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Effect of Fuel Structure on Emissions from a Spark-Ignited Engine. 3. Olefinic Fuels

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A single-cylinder, production-type engine has been run at four operating conditions on four olefinic fuels (ethylene, 1-butene, 1-hexene, and diisobutylene) and two blends (*n*-hexane with toluene and 20% diisobutylene with a fully blended gasoline). Engine-out hydrocarbon (HC) emissions (total and species), NO_x, CO, and CO_2 have been measured. Total HC emissions from the olefinic fuels increase with the molecular weight of the fuel (e.g., from 320 ppm C_1 for ethylene to 1420 ppm C_1 for diisobutylene during lean operation). The HC emission for each olefin is lower, and the NO_x emission is higher than that of the corresponding alkane. 1,3-Butadiene is significant for the straight-chain terminal olefins, 1-butene and 1-hexene, but is much less important for the highly branched olefin, diisobutylene. For the diisobutylene–gasoline blend, the mole fractions of products unique to diisobutylene combustion can be predicted to within 10% based on data from diisobutylene, gasoline, and the concentration of diisobutylene in the blend. Thus, the exhaust emissions are approximately additive. For the hexane–toluene blend, no appreciable formation of alkyl-substituted toluenes is observed.

Introduction

In recent publications (*1, 2*), we have demonstrated the critical role that fuel structure plays in determining both the total hydrocarbon (HC) emissions and the distribution of species in the engine-out exhaust from spark-ignited engines. During these previous experiments, a single-cylinder engine with no catalytic after-treatment was fueled with single-component hydrocarbons including alkanes, aromatics, and naphthenes. The current experiments extend those studies to include olefinic fuels and a mixture of a single-component hydrocarbon with a fully blended gasoline. Olefins can comprise a significant fraction of current gasoline fuels, and a determination of the types of partial combustion products formed by olefinic fuels is important to gaining a better understanding of the effect of fuel structure on hydrocarbon emissions from spark-ignited engines. In these experiments, we examine the emissions from three olefinic fuels (ethylene, 1-butene, and diisobutylene) which are conjugate to paraffins studied previously (ethane, *n*-butane, and isooctane). Experiments were also performed using a longer straight-chain olefin, 1-hexene, and its conjugate alkane, *n*-hexane.

In addition, a blend of diisobutylene with gasoline has been tested. The experiment with the diisobutylene–gasoline mixture was carried out specifically to examine whether the same fraction of several characteristic combustion products was formed from the diisobutylene in the mixture as was observed from the pure fuel. This experiment was performed to verify that studies of single-component fuels can provide accurate information concerning HC emissions from fuel blends.

The data from our engine, which is not equipped with a catalyst, represent engine-out rather than tailpipe emissions. However, a considerable fraction of the total urban driving cycle emissions from a catalyst-equipped vehicle exits prior to catalyst light-off, and these pre-light-off emissions should be essentially engine-out exhaust. Even after catalyst light-off, fully 50% of the *tailpipe* emissions may be unburned fuel. For these reasons, measurements of engine-out emissions from single-component fuels can provide important information regarding the effect of fuel structure on tailpipe exhaust during a driving cycle test. Finally, although a single-cylinder engine is used in these experiments, the head and piston have geometries typical of modern multicylinder engines and should provide useful information concerning production vehicles.

Experiment

The single-cylinder engine has been described in detail (*1, 2*). As in the earlier experiments, the baseline engine condition was a fuel–air equivalence ratio (Φ) of 0.9 (fuel-lean), MBT spark timing [defined as the spark advance required to yield peak cylinder pressure at 13° (crank angle) after top dead center], 1500 rpm, 90 °C coolant temperature, 73 °C oil temperature, and a load of 3.8 bar IMEP. No exhaust gas recirculation was added to the intake mixture in these experiments. This steady-state condition is typical of a midspeed, low-to-midload cruise. In addition, experiments were carried out at either 2500 rpm, MBT-12° spark advance (retarded timing), or $\Phi = 1.15$ while keeping the other conditions as defined for baseline. The liquid fuels were introduced through an injector located in the intake port. The start of injection was at 660 crank angle degrees (0 CAD = top dead center of compression), and the fuel injection continued for approximately 45 crank angle degrees. Thus, injection occurred during the compression stroke with the intake valve closed.

For the liquid fuels, the exhaust gas sampling and the gas chromatographic (GC) analysis techniques were identical to those described earlier (*1, 2*). The only difference from the analyses of ref 1 was that the gaseous as well as the liquid fuels were analyzed using the GC method described in ref 3. This method assumes that the FID response per carbon atom in a molecule is identical for all species. Limited tests with certified standards indicate that this approximation is accurate to ±5% for most species; however, recent measurements of the response factor of methane indicate that it is 30% larger than that of the higher molecular weight species. Thus, all measurements using the GC method of ref 3 yield methane mole fractions which are 30% too large. The methane mole fractions in Tables I–VII are uncorrected for this response change to allow comparison with most of the data in our previous publications. Comparison of the methane emission from the gaseous fuels in ref 1 with the current measurements requires making this correction

Table I. Exhaust Species for Ethane, Propane, Toluene, and Isooctane Fuels[a]

exhaust species	C_2H_6, base	C_3H_8, base	$n\text{-}C_4H_{10}$, base	C_8H_{18}, base	C_8H_{18}, $\Phi = 1.15$	C_7H_8, base	C_7H_8, $\Phi = 1.15$
methane	10	25	22	32	326	10	83
acetylene	13	30	29	38	258	54	181
ethylene	193	219	276	66	178	16	22
ethane	257	10	8	16	45		
allene				14	20	3	
propyne				20	22	6	
propylene		121	153	157	174	5	
propane		408					
1,3-butadiene			7	8	8	7	4
1-butene			14				
isobutene				390	339		
n-butane			387				
2-methyl-1,3-butadiene				5	10		
2-methyl-1-butene				13	11		
methacrolein				21	<1		
isooctane				801	1454		
benzene				6	9	95	257
toluene						1626	2569
ethylbenzene						13	15
styrene						7	6
benzaldehyde						75	18
sum of GC (ppm C_1)[b]	475	836	912	1722	2958	1972	3222
unburned fuel (%)[c]	54	49	43	47	49	82	80
total HC (hot FID)[d]	504	828	890	1776	2821	2139	3520
NO_x (ppm)[e]	2043	2276	na	2193	662	na	na
CO (ppm)[e]	420	437	500	557	40160	760	49140
CO_2 (%)[e]	10.1	10.5	10.9	11.0	9.6	13.7	12.2
O_2 (%)[e]	1.9	1.8	2.0	2.0	0.2	2.0	0.16
MBT spark timing[f]	18	20	21	27	20	26	20

[a] These data are species mole fractions (ppm C_1) in undiluted exhaust samples. ppm C_1 (species i) = ppm(i) × carbon no. (i). Fuel and engine condition specified at top of column. na = data not available for this species. [b] Sum of the carbon content of all GC peaks contained in the chromatogram assuming that the carbon response of all species is the same. Includes GC peaks not included in table. [c] Contribution of unburned fuel to sum of GC. [d] Total HC emissions (ppm C_1) measured by the hot FID emissions instrument connected to the exhaust pipe by a heated sample line. [e] Mole fractions measured by engine emissions console instruments corrected to fully wet sample condition. NO_x not measured for toluene. [f] Spark advance for MBT operation (degrees before top dead center).

because in ref 1 the emissions from gaseous fuels were calibrated with individual standards for each species.

Primarily, hydrocarbons were measured; with the exception of benzaldehyde and methacrolein, oxygenated organics were not included in the analysis. An exhaust sample at baseline condition from 1-hexene fuel was analyzed three times over a period of 24 h to assess its stability. None of the species with the exception of 1,3-butadiene and cyclopentadiene showed a significant concentration change. Butadiene decreased at a rate of ~10%/h in this fuel-lean sample. The cyclopentadiene loss rate was much faster. The loss rates of both 1,3-butadiene and cyclopentadiene are consistent with those observed previously using cyclohexane fuel (2).

CP-grade ethylene (99%) and 1-butene (99%) were used in the experiments. The diisobutylene contained 76.9% 2,4,4-trimethyl-1-pentene, 18.4% 2,4,4-trimethyl-2-pentene, 2% isomeric octanes, and 2.7% unidentified impurities. The purity of the 1-hexene was 96%, with four other isomeric hexenes each present at approximately 1% mole fraction. The gasoline was a blend having 91 research octane and a T_{90} distillation point of 157 °C. The carbon content of this fuel consists of 69% saturates, 30% aromatics, and less than 1% olefins; the fractions of the total carbon number represented by selected major components as determined by GC analysis of the gasoline have been presented in Table I of ref 2. Prior to running each new fuel, the engine fuel system was purged with that fuel to remove any contamination from the previous sample.

Total Emissions Results

Table I presents the mole fractions of the major species determined by GC analyses of single experiments for ethane, propane, butane, isooctane (2,2,4-trimethylpentane), and toluene fuels at the baseline operating condition; fuel-rich results are also included for isooctane and toluene. These data provide a cross comparison of the current results with those obtained earlier (1, 2). For each fuel, all measurements of the total HC agree to within 10%, and all major HC species and most minor species agree to better than ±15% from the mean of all of the experiments that have been carried out over a period of 2 years. The species agreement is best for the liquid fuels, which have been analyzed by the same GC technique during the entire period and are somewhat worse for the gaseous fuels which have been analyzed by the two techniques. Repeat baseline experiments were carried out for propane, diisobutylene, and 1-hexene during the current series of experiments. The mole fractions from these repeat experiments agreed to ±10–15% from the mean for all species. Thus, the experimental reproducibility is sufficient to observe changes of approximately 25% in the mole fractions of individual exhaust species and 10% in total emissions for single measurements during the current series of experiments.

Tables I–VII contain the GC mole fractions of the major HC species in the engine-out exhaust for the fuels tested as well as the engine emissions console measurements of total HC (using the hot FID), NO_x, CO, CO_2, and O_2 (all corrected to wet exhaust condition). The MBT spark

Table II. Measured Species in Exhaust for Ethylene Fuel[a]

exhaust species	base	MBT −12°	Φ = 1.15	2500 rpm
methane	14	11	134	14
acetylene	18	16	185	19
ethylene	280	120	854	137
ethane	<2	<2	20	<2
sum of GC (ppm C_1)[b]	317	149	1216	174
unburned fuel (%)[c]	88	81	70	79
total HC (hot FID)[d]	320	138	1124	140
NO_x (ppm)[e]	4040	2440	900	>2490
CO (ppm)[e]	350	313	44400	300
CO_2 (%)[e]	11.8	11.8	9.8	11.7
O_2 (%)[e]	1.7	1.7	0.1	1.8
MBT spark timing[f]	12		10	13

[a] These data are species mole fractions (ppm C_1) in undiluted exhaust samples. ppm C_1 (species i) = ppm(i) × carbon no. (i). Engine condition specified at top of column. [b] Sum of the carbon content of all GC peaks contained in the chromatogram, assuming that the carbon response of all species is the same. Includes peaks not presented in table. [c] Contribution of unburned fuel to sum of GC. [d] Total HC emissions (ppm C_1) measured by the hot FID emissions instrument connected to the exhaust pipe by a heated sample line. [e] Mole fractions measured by engine emissions console instruments corrected to fully wet condition. [f] Degrees before top center.

advance for each fuel is included for reference. Also presented is the percentage contribution of unburned fuel to the total emissions determined by the GC. Because gasoline contains many components, no unburned fuel contribution for this fuel or for the diisobutylene–gasoline blend is included. The instrument for measuring NO_x had a maximum range of 2465 ppm (corrected to wet sample), and for emissions levels higher than this value, only the upper limits are presented except for the case of ethylene at baseline condition for which the range was extended.

The trends in total HC emissions for the pure alkene fuels are similar to those observed for alkanes (1). As the molecular weight of the fuel increases, the total emissions measured by the hot FID increase for all four engine conditions [e.g., at baseline: 320 ppm C (ethylene); 623 (1-butene); 1100 (1-hexene); 1418 (diisobutylene)]. For the three lean-operating conditions, the HC emissions from the olefinic fuels are 20–50% lower than those observed for the conjugate alkanes [see ref 1 and Table I]. The largest difference is observed for ethylene fuel and the percentage difference decreases as the molecular weight of the fuel increases. During either high-speed or retarded-spark operation, all olefin fuels show large decreases in the total HC emissions, again similar to the alkane fuel results.

Species Measurements

Ethylene Fuel. Data for ethylene fuel are presented in Table II. For all conditions, the major HC species emitted is ethylene, ranging from 88% of the total HC emissions at baseline to 70% during rich operation. At Φ = 1.15, methane is an important exhaust species even though this fuel has no methyl group. This emphasizes the fact that methane formation can occur in the postflame-burned gas of rich flames by H atom addition to ethylene as has been observed during studies of burner-stabilized ethylene–air flames (4). Acetylene is also a significant product during rich combustion as for all other fuels tested (1, 2).

During lean operation, the total HC emissions from ethylene fuel are the lowest for any fuel tested in our engine, falling to 140 ppm C for retarded-spark or 2500 rpm operation. These are also the lowest engine-out emissions reported from any premixed, hydrocarbon-fueled, spark-ignited engine to our knowledge. Crevice storage will dominate the source terms of HC emission for lean operation on nonaromatic fuels having eight or fewer carbon atoms, because oil absorption will be a small effect (5). Thus, ethylene might be expected to exhibit total hot FID HC emissions similar to isooctane rather than 5–8 times less (see Tables I, II, and data in ref 1). This emphasizes the critical role that fuel structure plays in the secondary burnup of HCs stored within the engine cylinder during flame passage.

An earlier publication (1) suggested that the rate of diffusion of HCs into the burned gas from thin-wall layers deposited by the descending piston might account for a portion of the direct dependence of HC emissions during lean operation on molecular weight for fuels heavier than methane. These results from ethylene fuel show that, during lean operation, the total HC emissions are 50–60% of those observed for ethane (see Table I and ref 1) after correction for the different initial carbon content of the two fuels at the same equivalence ratio. A much smaller difference is seen during rich operation (1). Because ethane and ethylene have very similar diffusion constants, a difference in reaction rates likely plays an important part in this result. Ethylene has an adiabatic flame temperature approximately 5% higher than ethane (6), and the increased temperature throughout the cycle (including that measured in the exhaust gas) might contribute to the increased burnup that is observed.

The NO_x emissions are much larger for ethylene than for ethane fuel for baseline (see Tables I and II), retarded-spark, and fuel-rich operation. At baseline, the NO_x from ethylene fuel is two times larger than for ethane. These results are consistent with the higher flame temperature of C_2H_4. CO emissions from ethane and ethylene are indistinguishable at base condition.

1-Butene Fuel. Table III presents the emissions data from 1-butene fuel. The total HC emissions, corrected for differences in initial carbon content, are 70% of those for butane fuel (see Table I and ref 1) during lean operation, a slightly smaller change than for the ethylene–ethane case. No significant difference is observed for rich operation (1). The CO emissions from 1-butene are indistinguishable from those of butane, while the NO_x emissions are 1.5 and 1.3 times greater during lean (retarded) or rich operation (where they could be measured), respectively, because of the higher flame temperature. This temperature difference decreases as the molecular weight of the olefin increases, and the effect on NO_x is smaller for butene than for ethylene.

The hydrocarbon species mole fractions and their trends show substantial differences from those of the conjugate alkane, n-butane. At baseline condition, the mole fraction of 1,3-butadiene is 62 ppm C for 1-butene but is 7 ppm C for n-butane fuel (see Table I). Thus, butadiene, which is defined as an air toxic in the Clean Air Act (7), contributes 10% to the total HC emissions from 1-butene while for n-butane fuel it is negligible. Propylene emissions from 1-butene are much smaller (38 ppm C) than from n-butane (153 ppm C) for lean operation (see Table I). However, they increase by a factor of 4 during rich running,
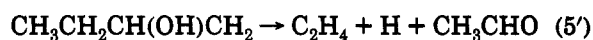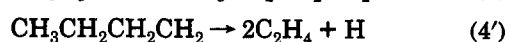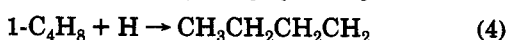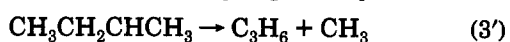
Table III. Measured Species in Exhaust for 1-Butene Fuel[a]

exhaust species	base	MBT −12°	Φ = 1.15	2500 rpm
methane	17	12	189	17
acetylene	39	34	219	42
ethylene	87	63	212	63
ethane	<1	<1	25	<1
allene	5	2	8	3
propyne	3	2	8	3
propylene	38	22	146	21
1,3-butadiene	62	34	51	42
trans-2-butene	6	3	12	4
cis-2-butene	2	1	7	<1
1-butene	291	121	787	81
sum of GC (ppm C_1)[b]	555	296	1679	279
unburned fuel (%)[c]	52	41	47	29
total HC (hot FID)[d]	623	330	1699	292
NO_x (ppm)[e]	>2465	1304	765	>2495
CO (ppm)[e]	498	467	42850	514
CO_2 (%)[e]	11.6	11.6	10.2	11.6
O_2 (%)[e]	2.0	2.2	0.15	2.0
MBT spark timing[f]	19		16	18

[a] These data are species mole fractions (ppm C_1) in undiluted exhaust samples. ppm C_1 (species i) = ppm(i) × carbon no. (i). Engine condition specified at top of column. [b] Sum of the carbon content of all GC peaks contained in the chromatogram, assuming that the carbon response of all species is the same. Includes GC peaks not included in table. [c] Contribution of unburned fuel to sum of GC. [d] Total HC emissions (ppm C_1) measured by the hot FID emissions instrument connected to the exhaust pipe by a heated sample line. [e] Mole fractions measured by engine emissions console instruments corrected to fully wet condition. [f] Spark advance for MBT operation (degrees before top dead center).

while for *n*-butane fuel, propylene emissions *decrease* slightly (ref 1 and correction). For a rich mixture, the ethylene mole fraction increases by a factor of 2.5 for 1-butene but only 1.2 for *n*-butane fuel (1). These trends differ because of differences in the chemistry of burnup for the two fuels.

For alkanes, β-scission and H-atom loss reactions play important roles in determining the combustion products emitted from the exhaust (1, 2, 8) once an alkyl radical is formed. As noted by Tsang (9), larger alkenes such as 1-hexene may also have molecular decomposition paths, forming products which cannot be explained by the simple picture of C–C and C–H bond-scission reactions of alkyl radicals. An alkyl radical is formed by H-atom abstraction for alkane fuels, while both abstraction and addition to the double bond can occur for alkenes. The following reactions can account for the most important combustion products of 1-butene fuel (1,3-butadiene, ethylene, propylene, acetylene, and methane):

$$1\text{-}C_4H_8 + X \text{ (OH,H)} \rightarrow CH_3CHCH=CH_2 + HX \quad (1)$$

$$CH_3CHCH=CH_2 \rightarrow CH_2=CHCH=CH_2 + H \quad (1')$$

$$1\text{-}C_4H_8 + X \rightarrow CH_2CH_2CH=CH_2 + HX \quad (2)$$

$$CH_2CH_2CH=CH_2 \rightarrow C_2H_4 + C_2H_2 + H \quad (2')$$

$$\rightarrow CH_2=CHCH=CH_2 + H \quad (2'')$$

$$1\text{-}C_4H_8 + H \rightarrow CH_3CH_2CHCH_3 \quad (3)$$

$$CH_3CH_2CHCH_3 \rightarrow C_3H_6 + CH_3 \quad (3')$$

$$1\text{-}C_4H_8 + H \rightarrow CH_3CH_2CH_2CH_2 \quad (4)$$

$$CH_3CH_2CH_2CH_2 \rightarrow 2C_2H_4 + H \quad (4')$$

$$1\text{-}C_4H_8 + OH \rightarrow CH_3CH_2CH(OH)CH_2 \quad (5)$$

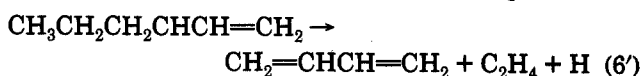$$CH_3CH_2CH(OH)CH_2 \rightarrow C_2H_4 + H + CH_3CHO \quad (5')$$
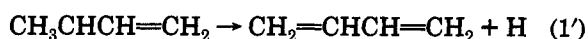
The reactions with unprimed numbers involve formation of alkyl radicals either by abstraction of H atoms or by addition of H or OH to the double bond. The reactions with primed numbers present possible reaction channels that can occur by either β-scission or H-atom loss. Two channels exist for butadiene formation. In contrast, *n*-butane fuel has no simple path for formation of butadiene via H-atom loss from an alkyl radical, and little butadiene is observed.

The H-atom addition reactions will be more important during rich operation because the H-atom concentration will be much higher in the burned gas than that of the OH radical, which is dominant under lean conditions. Based on the above mechanism, propylene and ethylene, the products formed from reactions 3 and 4, should increase in importance during rich operation as is observed. The effect is particularly pronounced for propylene, because the addition of an H atom to a double bond is its principal source in this mechanism. Both abstraction and addition paths could form ethylene even for a lean mixture. Abstraction reaction 2 should be slower than reaction 1 because of the weakness of the allylic C–H bond. Thus, ethylene formed during lean operation may come from the addition of OH to the double bond (reaction 5), which can be an important channel for larger alkenes at high temperature (10). No substantial increase in either ethylene or propylene was observed during rich operation for *n*-butane fuel (1), supporting the above interpretation.

The *sec*-butyl radical formed by reaction 3 could lose an H atom to form 2-butene. The fact that the 2-butene mole fraction is much less than that of propylene suggests that C–C bond scission is preferred over H-atom loss as a decomposition path for *sec*-butyl radicals [see analogous rates for the *n*-propyl radical (11) for which β-scission is 6 times faster at 1500 K].

For high-speed or retarded-spark operation, the total hot FID hydrocarbon emissions decrease because of the increased burnup caused by higher late-cycle cylinder temperatures and higher exhaust temperatures. This is reflected in a reduction in the percentage contribution of unburned fuel to the total emissions as was observed for alkane fuels (1, 2).

1-Hexene Fuel. Trends similar to those of 1-butene are observed for 1-hexene as shown in Table IV. Again, 1,3-butadiene is a significant exhaust emission (8% of total HC at baseline). For this fuel, butadiene and ethylene can be formed by β-scission of the alkyl radical generated by H abstraction from an allylic hydrogen:

$$1\text{-}C_6H_{12} + X \rightarrow CH_3CH_2CH_2CHCH=CH_2 + HX \quad (6)$$

$$CH_3CH_2CH_2CHCH=CH_2 \rightarrow CH_2=CHCH=CH_2 + C_2H_4 + H \quad (6')$$

Propylene could be formed by β-scission of the CH_3-$CHCH_2CH_2CH=CH_2$ radical. However, this reaction should form allene and propyne, but neither of these species is observed in appreciable quantity. Both ethylene and propylene show significant increases during rich operation, and these products can be formed by H-atom addition to the double bond. A detailed explanation of the sources of the combustion products is more difficult than for 1-butene because of the larger number of reactions that can take place. For example, propylene can be formed

Table IV. Measured Species in Exhaust for 1-Hexene[a]

exhaust species	base	MBT -12°	Φ = 1.15	2500 rpm
methane	16	9	192	11
acetylene	48	48	272	48
ethylene	239	162	414	131
ethane	6	<1	29	<1
allene	4	2	7	2
propyne	4	3	7	3
propylene	109	55	188	43
1-butene	16	7	41	5
1,3-butadiene	94	48	59	38
isobutene	<1	<1	<1	<1
cyclopentadiene	8	4	6	4
1-hexene	367	117	843	44
benzene	6	4	6	5
sum of GC (ppm C_1)[b]	994	486	2129	348
unburned fuel (%)[c]	37	24	40	13
total HC (hot FID)[d]	1110	660	2010	390
CO (ppm)[e]	760	780	43000	810
CO_2 (%)[e]	11.7	11.7	10.4	11.7
O_2 (%)[e]	2.0	1.9	0.15	1.9
MBT spark timing[f]	21		18	18

[a] These data are species mole frarctions (ppm C_1) in undiluted exhaust samples. ppm C_1 (species i) = ppm(i) × carbon no. (i). Engine condition specified at top of column. [b] Sum of the carbon content of all GC peaks contained in the chromatogram, assuming that the carbon response of all species is the same. Includes GC peaks not included in table. [c] Contribution of unburned fuel to sum of GC. [d] Total HC emissions (ppm C_1) measured by the hot FID emissions instrument connected to the exhaust pipe by a heated sample line. [e] Mole fractions measured by engine emissions console instruments corrected to fully wet condition. NO_x not measured for 1-hexene. [f] Spark advance for MBT operation (degrees before top dead center).

Table V. Measured Species in Exhaust for n-Hexane–Toluene Mixture (50/50 vol)[a]

exhaust species	base	MBT -12°	Φ = 1.15	2500 rpm
methane	12	10	132	12
acetylene	46	57	219	64
ethylene	136	130	193	117
ethane	4	<1	13	<1
allene	3	2	4	2
propyne	5	5	5	5
propylene	61	48	56	39
1-butene	29	21	21	15
1,3-butadiene	18	16	10	13
isobutene	<1	<1	<1	<1
1-pentene	8	5	6	4
cyclopentadiene	10	7	19	3
methylcyclopentane[a]	20	10	55	5
1-hexene	<1	2	3	<1
n-hexane	157	73	415	35
benzene	47	48	178	42
toluene	558	355	1146	227
ethylbenzene	8	6	18	4
styrene	6	6	6	4
benzaldehyde	na	41	15	29
sum of GC (ppm C_1)[b]	1158	862	2563	636
unburned fuel (%)[c]	62	50	61	41
total HC (hot FID)[d]	1404	990	2889	753
CO (ppm)[e]	716	832	43450	920
CO_2 (%)[e]	12.4	12.3	11.2	12.5
O_2 (%)[e]	2.0	2.1	0.16	2.0
MBT spark timing[f]	23		19	22

[a] These data are species mole fractions (ppm C_1) in undiluted exhaust samples. ppm C_1 (species i) = ppm(i) × carbon no. (i). Methylcyclopentane is a contaminant in the fuel mixture (5% of total carbon content). Engine condition specified at top of column. na = data not available for this species. [b] Sum of the carbon content of all GC peaks contained in the chromatogram, assuming that the carbon response of all species is the same. Includes GC peaks not included in table. [c] Contribution of unburned fuel to sum of GC. [d] Total HC emissions (ppm C_1) measured by the hot FID emissions instrument connected to the exhaust pipe by a heated sample line. [e] Mole fractions measured by engine emissions console instruments corrected to fully wet condition. NO_x not measured. [f] Spark advance for MBT operation (degrees before top dead center).

by a molecular decomposition channel according to the mechanism of Tsang (9).

These results from 1-hexene fuel can be used to shed light on an observation made when running this engine on cyclohexane (2). At baseline condition, approximately 5% of the exhaust HC from cyclohexane fuel is benzene, which has also been observed in oxidation studies (12). We noted that two possible paths of benzene formation were (1) successive dehydrogenation or (2) reaction of butadiene with acetylene. At baseline, 1-hexene fuel produces one-tenth of the benzene mole fraction observed from cyclohexane, although the butadiene and acetylene mole fractions are only 25% lower. This suggests that the primary source of benzene emission from cyclohexane fuel is not a reaction between butadiene and acetylene.

High-speed or retarded-spark operation produces a substantial reduction in HC emissions, and the contribution of unburned fuel to the exhaust emissions falls, as was observed for 1-butene. For 1-hexene fuel at 2500 rpm, the contribution of unburned fuel to these emissions falls to only 13%.

n-Hexane Fuel. As was the case with the lower molecular weight alkenes, it is useful to compare the emissions from 1-hexene to those from n-hexane. However, it is not possible to run this engine on n-hexane because of its low octane number. For this reason, a (50-50) mixture by volume of n-hexane with toluene was prepared (octane = 73). A GC analysis of this fuel mixture showed that the carbon content consisted of 36% n-hexane, 57% toluene, and 5% methylcyclopentane (a contaminant in the hexane). Toluene was chosen as the high-octane co-mixed fuel because only 1,3-butadiene (or acetylene and methane emissions under rich conditions) gives significant interference with the exhaust species expected
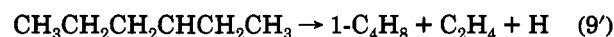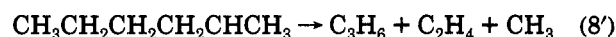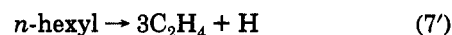
from n-hexane fuel (see Table I). Table V presents the emissions data from this mixture.

Similar to the other n-alkane fuels (1), ethylene and propylene are major combustion-generated exhaust species from n-hexane fuel, and 1-butene is also formed. The mole fraction of ethylene approaches that of the unburned hexane. Toluene produces little of these three species. Approximately 60% of the methane and acetylene emissions from this mixture arise from the toluene component of the fuel (see Table I). Formation of ethylene, propylene, and 1-butene can be rationalized based on H-atom abstraction from the three different types of H atoms present in n-hexane and the following C–C β-scission and H-atom loss reactions:

$$n\text{-hexyl} \rightarrow 3C_2H_4 + H \tag{7'}$$

$$CH_3CH_2CH_2CH_2CHCH_3 \rightarrow C_3H_6 + C_2H_4 + CH_3 \tag{8'}$$

$$CH_3CH_2CH_2CHCH_2CH_3 \rightarrow 1\text{-}C_4H_8 + C_2H_4 + H \tag{9'}$$

The n-hexyl radical could form 1-hexene by H-atom loss, but the 1-hexene contribution is at or below the detectability limit of the GC. Once again, this verifies that if C–C bond scission is possible, it dominates over C–H bond scission. The propylene mole fraction does not increase as the mixture is switched from lean to rich as was observed with 1-hexene fuel, and the percentage increase in ethylene

is smaller. This provides additional support for the suggestion that a portion of the propylene and ethylene arises from H addition to the double bond in the case of 1-hexene fuel.

1,3-Butadiene is observed in the exhaust from this fuel mixture. Approximately 25% of this species comes from the toluene component (see Table I), and it is likely that a portion arises from the methylcyclopentane contaminant in the hexane. We have observed previously that substantial 1,3-butadiene forms from combustion of methylcyclohexane (2) and similar reaction paths exist for formation from methylcyclopentane. Because of this interfering source, it is not possible to estimate the yield of butadiene from n-hexane accurately. However, an upper limit to the butadiene production from n-hexane can be calculated by assuming that the butadiene remaining after correcting for the toluene contribution comes from the n-hexane. This upper limit, after correction for the percentage of hexane in the mixture, is 46% of that observed from 1-hexene. From this result and that of 1-butene, it appears that a straight-chain terminal olefin produces more butadiene than a straight-chain alkane. In experiments using a pulsed-flame combustor (13), 1-hexene produced four times as much butadiene as did n-heptane, supporting this statement, although a cleaner measurement of butadiene production from n-hexane in an engine is needed.

This mixture of an alkane with an aromatic produced only minor amounts of alkyl-substituted benzenes other than the fuel component toluene (8 ppm C ethylbenzene and 6 ppm C styrene) at baseline condition, and these species are present when pure toluene is used as fuel (see Table I). Thus, these data support the contention that the substituted benzenes found in the exhaust of spark-ignited engines arise primarily from the fuel and are not formed in appreciable quantity by addition of alkyl radicals to aromatic rings.

Diisobutylene Fuel. This fuel contains two isomeric alkenes which have the same carbon atom structure as isooctane (see the Experiment section). The diisobutylene emissions data in Table VI can be compared with the results from its conjugate alkane fuel in Table I and ref 1. Similar to the other olefins, the HC emissions at baseline are lower (20%) and the NO$_x$ emissions are slightly higher (13%), but these differences are much smaller than those of the lower molecular weight olefins. The total emissions for alkenes and their conjugate alkanes approach one another as the molecular weight increases because the double bond represents a smaller portion of the molecular structure, resulting in a similar flame temperature for the two types of fuels.

For baseline operation, the mole fractions of combustion products are very similar for diisobutylene and isooctane with the exceptions of 2-methyl-1,3-butadiene and the unidentified species, both of which are essentially absent for isooctane fuel. The unidentified hydrocarbon is characteristic of diisobutylene combustion and decreases by a factor of 6 for rich mixtures. This large decrease is typical of that observed for methacrolein (for isooctane or diisobutylene fuels) and for benzaldehyde (using toluene fuel). Thus, it seems likely that the species is an oxygenated product. With a fuel-rich mixture, the mole fractions of isobutene and 2-methyl-1-butene increase by factors of 2–3 for diisobutylene fuel while for isooctane the mole fractions of both products decrease slightly.

Table VI. Measured Species in Exhaust for Diisobutylene Fuel[a]

exhaust species	base	MBT -12°	Φ = 1.15	Φ = 1.0	2500 rpm
methane	31	28	340	72	36
acetylene	40	48	289	94	63
ethylene	70	81	158	83	85
ethane	12	10	46	38	10
allene	34	25	68	59	25
propyne	30	27	56	43	29
propylene	124	100	147	109	86
1,3-butadiene	10	9	17	12	9
isobutene	337	211	789	505	166
2-methyl-1,3-butadiene	44	27	53	45	20
2-methyl-1-butene	23	13	73	57	10
methacrolein	50	40	16	22	31
unidentified[g]	40	35	3	21	18
2,4,4-trimethyl-1-pentene	292	115	511	258	47
2,4,4-trimethyl-2-pentene	88	38	189	94	19
benzene	11	12	31	15	13
sum of GC (ppm C$_1$)[b]	1335	885	2994	1638	695
unburned fuel (%)[c]	28	17	23	21	9
total HC (hot FID)[d]	1418	968	2871	1670	757
NO$_x$ (ppm)[e]	2480	878	682	2333	>2520
CO (ppm)[e]	718	886	44140	3222	900
CO$_2$ (%)[e]	11.6	11.6	10.1	12.4	11.6
O$_2$ (%)[e]	2.1	2.2	0.2	0.5	2.0
MBT spark timing[f]	25		19	23	23

[a] These data are species mole fractions (ppm C$_1$) in undiluted exhaust samples. ppm C$_1$ (species i) = ppm (i) × carbon no. (i). [b] Sum of the carbon content of all GC peaks contained in the chromatogram, assuming that the carbon response of all species is the same. Includes GC peaks not included in table. [c] Contribution of unburned fuel to sum of GC. [d] Total HC emissions (ppm C$_1$) measured by the hot FID emissions instrument connected to the exhaust pipe by a heated sample line. [e] Mole fractions measured by engine emissions console instruments corrected to fully wet condition. [f] Spark advance for MBT operation (degrees before top dead center). [g] Unidentified hydrocarbon unique to diisobutylene combustion.

As mentioned in the discussion of 1-hexene, rationalization of the combustion products based solely on β C–C bond scission and H-atom loss reactions of alkyl radicals becomes more difficult for large alkenes. Isobutene and allene (or propyne) are important products formed from β C–C bond scission of alkyl radicals. However, no such path exists for formation of propylene, which is also a significant product. Addition to the double bond and molecular decomposition channels may become important in generating certain products. Propylene can certainly be generated by the addition of H to the double bond, but this path cannot explain its formation during lean operation. The presence of increased H-atom concentration at Φ = 1.15 could contribute to the increased isobutene production during rich operation. However, a better understanding of the exhaust species distribution for diisobutylene fuel must await additional laboratory studies of the combustion chemistry of this fuel.

Unburned fuel contributes less to the total HC emissions for diisobutylene fuel under all operating conditions than for any of the other fuels tested. Comparison of the baseline diisobutylene data in Table VI to that obtained for isooctane in Table I shows that the fuel contribution for diisobutylene is 28% while that of isooctane is 47%. As with all other alkane and alkene fuels (C$_3$ and heavier), operation at high speed or with retarded-spark timing results in a substantial reduction of total HC emissions

Table VII. Comparison of Diisobutylene–Gasoline Mix (20/80 mass) to Gasoline[a]

exhaust species	mix base	mix $\Phi = 1.15$	gasoline base	gasoline $\Phi = 1.15$
methane	21	228	23	214
acetylene	35	224	43	221
ethylene	121 [124]	188 [192]	136	199
ethane	7	27	9	23
allene	11	17	6	6
propyne	10	15	9	8
propylene	115	111	110	107
1,3-butadiene	22	15	23	15
isobutene	128 [128]	199 [216]	77	75
n-butane	11	19	13	24
2-methyl-1,3-butadiene	16 [16]	14 [16]	9	7
2-methyl-1-butene	10	17	8	7
isopentane	53 [52]	99 [98]	65	121
n-pentane	33	66	40	81
methacrolein	11 [12]	<1 [3]	2	<1
unidentified	10 [8]	2 [2]		
2,4,4-trimethyl-1-pentene	65 [58]	98 [101]		
2,4,4-trimethyl-2-pentene	20 [17]	36 [37]		
2,2,4-trimethylpentane	57 [58]	115 [110]	72	136
benzene	37	96	46	111
toluene	130 [132]	242 [222]	164	275
xylenes	51	104	66	107
ethylbenzene	12	23	15	24
trimethylbenzenes	24	45	31	43
sum of GC (ppm C_1)[b]	1264	2461	1296	2307
total HC (hot FID)[c]	1536	2722	1476	2649
NO_x (ppm)[d]	2480	686	2463	773
CO (ppm)[d]	588	44100	552	41993
CO_2 (%)[d]	11.7	10.3	11.8	10.4
O_2 (%)[d]	2.2	0.2	2.1	0.2
MBT spark timing[e]	25	19	24	20

[a] These data are species mole fractions (ppm C_1) in undiluted exhaust samples. ppm C_1 (species i) = ppm(i) × carbon no. (i). Entries in brackets are the predicted values based on the data for the individual components in Table VI (diisobutylene) and Table VII (gasoline)—see text. [b] Sum of the carbon content of all GC peaks contained in the chromatogram, assuming that the carbon response of all species is the same. Includes GC peaks not included in table. [c] Total HC emissions (ppm C_1) measured by the hot FID emissions instrument connected to the exhaust pipe by a heated sample line. [d] Mole fractions measured by engine emissions console instruments corrected to fully wet condition. [e] Spark advance for MBT operation (degrees before top dead center).

accompanied by a reduced contribution of unburned fuel. This is particularly pronounced for diisobutylene at 2500 rpm where the unburned fuel contributes only 9% to the total HC emissions.

Diisobutylene–Gasoline Mixture. Based on GC analyses, the carbon content of this mixture is comprised of 19.7% diisobutylene and 80.3% gasoline. Table VII presents the emissions observed both from the mixture and from gasoline for both baseline and rich operation. Included in parentheses for selected species are the mole fractions (MF) predicted for the mixture based on the assumption that the mole fraction of species i emitted from the mixture is a linear combination of the emissions from the individual mixture components:

$$MF_i = 0.197 MF_i(\text{diisobutylene}) + 0.803 MF_i(\text{gasoline})$$

The species selected for comparison include the two fuel components from diisobutylene, selected fuel components from gasoline, and selected products which have as their source primarily one or the other fuel components. For

virtually all of the species compared, the predicted value agrees with that measured to within 10%. This provides firm evidence that the composition of the exhaust gas from a multicomponent fuel mixture can be estimated with some accuracy based on exhaust measurements for the individual components.

Conclusions

Four alkenes (ethylene, 1-butene, 1-hexene, and diisobutylene) were tested as fuels in a single-cylinder engine. The total HC emissions increased with increasing molecular weight of the fuel as was observed previously for alkane fuels. Total engine-out HC emissions from the alkene fuels were lower than those of their conjugate alkanes during lean operation. The largest difference was observed for ethylene under lean operating conditions where the emissions were 45% lower than those of ethane after correction for the different initial carbon content of the intake mixtures. Smaller differences were observed between the alkene and its conjugate alkane as the molecular weight of the fuel increased and when running the engine fuel-rich. Straight-chain terminal alkene fuels produced significant exhaust emissions of 1,3-butadiene, which is defined in the Clean Air Act (7) as an air toxic. These results identify a possible source of butadiene emissions, whose specific precursors have been in some doubt (14), although a correlation between 1,3-butadiene emissions and olefin content of the fuel has been observed (15). The branched alkene, diisobutylene, produced much less 1,3-butadiene, but a significant amount of 2-methyl-1,3-butadiene was emitted.

NO_x concentrations were higher for the alkenes than for their conjugate alkanes because of the higher alkene flame temperature. This difference became smaller as the molecular weight of the alkene increased. No significant difference in CO emissions was observed for the alkene–alkane pairs, although the total CO emissions increased somewhat with molecular weight.

The combustion products present in the exhaust from ethylene and 1-butene can be rationalized based on C–C and C–H bond-scission reactions of alkyl radicals formed either by H-atom abstraction or H-atom addition to the double bond. For the higher molecular weight alkene fuels, such a reaction mechanism cannot explain all of the products formed, and other reactions must play roles in the burnup process.

A mixture of diisobutylene with gasoline was tested, and the species emissions were compared to those of pure diisobutylene and pure gasoline. The mole fractions of products which are characteristic of diisobutylene combustion can be predicted to within 10% based on the emissions data from diisobutylene, gasoline, and the known concentration of diisobutylene in the fuel mixture. Thus, exhaust emissions data from single-component fuels can be useful in predicting the emissions from fuel mixtures.

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