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The Effects of MTBE/Ethanol Additives on Toxic Species Concentration in Gasoline Flame

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Methyl tert-butyl ether (MTBE) and ethanol as gasoline fuel additives can enhance gasoline fuel octane value. This study evaluates the effects of these oxygenated additives (MTBE and ethanol) at 10% by volume on the main combustion intermediates in a low-pressure laminar premixed gasoline flame using synchrotron radiation. The photoionization mass spectra of three flames were presented, and the temperatures of flames were measured by a thermocouple. The relative concentrations of five typical combustion toxic species in the gasoline, gasohol, and MTBE/gasoline flame were compared. It is observed that ethanol and MTBE both delay the oxidation of aromatics in gasoline, and MTBE plays a more obvious role than ethanol. It is also shown that the addition of ethanol leads to an increased concentration of acetaldehyde, whereas the addition of MTBE has no significant effect on the concentration of acetaldehyde. The results obtained provide data for the analysis of intermediates and radicals in flames, which is of use in establishing the chemical kinetic processes of gasoline/oxygenated additive flames.

Introduction

With the development of the automobile industry and the rapid increase of vehicle population, more and more attention is paid to the corresponding problems of energy shortage and environmental pollution. Taking into account saving energy and environmental protection, many investigations have been conducted in the improvement of engine structures and fuel properties.^{1–3} Among these means, fuel additives and alternative fuels are two effective paths to improve the properties of fuels.

Methyl tert-butyl ether (MTBE) has widely been applied to gasoline as an octane enhancer and further to reduce carbon monoxide and ozone.^{4,5} It dominates over other oxygenates in the European and Asian market. However, its mere presence in underground water has aroused concern about possible adverse effects.^{6,7} As MTBE is a frequent contaminant of some shallow

groundwater⁸ and has an irritation effect on eyes or lungs,⁹ the US EPA has issued an ANPR (Advance Notice of Proposed Rulemaking) under TSCA (Toxic Substance Control Act) to eliminate or limit the use of MTBE as a fuel additive in gasoline in the year 2000. Ethanol has been regarded as an attractive renewable alternative fuel with a higher octane number and faster combustion speed than gasoline, which can be derived from domestic crops, such as sugar cane, corn, sorghum, grains, and potatoes. Therefore, it can also be used as a gasoline additive for octane number enhancement and improves emissions from spark-ignition engines. Currently, several countries such as USA and Brazil¹⁰ and some regions in China are using gasohol to fuel vehicles.¹¹ As more and more gasoline are blended with the oxygenates such as MTBE and ethanol, their emissions raise people's concern, especially unregulated emissions, such as aldehydes and benzene.

Comparative effects of MTBE and ethanol additions into gasoline on exhaust emission were performed on the SI engine.¹² The unregulated exhaust emissions (benzene, formaldehyde, and acetaldehyde) have been investigated by GC-FID. The results showed that the effect of ethanol on benzene emission was worse than that of MTBE, which was a contrast with formaldehyde emission. The difference in the acetaldehyde comparison depended on the engine conditions, especially the engine speed.

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Table 1. The Main Properties of the Test Gasoline

fuel	RON	distillation range (°C)				the contents of alkene and aromatic hydrocarbons (%)		density (kg/l)
		10%	50%	90%	100%	alkene	aromatic	
gasoline	92.1	59	105	159	184	29	24	0.737

Table 2. The Main Properties of MTBE and Ethanol

molecular formula	molecular weight	RON	MON	autoignition temperature (°C)	boiling point (°C)	density (g/mL)	LHV (MJ/kg)	oxygen content (% mass)
C ₅ H ₁₂ O	88	102	118	375	55.2	0.74	34.9	18.2
C ₂ H ₆ O	46	106	92	434	78.4	0.7893	26.8	34.8

In this case, it is of great significance to further study the combustion mechanism of gasoline with oxygenated compounds (ethanol and MTBE) in flame. As far as oxygenate additives are concerned, the research that already exists is not scarce, but has usually not focused on the effect of different oxygenates in gasoline. Inal and Senkan¹³ have studied the effect of the addition of three fuel oxygenates (methanol, ethanol, and MTBE) on the formation of PAHs in premixed *n*-heptane flames. Huang et al.¹⁴ investigated the premixed gasoline/oxygen/argon flame with an approximated fuel equivalence ratio of 0.75 using the tunable synchrotron vacuum ultraviolet photoionization and molecular-beam sampling mass spectrometry. About 80 species produced in the flame have been identified, and mole fraction profiles of these species are plotted at the selected photon energies; the temperature was also measured. Yao et al.¹⁵ have also studied the combustion intermediates in low-pressure premixed MTBE/gasoline/oxygen flame probed via synchrotron radiation with synchrotron radiation photoionization technique and obtained a better understanding on those components production history as well as their distribution profile in flame.

This paper focuses on comparing the concentrations of five typical kinds of toxic species that are recognized as harmful to the human body, at the different sampling position in flames with the absence and presence of oxygenated additives with the method of MBMS combining with tunable synchrotron radiation photoionization technique. Meanwhile, the effects of MTBE and ethanol on the antiknocking and emission characteristics of gasoline fuel have been also analyzed.

Experimental Section

Fuel Properties. Alcohol has been used as a fuel for internal combustion engines since their invention. Mixing 10% alcohol with 90% gasoline produces "gasohol". In this study, standard gasoline and gasoline blended with 10% MTBE and ethanol were investigated to compare their combustion species using synchrotron radiation. Detailed information about the properties of the base fuel and of MTBE and ethanol (HPLC grade, 99.7%) are shown in Tables 1 and 2, respectively.

Preparation of Mixtures and Light Beam. Gasoline fuel was vaporized and combined with oxygen and argon at a temperature of 200°. During the experiment, argon was used as the carrier gas. The fuel flow rate was 1.0 mL/min, and the oxygen and argon flow rates were 1.6 SLM (standard liter per minute) and 1.3 SLM, respectively. The fuel and gas flow rates are precisely controlled by a syringe pump made by ISCO Co. Ltd. and a mass flow controller from MKS Co. Ltd., respectively. To start the experiment, a mixture of hydrogen/oxygen/argon was introduced into the burner

Table 3. Chemical Formulae for the Species Involved

mass	formula	species	literature (eV)	measured (eV)
28	C ₂ H ₄	ethylene	10.5138	10.51
44	C ₂ H ₄ O	acetaldehyde	10.229	10.23
78	C ₆ H ₆	benzene	9.25	9.24
92	C ₇ H ₈	toluene	8.828	8.83
106	C ₈ H ₁₀	xylene <i>p</i> - <i>o</i> - or <i>m</i> -	8.44	8.45
			8.55 or 8.56	8.55

and ignited by a tungsten filament. Then, gasoline was introduced and ignited by the hydrogen flame. Hydrogen was not cut off until the gasoline flame reached stable status.

Synchrotron radiation from a bend magnet of the 800 MeV electron storage ring of NSRL (National Synchrotron Radiation Laboratory in China) was monochromized with a 1.0 m Seya-Namioka monochromator. The radiation passed through a prepositive condensing lens, monochromator, postpositive condensing lens, and finally reached the photoionization chamber. Energy resolution of the monochromator was $E/\Delta E \approx 500$. An MgF₂ window of 1.0 mm thickness was used in order to abate higher-order radiation of the dispersed light in the photon energy region over 1150 Å. Because vacuum ultraviolet light is easily absorbed by air, it should be transmitted in high vacuum conditions, which were maintained at about 10⁻⁸ Pa.

Experimental Apparatus. The experimental setup is detailed in ref 16. Test equipment used includes a low-pressure flame chamber, a differentially pumped chamber with flame-sampling system, and a photoionization chamber with reflection time-of-flight mass spectrometer (RTOF-MS). The pressure in the combustion chamber was measured by a capacitance manometer and was adjusted between 2.8×10^4 and 9.7×10^4 Pa by an exhaust throttle valve. The burner with diameter 6.0 cm was connected with a stepper motor controlled by computer and is moved toward or away from the fixed sampling cone to record mass spectra at any desired position. A limit switch was placed 1.5 mm away from the burner surface, from which point the reference position of the spatial curves was defined. A special fire-resistant quartz cone of 500 μm diameter orifice and 110.0 nm diameter base was used to sample from flame along the flow axis. Through a differentially pumped chamber and a nickel skimmer, an ultraphonic molecular beam was formed and entered into the photoionization chamber. The molecular beam intersected the photon beam in the photoionization chamber. Molecules absorbed the energy of the photons and were ionized. The ions transfer the RTOF-MS under the effect of the electric field. The vacuum was maintained by several mechanical pumps, turbo molecular pumps, roots pumps, and ionic pumps.

Results and Discussion

Comparison of Mass Spectrum of Gasoline, MTBE/gasoline, and Gasohol Flame. The pure gasoline flame was considered as a reference flame to compare with oxygenates containing flames. The photoionization mass spectra for reference gasoline, MTBE/gasoline, and gasohol flames are shown in Figure 1, panels a–c, at 3.0 mm distance from the burner

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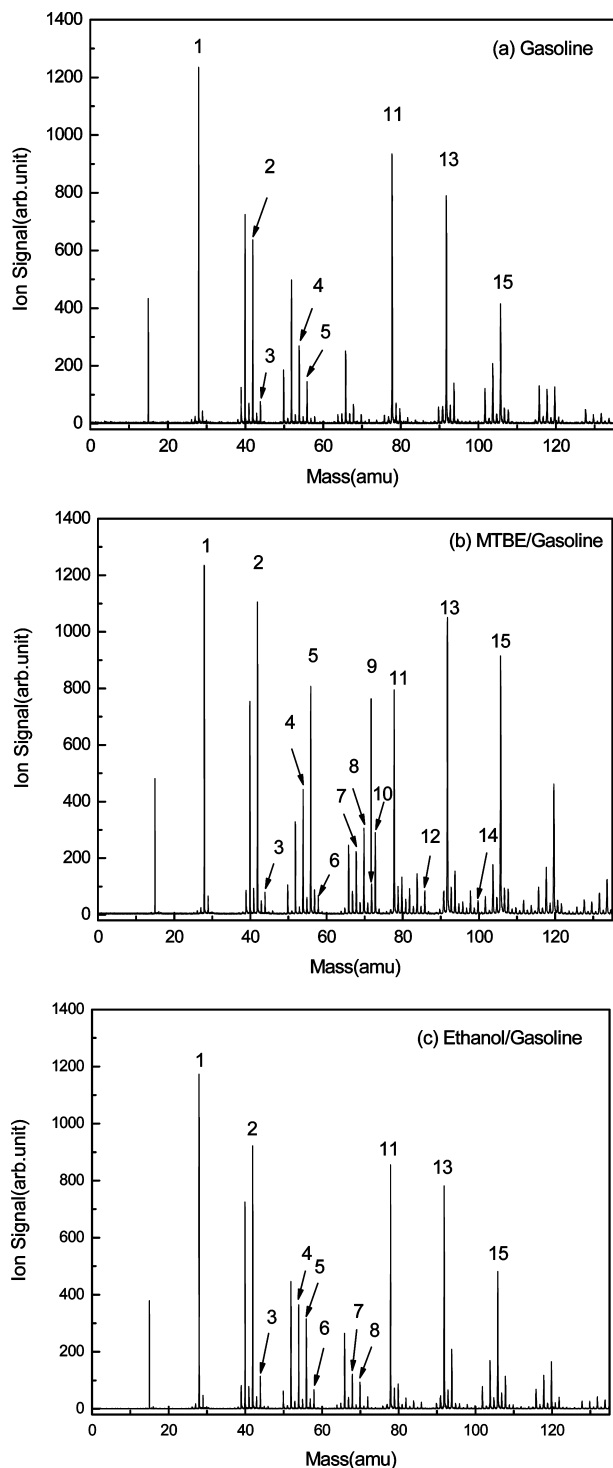


Figure 1. Photoionization mass spectrum of gasoline, MTBE/gasoline, and gasohol flame, respectively, recorded at a position 3.0 mm at 10.78 eV photon energy (1150 Å) for 100 s. Peaks: 1 = ethylene; 2 = propylene; 3 = acetaldehyde; 4 = 1,3-butadiene; 5 = 2-butylene; 6 = butane; 7 = 1,3-pentadiene; 8 = 2-methyl,2-butylene; 9 = pentane; 10 = butoxy; 11 = benzene and fulvene; 12 = hexane; 13 = toluene; 14 = heptane; 15 = xylene.

using the 10.78 eV of photon energy and sampling time of 100 s. At this sampling position, there are the strongest signals of intermediate species and free radicals. The Y-axis presents the ion intensity in arbitrary units from the data processed results.

Comparing panels a–c in Figure 1, it can be observed that there are some species in the gasohol and MTBE/gasoline flames that are different than in the gasoline flame, such as butane, 1,3-pentadiene, and 2-methyl,2-butylene. Besides those, some

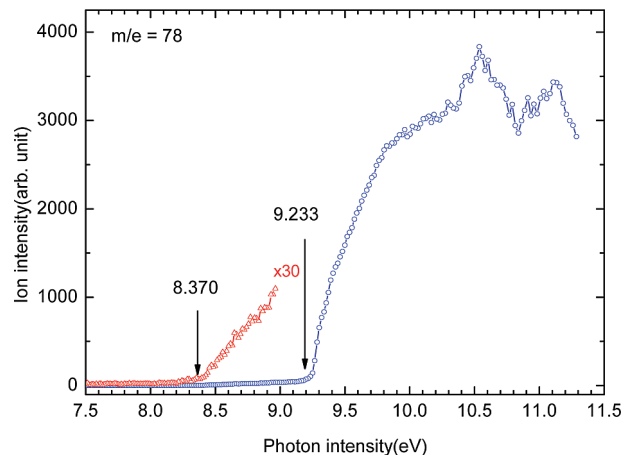


Figure 2. Photoionization efficiency curve for $m/e = 78$ (C_6H_6) in the base flame.

species, such as pentane, hexane, and heptane, are only detected in the MTBE/gasoline flame. These species are alkane or the split product of alkane.^{16,17} For example, butane and pentane are the split product of octane; 1,3-pentadiene and 2-methyl,2-pentane are the product of butane and isopentane dehydrogenation. In general, some alkane-containing fuels, when used in engines, can increase the antiknock performance. Similarly, gasohol can also reduce the engine knocking to some extent compared with pure gasoline.¹⁸ However, Figure 1a shows that there are no alkanes detected from gasoline, whereas there are some alkanes in the MTBE/gasoline and gasohol flame from Figure 1, panels b and c, although the fuel contains approximately 47% alkanes. This result is in good agreement with that presented in the literature.¹⁹ The reason for this may be that MTBE and ethanol react with the some radicals from the fuel and oxygen that start the combustion, in turn increasing the ignition delay and leading to an increased octane number. That is to say, they act as radical scavengers and retard the overall fuel oxidation.

Identification of Species. The identification of the species is made with measurements of masses and ionization thresholds. The photoionization efficiency (PIE) spectra of most flame intermediates were measured ranging from 7.75 to 11.00 eV. Figure 2 shows the photoionization efficiency curve for $m/z = 78$ (C_6H_6) sampled from the each of the flames with photon energy between 7.5 and 11.5 eV. From the figure, it is clearly observed that there are two thresholds near 8.37 eV and 9.23 eV. The readings agree with the ionization energy data of benzene (IE = 9.24 eV) and fulvene (IE = 8.36 eV) in ref 20. Therefore, it is considered that there are two species produced in these flames: benzene and fulvene, whose mass-to-charge ratio is 78. It can be concluded that fulvene has been identified as an isomer of benzene. The photoionization efficiency of each substance was measured during the flame combustion process, and each ion peak on PIE was recorded and identified, compared with the PIE value in the literature. Therefore, the isomers of species can be distinguished with measurements of photoionization mass spectrometry and photoionization efficiency spectra.

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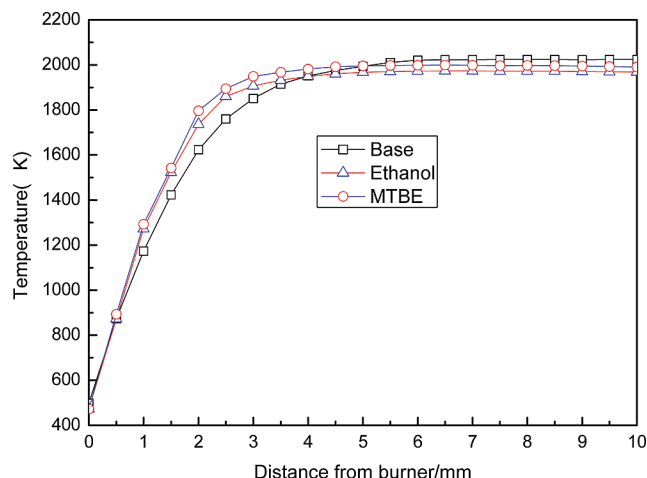


Figure 3. Temperature profiles of gasoline, MTBE/gasoline, and gasohol flames.

Profiles of Combustion Temperature. Flame temperature was measured with a Pt/Pt-13% Rh thermocouple coated with an $\text{Y}_2\text{O}_3\text{--BeO}$ antioxidation surface and with a diameter of 0.076 mm. The thermocouple was located 15.0 mm upstream of the sampling cone so as not to affect the flame structure. The uncertainty in temperature is ± 100 K.

The temperature profiles for gasoline, MTBE/gasoline, and gasohol flame are shown in Figure 3. The data points represent the experimental results and the solid lines represent the trends in all the figures presented here. It is seen that there is not much difference in the temperature profile for these three flames with maximum flame temperature in the range 1950–2025 K. The results show that the flame temperatures in the gasohol and MTBE/gasoline flames are a little higher than that in the gasoline flame in the range from 1.0 to 4.0 mm. As can be seen from Figure 3, gasoline reaches its maximum temperature at the distance of about 6.5 mm, whereas the maximum temperatures in gasohol and MTBE/gasoline are obtained at 4.5 mm. It is evident that gasohol and MTBE/gasoline have a higher combustion speed than the gasoline flame. These results are in accordance with those already presented in the literature.^{21,22} The reason may be that gasoline contains a large amount of toluene that has a significantly lower burning velocity than benzene, thereby leading to the relatively low flame speed; and when 10% of gasoline was substituted by oxygenate, toluene was correspondingly substituted, and this then lead to the higher flame speed.²³ Further, the flame temperature of gasoline is slightly higher than gasohol and MTBE/gasoline at positions above 5.0 mm, due to the fact that gasoline has a higher heating value compared with ethanol and MTBE.¹⁶

Comparison of Spatial Profiles of Combustion Species. Spatial profiles were recorded by moving the burner away from the quartz probe and scanning the flame. The position of the limit switch was considered to be the position 0 mm, and the concentration of species in the gasoline/oxygen flame at this position was considered to be the reference concentration. The data processing method used in this paper was adopted from the method described by Cool et al.^{24,25} The concentrations have an uncertainty of $\pm 25\%$.

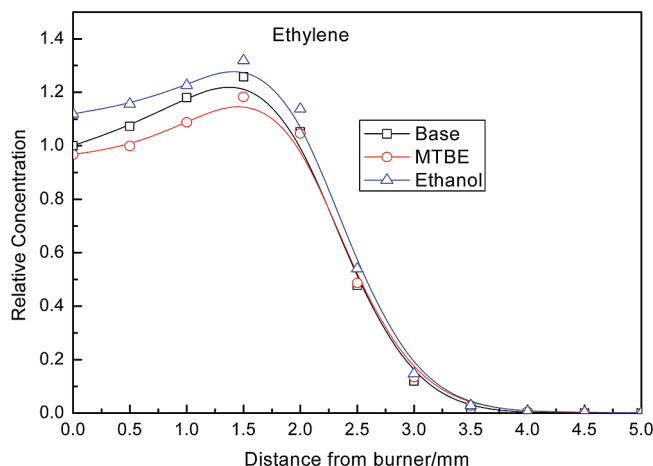


Figure 4. Relative concentration of ethylene in gasoline, MTBE/gasoline, and gasohol flames.

The spatial profiles of ethylene in gasoline, gasohol, and MTBE/gasoline flames are presented in Figure 4. As seen in the figure, the concentration of ethylene increases when ethanol is added into gasoline, whereas it slightly decreases when MTBE is added. Straight-chain hydrocarbons are the fuel compounds enhancing the formation of ethylene most, owing to the C_2 radicals formed from β -scissions.^{16,17,26,27} That the concentration of ethylene in the flame of MTBE/gasoline is slightly lower than that in gasoline may be the result of a “diluting effect”, when 10% of gasoline is replaced by MTBE. As far as ethanol is concerned, it has some inhibiting effect on the decomposition of the straight-chain hydrocarbon, but the concentration of ethylene is slightly higher than that in gasoline because ethylene can also be formed by ethanol dehydration. In addition, alkenes are unsaturated chemical compounds containing at least one carbon–carbon double bond that can be more easily broken down and have faster combustion speed than saturated alkanes. Hence, the higher concentrations of alkenes from the gasohol combustion process increase the fuel burning speed. So this is likely to be another reason why the gasohol flame has a relatively higher combustion speed than gasoline.

Figure 5 gives the spatial profile of acetaldehyde in gasoline, gasohol, and MTBE/gasoline flames. As can be seen from Figure 5, the concentration of the acetaldehyde is more than 2 times higher in the gasohol flame than that in pure gasoline. This result is in good agreement with other investigations on the emission characteristics of spark ignition engines operating with alcohol-containing fuels.^{28–31} These and other researchers have found an increase in aldehydes emission when the alcohol is applied. It is therefore worthwhile to study further the processes of aldehydes emissions when ethanol is fueled in engines. Compared with the gasohol flame, the concentration of acetaldehyde is almost the same in the MTBE/gasoline flame as in the pure gasoline flame. This is in good agreement with the conclusion

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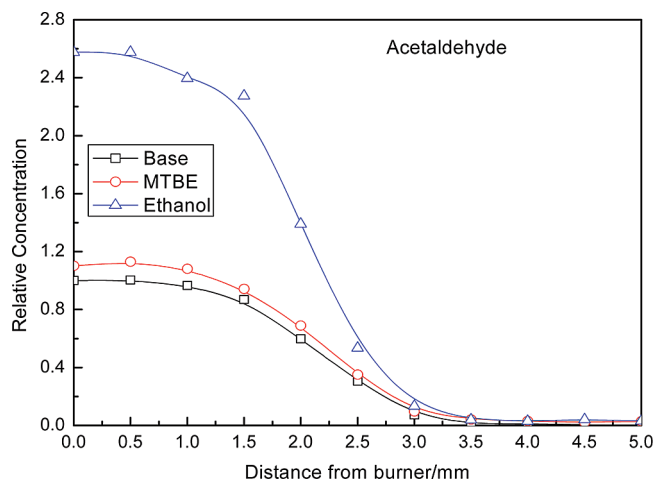


Figure 5. Relative concentration of acetaldehyde in gasoline, MTBE/gasoline, and gasohol flames.

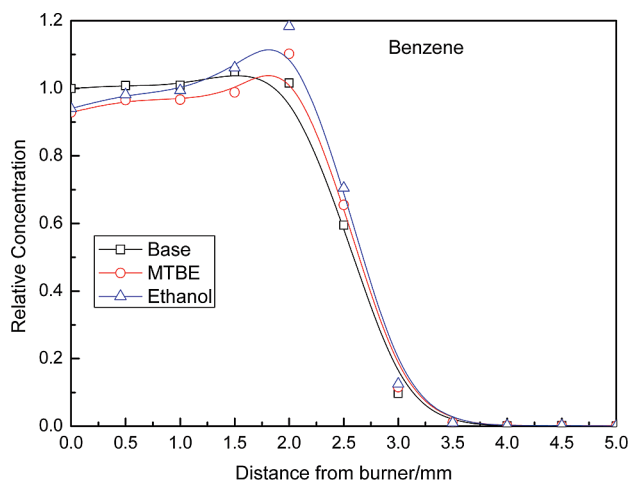


Figure 6. Relative concentration of benzene in gasoline, MTBE/gasoline, and gasohol flames.

that MTBE has no significant effect on the emission of acetaldehyde,³² but there is also some literature reporting that the addition of MTBE increases acetaldehyde.¹² The differences may be due to different test engines, different controlling strategies, and the uncertainties of the experimental apparatus.

The comparisons of some major aromatic hydrocarbon concentrations in the gasoline, gasohol, and MTBE/gasoline flames are presented in Figures 6–8, respectively. The concentration of benzene in the gasoline flame stays almost the same at the position ranging from 0–1.5 mm, which means that there is a trade-off between the consuming and forming of benzene. In contrast, benzene increases significantly in gasohol and MTBE/gasoline from position 0 to 2.0 mm, which means that the forming of benzene outweighs the consumption of benzene in these flames. In other words, we find that benzene is being formed in the primary flame zone, which is in agreement with the result found by Pedersen et al.³³ The concentration of benzene is a result of two combining factors. The one is the content of fuel aromatics, which according to results in the literature,^{16,17} benzene in flame is clearly produced from fuel

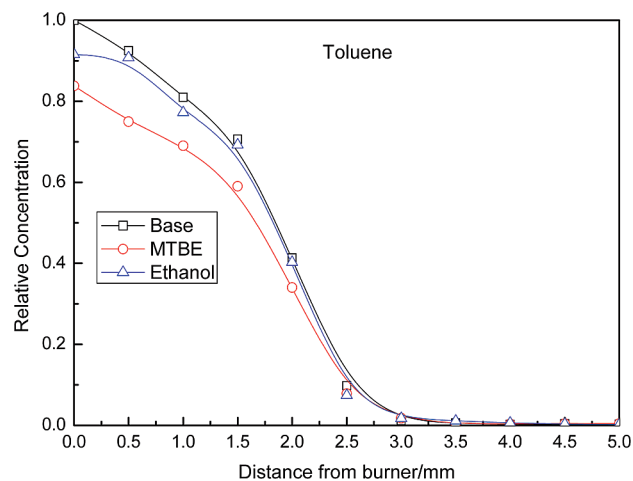


Figure 7. Relative concentration of toluene in gasoline, MTBE/gasoline, and gasohol flames.

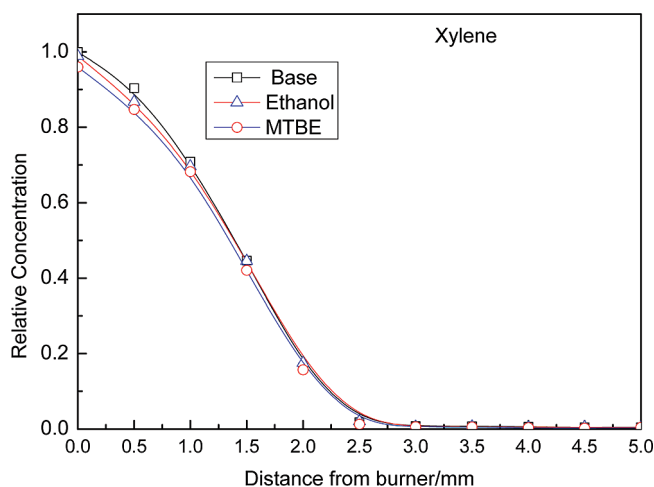


Figure 8. Relative concentration of xylene in gasoline, MTBE/gasoline, and gasohol flames.

aromatics. The other factor is that the addition of oxygenated compounds inhibits the oxidation of benzene, which is in agreement with the modeling results found by Böhm and Braun-Unkhoff,³⁴ who showed that lower concentrations (5–20%) of MTBE and ethanol being added into benzene increased the soot volume fraction. So when 10% of gasoline was substituted by MTBE or ethanol, the soot volume fraction increased and the concentration of benzene increased correspondingly. As we can see in figure 6, at position 0 mm, benzene concentration in MTBE/gasoline and gasohol is about 10% lower than that in the gasoline flame. But the inhibiting effect of oxygenates makes the benzene concentration slightly increase.

Figure 7 shows that the toluene in MTBE/gasoline and gasohol flames is lower than in gasoline flame, which agrees with the results found by Zervas et al.^{16,17} The figure also shows that toluene has a lower concentration at the limit switch position for the MTBE/gasoline and gasohol flames than for the gasoline flame. Since toluene reduces to approximately zero at the same distance from the burner, then the rates at which toluene reduces in the MTBE/gasoline and gasohol flame are less than in the gasoline flame. So, we can deduce that MTBE and ethanol both delay the oxidation of toluene, and MTBE plays a more obvious role than ethanol.

As can be seen in Figure 8, the relative concentrations of xylene are almost the same rate in all the flames. Zervas et al.^{16,17}

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show that the addition of oxygenated compounds to fuel *R* decreases exhaust *o*-xylene, but we could not confirm this correlation. The difference may come from different reference fuel. Some authors present other correlations, but using synthetic fuel blends containing many hydrocarbons and oxygenated compounds, whereas we use commercial gasoline as reference fuel to specialize on gasoline fuel. No detailed explanations are currently available for the difference, and this needs further study.

Conclusions

In this research, with the tunable wavelength, photon energy synchrotron radiation, flame-sampling molecular beam time-of-flight mass spectrometry (TOF-MS), the intermediates in three flames (gasoline, MTBE/gasoline, and gasohol) were measured. The spatial profiles of five typical kinds of combustion species (ethylene, acetaldehyde, benzene, toluene, and xylene) have been analyzed and compared. On the basis of the experimental results, the following conclusions can be drawn.

- (1) Blending oxygenated additives with gasoline resulted in a higher combustion speed from temperature measurement.
- (2) MTBE has no significant effect on the emission of acetaldehyde, whereas the addition of ethanol increases the emission of acetaldehyde dramatically.
- (3) The concentration of toluene is lower in the flame of gasohol and MTBE/gasoline than for gasoline.
- (4) Ethanol and MTBE act as radical scavengers and retard the overall fuel oxidation.

These results should be useful in the developing the chemical kinetic modeling of gasoline/oxygenate additive flames.

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