MECHANISM REDUCTION BY NECESSITY ANALYSIS: A GAS-PHASE REACTION MECHANISM OF ISO-OCTANE

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ABSTRACT

In this study, skeletal mechanisms for the CPOX of iso-octane and non-catalytic study of gas composition after CPOX process are obtained by the Necessity Analysis. It is shown that skeletal mechanisms with 61-62% less species and 57-59% less reactions than the detailed mechanism allow accurate prediction of the species distributions in the batch reactor. Additionally, selected skeletal mechanism is simulated for the numerical prediction of iso-octane, hydrogen and soot-precursors within the plug flow reactor after reforming. Plug flow simulations also proved the applicability of the skeletal mechanism for the considered non-catalytic cases.

Reduction procedure

The necessity analysis method [1] is used for the reduction of iso-octane detailed mechanism that consists of 857 species and 7193 reactions [2]. This reduction method considers sensitivity coefficients of each species in each reaction separately and couples them with reaction flow calculations for each reaction. The idea of coupling sensitivity coefficients and reaction flow calculations, of each species in each reaction is considering the effects at each instant.

Sensitivity coefficients are calculated in [3] through DETCHEM^{BATCH} code. The flow of atom a between species i and species j, through formation or consumption, is multiplied with the sum of each species' sensitivity coefficients for forward and backward reactions and total amount of formation and consumption between species are summed as follows,

$$f_{ij} = \sum_{a=1}^{N_a}\left(\sum_{k=1}^{N_R}\left|r_k \nu'_{jk}\nu''_{ik}\frac{n_j^a}{\Delta n_k^a}[S_{(i,k)}+S_{(j,k)}]\right| + \sum_{k=1}^{N_R}\left|r_k \nu''_{jk}\nu'_{ik}\frac{n_j^a}{\Delta n_k^a}[S_{(i,k)}+S_{(j,k)}]\right|\right) \quad (1)$$

$$c_{ij} = \sum_{a=1}^{N_a}\left(\sum_{k=1}^{N_R}\left|r_k \nu''_{jk}\nu'_{ik}\frac{n_j^a}{\Delta n_k^a}[S_{(i,k)}+S_{(j,k)}]\right| + \sum_{k=1}^{N_R}\left|r_k \nu'_{jk}\nu''_{ik}\frac{n_j^a}{\Delta n_k^a}[S_{(i,k)}+S_{(j,k)}]\right|\right) \quad (2)$$

where f_{ij} and c_{ij} are total amount of formation and consumption between species through forward and backward reactions, r_k is the reaction rate coefficient of reaction k, ν'_{jk}, ν''_{jk}, ν'_{ik} and ν''_{ik} are the stoichiometric coefficients of species i and species j in reaction k, $n_j^a/\Delta n_k^a$ is the ratio of the number of atoms n_j^a to the total number of atoms transported in the reaction, $S_{(i,k)}$ and $S_{(j,k)}$ are the sensitivity coefficients of species i and species j in reaction k. Each species is assigned a necessity value via equation (3).

$$N_i = \max(f_{ij}, c_{ij}) \quad (3)$$

where, Ni is the necessity value of species i (all species' necessity values). Skeletal mechanisms are obtained after the removal of unnecessary species, defined by various cut-off levels with respect to the necessity values of each species, from the detailed mechanism.

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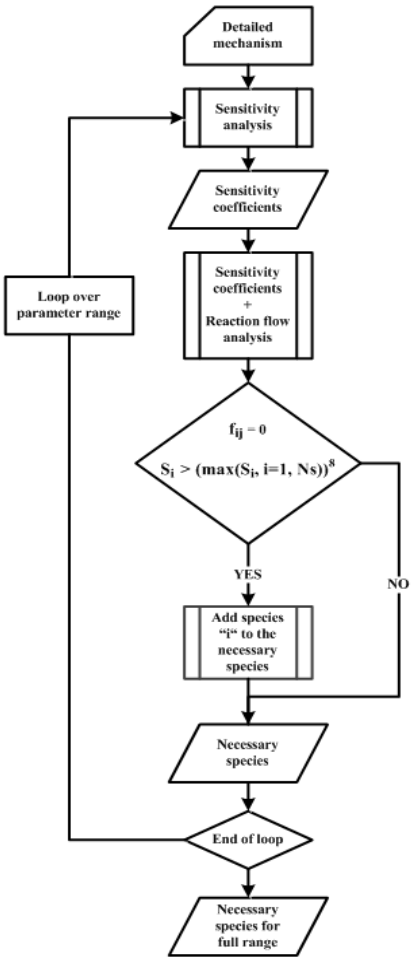

Figure 1. Flow diagram of the necessity method

Table 1. Initial parameters for C/O=2.0

Parameter	Value	Parameter	Value
Volume (m^3)	2.83 E-06	Pressure (Pa)	101325
Diameter (m)	0.019	Temperature (K)	998.26
Radius (m)	9.50 E-03	C/O	2.0
Length (m)	1.00 E-02	Simulation Time (s)	4.2 E02
Area (m^2)	2.83 E-04		

Table 2. Initial mole fractions for C/O=2.0

Species	Mole Fraction
IC_8H_{18}	6.67E-02
N_2	8.00E-01
O_2	1.33E-01

Table 3. Initial parameters of batch simulation for C/O=0.8

Parameter	Value	Parameter	Value	Parameter	Value
Volume (m^3)	2.83 E-06	Length (m)	1.00 E-02	Temperature (K)	1374.85
Diameter (m)	0.019	Area (m^2)	2.83 E-04	C/O	0.8
Radius (m)	9.50 E-03	Pressure (Pa)	101325	Simulation Time (s)	4.2 E-02

Table 4. Initial mole fractions for C/O=0.8

Species	Mole Fraction	Species	Mole Fraction	Species	Mole Fraction
IC_8H_{18}	3.33E-02	N_2	8.00E-01	O_2	1.67E-01

Results and Discussion

Results of the CPOX of iso-octane, to predict important species distribution in the batch reactor were already given in [1] for two different conditions, i.e., for C/O=1.6 and C/O=1.2. In the present study, additional simulation results of the CPOX of iso-octane in the batch reactor are given, i.e., for a very rich condition C/O=2.0 and for a lean condition C/O=0.8. The reason to include these two conditions is to prove the applicability of the method for different operating conditions, not only at a certain limited range. Results of the plug flow simulations for the non-catalytic study

of gas composition after reforming are also given in detail. Since we consider partial oxidation, we employ plug flow simulations just for the rich conditions. Results carried out from the batch and plug flow reactor simulations can be examined under two main categories: 1) obtaining the optimal skeletal mechanism for the accurate and fast prediction of species distributions, 2) further investigation of CPOX and non-catalytic processes.

Simulations are performed within the batch reactor for two different conditions respectively, i.e, for a rich (C/O=2.0) and lean (C/O=0.8) condition. Parameters and initial mole fractions for C/O=2.0 are given in detail in Table 1 and Table 2. Species distribution predictions in CPOX of iso-octane, as a function of time, in the batch reactor for C/O=2.0 case are shown in (Fig.2). As seen in the figure, skeletal mechanism with 320 species gives similar results to the detailed mechanism for all considered species. Number of the remaining reactions corresponding to the skeletal mechanism is 2933. If more species and reactions are deleted, skeletal mechanism results start deviating from the detailed mechanism results.

Maximum error level for the prediction of species distribution is obtained around 4%. Error level mentioned here refers to the deviation of the mole fraction results of the skeletal mechanisms from the detailed mechanism according to the equation (4),

$$\text{Error} = \left(\frac{X_{det} - X_{skel}}{X_{det}} \right) \cdot 100\,\% \qquad (4)$$

where X_{det} represents mole fraction of the detailed mechanism, and X_{skel} mole fraction of the skeletal mechanism [24]. Second simulation for the CPOX of iso-octane is performed for the lean condition (C/O=0.8). Parameters and initial mole fractions for C/O=0.8 at 4.2E-02 seconds are given in Table 3 and Table 4. As seen in (Fig. 3), skeletal mechanism with 315 species and 3127 reactions gives similar species distribution predictions to the detailed mechanism for considered species.

The process of CPOX of i-octane for different C/O ratios is examined further. Full conversion of i-octane is obtained in fuel lean mixture which results in increasing H_2O and CO_2 selectivity. It is the result of full conversion of i-octane (i-C_8H_{18}). The amount of oxygen is too little for full conversion at fuel rich conditions. 56 % conversion of i-octane is obtained at C/O=2.0 condition. Methane dominates by-products at fuel lean conditions that is followed by acetylene (C_2H_2) and ethylene (C_2H_4). Iso-butylene and propylene selectivity increases under fuel rich conditions. Methane also has high selectivity under fuel rich conditions. In contrast, acetylene and ethylene selectivity decreases with the increasing C/O ratios.

Conclusions

The main purpose of this study was to obtain skeletal mechanisms via application of the considered reduction procedure for different CPOX cases in the batch reactor and also non-catalytic cases in the plug flow reactor in order to make a fast and accurate numerical prediction of the important species distributions for further investigation of the CPOX and non-catalytic processes. It was seen that the skeletal mechanisms allowed consistent predictions of the species distributions for the CPOX of iso-octane in the batch reactor by deleting up to 62-63% species and 57-59% reactions from the detailed mechanisms for the considered conditions.

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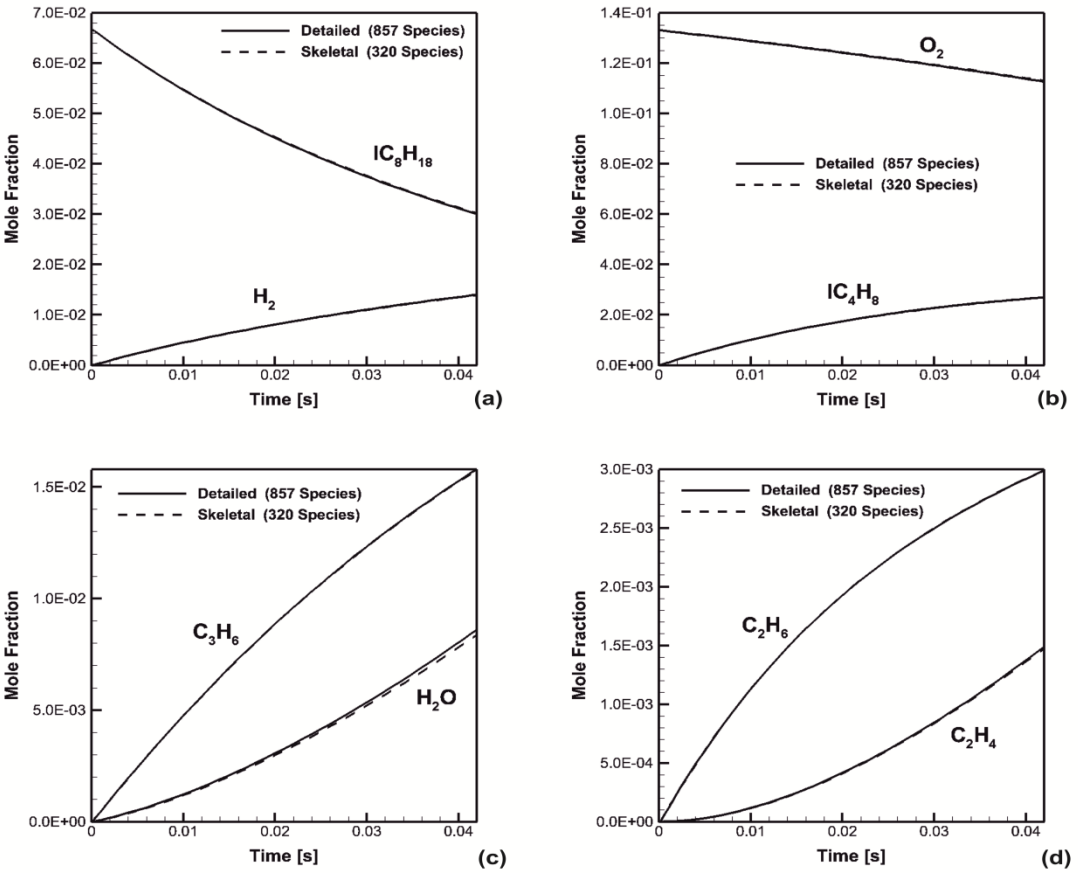

Figure 2. Species distribution predictions in CPOX of iso-octane: very rich condition C/O=2.0

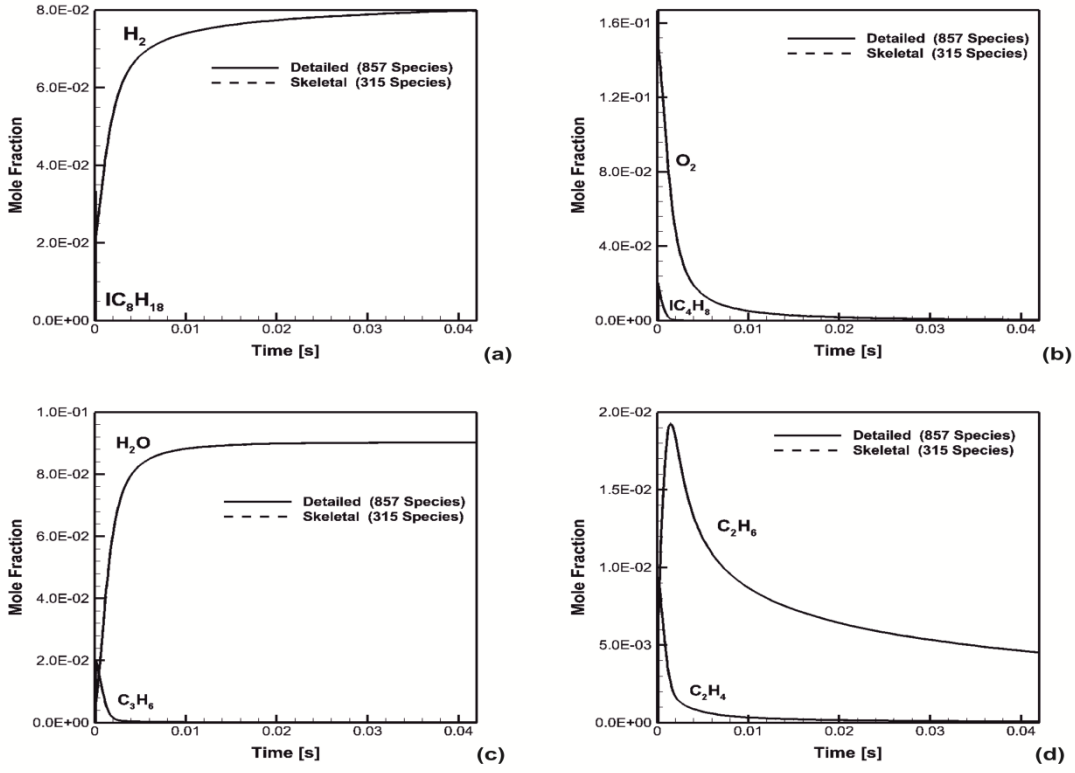

Figure 3. Second simulation for the CPOX of iso-octane: lean condition (C/O=0.8)