

Combustion and Flame 132 (2003) 219-239

Two-stage ignition in HCCI combustion and HCCI control by fuels and additives

Shigeyuki Tanaka*, Ferran Ayala, James C. Keck, John B. Heywood

Sloan Automotive Laboratory, Massachusetts Institute of Technology, Cambridge, MA, USA

Received 27 February 2002; received in revised form 23 July 2002; accepted 6 August 2002

Abstract

A Rapid Compression Machine (RCM) has been used to study the effects of fuel structure and additives on the Homogeneous Charge Compression Ignition (HCCI) of pure hydrocarbon fuels and mixtures under welldetermined conditions. Such information is needed for understanding ignition delays and burning rates in HCCI engines, and "knock" in spark-ignition engines. It is also valuable for validating basic chemical kinetic models of hydrocarbon oxidation. The pure fuels used in the study include: paraffins (n-heptane, iso-octane), cyclic paraffins (cyclohexane, methylcyclohexane), olefins (1-heptene, 2-heptene, 3-heptene), cyclic olefins (cyclohexene, 1,3-cyclohexadiene), and an aromatic hydrocarbon (toluene). The additives were 2-ethyl-hexyl-nitrate and di-tertiary-butyl-peroxide. It was found that fuels which contained the structure -CH₂-CH₂-CH₂- showed twostage ignition with relatively short ignition delays and that the ignition delay depended strongly on the energy released during the first-stage. For primary reference fuel mixtures (n-heptane + iso-octane), the ignition delay depended only on the molar ratio of n-heptane to oxygen and was independent of the octane number (percent iso-octane). On the other hand, the burn rate depended on both these parameters, which uniquely determine the equivalence ratio. When additives were included in the air/fuel mixtures, the ignition delay was reduced but the burn rate was not affected. These results indicate that for HCCI combustion, the ignition delay and the burn rate can be independently controlled using various fuel mixtures and additives. © 2003 The Combustion Institute. All rights reserved.

1. Introduction

Reducing exhaust emissions and increasing the fuel efficiency of internal combustion engines are of global importance. In this regard, diesel engines are attractive because of their relatively high efficiency. Unfortunately, they produce greater NOx emissions and particulate matter (PM) than spark-ignition engines. Therefore, it would be desirable to reduce emissions from diesel engines and increasingly strict emissions regulations are being placed on them. However, because diesel combustion involves turbulent diffusion flames that produce locally rich lowtemperature and locally lean high-temperature regions, it is difficult to reduce both NOx and PM simultaneously and still maintain high efficiency. One way to achieve both of these objectives would be to use HCCI combustion, which is currently being investigated because of its potential for producing uniform mixtures under lean conditions. The concepts of HCCI have been applied to a two-stroke engine as Active Thermo-Atmosphere Combustion (ATAC) by Onishi et al. [1]. Najt et al. [2] studied HCCI combustion in a four-stroke engine and found that the oxidation kinetics of hydrocarbon fuels could have an important effect on the operation of such an

^{*} Corresponding author. Tel.: +81-480-42-2215; fax: +81-480-42-3790.

E-mail address: shigeyuki-tanaka@cosmo-oil.co.jp (S. Tanaka).



Fig. 1. General oxidation scheme for heavy hydrocarbons at low and high temperatures.

engine. HCCI combustion has also been studied by a number of other investigators [3–10] to obtain a better understanding of the phenomena responsible for the significant reduction of NOx and soot emissions observed.

For HCCI engines, the critical problems are the control of ignition timing and combustion rate [11]. These are determined primarily by low temperature oxidation reactions of the fuel/air mixture in which fuel structure and mixture composition plays an important role. A number of prior studies of the HCCI combustion of light paraffinic hydrocarbons such as methane, propane, butane, pentane, n-heptane, and iso-octane for which the oxidation processes are relatively well understood have been reported [9,12–14]. However, there is relatively little information about more complex fuels such as cyclic paraffins, olefins, and aromatics, which exist in petroleumbased fuels.

The use of fuel mixtures has been proposed as one possible method for controlling HCCI combustion [15–17]. However the combustion mechanism for mixtures has not yet been well established. Additives, such as nitrates and peroxides, used as cetane improvers in diesel fuel to enhance its ignition quality are also of interest. These additives generate radicals through thermal decomposition during the initiation stage of combustion, which strongly affect the HCCI combustion of the air/fuel mixture.

In this study, the effects of fuel structure, mixture composition, and additives on HCCI combustion

were investigated using a Rapid Compression Machine (RCM). Such information is needed for understanding ignition delays and burning rates in HCCI engines and "knock" in spark-ignition engines. It is also valuable for validating basic chemical kinetic models of hydrocarbon oxidation. The fuels investigated included paraffins (n-heptane, iso-octane), cyclic paraffins (cyclohexane, methylcyclohexane), olefins (1-heptene, 2-heptene, 3-heptene), cyclic olefins (cyclohexene, 1,3-cyclohexadiene), and an aromatic hydrocarbon (toluene). The additives (2-ethyl-hexylnitrate and di-tertiary-butyl-peroxide) studied are representative of cetane improvers used in diesel fuel. The results indicate that ignition delays and burning rates in HCCI combustion can be independently controlled by varying fuel composition, initial temperature, and equivalence ratio.

2. Auto ignition of hydrocarbon/air mixtures

The auto-ignition of hydrocarbon/air mixtures has been the subject of numerous prior experimental and theoretical investigations [18–22]. These investigations indicate that for heavy hydrocarbons, HCCI combustion is a two-stage process involving a low temperature cycle followed by a high temperature cycle. The most important reaction paths in the kinetic model are shown in Fig. 1. Reaction is initiated by the abstraction of H from a fuel molecule (RH) by O_2 to form an alkyl radical R and HO₂. At low temperatures, the addition reaction $R + O_2 = RO_2$ initiates a highly exothermic cycle producing H2O and an alkylperoxide O=ROOH. This cycle continues until the temperature rises to a value where the competing reaction $R + O_2 = Olefin + HO_2$ becomes important terminating the first-stage of combustion. At this point, the second-stage, involving slightly exothermic high-temperature reactions, which produce an Olefin and H₂O₂, begins and the rate of temperature rise drops sharply. Thereafter, the temperature continues to rise slowly until the reaction $H_2O_2 + M = OH + OH + M$ becomes important terminating the second stage and initiating a branched thermal explosion. During the explosive stage, O=ROOH and Olefin decompose irreversibly to H₂O and CO. Finally CO is converted to CO₂ in the reaction $CO + OH = CO_2 + H$. The most important reactions determining the overall ignition delay are the initiation reaction, the internal isomerization reaction, and the reaction $R + O_2 = Olefin + Olefin + O_2 = Olefin + O$ HO₂. These reactions are exceedingly sensitive to both fuel structure and temperature and the control of the HCCI combustion process depends on being able to identify and mix fuels and additives with the desired characteristics.

Several nitrate or peroxide compounds have used to improve the ignition quality of diesel fuels. These compounds generate radicals by thermal decomposition before auto-ignition of the air/fuel mixture and advance the timing in diesel engines [23-25]. 2-ethyl-hexyl-nitrate (2EHN) is one such additive used in diesel fuels because of its low cost and high effectiveness. 2-ethyl-hexyl-nitrate decomposes to produce nitrogen dioxide (NO₂) and alkoxy radicals $C_8H_{17}O$. Di-tertiary-butyl-peroxide (DTBP) is often used because it does not contain nitrogen. Di-tertiarybutyl-peroxide decomposes at low temperatures to produce two alkoxy radicals (CH₃)₃CO. Alkoxy radicals have high reactivity and produce fuel radicals, R, which accelerate the ignition process. The bond energies of RO-NO₂ and (CH₃)₃CO-OC(CH₃)₃ are relatively weak compared to that of the R-H involved in the initiation reaction, $RH+O_2 = R+HO_2$. Therefore, relatively small concentrations of these additives produce significant effects on ignition delay times but have little effect on the maximum energy release rates. Thus they could be useful for the independent control of ignition timing in HCCI engines.

3. Experimental apparatus and procedures

3.1. Rapid compression machine

A diagram of the rapid compression machine (RCM) used to investigate the effects of fuels and

additives on HCCI combustion in this study is shown in Fig. 2 and its specifications are shown in Table 1. The cylinder bore was 5.08 cm and the stroke was variable. The volume of combustion chamber was fixed at 12.95 cc and the compression ratio was fixed at 16. The RCM was controlled by a combined hydraulic and pneumatic system. The combustion chamber and the gas supply lines could be heated to control the initial temperature of air/fuel mixture.

3.2. Test fuels and additives

The fuel mixtures used in this study of HCCI combustion included paraffins (n-heptane, iso-octane), cyclo-paraffins (cyclo-hexane, methyl-cyclo-hexane), olefin (1-heptene, trans-2-heptene, trans-3-heptene), cyclic-olefins (cyclohexene, 1,3-cyclohexadiene), and an aromatic hydrocarbon (toluene). 2-ethyl-hexylnitrate and di-tertiary-butyl-peroxide were used to investigate the effect of additives. The properties of these fuels and their purity levels are summarized in Table 2. They were chosen to include a wide range of structures and are representative of the components of gasoline and diesel fuel used in prior HCCI investigations.

3.3. Experimental procedures

As can be seen in Fig. 2, the RCM contains two main oil chambers separated by a fast acting valve. When the fast-acting valve is open, both of these chambers are connected. The outer chamber is the main oil reservoir, which operates at relatively low pressure. The center chamber is the speed control chamber and is designed for high pressures. The fast-acting valve can be locked in the closed position by high-pressure oil in the small chamber behind it.

The experimental procedure was as follows: With the fast-acting valve open, the outer oil chamber was pressurized with nitrogen to lift the piston. The chambers were then isolated by lowering the fast acting

Specifications of rapid compression machine

Cylinder bore	5.08 cm
Maximum stroke	11.0 cm
Maximum compression ratio	19.0
Clearance height	0.6–2.0 cm
Piston length	17.2 cm
Piston mass	0.97 kg
Maximum driving pressure	3.45 MPa
Maximum piston speed	10 m/s
Maximum compression pressure	7 MPa
Compression time	10-30 ms
Maximum compression temperature	1300 K

	n-Heptane i-Octane C7H16 C8H18		1-Heptene C7H14	trans-2-Heptene C7H14	trans-3-Heptene C7H14		
MW	100.2034	114.2302	98.1876	98.1876	98.1876		
Density@ 277 K g/cm3	0.684	0.692	0.697	0.701	0.698		
Boiling point K	371.4	372.2	366.3	371	369		
Q _{LHV} kJ/kg	44566	44310	44300	44183	44191		
RON	0	100	76.4	92.7	94		
MON	0	100	63.4	80.8	80.1		
Sensitivity	ity 0 0		13	11.9	13.9		
Purities %	99+	99+	99+	99	99		
	Cyclohexane C6H12	Methyl cyclohexane C7H14	Cyclohexene C6H10	1,3-cyclohexadier C6H8	e Toluene C7H8		
MW	84.1608	98.1876	82.145	80.1292	92.1402		
Density @277 K g/cm3	0.779	0.769	0.811	0.8616	0.867		
Boiling point K	353.7	374	356	353	383.6		
Q _{LHV} kJ/kg	43450	43380	42886	41401	40589		
RON	83	74.8	83.9	74.8	120		
MON	77.2	71.1	63	53	103.5		
Sensitivity	5.8	3.7	20.9	21.8	16.5		
Purities %	99.9+	99+	99+	97	99.8		



Fig. 2. Experimental apparatus: RCM.

Table 2

Properties of test fuels



Fig. 3. Example of a pressure-time history obtained in the RCM. Fuel: iso-octane. Equivalence ratio: 0.4. Initial temperature and pressure: 318 K and 0.1 MPa, respectively. Compression ratio: 16.

valve with pressurized nitrogen and locking it in place with high-pressure oil. The combustion chamber was evacuated to a pressure below 13 Pa and an appropriate amount of fuel was injected to produce the desired fuel mixture. The method of partial pressures was used and a 10-min interval was allowed insure to complete evaporation of the fuels before the pressures were measured. Dry air was then introduced into the combustion chamber and another 10min interval was allowed for the air/fuel mixture to become homogeneous and equilibrate with the wall temperature. After the combustion chamber was charged, the driving chamber was pressurized with nitrogen. The compression stroke was initiated by releasing the locking pressure on the fast-acting valve. The valve opens and the force balance between the pressurized driving gases above piston and the pressurized oil underneath is broken. The piston is accelerated by the driving gas, which compresses the gases inside the combustion chamber. At the end of compression, high pressure generated by a pin and groove stopping mechanism slows the piston down. In this study, the total piston travel time was 10 ms, the deceleration time was 0.48 ms and the effective compression time was approximately 2.0 ms.

The pressure-time histories were recorded during compression and combustion of the air/fuel mixtures using a Kistler pressure transducer. Pressure-time histories were also recorded for the compression of an inert air/CO₂ mixture having same specific heat ratio, as the air/fuel mixtures at a temperature of 800 K and pressure of 4 MPa. The pressure difference between the air/fuel and air/CO₂ mixtures was used to determine the energy release from the air/fuel mixtures. A typical example of such a pressure-time history is shown in Fig. 3. In this figure, time is set equal to zero at the inflection point in the pressure trace during compression. The end of compression was defined as the time at which peak pressure occurred in the air/CO₂ compression. The adiabatic core temperature, Tac, during the compression was calculated from the measured pressure by using the isentropic relations.

The pressure difference, dP, between the air/fuel and air/CO_2 records in Fig. 3 is shown in Fig. 4. The dPmax is defined as the maximum value of the dP. The temperature increase, dTac, of the core gas at the end of compression was calculated from measured pressure using the ideal gas law under constant volume conditions. The ignition delay, ti, for the air/fuel mixtures is defined as the time at which dP reached 20% of dPmax point. The ignition delay is divided into t1 (first stage induction time) and t2 (second stage induction time). The pressure increases during first stage and second stages are denoted dP1 and dP2, respectively. The burn rate for the explosive phase of combustion is defined as the average rate of pressure increase during the time in which dP rises from 20% to 80% of dPmax.

For fast burn rates, high frequency oscillations



Fig. 4. Definition of symbols used in this paper.

similar to those seen on the pressure traces in "knocking" spark-ignition engines were observed near dPmax. The frequency of these oscillations is approximately 20 kHz, which is very much lower than the 100 kHz characteristic frequency of the Kistler gauge but close to the estimated frequencies of acoustical waves in the test gas and metal cylinder. In engines, these oscillations have been attributed to shock waves produced by auto ignition of the "end gas" and it is assumed that these shock waves cause "ringing" of the metal cylinder that is picked up by the pressure transducer. However, since there is no mechanism for producing significant pressure gradients in the gas during HCCI combustion, it is most likely that, in this case, the "ringing" of the metal cylinder is due to the high impulsive load produced directly by the explosion of the test gas. In either case, the amplitude of such high frequency oscillations provides a measure of the "knock" intensity and stresses in metal engine parts occurring under various operating conditions.

4. Results and discussion

The test matrix showing all experimental conditions investigated is shown in Table 3. Also included are the temperature increment, dTeq, for a constant-volume adiabatic combustion process and the equilibrium pressure, dPeq, calculated from dTeq using the ideal gas law. All the test results are summarized in Table 4. The repeatability of the measurements for three primary fuel mixtures with octane numbers of 0, 90, and 100 is shown in Fig. 5. It can be seen that the repeatability was excellent and that the fractional errors in the peak pressures and ignition delay times were less than plus or minus 3%. This means that RCM measurements of the type made in this study are excellent for accurately evaluating fuel and additive effects on HCCI combustion.

4.1. Knock index and HCCI burn rate

In this work, the knock index, KI, is defined as the amplitude in MPa of the high frequency oscillations occurring near the maximum pressure as seen in Fig. 4. The measured dependence on burn rate is shown in Fig. 6. It can be seen that below a burn rate of approximately one MPa/ms, KI is effectively zero while above this value; KI varies linearly with the burn rate. As discussed in section 3.3 above, these oscillations are most likely caused by pickup of acoustical waves in the metallic parts of the RCM. It is important to limit the amplitude of such oscillation because they cause undesirable noise and can seriously damage the parts of HCCI engines. This can be done by controlling the burn rate, which requires an understanding of the effects of fuel structure and additives on HCCI combustion.

Table 3	
Test matrix	

						Pi = 0.1 MPa,			CR = 16,	dPeq ^b	dTeq ^c
	Fuel	Additive	RON	MON	Phi	Ti (K)	Y	Pc (MPa)	Tc (K) ^a	(MPa)	(K)
1	n-heptane	w/o	0	0	0.5	318	1.335	4.04	805	8.53	1699
2	n-heptane	w/o	0	0	0.4	318	1.345	4.16	827	7.04	1401
3	n-heptane	w/o	0	0	0.3	318	1.355	4.28	851	5.46	1085
4	n-heptane	w/o	0	0	0.2	318	1.365	4.40	875	3.74	744
5	n-heptane	w/o	0	0	0.4	305	1.347	4.19	798	7.39	1409
6	n-heptane	w/o	0	0	0.4	330	1.343	4.14	854	6.75	1393
7	n-heptane	w/o	0	0	0.4	341	1.341	4.12	878	6.50	1385
8	PRF50	w/o	50	50	0.4	318	1.345	4.16	827	7.04	1401
9	PRF/5	W/O	75	75	0.4	318	1.345	4.16	827	7.04	1400
10	PKF90 DDE00	W/O	90	90	0.5	318 219	1.335	4.04	805	8.51	1095
11	PRF90 DDE00	w/0	90	90	0.4	210	1.545	4.10	027 951	7.04 5.44	1400
12	PKF90 DDE00	W/O	90	90	0.5	318 219	1.333	4.28	851 975	5.44 2.74	1082
13	PRF90 DDE00	w/0	90	90	0.2	205	1.303	4.40	873 709	5.74 7.20	144
14	PKF90 DDE00	w/0	90	90	0.4	220	1.547	4.19	798 854	674	1408
15	PKF90 DDF00	w/0	90	90	0.4	330 341	1.343	4.14	834 878	0.74 6.40	1391
17	iso octane	w/0	100	100	0.4	318	1 3 3 5	4.12	805	0.49 8 5 1	1604
19	iso octane	w/0	100	100	0.5	318	1.335	4.04	805	7.04	1400
10	iso-octane	w/0 w/0	100	100	0.4	318	1.343	4.10	851	7.04 5.45	1400
20	iso-octane	w/o	100	100	0.5	318	1.355	4.20	875	3.74	7/3
20	iso-octane	w/0	100	100	0.2	305	1.303	4.40	798	7 30	1408
21	iso-octane	w/0 w/0	100	100	0.4	330	1.347	4.19	854	675	1392
22	iso-octane	w/o	100	100	0.4	341	1 341	4.14	878	6.50	1384
23	cyclo hexane	w/o	83	77.2	0.4	318	1 345	4.12	827	7.04	1401
25	methylcyclohexane	w/o	74.8	71.1	0.4	318	1 345	4.16	827	7.04	1401
26	1-heptene	w/o	76.4	63.4	0.4	318	1.345	4.16	827	7.19	1430
27	2-heptene	w/o	92.7	80.8	0.4	318	1.345	4.16	827	7.17	1427
28	3-heptene	w/o	94	80.1	0.4	318	1.345	4.16	827	7.17	1427
29	cvclohexene	w/o	83.9	63	0.4	318	1.345	4.16	827	7.17	1427
30	1.3-cvclohexadiene	w/o	74.8	53	0.4	318	1.345	4.16	827	7.18	1429
31	toluene	w/o	120	103.5	0.4	318	1.345	4.16	827	7.20	1433
32	TSF 74/26	w/o	93.4	81.5	0.4	318	1.345	4.16	827	7.17	1426
33	TSF 74/21/5	w/o	96.7	85.2	0.4	318	1.345	4.16	827	7.16	1425
34	TSF 74/16/10	w/o	99.8	88.7	0.4	318	1.345	4.16	827	7.16	1425
35	PRF90	2EHN 0.5%	76.5	80.2	0.4	318	1.345	4.16	827	7.04	1400
36	PRF90	2EHN 1%	68.7	75.6	0.4	318	1.345	4.16	827	7.04	1400
37	PRF90	2EHN 2%	57	68.2	0.4	318	1.345	4.16	827	7.04	1400
38	PRF90	2EHN 2%	57	68.2	0.4	305	1.347	4.19	798	7.39	1408
39	PRF90	2EHN 2%	57	68.2	0.4	330	1.343	4.14	854	6.74	1391
40	PRF90	2EHN 2%	57	68.2	0.4	341	1.341	4.12	878	6.49	1383
41	PRF90	DTBP 0.5%	81.4	84.2	0.4	318	1.345	4.16	827	7.04	1400
42	PRF90	DTBP 1%	77.4	80.5	0.4	318	1.345	4.16	827	7.04	1400
43	PRF90	DTBP 2%	71.1	77.1	0.4	318	1.345	4.16	827	7.04	1400
44	PRF90	DTBP 2%	71.1	77.1	0.4	305	1.347	4.19	798	7.39	1408
45	PRF90	DTBP 2%	71.1	77.1	0.4	330	1.343	4.14	854	6.74	1391
46	PRF90	DTBP 2%	71.1	77.1	0.4	341	1.341	4.12	878	6.49	1383
47	iso-octane	2EHN 0.5%	92	92	0.4	318	1.345	4.16	827	7.04	1400
48	iso-octane	2EHN 1%	88	86	0.4	318	1.345	4.16	827	7.04	1400
49	iso-octane	2EHN 2%	80	80	0.4	318	1.345	4.16	827	7.04	1400
50	iso-octane	2EHN 2%	80	80	0.4	305	1.347	4.19	798	7.39	1408
51	iso-octane	2EHN 2%	80	80	0.4	330	1.343	4.14	854	6.75	1392
52	iso-octane	2EHN 2%	80	80	0.4	341	1.341	4.12	878	6.50	1384
53	iso-octane	DTBP 0.5%	95.4	94.6	0.4	318	1.345	4.16	827	7.04	1400
54	iso-octane	DTBP 1%	92.7	91.2	0.4	318	1.345	4.16	827	7.04	1400
55	iso-octane	DTBP 2%	89.6	87.1	0.4	318	1.345	4.16	827	7.04	1400
									(continu	ed on nex	ct page)

(con	continued)												
						Pi = 0.1 MPa,			CR = 16,	dPeq ^b	dTeq ^c		
	Fuel	Additive	RON	MON	Phi	Ti (K)	Y	Pc (MPa)	Tc (K) ^a	(MPa)	(K)		
56	iso-octane	DTBP 2%	89.6	87.1	0.4	305	1.347	4.19	798	7.39	1408		
57 58	iso-octane iso-octane	DTBP 2% DTBP 2%	89.6 89.6	87.1 87.1	0.4 0.4	330 341	1.343 1.341	4.14 4.12	854 878	6.75 6.49	1392 1383		

^a Tc is calculated from measured Pc by isentropic relationships.

^b dPeq is calculated from dTeq by the ideal gas law.

^c dTeq is a temperature increment for a constant-volume adiabatic combustion process.

4.2. The effects of fuel structure on HCCI combustion

The HCCI combustion characteristics of several pure hydrocarbons were measured for the fixed conditions: initial pressure = 0.1 MPa, initial temperature = 318 K, and equivalence ratio = 0.4. The fuels used were: n-heptane, iso-octane, cyclo-hexane, methyl-cyclo-hexane, 1-heptene, trans-2-heptene, trans-3-heptene, cyclo-hexene, 1,3-cyclohexadiene, and toluene. The results for saturated and unsaturated compounds are shown in Figs. 7 and 8, respectively. It can be seen that the HCCI combustion characteristics are strongly affected by the fuel structure. All the saturated compounds and the olefins, 1-heptene and trans-2-heptene, showed two-stage ignition. On the other hand, trans-3-heptene and the cyclic unsaturated compounds, cyclohexene and 1,3-cyclohexadiene, showed single-stage ignition. Toluene could not be ignited under the conditions studied. The absence of a two-stage ignition is most likely associated with a low heat release in the first-stage cycle. For two-stage ignition, the dP at the end of first-stage, dP1, increased in the order: iso-octane < cyclo hexane < 2-heptene <1-heptene = methylcyclohexane < n-heptane. However, the pressure increase, dPi, at the end of the second stage occurred at constant value of approximately 1.0 MPa for all fuels. This corresponds to a temperature rise of 200 K, which added to the compression temperature of 827 K leads to an ignition temperature of approximately 1027 K for the explosive phase.

The ignition delays and the burn rates for all the pure fuels are summarized in Fig. 9. It can be seen that both the ignition delays and the burn rates are strongly affected by fuel structure. Ignition delays for the fuels increased in the order: n-heptane < 1-heptene < methylcyclohexane = 2-heptene < 1,3-cy-clohexadiene = 3-heptene = cyclohexane < cyclohexae = iso-octane \ll toluene (not ignited). First-stage induction times (t1) increased in the order: n-heptane < 1-heptene = 2-heptene = methylcyclohexane < iso-octane < cyclohexae. Finally, sec-

ond-stage induction times increased in the order: n-heptane < 1-heptene < methylcyclohexane = 2-heptene < cyclohexane < iso-octane. Burn rates increased in the order: iso-octane = 1,3-cyclohexadiene < cyclohexane < cyclohexene < 2-heptene = 3-heptene < 1-heptene < n-heptane = methylcyclohexane. Iso-octane and unbranched cyclic compounds have the slowest burn rates. n-heptane, methylcyclohexane, and straight chain olefins have the fastest burn rates.

As shown in Figs. 7 and 8, both single- and two-stage ignition was observed in this study. Singlestage ignition occurred in the combustion of 3-heptene, cyclohexene, and 1,3-cyclohexadiene while two-stage ignition occurred for n-heptane, 1-heptene, 2-heptene, methylcyclohexane, cyclohexane, and isooctane. In general, two-stage ignition is associated with internal isomerization reactions in peroxy radicals. These can occur most easily in complex molecules containing the structure -CH2-CH2-CH2- which allows the formation of low strain 6-member rings containing C-C-C-O-O-H [26]. This is true for all of the molecules that showed two-stage ignition listed above. However, it is also true for cyclohexene but in this case the formation of 6-member rings involving C-C-C-O-O-H is inhibited by the fact the C-C-C structure is already part of a complete 6-member carbon ring. Single-stage ignition is controlled by the same reaction mechanisms responsible for the oxidation of low molecular weight hydrocarbons in which internal isomerization cannot occur [21, 22]. The failure of toluene to ignite under the conditions studied can be associated with the high activation energy required to abstract H from primary carbon sites on the attached methyl group and the absence of the requisite -CH2-CH2-CH2- structure in the molecule.

4.3. HCCI combustion of primary reference fuels

The HCCI combustion characteristics of n-heptane and iso-octane mixtures were also studied in the RCM. Mixtures of these fuels are referred to as primary reference fuels (PRFs) and are used to establish

Table 3

Table 4

Result matrix

	Fuel	Additive	Phi	Ti (K)) $Pi = 0.1 MPa$,		CR = 16,		dP2	dPi	Burn Rate	K I	dPmax
					t1 (ms)	12 (ms)	ti (ms)	dP1 (MPa)	(MPa)	(MPa)	(MPa/ms)	(MPa)	(MPa)
1	n-heptane	w/o	0.5	318	0.160	0.505	0.665	1.38	0.16	1.54	94.3	9.27	7.70
2	n-heptane	w/o	0.4	318	0.164	0.463	0.627	1.11	0.16	1.27	51.9	2.41	6.35
3	n-heptane	w/o	0.3	318	0.165	0.615	0.780	0.8	0.07	0.87	7.6	0.64	4.34
4	n-heptane	w/o	0.2	318	0.165	0.815	0.980	0.4	0.05	0.45	1.3	0.02	2.24
5	n-heptane	w/o	0.4	305	0.301	0.544	0.845	1.31	0.07	1.38	51.5	3.64	6.88
6	n-heptane	w/o	0.4	330	0.102	0.343	0.445	0.8	0.37	1.17	48.0	3.67	5.87
7	n-heptane	w/o	0.4	341	0.100	0.275	0.375	0.75	0.33	1.08	77.3	2.15	5.42
8	PRF50	w/o	0.4	318	0.200	0.875	1.075	0.68	0.55	1.23	37.9	1.31	6.15
9	PRF75	w/o	0.4	318	0.300	1.985	2.285	0.54	0.66	1.19	35.7	1.67	5.97
10	PRF90	w/o	0.5	318	0.500	3.395	3.895	0.46	0.98	1.44	74.8	5.32	7.18
11	PRF90	w/o	0.4	318	0.500	5.343	5.843	0.36	0.78	1.13	18.0	0.55	5.66
12	PRF90	w/o	0.3	318	0.500	7.745	8.245	0.25	0.55	0.80	3.6	0.04	4.00
13	PRF90	w/o	0.2	318	0.500	12.245	12.745	0.19	0.29	0.48	0.4	0.04	2.39
14	PRF90	w/o	0.4	305	0.500	5.665	6.165	0.40	0.68	1.08	14.8	0.77	5.42
15	PRF90	w/o	0.4	330	single-stag	ge	5.045	_		0.98	14.9	0.38	4.89
16	PRF90	w/o	0.4	341	single-stag	ge	5.025	_	_	0.96	14.4	0.31	4.79
17	iso-octane	w/o	0.5	318	1.200	6.225	7.425	0.25	1.19	1.44	44.1	3.33	7.20
18	iso-octane	w/o	0.4	318	1.230	10.090	11.320	0.21	0.86	1.08	12.0	0.48	5.39
19	iso-octane	w/o	0.3	318	1.250	15.045	16.295	0.16	0.52	0.68	1.7	0.04	3.42
20	iso-octane	w/o	0.2	318	1.250	29.415	30.665	0.10	0.25	0.35	0.1	0.04	1.73
21	iso-octane	w/o	0.4	305	1.230	10.605	11.835	0.25	0.79	1.04	9.0	0.50	5.22
22	iso-octane	w/o	0.4	330	single-stag	ge	11.905	_	_	0.96	9.6	0.14	4.80
23	iso-octane	w/o	0.4	341	single-stag	ge	9.165	_	_	0.89	7.0	0.11	4.47
24	cyclo hexane	w/o	0.4	318	2.790	2.302	5.092	0.43	0.71	1.14	15.4	0.36	5.71
25	methylcyclohexane	w/o	0.4	318	0.410	1.765	2.175	0.55	0.67	1.21	53.1	1.70	6.07
26	1-heptene	w/o	0.4	318	0.625	0.925	1.550	0.59	0.69	1.28	49.1	2.24	6.39
27	2-heptene	w/o	0.4	318	0.688	1.517	2.205	0.51	0.66	1.18	35.6	2.02	5.88
28	3-heptene	w/o	0.4	318	single-stag	ge	4.825	_		1.16	36.0	1.47	5.82
29	cyclohexene	w/o	0.4	318	single-stag	ge	7.898	_		1.15	17.9	0.63	5.77
30	1,3-cyclohexadiene	w/o	0.4	318	single-stag	ge	4.505	_		1.12	12.9	0.33	5.61
31	toluene	w/o	0.4	318	no ignited	-	_	_	_	_	_	_	_

(continued on next page)

(continued)

Fuel 32 TSF 74/26 33 TSF 74/21/5 34 TSF 74/16/10 35 PRF90 36 PRF90 37 PRF90 38 PRF90 39 PRF90 40 PRF90 41 PRF90 42 PRF90	Fuel	Additive		Ti (K)	Pi = 0.1 MPa,		CR = 16,		dP2	dPi	Burn Rate	ΚI	dPmax
					t1 (ms)	12 (ms)	ti (ms)	dP1 (MPa)	(MPa)	(MPa)	(MPa/ms)	(MPa)	(MPa)
32	TSF 74/26	w/o	0.4	318	0.900	7.988	8.888	0.33	0.79	1.12	8.4	0.23	5.61
33	TSF 74/21/5	w/o	0.4	318	1.000	10.802	11.802	0.19	0.86	1.05	4.2	0.11	5.25
34	TSF 74/16/10	w/o	0.4	318	1.050	14.608	15.658	0.10	0.97	1.06	4.7	0.06	5.30
35	PRF90	2EHN 0.5%	0.4	318	0.100	4.505	4.605	0.37	0.77	1.14	22.0	0.58	5.68
36	PRF90	2EHN 1%	0.4	318	0.100	4.215	4.315	0.44	0.68	1.12	20.2	0.50	5.59
37	PRF90	2EHN 2%	0.4	318	0.100	4.125	4.225	0.45	0.67	1.12	20.7	0.55	5.60
38	PRF90	2EHN 2%	0.4	305	0.100	4.475	4.575	0.50	0.87	1.37	23.1	0.93	6.83
39	PRF90	2EHN 2%	0.4	330	0.100	3.305	3.405	0.30	0.89	1.19	21.4	0.67	5.93
40	PRF90	2EHN 2%	0.4	341	0.100	2.595	2.695	0.20	0.92	1.12	17.6	0.59	5.62
41	PRF90	DTBP 0.5%	0.4	318	0.010	3.905	3.915	0.45	0.68	1.13	19.0	0.43	5.66
42	PRF90	DTBP 1%	0.4	318	0.010	3.125	3.135	0.47	0.69	1.16	21.5	1.10	5.81
43	PRF90	DTBP 2%	0.4	318	0.010	2.685	2.695	0.56	0.63	1.19	23.0	0.45	5.96
44	PRF90	DTBP 2%	0.4	305	0.010	3.485	3.495	0.55	0.85	1.40	22.1	1.04	7.00
45	PRF90	DTBP 2%	0.4	330	0.010	2.075	2.085	0.35	0.83	1.18	26.1	0.59	5.90
46	PRF90	DTBP 2%	0.4	341	0.010	1.755	1.765	0.30	0.87	1.17	23.7	0.71	5.87
47	iso-octane	2EHN 0.5%	0.4	318	0.100	9.725	9.825	0.25	0.81	1.06	10.5	0.24	5.28
48	iso-octane	2EHN 1%	0.4	318	0.100	8.525	8.625	0.26	0.81	1.07	13.2	0.14	5.33
49	iso-octane	2EHN 2%	0.4	318	0.100	8.375	8.475	0.26	0.78	1.04	8.9	0.17	5.19
50	iso-octane	2EHN 2%	0.4	305	0.100	10.145	10.245	0.32	0.93	1.25	13.1	0.43	6.26
51	iso-octane	2EHN 2%	0.4	330	0.100	6.925	7.025	0.23	0.80	1.03	10.1	0.21	5.14
52	iso-octane	2EHN 2%	0.4	341	0.100	5.455	5.555	0.20	0.80	1.00	9.6	0.14	5.01
53	iso-octane	DTBP 0.5%	0.4	318	0.010	7.575	7.585	0.27	0.78	1.05	11.2	0.19	5.24
54	iso-octane	DTBP 1%	0.4	318	0.010	6.885	6.895	0.34	0.71	1.05	11.9	0.12	5.24
55	iso-octane	DTBP 2%	0.4	318	0.010	5.525	5.535	0.36	0.69	1.05	12.1	0.21	5.26
56	iso-octane	DTBP 2%	0.4	305	0.010	7.385	7.385	0.40	0.86	1.26	19.5	0.57	6.31
57	iso-octane	DTBP 2%	0.4	330	0.010	4.355	4.365	0.35	0.73	1.08	13.5	0.31	5.38
58	iso-octane	DTBP 2%	0.4	341	0.010	2.915	2.925	0.30	0.75	1.05	16.0	0.55	5.24



Fig. 5. The repeatability of experiments for three PRFs with octane numbers of 0, 90, and 100. Equivalence ratio: 0.4, Initial temperature: 318 K, Initial pressure: 0.1 MPa. Compression ratio: 16.

the octane rating scale. The octane number, ON, of a PRF is defined as the volume percentage of isooctane in the PRF. PRFs with octane numbers of 0, 50, 75, 90, and 100 were included in this study. Plots of the pressure rise, dP, as a function of time for each PRF mixture are shown in Fig. 10. The equivalence ratio was fixed at 0.4 and initial temperature and pressure were fixed at 318 K and 0.1 MPa, respectively. It can be seen that both the first- and secondstage induction times increase as the octane number increases, that is, as the amount of iso-octane in the PRF increases. It can also be seen that the dP1 at the end of the first stage decreases as the octane number increase while the dP at the end of the second stage



Fig. 6. Dependence of the KI on the burn rate.



Fig. 7. The HCCI combustion characteristics of some saturated hydrocarbons. Equivalence ratio: 0.4, Initial temperature: 318 K, Initial pressure: 0.1 MPa. Compression ratio: 16.

is constant as previously noted. Because dP is a measure of the temperature rise in the gas mixture due to chemical energy release and temperature is the most important parameter controlling the rate of branching reactions responsible for the explosive phase, this suggest that the second-stage induction time is just the time required for the energy released by second-stage reactions to raise the temperature from the value produced by first-stage reactions to the ignition temperature.

The sensitivity of the ignition delay to the octane number can now be explained by noting that the energy



Fig. 8. The HCCI combustion characteristics of some unsaturated hydrocarbons. Equivalence ratio: 0.4, Initial temperature: 318 K, Initial pressure: 0.1 MPa. Compression ratio: 16.



Fig. 9. Summary of ignition delays and burn rates for all fuels. Equivalence ratio: 0.4. Initial temperature and pressure: 318 K and 0.1 MPa, respectively. Compression ratio: 16.



Fig. 10. HCCI combustion characteristics of PRFs. Equivalence ratio: 0.4, Initial temperature: 318 K, Initial pressure: 0.1 MPa. Compression ratio: 16.



Fig. 11. HCCI combustion characteristics of TSFs. Equivalence ratio: 0.4, Initial temperature: 318 K, Initial pressure: 0.1 MPa. Compression ratio: 16.

released in the first stage is due almost entirely to fast reactions involving n-heptane. That is to say, if the fuel is all n-heptane (octane number = 0), fast highly exothermic first-stage reactions alone are sufficient to raise the gas temperature from its value at the end of compression to the ignition temperature in a small fraction of a millisecond. On the other hand, if the fuel is all iso-octane (octane number = 100), the temperature rise is due solely to slow only slightly exothermic reactions and takes many milliseconds.

4.4. HCCI combustion of toluene standard fuels

The HCCI combustion characteristics of mixtures of toluene, n-heptane, and iso-octane referred to as toluene standard fuels (TSFs) were also investigated in this study. The volume percentage of toluene was 74% for all TSFs. The amount of n-heptane and iso-octane in TSFs was varied to produce octane numbers of 93.4, 96.7, and 99.8. The equivalence ratio was fixed at 0.4 for each TSF and the initial temperature and pressure were fixed at 318 K and 0.1 MPa, respectively. The test results are shown in Fig. 11. Two-stage ignition was observed for all TSFs. As in the case of PRFs, the ignition delay increases with the octane number. The first-stage induction times, t1, for TSFs are almost same as those for PRFs with the same octane number. However, the second-stage induction times, t2, are somewhat longer due to the slower rate of second-stage reactions in mixtures containing a high percentage of toluene.

4.5. Dependence of ignition delay on first-stage pressure rise

In the preceding sections, a qualitative relationship was suggested between the ignition delay for HCCI combustion and the energy released in the first-stage reactions during two-stage ignition. Quantitative results are presented in Fig. 12, which shows that ignition delays for all fuels exhibiting two-stage combustion characteristics are strongly correlated with the pressure increase occurring during the first stage. The ignition delay decreases as the pressure increase and approaches zero at dP \gg 1.0MPa which is approximately the same dP at which the explosive stage was observed to begin.



Fig. 12. Dependence of ignition delays on first-stage pressure increases for all fuels.



Fig. 13. Ignition delays and burn rates plotted as a function of RON for all fuels. Equivalence ratio: 0.4. Initial temperature and pressure: 318 K and 0.1 MPa, respectively. Compression ratio: 16.

4.6. Effect of octane number on ignition delay and burn rate

The research octane number (RON) of a general fuel is defined as the octane number of the PRF that has the same knock intensity as the general fuel when both are measured in a Cooperative Fuel Research (CFR) engine running under specified operating conditions. In this study, ignition delays and burn rates were measured in an RCM for a variety of fuels including PRFs. The results for all fuels used are shown as a function of RON in Fig. 13. Although the ignition delay appears to increase and the burn rate to decrease as RON increases, there is considerable scatter in the data and the correlation is relatively weak. A cross plot of the ignition delay times as a function of burn rates is shown in Fig. 14. Here the correlation is slightly better and it can be seen



Fig. 14. Dependence of burn rates on the ignition delays for all fuels. Equivalence ratio: 0.4. Initial temperature and pressure: 318 K and 0.1 MPa, respectively. Compression ratio: 16.



Fig. 15. The time history of PRF90 at different equivalence ratios. Initial temperature and pressure: 318 K and 0.1 MPa, respectively. Compression ratio: 16.

that the ignition delay decreases roughly as the reciprocal of the burn rate in agreement with prior observations.

4.7. Effect of equivalence ratio on HCCI combustion

As previously noted, the ignition delay in twostage HCCI combustion depends strongly on the energy release during the first-stage, which in turn depends on the equivalence ratio and the octane number. To investigate this dependence, mixtures of n-heptane and iso-octane with different equivalence ratios and octane numbers were studied. The initial temperature and pressure were fixed at 318 K and 0.1 MPa, respectively. n-heptane and iso-



Initital Temp.: 318K, Initial Pressure: 0.1MPa, Compression Ratio: 16

Fig. 16. Contour plot of the ignition delay for PRFs as a function of RON and equivalence ratios. Initial temperature and pressure 318 K and 0.1 MPa, respectively. Compression ratio: 16.



Initital Temp.: 318K, Initial Pressure: 0.1MPa, Compression Ratio: 16

Fig. 17. Contour plot of the burn rate for PRFs as a function of RON and equivalence ratio. Initial temperature and pressure: 318 K and 0.1 MPa, respectively. Compression ratio: 16.



Fig. 18. Dependence of the ignition delay on the n-heptane/oxygen mole ratio for various PRFs and equivalence ratios (Phi)



Fig. 19. dP vs. time histories for two PRFs with the same n-heptane/oxygen mole ratio at different equivalence ratios

octane were used because, as previously noted, the former showed the largest energy release during first-stage while the latter showed the smallest.

The pressures-time curves for PRF90 at different equivalence ratio are shown in Fig. 15. The first-stage induction time is very small for all equivalence ratios. However, as the equivalence ratio decreases, the energy release from first-stage decreases and the ignition delay becomes longer. As would be expected from previous discussion, the knock-intensity and burn rate decrease strongly as the equivalence ratio decreases.

Three-dimensional plots of the ignition delay and burn rate as a function of equivalence ratio and research octane number are shown in Fig. 16 and 17. The ignition delay decreases with decreasing RON and increasing equivalence ratio. The burn rate shows the opposite trend, however, the effect of equivalence ratio on the burn rate is much stronger than that of RON.

The ignition delays for all RONs and equivalence ratios were re-plotted as a function of the iso-octane/O₂ and n-heptane/O₂ ratios in Fig. 18. It can be seen that ignition delays are strongly correlated with the n-heptane/O₂ ratio independent of the RON or equivalence ratio. On the other hand, Fig. 15 shows that the total energy release depends strongly on the equivalence ratio. Thus, for PRFs the ignition delay and the total energy release can be controlled independently. This is further illustrated in Fig. 19, which shows two pressure-time curves for a fixed n-heptane/O₂ ratio at equivalence ratios of 0.2 and 0.5. In both cases, the ignition delay is about 1.0 ms, as indicated by the arrows, however the total energy release and burn rate are very much higher at the higher equivalence ratio. The ability to control the ignition delay and energy release rate is, of course, just what is required for the design of HCCI engines.

4.8. Effect of additives on HCCI combustion

The effects of additives on HCCI combustion were also investigated using the RCM. The additives used were 2-ethyl-hexyl-nitrate (2EHN) and di-tertiary-butyl-peroxide (DTBP). PRF90 and PRF100 (iso-octane) were used as base fuels.

The pressure-time histories for air/PRF90 mixtures without additives and with 2% by volume of di-tertiary-butyl-peroxide or 2-ethyl-hexyl-nitrate are shown in Fig. 20. It can be seen that the additives increased the energy release from first-stage and decreased the ignition delay time in agreement with prior observations. It can also be seen that di-tertiarybutyl-peroxide has a larger effect on the ignition delay than 2-ethyl-hexyl-nitrate. As previously discussed, the reduction in the ignition delay is due to the initiation of combustion by alkoxy radicals produced in the dissociation of the additives. These in turn react rapidly with the fuel to produce alkyl radicals, R, which initiate the low temperature cycle. Because the dissociation energies of di-tertiary-butylperoxide and 2-ethyl-hexyl-nitrate are approximately the same, the smaller ignition delay associated with di-tertiary-butyl-peroxide may be attributed to the fact that it produces twice as many active alkoxy radicals as 2-ethyl-hexyl-nitrate when it dissociates.



Fig. 20. dP versus time histories for PRF90/air mixtures with 2 vol.% of the additives: DTBP and 2EHN. Equivalence ratio: 0.4. Initial temperature and pressure: 318 K and 0.1 MPa, respectively. Compression ratio: 16.

It may be noted that additives produce exactly the same effect as adding n-heptane to a mixture. However, the effects are larger for the additives because the activation energies for the initiation reactions are lower than those for n-heptane.

The correlation between ignition delay and firststage pressure rise for the above air/fuel mixtures is shown in Fig. 21 along with the data from Fig. 12. It can be seen that the correlation is preserved even when additives are included in the air fuel mixtures.

The ignition delays and burn rates are plotted as a function of volume percent additive for PRF90 and PRF100 (iso-octane) base fuels in Fig. 22. For both



Fig. 21. Dependence of the ignition delay on the first-stage pressure increase for all fuels: w/o the additives, DTBP and 2EHN.

additives, the ignition delays decreased as the volume percent additive increased. As previously noted, the affect of di-tertiary-butyl-peroxide on the ignition delay was larger than that of 2-ethyl-hexyl-nitrate. However, the volume percent of the additives used was too small to affect the burn rates.

4.9 Effect of initial temperature on HCCI combustion

The effect of initial gas temperature on the ignition delay and burn rate is shown in Figs. 23 and 24 for fuels with and without additives. In all cases, the ignition delay decreased as the initial gas temperature increased while the burn rate remained essentially constant. There is some slight evidence of a negative temperature coefficient between 830 K and 850 K for the case of iso-octane/air mixtures without additives but additional data are needed to establish this.

A conceptual model for controlling HCCI combustion using fuel composition, initial gas temperature, and equivalence ratio shown in Fig. 25. Ignition delay can be controlled using the n-heptane and oxygen mole ratio, the initial temperature, and the additive dosage and for PRFs, the total pressure increase and burn rate can be independently controlled using the equivalence ratio and octane number.

5. Summary and conclusions

In this study, the affects of fuel structure, equivalence ratio, additives, and initial gas temperature on HCCI combustion were investigated using a rapid



Fig. 22. Ignition delays and burn rates plotted as a function of dosage of the additives: DTBP and 2EHN. Equivalence ratio: 0.4. Initial temperature and pressure: 318 K and 0.1 MPa, respectively. Compression ratio: 16.

compression for a variety pure fuels and mixtures under conditions similar to those encountered in diesel engines. Such information is needed for understanding ignition delays and burning rates in HCCI engines and "knock" in spark-ignition engines. It is also valuable for validating basic chemical kinetic models of hydrocarbon oxidation.

On the basis of the information obtained, the following conclusions about HCCI combustion can be drawn:

 Both the ignition delays and the burn rates of heavy hydrocarbon fuels are strongly affected by fuel structure. Fuels including the structure -CH₂-CH₂-CH₂-, which allows the formation of 6-member low strain C-C-C-O-O-H rings, showed two-stage ignition with relatively short ignition delays in agreement with previously reported data.



Fig. 23. The effect of the initial temperature on the ignition delay for two PRF/air mixtures with additives. Equivalence ratio: 0.4. Initial pressure: 0.1 MPa. Compression ratio: 16.

- Ignition delays for all fuels exhibiting twostage combustion characteristics are strongly correlated with the first-stage pressure increase and the ignition delay decreases as the firststage pressure increase becomes larger.
- 3. When n-heptane and iso-octane mixtures (PRFs) are used as fuels, the ignition delays are a function only of the n-heptane to oxygen mole ratio. However, the total pressure rise and burn rates are functions of both the octane number and the equivalence ratio.
- 4. The ignition delays become significantly shorter when small amounts of di-tertiary-butyl-peroxide or 2-ethyl-hexyl-nitrate are added to the air/fuel mixtures or the initial temperature is increased but the total pressure increase and burn rate is not affected.



Fig. 24. The effect of initial temperature on the burn rate for two PRF/air mixtures with additives. Equivalence ratio: 0.4. Initial pressure: 0.1 MPa. Compression ratio: 16.

HCCI Controlling by PRFs with Additives



Fig. 25. Conceptual model for controlling HCCI combustion.

5. The results show that the ignition delay time, total pressure increase, and burn rate can be independently controlled using the n-heptane to oxygen mole ratio, additives, and the initial temperature to fix the ignition delay time and the equivalence ratio and octane number to fix the total pressure increase and burn rate.

Acknowledgment

The authors wish to thank the COSMO OIL CO., LTD. and COSMO Research Institute of Japan for their financial support and their permission to publish this article.

References

- S. Onishi, S.H. Jo, K. Shoda, P.D. Jo, S. Kato, Society Automotive Engineers SAE-790501, 1979.
- [2] P.M. Najt, D.E. Foster, Society of Automotive Engineers SAE-830264, 1983.
- [3] R.H. Thring, Society of Automotive Engineers SAE-892068, 1989.
- [4] T.W. Ryan, T.J. Callahan, Society of Automotive Engineers SAE-961160, 1996.
- [5] Y. Takeda, K. Nakagome, K. Niimura, Society of Automotive Engineers SAE-961163, 1996.

- [6] Y. Ishibashi, M. Asai, Society of Automotive Engineers SAE-960742, 1996.
- [7] K. Nakagome, N. Shimazaki, K. Niimura, S, Kobayashi. Society of Automotive Engineers SAE-970898, 1997.
- [8] H. Yokota, Y. Kudo, H. Nakajima, T. Kakegawa, T. Suzuki, Society of Automotive Engineers SAE-970891, 1997.
- [9] M. Christensen, P. Einewall, B. Johansson, Society of Automotive Engineers SAE-972874, 1997.
- [10] S. Kimura, O. Aoki, H. Ogawa, S. Muranaka, Y. Enomoto, Society of Automotive Engineers SAE-1999-01-3681, 1999.
- [11] R.H. Stanglmaier, C.E. Roberts, Society of Automotive Engineers SAE-1999-01-3682, 1999.
- [12] M. Christensen, A. Hultqvist, B. Johansson, Society of Automotive Engineers SAE-1999-01-3679, 1999.
- [13] M. Christensen, B. Johansson, P. Amneus, F. Mauss, Society of Automotive Engineers SAE-980787, 1998.
- [14] T. Tsurushima, N. Shimazaki, Y. Asaumi, Int. J. Engine Research 1 (2000) 337.
- [15] M. Furutani, Y. Ohta, M. Kono, M. Hasegawa. Proceeds of the Fourth International Symposium COMO-DIA, 1998, p. 173.
- [16] T. Kaimai, H. Tsunemoto, H. Ishitani, Society of Automotive Engineers SAE-1999-01-1509, 1999.
- [17] R.H. Stanglmaier, T.W. Ryan III, J.S. Souder, Society of Automotive Engineers SAE-2001-01-1897, 2001.
- [18] R.A. Cox, J.A. Cole, Combust. Flame 60 (1985) 109.
- [19] S.W. Benson, Prog. Energy Combust. Sci. 7 1981 125, see also Oxidation Communication 2 (1982) 169.
- [20] H. Hu, J. Keck, J, Society of Automotive Engineers SAE-872110, 1987.
- [21] R.W. Walker, C. Morley, in: R.G. Compton, G. Hancock, and M. J. Pilling (Eds.), Comprehensive Chemical Kinetics, vol. 35. Elsevier, New York, 1997, p. 9.
- [22] I. Glassman, Combustion, 3rd ed. Academic Press, 1996, p. 84.
- [23] P.Q.E. Clothier, B.D. Aguda, A. Moise, H.O. Pritchard, Chem. Soc. Rev. 22 (1993) 101.
- [24] M.A.R. AI-Rubaie, J.F. Griffiths, C.G.W. Sheppard, Society of Automotive Engineers SAE-912333, 1991.
- [25] K. Hashimoto, Y. Akutsu, M. Arai, M. Tamura, Sekiyu Gakkaishi 41 (1998) 341.
- [26] R.T. Pollard, in: C.H. Bamford, C.F.H. Tipper, Eds., Comprehensive Chemical Kinetics, vol. 17. Elsevier, New York, 1977, p. 249.