

# Universal Rule of Hydrocarbon Oxidation

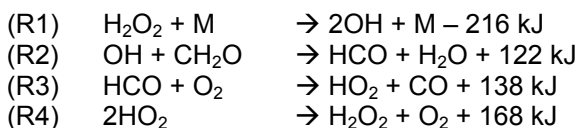
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## INTRODUCTION

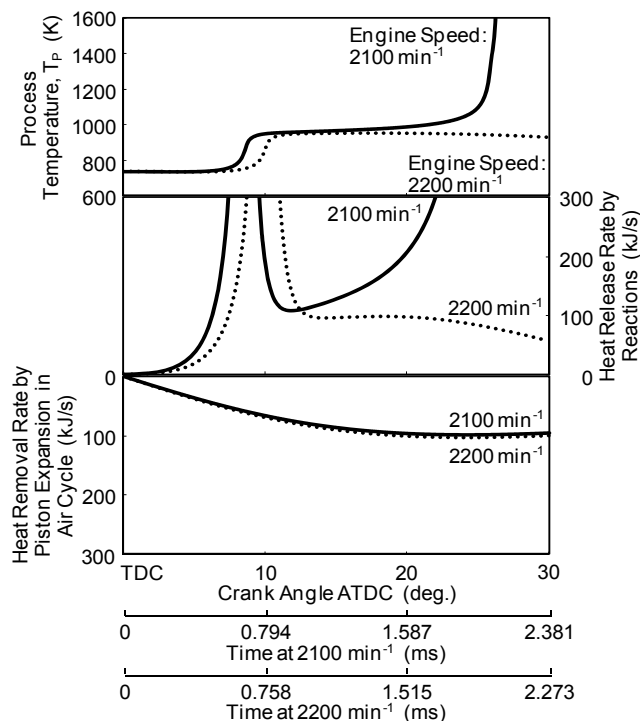
Hydrocarbon oxidation is composed of four stages, LTO (low temperature oxidation), NTC (negative temperature coefficient), thermal ignition preparation and thermal ignition. The LTO range is controlled by the sequential, primary and secondary  $O_2$  addition processes and the beta scission reactions of the oxidation products[7]. Major products in the LTO and NTC ranges are alkenes and oxygen-containing small species such as aldehydes and  $H_2O_2$ .

In the preceding studies [1-5], the authors found that the reaction loop composed of Reactions (R1) to (R4) plays a predominant role, named it as “ $H_2O_2$  Reaction Loop” and suggested that it may be a Universal Rule which can be applied to various hydrocarbons.



Between the LTO range and the thermal ignition range in which branching chain reactions in the Hydrogen-Oxygen system reaction mechanism are dominant, there is the thermal ignition preparation range. In this range, branching chain reactions of Hydrogen-Oxygen system are suppressed by the competing H and  $O_2$  recombination reaction generating  $HO_2$ .

Figure 1 shows an example of modeling result of HCCI (homogeneous-charge compression ignition) engine operation [2]. When the engine speed is  $2100 \text{ min}^{-1}$ , HCCI combustion was realized, when it increases to  $2200 \text{ min}^{-1}$ , however, thermal ignition cannot be observed. During the relatively long thermal ignition preparation period, the gradual heat release by chemical reactions competes with the internal energy removal by expansion. In case of the engine speed of  $2100 \text{ min}^{-1}$ , the heat formation by chemical reactions prevails over the heat removal. As a result, gradual temperature increase continues up to the Hydrogen-Oxygen system reaction dominant temperature. When the engine speed increased up to  $2200 \text{ min}^{-1}$  the heat removal rate increases and prevails over the heat release rate by ignition preparation reactions. Therefore the temperature increase up to the thermal ignition initiation condition does not take place. Thermal ignition takes place before TDC in most of experimental HCCI engines [6-8]. A



**Figure 1** Influence of engine speed on heat release rate by reactions and heat removal rate by adiabatic expansion (fuel: DME, displacement:  $619.2 \times 10^{-6} \text{ m}^3$ , compression ratio: 10 to 1, temperature at BDC: 330 K, pressure at BDC: 0.1 MPa,  $\phi$ : 0.5) [2]

major factor preventing the HCCI technology to be brought into the real world is its narrow operation zone. When the ignition delay period is stretched and enters into the expansion stroke, it is believed, to realize thermal ignition is difficult. Whether HCCI combustion takes place or not in an expansion stroke is decided by the competition of heat release by reactions and internal energy removal by adiabatic expansion.

As shown in this example, it will be essential to clarify factors controlling the heat release in the thermal ignition preparation range in inspecting influence of chemical reactions to engine combustion.

The phenomena in internal combustion engines are controlled not only by the chemical process but also by the physical process, such as mixing, turbulence and heat transfer. Because of the computational burden, detailed turbulent combustion modeling cannot adopt full kinetics model composed of thousands of elementary

reactions. In many cases, however, if chemical kinetics modeling can give local and instantaneous heat release rates, turbulent combustion modeling can simulate the phenomena. This study is an approach to understand and to formulate heat release timing and rates based on the understanding of detailed reaction kinetics.

## MODELING PROCEDURE

**CONTRIBUTION MATRIX** - One of the authors had defined "Contribution Matrix" for extracting important reaction paths from a reaction scheme and reducing the mechanism [14]. Elements of the contribution matrix are the contribution ratios of important elementary reactions to formation or removal of a species, or heat release or absorption at each moment in a reaction process.

Elements of the contribution matrix are defined by Equations (1) or (2).

$$CFR_{ij, T_P} = \frac{FR_{ij, T_P}}{\sum_{j=1}^{2N} \text{abs}(FR_{ij, T_P})} \times 100 [\%] \quad (1)$$

$$CHR_{j, T_P} = \frac{HR_{j, T_P}}{\sum_{j=1}^N \text{abs}(HR_{j, T_P})} \times 100 [\%] \quad (2)$$

Here,  $CFR_{ij, T_P}$  is the contribution ratio of the  $j^{\text{th}}$  forward or backward elementary reaction to formation of the  $i^{\text{th}}$  species at a process temperature  $T_P$ .  $CFR_{ij, T_P}$  is the formation rate of the  $i^{\text{th}}$  species by the  $j^{\text{th}}$  forward or backward elementary reaction at  $T_P$ .  $N$  is the number of elementary reactions in a reaction mechanism. The negative values of them represent removal of the species. The forward and backward reactions were separated to find reaction paths. Since the denominator was defined as the sum of the absolute values, the sum of either positive contribution ratios or negative ones at the same temperature is to be approximately 50 or -50 % respectively, when the species is in the quasi-steady state.

$CHR_{j, T_P}$  is the contribution ratio of the  $j^{\text{th}}$  elementary reaction to heat release at a process temperature  $T_P$ .  $HR_{j, T_P}$  is the heat release rate by the  $j^{\text{th}}$  elementary reaction at  $T_P$ . The negative values of them represent heat absorption. The forward and backward reactions were united as for heat release.

Contribution matrices are constructed for formation or removal of every species in a reaction mechanism or heat release. In each matrix, unimportant elementary reactions whose contribution ratios do not exceed a threshold value are eliminated.

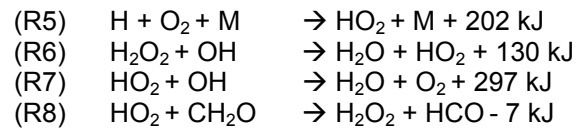
## FOUR REACTION GROUPS

The authors propose to classify elementary reactions into the following four groups.

- 1) Fuel series reactions
- 2) Fuel fragment reactions
- 3)  $H_2O_2$  loop reactions
- 4) Hydrogen-Oxygen system reactions

Contribution matrices to  $O_2$ ,  $OH$ ,  $H_2O_2$ ,  $HO_2$  and other species are also analyzed [2]. It was shown that in all of the cases, above mentioned grouping is valid.

Fuel series reactions are defined as those containing hydrocarbons and their oxides with the same carbon number as the original fuel. Fuel fragments reactions are the reactions of fuel fragments and their oxides excluding  $CH_2O$ ,  $HCO$ .  $H_2O_2$  loop reactions are the reactions composing  $H_2O_2$  reaction loop, Reactions (R1) to (R4). Sub-reactions (R5) to (R8) which supply or scavenge the key species of  $H_2O_2$  loop are included in this group.



Hydrogen-Oxygen system reactions are the reactions of species containing only O and H excluding Reactions (R1) to (R8). Reaction (R9) which takes place simultaneously with Hydrogen-Oxygen system reactions is included in this group.



At the beginning of oxidation process, that is, until the temperature increases up to about 950 K, fuel series reactions promote the oxidation process. In the temperatures ranging from about 950 to 1500 K, fuel fragment reactions and  $H_2O_2$  loop reactions control the process. When the temperature is higher than about 1500 K, Hydrogen-Oxygen system reactions make the process to proceed.

## $H_2O_2$ REACTION LOOP

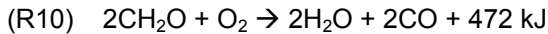
The absolute heat release rates of dominant elementary reactions are plotted against the process temperature in Figure 2. When the temperature increases to NTC range temperature, the rates of almost all reactions begin to decrease. The only exception is the  $H_2O_2$  decomposition reaction, Reaction (R1). This reaction rate continues to increase keeping the apparent activation energy approximately constant. Supported by Reaction (R1), the rates of other reactions, which have once fallen down, begin to increase again at about 950 K.

The heat formation rates by four reaction groups are shown in Figure 3. In the thermal ignition preparation

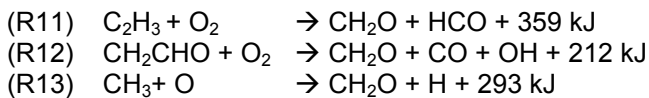
range, fuel series reactions are completed. Hydrogen-Oxygen system reactions play only a minor role. Major reactions are the  $\text{H}_2\text{O}_2$  loop reactions and fuel fragments reactions.

In the thermal ignition preparation range, Reactions (R1) to (R4) show similar activation energies and reaction rates. The rate constants of Reactions (R2) to (R4) are significantly larger than that of Reaction (R1) and their activation energies are very small. These suggest that Reactions (R1) to (R4) compose a reaction loop in which the rate determining process is Reaction (R1), as schematically shown in Figure 4.

On the assumption that 100 % of OH, HCO and  $\text{HO}_2$  generated by the  $\text{H}_2\text{O}_2$  loop reactions, are consumed by the succeeding reactions, the overall reaction is to be Reaction (R10). This is a reaction to release a considerable amount of heat from  $\text{CH}_2\text{O}$  without consuming  $\text{H}_2\text{O}_2$ .



Fuel fragments reactions proceed simultaneously with  $\text{H}_2\text{O}_2$  loop reactions. Major fragments reactions are Reactions (R11) to (R13).

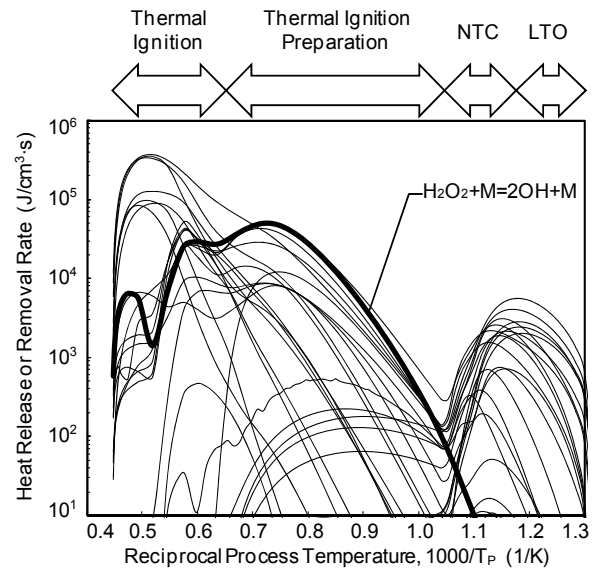


These reactions support the  $\text{H}_2\text{O}_2$  loop reactions by supplying the key species for  $\text{H}_2\text{O}_2$  loop reactions,  $\text{CH}_2\text{O}$ , HCO and OH.

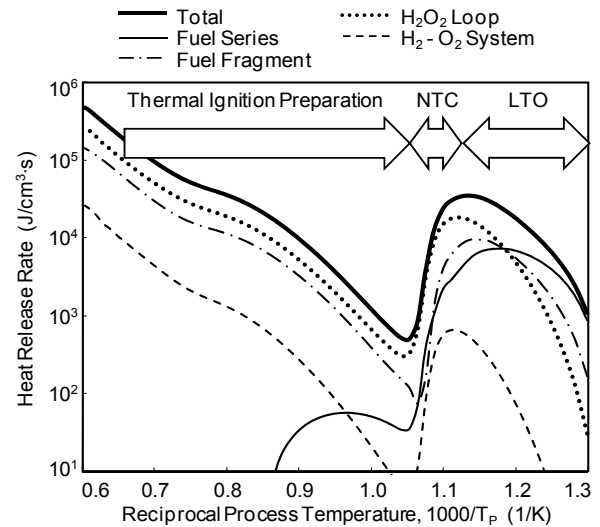
Sub-reactions, Reactions (R5) to (R8) also participate in the process. Reaction (R5) enhances the  $\text{H}_2\text{O}_2$  loop reactions by supplying  $\text{HO}_2$  using H generated mainly by Reaction (R13). In the real process, Reactions (R8) and (R11) to (R13) contribute to supply additional  $\text{H}_2\text{O}_2$ . Reactions (R6) and (R7) interfere with the  $\text{H}_2\text{O}_2$  loop reactions by scavenging the key species, OH and  $\text{HO}_2$ . The major reaction path in the thermal ignition preparation range can be expressed by  $\text{H}_2\text{O}_2$  reaction loop. If it is complete,  $\text{H}_2\text{O}_2$  concentration will be kept constant. Judging from the fact that  $\text{H}_2\text{O}_2$  continues to increase gradually during the thermal ignition preparation range, the enhancing effects by the fuel fragments reactions and  $\text{H}_2\text{O}_2$  loop sub-reactions seem to overcome the negative effects of radical scavenging.

## GLOBAL REACTION PROCESS OUTLOOK

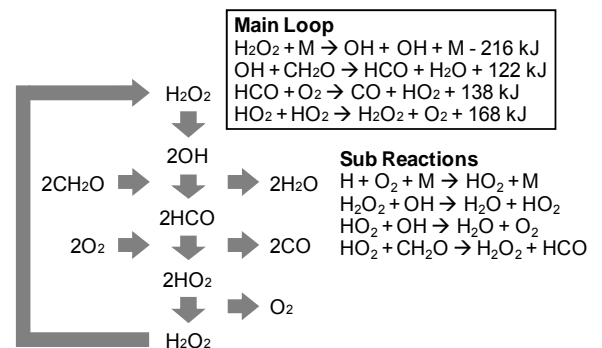
**ANALYSES BY O AND C ATOMIC BALANCE** – In order to clarify overall reactions at each moment, balance analyses of O and C atoms were performed. By LTO and NTC, major portion of fuel is converted to fragments and their oxides.  $\text{C}_7\text{-O}$ , hydrogen oxides containing seven C atoms and at least one O atom, shows an overshoot during the LTO and NTC period, which can be explained by ceiling temperature model [1]. Other oxides continue to increase during that period. Major fragments



**Figure 2** Absolute values of heat release or removal rates by major elementary reactions plotted against process temperature,  $T_P$  (fuel:  $n\text{-C}_7\text{H}_{16}$ ,  $T_0$ : 759 K,  $p_0$ : 2 MPa,  $\phi$ : 0.5)



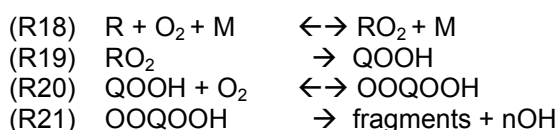
**Figure 3** Heat release rates by four groups (fuel:  $n\text{-C}_7\text{H}_{16}$ ,  $T_0$ : 759 K,  $p_0$ : 2 MPa,  $\phi$ : 0.5)



**Figure 4**  $\text{H}_2\text{O}_2$  reaction loop

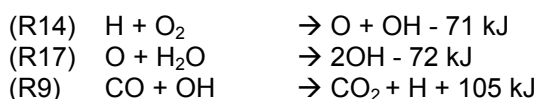
in the thermal ignition preparation phase are aldehydes containing 1 to 3 C atoms. Relatively large amounts of CO and H<sub>2</sub>O are generated during the LTO and NTC phases. During the thermal ignition preparation phase, the concentrations of aldehydes and H<sub>2</sub>O<sub>2</sub> are kept almost constant. Looking the C balance during the thermal ignition preparation period, carbons in C<sub>7</sub>, that is hydrocarbons containing seven C atoms and their oxides are converted to fragments and some fragments are converted to CO mainly by Reaction (R3), thus CO continues to increase. H<sub>2</sub>O formation starts at LTO, however, CO conversion into CO<sub>2</sub> takes place with the Hydrogen-Oxygen system reactions, that is, in the thermal ignition period by Reaction (R9).

**DEPENDENCE ON EQUIVALENCE RATIO** –The reaction process in the LTO and NTC phases is controlled by Reactions (R18) to (R21) [1].

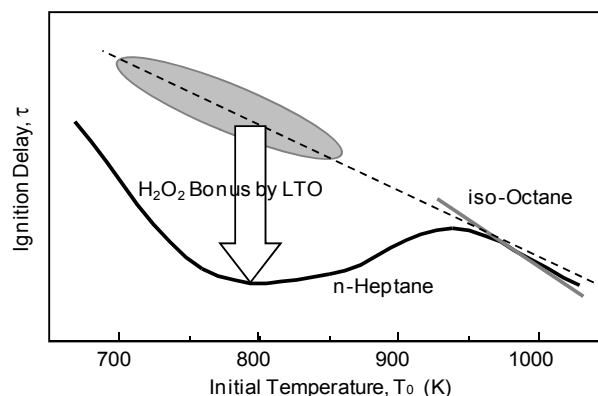


Expressing the rate of Reaction (Ri) as  $r_i$ , RO<sub>2</sub> formation rate by Reaction (R18), that is, ( $r_{18} - r_{-18}$ ) and RO<sub>2</sub> removal rate by Reaction (R20),  $r_{20}$  crosses earlier, that is, at a lower temperature when the equivalence ratio is low.

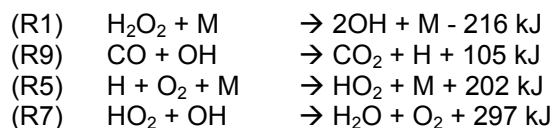
In the ignition preparation range, heat release phenomena can be explained by the H<sub>2</sub>O<sub>2</sub> reaction loop model in all of the cases. When the equivalence ratio is 0.5 or 1.0, the thermal ignition scheme is expressed by Reactions (R14), (R17) and (R9).



When the equivalence ratio is 0.25, however, the thermal ignition process is different. Because the temperature does not increase to the thermal ignition temperature defined as a cross point of Reactions (R5) and (R14). The main path can be expressed by the following scheme.



**Figure 5** H<sub>2</sub>O<sub>2</sub> bonus by LTO



Because large portion of H<sub>2</sub>O<sub>2</sub> is consumed by this timing, the reaction rate in this phase is significantly lower than those of the higher equivalence ratio cases.

**ROLES OF EACH REACTION PHASE** - The global mechanism of hydrocarbon oxidation is summarized in Table 1. A role of the LTO and NTC range reactions is to accumulate CH<sub>2</sub>O and H<sub>2</sub>O<sub>2</sub>. A role of the thermal ignition preparation reactions is to increase the temperature to initiate the thermal ignition. When the LTO and NTC ranges do not exist, CH<sub>2</sub>O and H<sub>2</sub>O<sub>2</sub> preparation proceeds simultaneously with the H<sub>2</sub>O<sub>2</sub> loop reactions. The thermal ignition is the Hydrogen-Oxygen system reactions, and CO conversion into CO<sub>2</sub> by the assist of OH takes place simultaneously with the Hydrogen-Oxygen system reactions.

Figure 5 shows the meaning of LTO and NTC range reactions schematically. The high and low octane number fuels show the similar ignition delays when the initial temperature is higher than NTC range temperatures. When the octane number is low, the LTO range reactions accumulate H<sub>2</sub>O<sub>2</sub> and enhance the H<sub>2</sub>O<sub>2</sub> loop reactions during the thermal ignition preparation

**Table 1** Summary of hydrocarbon oxidation global mechanism

Range	Low Octane Number Fuels (n-Heptane, DME)		High Octane Number Fuels (iso-Octane)	
	Dominant Reactions	Role	Dominant Reactions	Role
LTO	Fuel Series Reactions (Primary and Secondary O <sub>2</sub> Addition)	Preparation of CH <sub>2</sub> O and H <sub>2</sub> O <sub>2</sub>	Not Exist	
NTC				
Thermal Ignition Preparation	H <sub>2</sub> O <sub>2</sub> Loop Reactions	Temperature Increase	Fuel Series Reactions	Preparation of CH <sub>2</sub> O and H <sub>2</sub> O <sub>2</sub>
			H <sub>2</sub> O <sub>2</sub> Loop Reactions	Temperature Increase
Thermal Ignition	H <sub>2</sub> -O <sub>2</sub> System Reactions CO+OH→CO <sub>2</sub> +H	Branching Chain CO Conversion to CO <sub>2</sub>	H <sub>2</sub> -O <sub>2</sub> System Reactions CO+OH→CO <sub>2</sub> +H	Branching Chain CO Conversion to CO <sub>2</sub>

phase.

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