{N_L} \left( \sum_{k=1}^{N_R} \left( \nu_{l,k} \prod_{j=1}^{N_L} ((c_L/N_L)^{\nu'_{j,k}}) \prod_{i=1}^{N_S-N_L} c_i^{\nu'_{i,k}} k_k \right) \right) \quad (1)$$

$$\omega_L = \sum_{k=1}^{N_R} \left( \sum_{l=1}^{N_L} ((\nu_{l,k}) c_L^{\sum_{i=1}^{N_L} \nu'_{i,k}}) \prod_{i=1}^{N_S-N_L} c_i^{\nu'_{i,k}} k_k \prod_{j=1}^{N_L} (1/N_L)^{\nu'_{j,k}} \right)$$

with  $N_R$  denoting the number of reactions,  $N_S$  the total number of species,  $N_L$  the number of species lumped to  $L$ ,  $c_x$  the concentration of species  $x$ ,  $\nu_{x,k} = \nu''_{x,k} \nu'_{x,k}$  is the net stoichiometric coefficient of species  $x$  in reaction  $k$  where  $\nu'$  indicates the reactants and the  $\nu''$  products,  $k_k$  the rate coefficient of reaction  $k$ . After lumping the new number of species is calculated together with the new rate coefficients and new stoichiometric coefficients of the lumped group:

$$N_s^* = N_S - N_L + 1$$

$$k_k^* = k_k \left( \frac{1}{N_L^{\nu'_{j,k}}} \right)^{\sum_{j=1}^{N_L} \nu'_{j,k}}$$

$$\nu_{L,k}^* = \sum_{l=1}^{N_L} \nu_{l,k}$$

$$\nu'_{L,k*} = \sum_{l=1}^{N_L} \nu'_{l,k}$$

Equation (1) therefore reads as:

$$\omega_L = \sum_{k=1}^{N_R} \left( \nu'_{L,k*} \prod_{i=1}^{N_s^*} (c_i^{\nu'_{i,k}}) k_{k*} \right) \quad (2)$$

where  $\nu'_{i,k} = \nu'_{L,k}$  for  $i = L$ . Further lumping of species transforms the source term sequentially in this manner. Finally the thermo data of the lumped pseudo-species are considered as the average of those of the isomers involved in the lump group.

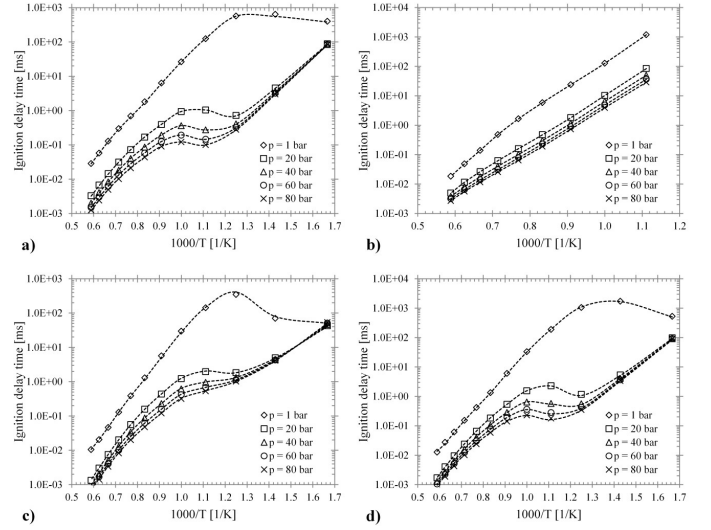


Fig. 2. Simulated ignition delay times at  $\phi = 1.0$  for detailed mechanism (symbols) and lumped mechanism (dashed line). Pure n-decane (a) ; Pure  $\alpha$ -methylnaphthalene (b) ; Pure methyldecanoate (c) ; European Diesel model (d): 0.71 n-decane - 0.23  $\alpha$ -methylnaphthalene - 0.06 methyldecanoate

#### IV. RESULTS AND DISCUSSION

Modelling of auto ignition has been carried out assuming constant-volume and homogeneous adiabatic conditions. The predicted ignition delay has been determined by the evaluation of the maximum temperature gradient. To comprehensively verify the effect of the lumping procedure on the mechanism performance, single fuel calculations were performed separately and a mixture including all three components was tested as well. The motivation behind the choice of the mixture, comprising 0.71 n-decane - 0.23  $\alpha$ -methylnaphthalene - 0.06 methyldecanoate in mole fraction, was on one hand side done based on the current legislation for european diesel by means of aromatic/biodiesel content allowed. On the other hand, the authors wanted to monitor potential influences of the lumping on the fuel-fuel interactions and therefore a blend, which is labelled as european Diesel model, was widely studied. In Figure 2 comparisons between ignition delay times predictions obtained using detailed and lumped mechanisms are presented for all sets of gas compositions considered. Overall a good agreement was found.

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