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Aldehydes and Methanol Emission Mechanisms and Characteristics from a Methanol/Gasoline-Fueled Spark-Ignition (SI) Engine

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Formaldehyde (HCHO), acetaldehyde (CH_3CHO), and methanol (CH_3OH) emission characteristics as well as their conversion efficiencies on the three-way catalytic converter (TWC) were investigated on a three-cylinder, spark-ignition (SI) engine when it ran on gasoline and M85 (gasoline/methanol = 15:85), respectively. In addition, their emission mechanisms were simulated on a plug flow reactor (PFR) model with the detailed kinetic mechanism of primary reference fuels as well. Simulation results show that there exist contribution zones for both HCHO and CH_3CHO emissions in pipes along with decrescent temperatures; it contains two subzones of the generation zone (Z_G) and the following generation−consumption zone (Z_{G-C}). Aldehydes emissions become the peak value at the critical point, and the critical temperature of HCHO is higher than that of CH_3CHO. The increase of the initial temperature and residence time of the gases in the pipe will move the aldehydes emissions from Z_G to Z_{G-C} along the emission profiles. The initial temperature of the exhaust pipe lies between the critical temperatures of HCHO and CH_3CHO; thus, the HCHO emission decreases while the CH_3CHO emission increases with the increase of the engine torque, i.e., initial temperature. With the increase of the engine speed, the decrease of the residence time takes the dominant role, the HCHO emission increases, while the CH_3CHO emission decreases. However, the initial temperature in TWC is higher than the critical temperature of CH_3CHO; the aldehydes conversion efficiencies decrease; and minus efficiencies appear at high engine speeds. Simulation results coincide well with the emission characteristics.

1. Introduction

With the growing concerns on environmental protection and worries about future oil supplies, nonpetroleum-based environmentally friendly alternative fuels have been widely studied since the 1970s. Methanol (CH_3OH), known as a methyl alcohol, has some advantages over gasoline. It has excellent combustion properties and better anti-knock characteristics.[1,2] Methanol engines have lower emissions and better power and thermal efficiency.[4−13] The advantages have made it the most attractive alternative fuel for the spark-ignition (SI) engine. However, more formaldehyde (HCHO) and unburnt methanol (CH_3OH) are emitted when the engine runs on methanol or methanol/gasoline blends.[10−14] HCHO and CH_3OH are both toxic pollutants, especially the HCHO, which is classified as a probable human carcinogen by the United States Environmental Protection Agency (U.S. EPA).

Because the hydrocarbon (HC) detector, flame ionization detector (FID), has an extremely limited response on HCHO,[15−17] it is commonly monitored with the 2,4-DNPH derivative method in engine tests.[11,12] However, exclusive of the sampling time, the complex sample pretreatments take over 1 h;[18] it is not endurable especially when a lot of testing points are needed. Because of restriction by the detecting method, limited test points of engine-out HCHO were investigated in the literature;[11,13] the HCHO emission characteristics can hardly be precisely reflected, not to mention the production mechanism of engine-out HCHO. Zervas et al. just investigated the influence of the fuels and equivalence ratio on the engine-out HCHO emission characteristics.[11,12] Because most electric controlled SI engines can now maintain the equivalence ratio around a unit, the influence of engine speed and torque on the HCHO emission characteristics is more important for application; however, related literature is rarely reported.[14] Thus, with the application of methanol on the SI engine and spread of the methanol vehicle, it is very important to find out the HCHO

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emission characteristics and the emission mechanisms from the methanol/gasoline blended fueled engine.

In this study, the emission characteristics of HCHO, acetaldehyde (CH_3CHO), and CH_3OH as well as their three-way catalytic converter (TWC) conversion efficiencies were experimentally investigated on the three-cylinder SI engine fueled with gasoline and M85 (gasoline/methanol = 15:85) fuel blend. In addition, their emission mechanisms were simulated on a plug flow reactor (PFR) model with the detailed kinetic mechanism of primary reference fuels as well. Simulation results explained well how the engine speed and torque influenced the characteristics of HCHO and CH_3CHO emissions and the TWC conversion characteristics.

2. Experimental Setup

A three-cylinder, electronic-controlled, port fuel injection, $JL368Q_3$ SI engine (bore, 68 mm; stroke, 72 mm; total displacement, 0.796 L; compression ratio, 9.4) was used for the investigation. There was no special retrofit on the engine except for the increase of cyclic fuel delivery quantity to keep its power. Commercial 93 gasoline was used as the base fuel; first grade industrial methanol with the purity of 99.9% was mixed with the fraction of 85% in volume; and the fuel blend was thus named M85. To prevent the problems of miscibility (e.g., methanol in the blends absorbs water from air), M85 was prepared before each experiment. No additives were used.

HCHO, CH_3CHO, and CH_3OH emissions were detected by gas chromatography (GC-2010, Shimadzu, Japan) consisting of a Gs-OxyPLOT capillary column (10 m × 0.53 mm inner diameter × 10 μm, Agilent Technologies) and a pulsed discharge helium ionization detector [PDHID, model D4-I-SH-17R, VICI (Valco Instrument Co., Inc.)] in Ar-PDHID mode. Before detection, the exhaust gas was first sampled in the bags made of fluoropolymer−ethylene−propylene (FEP) and then heated at 80 °C to prevent water from condensing. Details can be seen in our previous work.[14,19]

3. Mechanism Simulation

To understand well the emission mechanisms of HCHO and CH_3CHO from gasoline combustion and how methanol affects its formation when some is blended in gasoline, the detailed oxidation mechanism of primary reference fuels, i.e., iso-octane/*n*-heptane (iC_8H_{18}/nC_7H_{16}) mixture, containing 1034 species and 4236 reactions, developed by Curran et al.,[20] is used on CHEMKIN with the module of the PFR to simulate the HC and methanol oxidation process in the exhaust pipe of the gasoline and M85 blend fueled engine. The length of the PFR is set as 100 cm with decrescent temperatures along the pipe at the interval of 5 °C/cm. The initial temperature (T_0) and the gas flow velocity sets are shown in Table 1. Inner pressure is 1 atm, and the equivalence air/fuel ratio is set as a unit. The HC emission from the gasoline engine is presented by a gas mixture consisting of 93%$_{vol}$ of iso-octane and 7%$_{vol}$ of *n*-heptane (named the 93 mixture), and the exhaust gas from the M85 engine is presented by the M85 mixture consisting of 85%$_{vol}$ of methanol and 15%$_{vol}$ of the 93 mixture. In this way, the oxidations of HC/methanol emissions in the exhaust pipe of the gasoline and M85 engine are simulated by the oxidations of 93 and M85 gas in PFR.

Table 1. Sets of the PFR

	fuel component			mole fraction
fuel	93		iC_8H_{18}	0.93
			nC_7H_{16}	0.07
	M85	93	iC_8H_{18}	0.15 × 0.93
			nC_7H_{16}	0.15 × 0.07
		CH_3OH		0.85
oxidizer	air	O_2		0.21
		N_2		0.79
dilution gas	argon			0.997
reactor parameters	length			100 cm
	flow velocity (v)	10 m/s	residence time (t_{res})	10 ms
		5 m/s		20 ms
		3 m/s		33 ms
	pressure			1 atm
temperature sets	1	$T = T_0 - 5x^a$, T_0 =		1300 K
	2			1200 K
	3			1150 K
	4			1100 K
	5			1050 K
	6			1000 K

[a] x is the distance to the reactor inlet (cm).

3.1. Oxidation Profile. HCHO and CH_3CHO are the two most simple and important oxygenated intermediate products of HC oxidation. As is well-known, there exist two effects for intermediate products, generation and consumption.

Figure 1 shows the HCHO and CH_3CHO concentration profiles along the reactor from 93 and M85 mixture oxidation at different initial temperatures. Although the two mixtures are different in composition, HCHO and CH_3CHO have the similar profiles along the reactor. The generated HCHO and CH_3CHO are soon consumed at high temperatures. Because the consumption rate is slowed down with the decrease of the initial and along-pipe temperature (T_0 and T_{pipe}), some HCHO and CH_3CHO are emitted at lower temperatures. No consumption process appears when T_0 is lower than a critical temperature (T_{cri}). There exists only the generation effect; thus, HCHO and CH_3CHO keep increasing along the reactor. As can be seen from Figure 2, with the decrease of T_0, the two-stage process, including generation and consumption, is gradually degraded to a one-stage process of consumption. The differences between the HCHO and CH_3CHO profiles from the 93 and M85 mixture are that the T_{cri} of CH_3CHO profile is higher than HCHO, the presence of methanol in the gas mixture reduces both of their T_{cri}, and the frozen temperature of HCHO reactions is around 950 K, while the frozen temperature of CH_3CHO reactions is around 850 K.

The profiles of the two aldehydes are not only affected by temperature but also influenced by the reaction time. The latter is studied by changing the velocity of the gas flow in the reactor, as seen in Figure 3. With the increase of the flow velocity, the residence time (t_{res}) of the gas mixture staying in the reactor is shortened, the generation process is prolonged, while the consumption process is weakened to disappear, and the two-stage processes are both degraded toward one-stage processes. Thus, the increase of t_{res}, i.e., the decrease of gas flow velocity, has a similar effect on the profiles of the aldehydes as the increase of T_0; they both move the profiles from a one-stage process to a two-stage process.

3.2. Formation Path. The typical two-stage processes are chosen to analyze the formation and oxidation paths of HCHO and CH_3CHO from 93 and M85 gases at the flow

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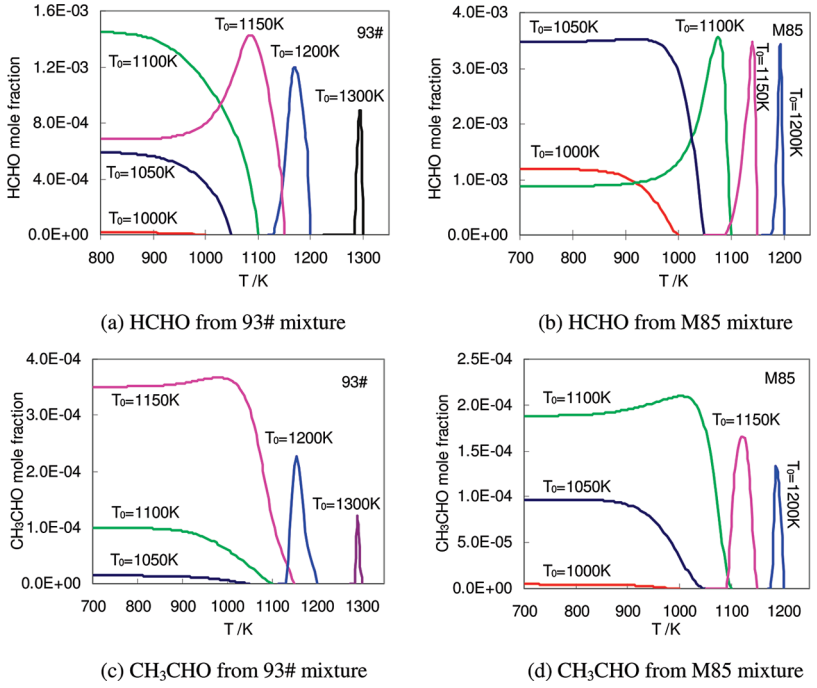
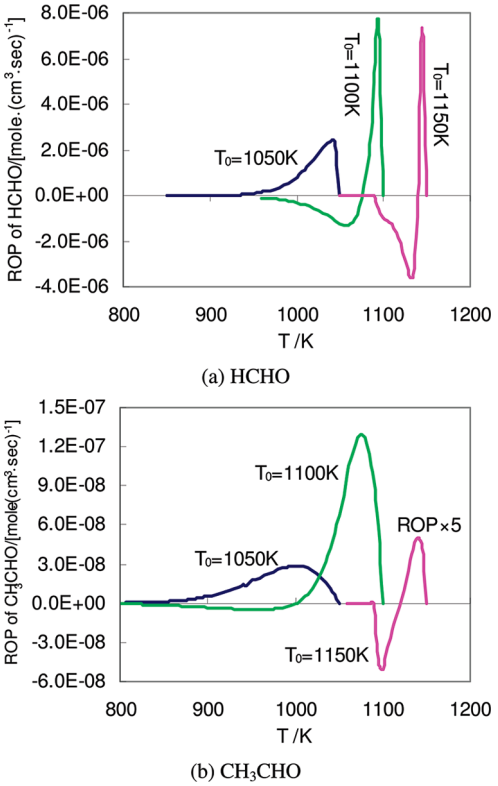


(a) HCHO from 93# mixture (b) HCHO from M85 mixture

(c) CH_3CHO from 93# mixture (d) CH_3CHO from M85 mixture

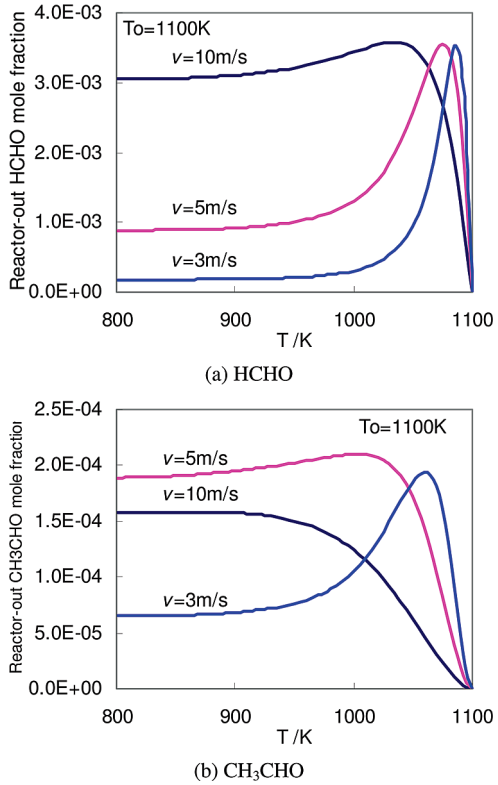
Figure 1. HCHO and CH_3CHO concentration profiles along the reactor at different initial temperatures. v = 5 m/s, and t_{res} = 20 ms.



(a) HCHO

(b) CH_3CHO

Figure 2. Total rate of production (ROP) profiles of HCHO and CH_3CHO from the M85 mixture at different initial temperatures. v = 5 m/s, and t_{res} = 20 ms.



(a) HCHO

(b) CH_3CHO

Figure 3. HCHO and CH_3CHO concentration profiles along the reactor at different gas flow velocities. T_0 = 1100 K.

velocity of 5 m/s, where the T_0 for 93 and M85 gas oxidation are 1150 and 1100 K, respectively, as seen in Figure 1. Figure 4 shows the top 20 sensitive reactions on HCHO production from the two-gas oxidation. Despite the common reactions of R45 and R112, the formation of HCHO in 93 gas mainly depends upon the following paraffin radical reactions concerning CH_3, C_3H_5, and iC_4H_7 radicals:

$$\text{R3} \quad CH_4+OH = CH_3+H_2O$$

$$\text{R24} \quad CH_3+CH_3 = C_2H_6$$

$$\text{R207} \quad iC_4H_8 = iC_4H_7+H$$

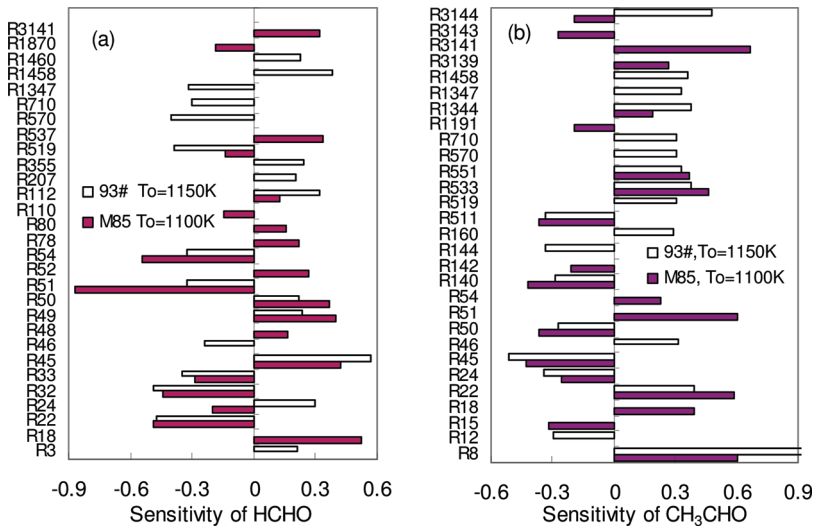


Figure 4. Sensitivity analysis plot for HCHO and CH_3CHO formation from 93 and M85 mixture oxidation.

$$\text{R355}\quad C_5H_{10} = iC_4H_7 + CH_3$$

$$\text{R1458}\quad CH_3 + O_2 = CH_2O + OH$$

$$\text{R1460}\quad C_3H_5 + O_2 = CH_2O + CH_3CO$$

while in the M85 mixture, the HCHO formation relies more on methanol reactions

$$\text{R18}\quad CH_3OH + HO_2 = CH_2OH + H_2O_2$$

$$\text{R78}\quad CH_3OH + OH = CH_2OH + H_2O$$

$$\text{R80}\quad CH_3OH + H = CH_2OH + H_2$$

It means that the formation path of HCHO is changed by the presence of methanol. As a result, the origination of HCHO is changed correspondingly from paraffin radicals to methanol. Figure 5 shows the normalized ROP of HCHO and CH_3CHO from 93 and M85 gases oxidation. The normalized ROP of HCHO formation is defined as the rate of individual ROP to total ROP. A total of 62% of HCHO in 93 gas is formed by the dehydrogenation of the methoxyl radical (CH_3O) and oxidation of the hydroxymethyl radical (CH_3) via the reactions R40 and R1458.

$$\text{R40}\quad CH_3O = CH_2O + H$$

$$\text{R1458}\quad CH_3 + O_2 = CH_2O + OH$$

While in M85 gas, 84% of HCHO is generated from the dehydrogenation of the methoxyl radical (CH_3O) and oxidation of the hydroxymethyl radical (CH_2OH) via the reactions R83 and R40, which are both the dehydrogenation products of methanol.

$$\text{R83}\quad CH_2OH + O_2 = CH_2O + HO_2$$

$$\text{R40}\quad CH_3O = CH_2O + H$$

CH_3CHO contains one more carbon atom than HCHO; its formation path is thus different from that of HCHO. The presence of methanol in M85 gas hardly changes the formation path of CH_3CHO from HC oxidation. The formation of CH_3CHO from 93 and M85 gases relies mainly on the

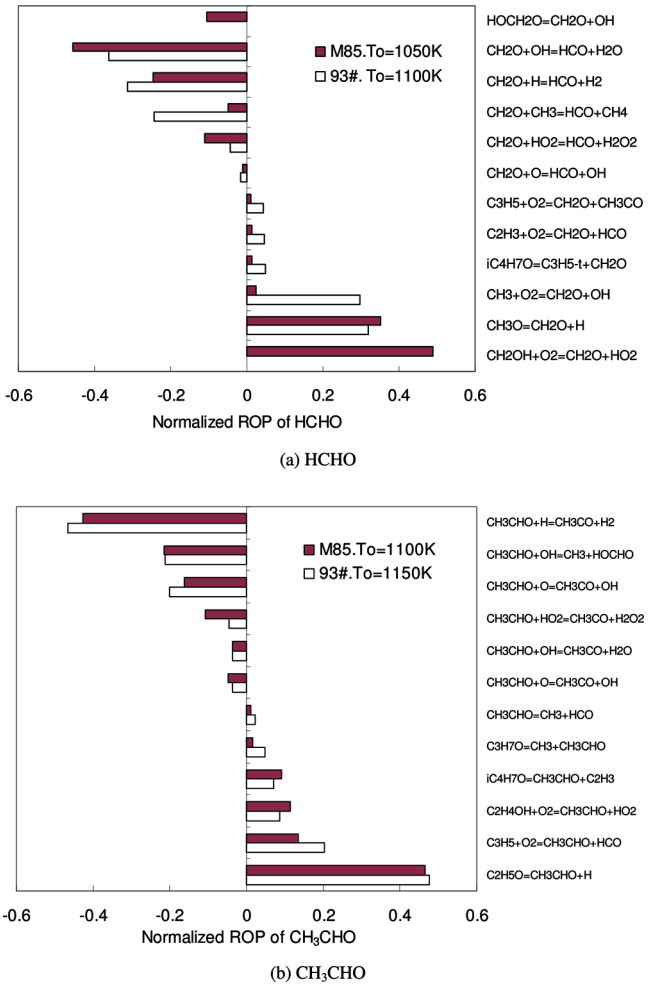


Figure 5. Normalized ROP plot for HCHO and CH_3CHO from 93 and M85 mixture oxidation.

following reactions concerning CH_3, C_2H_5, C_2H_5O, C_3H_5, and iC_4H_9 radicals:

$$\text{R22}\quad CH_3 + HO_2 = CH_3O + OH$$

$$\text{R533}\quad C_2H_5 + HO_2 = C_2H_5O + OH$$

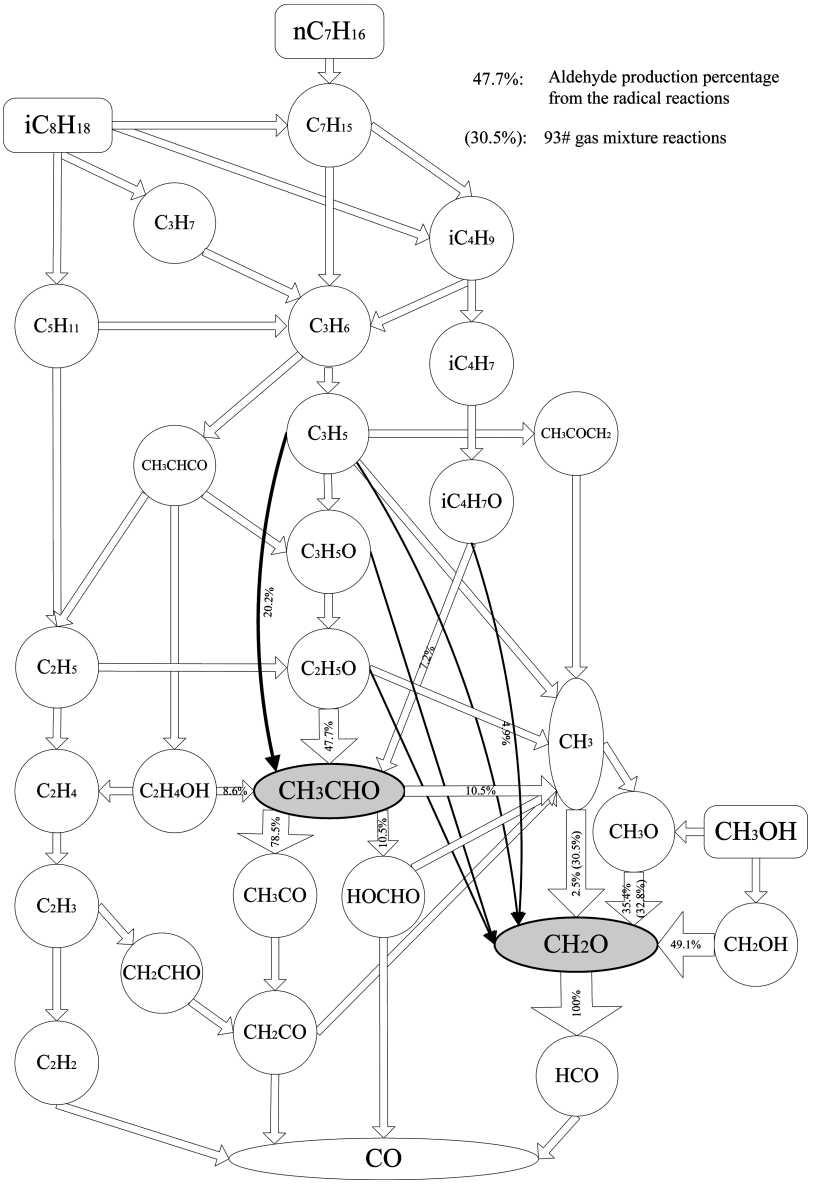


Figure 6. HCHO and CH_3CHO production path diagram from 93 and M85 mixture oxidation.

$$\text{R551} \quad C_2H_5O = CH_3CHO + HO$$

$$\text{R1344} \quad C_3H_5 + O_2 = CH_3CHO + HCO$$

$$\text{R1458} \quad CH_3 + O_2 = CH_2O + OH$$

$$\text{R3141} \quad iC_8H_{18} = tC_4H_9 + iC_4H_9$$

In comparison to the production sensitivity of HCHO, it can be inferred that C_2 radicals play an important role on CH_3CHO production. Actually, as can be seen in Figure 5b, 57.7 and 56.3% of CH_3CHO in both 93 and M85 gases originated from C_2H_5O and C_2H_4OH radicals via the following reactions:

$$\text{R551} \quad C_2H_5O = CH_3CHO + H$$

$$\text{R516} \quad C_2H_4OH + O_2 = CH_3CHO + HO_2$$

Another 22.6 and 27.4% from 93 and M85 gases originated from the C_3 and C_4 radials via the reactions R3144 and R719.

$$\text{R1344} \quad C_3H_5 + O_2 = CH_3CHO + HCO$$

$$\text{R719} \quad iC_4H_7O = CH_3CHO + C_2H_3$$

All of the HCHO is consumed via the path of HCHO → HCO. However, CH_3CHO has multiple consumption approaches: over 99% of CH_3CHO is consumed to CH_3CO, HOCHO, and CH_3 radicals, where 77.9 and 78.5% from 93 and M85 gases consume through the path of CH_3CHO → CH_3CO and the other 21.4 and 21.1% from 93 and M85 gases consume in the way of CH_3CHO → CH_3/HOCHO, respectively.

On the basis of the sensitivity and ROP analysis, the HCHO and CH_3CHO formation paths in both 93 and M85 gases are visualized in Figure 6. HCHO from 93 mixture oxidation has various originations; it can be formed from C_1-C_4 paraffin radicals. However, the methanol in M85 gas not only shortens the formation path of HCHO to two steps but also simplifies the originations from multiple to two channels, i.e., CH_3OH → CH_2OH/CH_3O → CH_2O. The

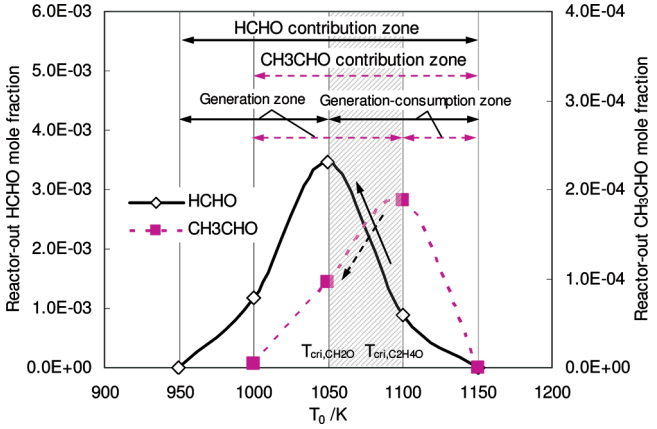


Figure 7. Influence of the initial temperature on the emissions of reactor-out aldehydes. v = 5 m/s.

simplification effects of methanol result in an increase of the HCHO concentration, as seen in Figure 1. The maximum concentration of HCHO in M85 gas is 2.3 times of that in 93 gas. However, methanol has a neglectable effect on CH_3CHO production. The lower maximum CH_3CHO concentration in M85 gas resulted from the lack of high-carbon HCs.

4. Results and Discussion

The SI engine was fueled with gasoline and M85 fuel blend and ran under stable operating conditions at given engine speeds and loads, respectively. The exhaust HCHO and CH_3OH were detected as well as the exhaust temperatures. The unit of engine speed, such as 2000 and 2500 revolutions per hour, are shortened as 2.0k and 2.5k r/min, on the margins of the figures.

4.1. HCHO and CH_3CHO Emissions. HCHO is an important intermediate product of HC oxidation; engine-out HCHO draws much attention because of its high toxicity, especially when methanol is used as fuel. The engine exhaust pipe has a similar HC input and temperature distribution with the PFR in the simulation; thus, engine-out HCHO and CH_3CHO have similar generation and consumption processes to that of the reactor. As can be seen in Figure 1, no HCHO and CH_3CHO will be emitted from the reactor when the initial temperature is too high or too low. There exists a temperature interval that contributes to aldehydes emission; the temperature interval is named the contribution zone here. Figure 7 is obtained from the HCHO and CH_3CHO concentration profiles in panels b and d of Figure 1. It shows the relationship between the initial temperature and the concentrations of reactor-out aldehydes. HCHO and CH_3CHO have similar profiles to the variation of T_0. The emissions at the left side of the peaks are caused by the one-stage process, and the emissions at the right side of the peaks are caused by the two-stage process, where the peak is the critical point of the two processes. The critical temperature of HCHO ($T_{cri,HCHO}$) is lower than that of CH_3CHO (T_{cri,C_2H_4O}).

The literature has proven that engine-out aldehydes are produced by HC partial oxidation events.[21] However, the in-cylinder temperature is always higher than the upper limit of the contribution zone. There exists a temperature drop at the open of the exhaust valve because of the sudden expansion of the exhaust gas. The oxidations that contribute to the aldehydes emissions begin here. As inferred in section 3.1, both the increase of the initial temperature (T_0) and residence time (t_{res}) will upgrade the aldehydes from Z_G to Z_{G-C}. The increase of the engine speed changes both the exhaust temperature, i.e., T_0, and t_{res}. When the exhaust gas stays in the tailpipe, T_0 is increased and t_{res} is reduced. The effect of t_{res} reduction takes the dominant role, and in the situation of T_0 lying between the $T_{cri,HCHO}$ and T_{cri,C_2H_4O}, as can be seen in Figure 7, the HCHO emission will increase, while the CH_3CHO emission will decrease with the increase of the engine speed. To a given engine speed, t_{res} is fixed. With the increase of the engine torque, i.e., T_0, the HCHO emission will decrease, while the CH_3CHO emission will increase. These coincide well with the emission characteristics of HCHO and CH_3CHO from the gasoline and M85 engines, as seen in Figures 8 and 9. At the end of high-load conditions, HCHO emissions increase a little. It can be considered rich in air/fuel mixture near the wide-open throttle (WOT) condition.

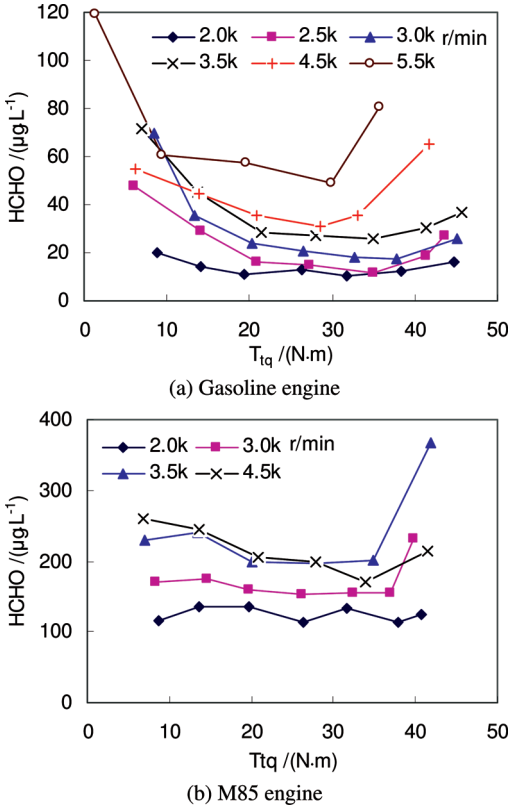


Figure 8. Characteristics of HCHO emission from the SI engine.

As analyzed above, HCHO mainly originated from C_1 radicals of CH_3, CH_3O, and CH_2OH, while CH_3CHO mainly originated from C_2 radicals, i.e., C_2H_5 and C_2H_5O, and methanol accelerates HCHO generation, while HCs contribute to CH_3CHO generation. Thus, because of the richness in methanol and lack in HCs in the M85 fuel blend, the emission of HCHO greatly increases; it is about 5 times the concentration of that from the gasoline engine, while CH_3CHO emission is less than half of that from the gasoline engine, as can be seen in Figure 10. It is almost proportional to the amount of cycle-supplied gasoline.

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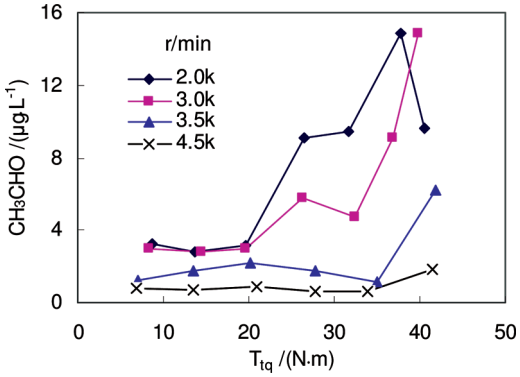
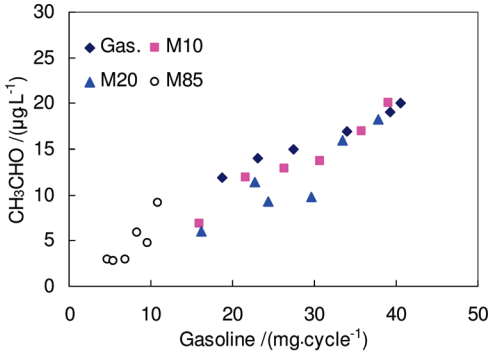
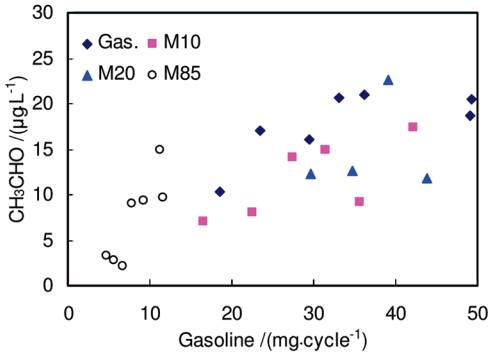


Figure 9. Characteristic of CH_3CHO emission from the M85 engine.



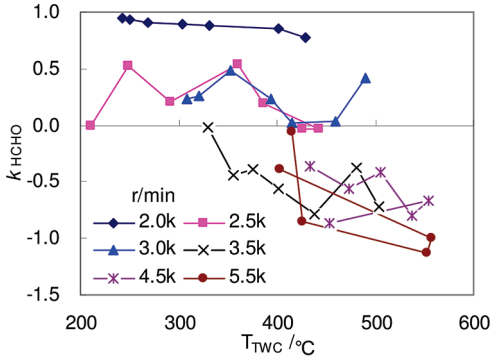
(a) 2000r/mim



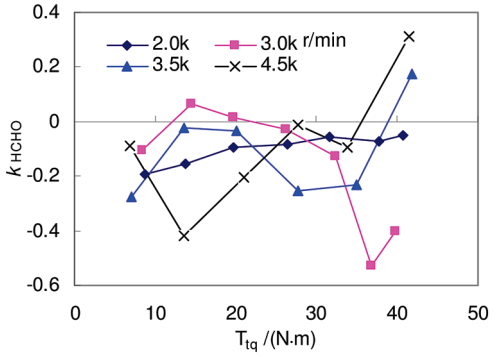
(b) 3000r/min

Figure 10. Relationship between CH_3CHO emission and cycle-supplied gasoline.

A three-way catalytic converter (TWC) can reduce the activation energy and, thus, hasten the reaction rate of feasible-in-thermodynamics reactions, but it cannot change the position of the reaction balance. Thus, the progresses of HCHO and CH_3CHO generation and consumption in normal TWC are similar to that in the exhaust pipe; the essential TWC conversion is to move the HC oxidations beyond the contribution zones in Figure 7. However, with the increase in engine speed, i.e., the decrease of t_{res}, the reactions are gradually drawn back to the contribution zone, the generation of the aldehydes from HC and methanol oxidation gradually exceeds the consumption of the existing ones in the exhaust pipe, and thus, the conversion efficiencies of HCHO and CH_3CHO (k_{HCHO} and k_{CH_3CHO}) decrease with the increasing engine speed. As can be seen in Figures 11



(a) Gasoline engine



(b) M85 engine

Figure 11. Characteristics of TWC conversion efficiencies on HCHO emission.

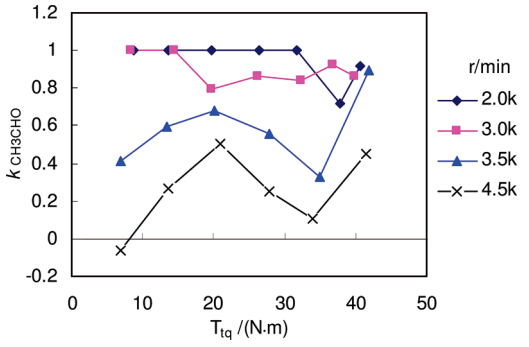
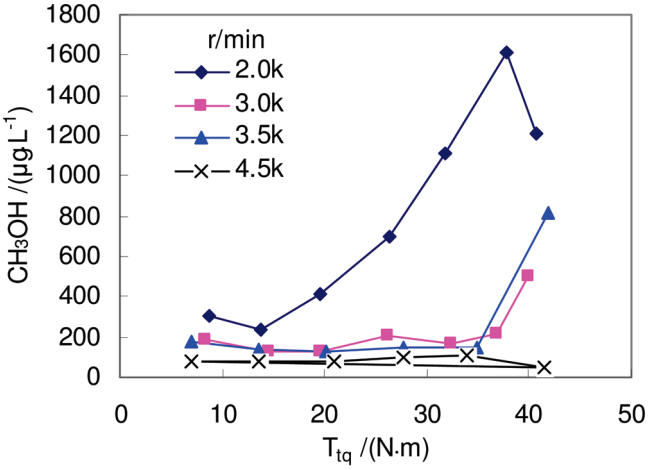


Figure 12. TWC conversion effects on CH_3CHO emission from the M85 engine.

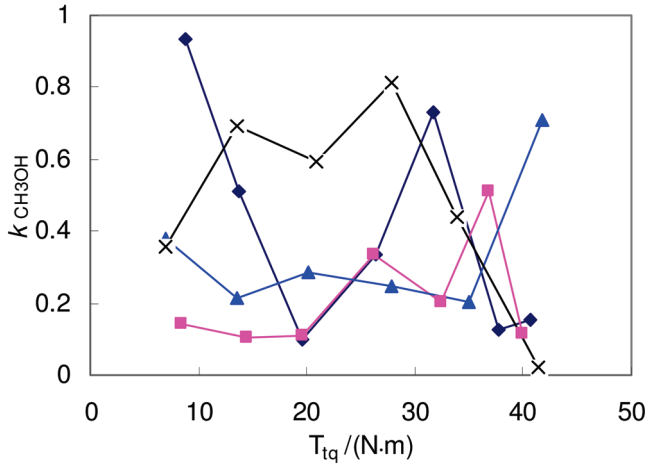
and 12, minus efficiencies appear at high engine speeds. This phenomenon is especially obvious for the M85 engine-out HCHO; it increases rather than decreases via the conversion of TWC at most operating conditions. Further studies must be performed to reduce the absolute HCHO emissions.

4.2. CH_3OH Emission. Although the literature shows that methanol can also be produced from isooctane, hexane,[11] and MTBE[22] oxidation from a recombination of a CH_3 and OH radical or CH_3O and H (free or abstraction of a HC), no methanol was detected from the gasoline engine in our experiments. CH_3OH emission is the unoxidized part of the unburned fuel methanol from the chamber crevice storage; thus, the temperature including in-cylinder and

(22) Stump, F. D.; Knapp, K. T.; Ray, W. D.; Siudak, P. D.; Snow, R. F. *J. Air Waste Manage. Assoc.* **1994**, *44*, 781–786.



(a) Before TWC



(b) TWC conversion efficiency

Figure 13. Characteristics of CH_3OH emission from the M85 engine.

exhaust temperatures determine the characteristic of CH_3OH emission via affecting its origination and oxidation progress. Similar to the emission characteristics from the M10 engine,[14] the residence time rarely affects the emission either.

M85 engine-out CH_3OH emission also decreases with the increasing engine speed, as can be seen in Figure 13a; however, it does not decrease with engine torque like the M10 engine-out ones. Because of the large rate of latent heat of vaporization to low heat value, which is 5.43% for the M85 blend while 0.68% for gasoline, both the in-cylinder and exhaust temperatures of the M85 engine are reduced. Thus, the quantity of residual CH_3OH from the crevice storage is increased, while its consumption is weakened. As a result, the M85 engine-out CH_3OH is much more than that from the M10 engine,[14] especially when the engine runs at 2000 revolutions/min; as high as 1600 μg/L CH_3OH is emitted. Meanwhile, the TWC conversion efficiencies (k_{CH_3OH}) vary from 10 to 80% under most operating conditions (Figure 13b). This makes CH_3OH emission a serious problem for the M85 engine. Further studies must also be performed to reduce the absolute CH_3OH emission.

5. Conclusions

The production mechanisms of HCHO and CH_3CHO emissions from the methanol/gasoline blend fueled engine were simulated with the detailed kinetic mechanism of primary reference fuels (iC_8H_{18}/nC_7H_{16}). The HCHO, CH_3CHO, and CH_3OH emissions characteristics as well as the TWC conversion efficiencies were studied on a three-cylinder SI engine when it ran on gasoline and M85 blend. The simulation results coincide well with the characteristics of the two aldehydes emissions.

There exist two effects for HCHO and CH_3CHO, generation and consumption. In the circumstance of pipe along with decrescent temperature, the emissions of HCHO and CH_3CHO from methanol and HC oxidation are controlled by two factors of initial temperature at the inlet of the pipe and the gas flow velocity, i.e., the residence time of the gas staying in the pipe. No HCHO and CH_3CHO will be emitted when the temperature is too high or too low because of the rapid consumption and the frozen generation, respectively. There exist contribution zones for both HCHO and CH_3CHO emissions, where the production of the aldehydes is gradually upgraded from the generation zone to the generation−consumption zone with the increase of the initial temperature and residence time. Thus, the emissions at the critical points have the peak values. Moreover, the critical temperature of HCHO is higher than that of CH_3CHO.

The initial temperature for exhaust pipe lies between the critical temperatures of HCHO and CH_3CHO; thus, the HCHO emission decreases and the CH_3CHO emission increases with the increase of engine torque, i.e., initial temperature. The increase of the engine speed will increase the initial temperature while decreasing the residence time, and the latter factor takes the dominant role; thus, HCHO emission increases while CH_3CHO decreases with the increase of the engine speed.

The situation in the TWC is rather similar to that in the exhaust pipe. However, the initial temperature is beyond the critical temperature of CH_3CHO. The generations of HCHO and CH_3CHO are both enhanced with the increase of the engine speed; as a result, their conversion efficiencies decrease and minus efficiencies appear at high engine speeds. Especially for the M85 engine-out HCHO, it increases after the conversion of TWC under most operating conditions.

HCHO mainly originated from C_1 radicals; thus, the M85 engine-out HCHO is about 5 times that from the gasoline engine; as much as 250 μg/L (about 180×10^{-6}) of HCHO is emitted at 4500 revolutions/min. CH_3CHO mainly originated from C_2 radicals. The presence of methanol has no effect on its emission, and it is nearly proportional to the amount of cycle-supplied gasoline.

CH_3OH emission is the part of unconsumed fuel methanol; it decreases with the increase of the engine speed. As high of a concentration as 1600 μg/L CH_3OH is emitted from the M85 engine at 2000 revolutions/min. The TWC has little effect on removing the CH_3OH emission; the conversion efficiency varies from 10 to 80%.

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Nomenclature

FID = flame ionization detector
HC = hydrocarbon

PFR = plug flow reactor
ROP = rate of production
SI = spark ignition
T_0 = initial temperature, K
T_{cri} = critical temperature, K
T_{pipe} = temperature alone the reactor pipe, K
t_{res} = residence time, ms
TWC = three-way catalytic converter
WOT = wide open throttle
Z_G = generation zone
Z_{G-C} = generation−consumption zone
PDHID = pulsed discharge helium ionization detector
k_{HCHO} and k_{CH_3CHO} = TWC conversion efficiencies of HCHO and CH_3CHO, respectively