

Precombustion of Fatty Acids and Esters of Biodiesel. A Possible Explanation for Differing Cetane Numbers¹

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ABSTRACT: Fatty acids of C₁₈ chainlength as well as their methyl, ethyl, *n*-propyl, and *n*-butyl esters were injected into a constant-volume combustion apparatus suitable for collecting material from the fuel spray prior to the onset of ignition. The collected material from this precombustion phase of the injection event was analyzed by gas chromatography–mass spectrometry. Compounds identified as forming during the precombustion phase were straight-chain and branched alkanes, alkenes, and cyclic hydrocarbons, as well as aldehydes, ketones, esters, substituted benzenes, and other species, such as furans. Some of the compounds formed during precombustion have low cetane numbers (CN). Low-cetane aromatic compounds were found more prominently for more unsaturated fatty compounds. Thus, the low CN of the intermediary precombustion species may constitute a possible partial explanation why some compounds, for example the more unsaturated fatty compounds, have relatively low CN.

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KEY WORDS: Biodiesel, cetane number, emissions, fatty acids, fatty esters, gas chromatography, mass spectrometry, precombustion.

Vegetable oils and animal fats and their derivatives, especially methyl esters, are of considerable interest as alternative diesel fuels (1), also known as biodiesel. Indeed, biodiesel is defined “as the mono alkyl esters of long-chain fatty acids derived from renewable lipid feedstocks, such as vegetable oils or animal fats, for use in compression ignition (diesel) engines” (2). Numerous studies have shown that most exhaust emissions encountered with conventional diesel fuel (petrodiesel) are reduced with biodiesel, with the exception of nitrogen oxides (NO_x) (1). Biodiesel also represents a domestic, renewable energy source.

When a diesel fuel is injected into the combustion chamber of a diesel engine, a brief time passes before the onset of ignition. During this so-called ignition delay time, the fuel passes through a pressure and temperature gradient until the conditions for ignition are attained. The ignition delay time is

the basis of the cetane number (CN), a prime diesel fuel quality index. The CN of a given compound is higher the shorter its ignition delay time is and *vice versa*. Hexadecane (also known as cetane) is the high-quality standard compound with a short ignition delay time and has been assigned a CN of 100 (3). The low-quality standard with a long ignition delay time is 2,2,4,4,6,8,8-heptamethylnonane (HMN) with an assigned CN of 15. Generally, fatty esters have CN values above that of conventional diesel fuel (petrodiesel), which should have a minimum CN of 40 (4). Note also that vegetable oils (containing triglycerides) have better ignition properties than their lower CN indicate (1).

The standard compounds on the cetane scale show that compound structure plays a significant role in determining the CN of a given material (5). Thus, branching reduces the CN (as demonstrated by the standard compounds of the cetane scale), but the presence, number, and position of double bonds in a fatty compound also influence CN (5,6). Therefore, more highly saturated fatty compounds have higher CN. The number of CH₂ groups is also significant. Therefore, the longer a saturated chain is, the higher the CN, and the larger the size of the alcohol moiety in fatty esters, the higher the CN.

The structure-dependent ignition delay time of a fuel can be influenced by compounds known as cetane improvers, which raise CN. Cetane improvers have been identified for fatty compounds that occur in biodiesel (5). Cetane improvers may have another important ramification, namely the reduction of NO_x exhaust emissions. It is known for petrodiesel that cetane improvers can reduce these exhaust emissions (7). Cetane improvers function by reducing the ignition delay and lowering the premixed fuel combustion temperature (7), thus lowering NO_x by inhibiting their formation, which occurs at high temperatures in the combustion chamber (7,8). Therefore, it appears feasible to attempt such an approach with biodiesel. The environmental significance of NO_x reduction is that these exhaust emissions are precursors of ozone (O₃), which is a primary component of urban smog. NO_x emissions are regulated in tailpipe emissions, while O₃ is regulated in ambient air.

The brief period of time after injection of the fuel into the combustion chamber before the onset of ignition may also be termed the precombustion phase. While passing through the precombustion temperature and pressure gradient, the fuel is

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subjected to chemical reactions during which species are formed that influence the subsequent combustion phase.

In previous work, we analyzed pure triglycerides, such as tripalmitin, tristearin, triolein, trilinolein, and trilinolenin (9–11). In an initial study (9), at 400°C in air or nitrogen, mainly fatty acids, various aliphatic hydrocarbons, and other compounds, such as aldehydes, were detected. Component patterns were largely independent of reaction conditions and starting materials. In a second study (10), where the precombustion products were separated as volatiles or semivolatiles, and the conditions were 450°C in air or nitrogen, unsaturated aliphatic hydrocarbons, unsaturated aldehydes, various aromatics, and polyaromatics were detected. Here the atmosphere had considerable influence on product formation. In this work, we studied stearic, oleic, linoleic, and linolenic acids as well as corresponding methyl, ethyl, propyl, and butyl esters for their precombustion behavior. Intermediate species, formed during precombustion, were trapped and analyzed.

EXPERIMENTAL PROCEDURES

All fatty acids and esters were obtained from Nu-Chek-Prep, Inc. (Elysian, MN), and were of purity >99% as indicated by the manufacturer and verified by random testing. Stearic, oleic, linoleic, and linolenic acids and their esters, as well as methyl *cis*-vaccenate [methyl 11(*Z*)-octadecenoate], were tested. These materials were injected under air into a constant-volume combustion apparatus (CVCA), designed to simulate the conditions that exist in a diesel engine and have been described previously (10; no motion pictures were prepared in the present work). Standard conditions were a temperature of 300°C and a pressure of 1.96 MPa. Experiments conducted under other conditions are noted in the text. Samples were collected as volatile and semivolatile materials.

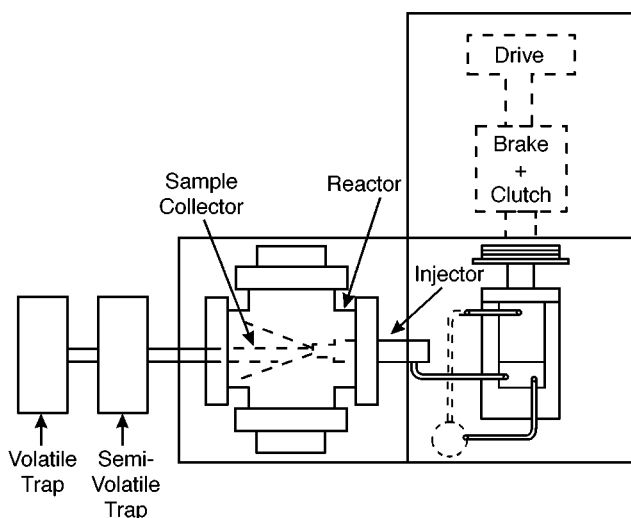


FIG. 1. Scheme of the constant-volume combustion apparatus designed to generate precombustion products (see text).

Figure 1 represents a schematic drawing of the CVCA. The CVCA used in the present work is a modification of a combustion bomb, originally developed as a reliable method for cetane testing, and offers other advantages (for example, less test material) compared to the standard cetane testing method (12). The modification suits the present experiments by attaching a trap system for collecting volatile and semivolatile species into which the precombustion gases are directed and then absorbed.

Semivolatiles were collected on polyurethane foam plugs. Materials from the plugs were extracted with dichloromethane in a Soxhlet extractor or by stirring with dichloromethane (Fisher Scientific, Fair Lawn, NJ) at room temperature for 2 h. Full extraction was controlled by gravimetric comparison of extracted plugs with unused plugs. Nuclear magnetic resonance (NMR) spectra of the extracts were obtained on a Bruker (Rheinstetten, Germany) ARX-400 spectrometer at 400 MHz for ^1H NMR and at 100 MHz for ^{13}C NMR.

The volatile samples were collected in TDU tubes (length 4.5 inches = 11.43 cm; outer diameter 0.25 inches = 0.635 cm; packed with Carbotrap 300; Supelco, Bellefonte, PA) customized to suit an OI Analytical (College Station, TX) purge and trap system which consisted of an MHC-16 multiple heater controller, a DPM-16 discrete purging multisampler, and a 4560 sample concentrator. After desorption and concentration on the purge and trap system, the samples were analyzed with a Hewlett-Packard (Palo Alto, CA) 5890 Series II gas chromatograph, equipped with a Supelco SPB-5 (length 60 m; 0.32 mm i.d.; 1.0 μm film thickness) column (temperature program: 15 min at 30°C, then 2°/min to 50°C, then 5°C/min to 100°C, then 10°/min. to 270°C, final hold 15 min at 270°C) and a Hewlett-Packard 5972 mass selective detector. Some spectra were checked by library search (Wiley 138 K library; obtained from Hewlett-Packard).

RESULTS AND DISCUSSION

Analysis by NMR of the semivolatile materials collected in the foam plug showed that they consisted mainly of unreacted starting material. The volatile samples, on the other hand, consisted of a complex mixture of different classes of compounds, as analysis by gas chromatography–mass spectrometry (GC–MS) with the purge-and-trap system showed. Therefore, the following evaluation deals exclusively with the volatile samples.

Two runs were conducted for each volatile sample. In the first run, some peaks, especially at lower elution temperature and shorter retention time, were extremely strong. Because we suspected that not all material was desorbed from the sampling tubes during the first run, and because we wanted to reveal peaks of materials “hiding” under strong peaks, a second run under identical desorption and GC–MS conditions was conducted. Our suspicion was indeed true for some materials. Generally, the second run displayed fewer and weaker peaks, and some materials identified in the first run were not detected in the second run. All

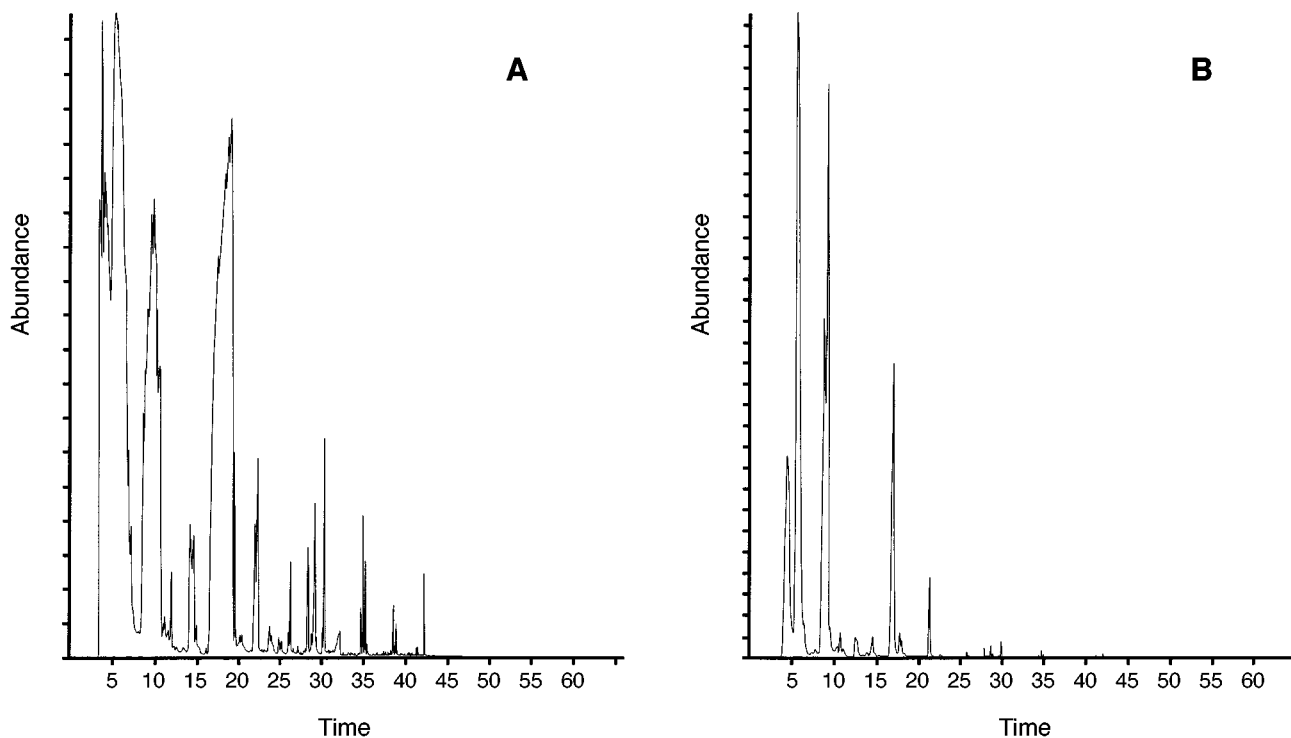


FIG. 2. Typical chromatograms (from precombustion of butyl oleate) of two consecutive GC-MS runs (A: first run; B: second run) for each sample. For details, see text.

tables contain data for both runs. Chromatograms for a series of two such runs are depicted in Figure 2.

The different kinds of thermally induced chemical reactions, such as those occurring here, are well known (13,14). One common type of reaction under the conditions used here results in radicals by cleavage of the hydrocarbon chain. The intermediary radicals can react in several ways (isomerization, disproportionation, recombination, etc.) to give species that differ from the starting material. Other possible reactions include decarboxylation (liberation of CO_2), oxidation, ring closure, cyclization, aromatization, and dehydrogenation. These reactions had also been observed previously in studies on the precombustion of triglycerides (9–11). Evidence for these reactions is presented here. The details of such reactions will not be discussed further, because they are well documented in the literature (13,14).

Numerous classes of compounds were identified in the present work. These classes of compounds include aliphatic hydrocarbons (saturated and unsaturated) as well as straight-chain and branched and likely cyclic species, aldehydes, ketones, aromatic hydrocarbons with aliphatic side chains, and shorter-chain esters. Interestingly, substituted furans were observed as well; these compounds had not been observed in the prior precombustion experiments on triglycerides (9–11). On the other hand, furans have been shown to arise during other combustion experiments with fossil fuels and biomass (15). Table 1 contains a list of compounds by elution sequence, whose nature was assigned as discussed in the next paragraph.

Not only by MS were compounds assigned to specific peaks. Just as essential was an evaluation of the physical properties of a suspected compound to be assigned to a peak. Especially, the boiling point was taken into consideration. Even when a library search indicated high probability for a specific assignment, this assignment was disregarded when the physical properties of the library search-assigned compound (particularly the boiling point) were not in agreement with the physical properties of the other compounds comprised in the elution sequence. Sometimes, assignments were made that disagreed with the primary results of the library search if mass spectra and boiling points pointed to a different specific compound.

Full quantitation of the individual species was not conducted, as was true also for the previous precombustion experiments on triglycerides, where compounds were reported in quantitation ranges (9–11). Quantitation ranges are reported here again. The reasons are: overlapping of peaks, inconclusive mass spectra due to possible isomers with similar physical properties, and fragmentary spectra, especially for compounds that were present in smaller amounts. Furthermore, no external standard could be used, because the experimental method is not amenable to it. Quantitation of compounds is, therefore, reported relative to the highest-intensity material in each sample. A similar procedure of using a parent compound for quantitation was conducted in one of the earlier studies (9). That many compounds were not identified in all samples may be a result of weak intensities and thus

TABLE 1
Elution Sequence of Some Compounds Identified in the Precombustion Samples^a

Compound	Retention time (min)
Acetaldehyde	4
Acetone	5.5–7.0
Methyl acetate	7.0–7.3
Propyl formate	11
2-Butanone	11.5–12
Methyl 2-propenoate	11.5–12
Propyl formate	11
Benzene	14
Branched alkene or alkane (see text)	17.2–21
Pentanal	19–20.5
Dimethyl-2-butanone	20.2
Ethyl 2-propenoate	22
Ethyl propanoate	22
Propyl acetate	22–23
Butyl formate	23.2
Toluene	26–27
2-Hexanone	28.5
Hexanal	29.0–29.5
Methyl 4-Pentenoate	30
Butyl acetate	30.5
Ethylbenzene	33.3–33.5
1,4-Dimethylbenzene	33.7
1,3-Dimethylbenzene	33.8
Trimethylcyclohexane	33.9–34.1
Trimethylcyclohexane	34.0–34.2
Methyl hexanone	34.4–34.5
1,2-Dimethylbenzene	34.8–34.9
Nonane	35.2–35.3
Benzaldehyde	36.6–36.7
Decane	38.8–38.9
Undecane	41.2–41.4
Dodecane	43.2–43.3

^aCompounds were identified by mass spectrometry and physical properties (see text). For example, this holds for the three isomeric dimethylbenzenes (xylenes), which appear in order of increasing boiling point. Mass spectra of these isomers are similar. Retention time ranges are often given because of slight retention time differences of the same compound from sample to sample. Not all structures were identified unambiguously. For example, the exact substitution nature of the trimethylcyclohexanes could not be established.

lack of full peak formation in the chromatogram. Not all experiments conducted are reported for all classes of compounds, for sake of brevity and clarity. The numerous unidentified peaks or those with ambiguous assignments are not reported, either, for space reasons, unless they represent major components that occurred in more than one sample.

Repeatability was checked by conducting three experiments with methyl linoleate under the same conditions. No significant deviations in the component pattern were identified, indicating satisfying replicability. Furthermore, experiments with methyl linoleate at 400°C with 2.3 MPa pressure and at 350°C with 2.12 MPa pressure did not indicate significant changes in the precombustion component pattern.

The intermediate species formed during precombustion have different ignition characteristics themselves. They arise during the precombustion phase and will therefore influence the further course of precombustion. A result of this observa-

tion is that the CN of the intermediary species formed during precombustion will thus influence the cetane number of the original starting material—in the present experiments, the fatty acids and esters.

Most intermediary species will have lower CN than the fatty compounds tested. This is clarified by the known influence of compound structure on the CN (5,6). Increased branching and decreasing chainlength (fewer CH₂ moieties) lower the CN. Aromatics, which may form *via* cyclization and dehydrogenation, have especially low CN (16).

Numerous alkanes, alkenes, and cycloaliphatic compounds were detected. Together, they constitute the most abundant classes of compounds in the present samples. On the other hand, full identification and assignment of these compounds pose significant problems, for two related reasons. With increasing chainlength, the number of possible isomers (with similar physical properties, such as boiling point) increases, and the mass spectra of the isomers are often similar because branching may occur at similar locations in the chain. The chainlength of the backbone of the branched alkanes may not even be identifiable unambiguously. At best, the approximate chainlength or total number of carbons may be deduced from the retention time. This is most conspicuously demonstrated for the strong peak at 18–20 min (consistently one of the strongest peaks in all GC–MS runs), for which no final assignment could be made. Based on retention time and corresponding likely physical properties, the compound is a branched C₇–C₈ alkane or alkene. The mass spectra of the scans with *m/z* 57 as base peak and *m/z* 41 as second most intense peak may point to an alkene (possibly 2,4,4-trimethyl-1-pentene, whose boiling point of 101.4°C would fit the elution sequence in terms of boiling points). On the other hand, an overlap of different compounds appears possible. Distinction between unsaturated compounds (alkenes) and cyclic compounds is often difficult because of mass spectral similarities and isomerism. Table 2 shows some saturated and unsaturated (cyclo-)aliphatic compounds.

Esters with chainlengths shorter (C₁–C₃) than those of the original starting materials were found in most samples. The shorter-chain esters identified are given in Table 3. Extension of the chain of the ester moiety was rarely identified and possibly arose from recombination of radical species.

The detection of aromatic compounds has further unique ramifications. First, they are easy to distinguish from other compounds, which often display mass-spectral similarities, by their typical aromatic fragmentation pattern. Thus, the relative number of aromatic components in a precombustion mixture is readily determined. Table 4 details the presence of aromatic compounds in the precombustion mixtures. They were detected mainly as alkylated species. Benzene was usually present only in small amounts; toluene was observed in nearly all samples.

Table 4 shows that aromatics with extended side-chains or more than one alkyl side-chain were found mainly for the more unsaturated starting materials, linoleic and linolenic acids and esters. Furthermore, although some oleate samples

TABLE 2
Straight-Chain and Branched Alkanes and Alkenes and Cycloaliphatic Compounds in the Precombustion Samples^{a,b}

Compound	18:0 Ac	18:0 Et	18:1 Ac	18:1 Me	18:1 Et	18:1 Δ11 Me	18:2 Ac	18:2 Me ^c	18:2 Me ^d	18:2 Et	18:3 Me	18:3 Et
Branched alkene/alkane	h/h	h/h	h/h	h/h	h/h	h/h	h/h	h/g	h/g	h/h	h/g	h/f
Trimethylcyclohexane ^e	—	a/a	—	—	—	—	—	—	—	—	—	a/a
Trimethylcyclohexane ^e	—	a/a	—	—	—	—	—	—	—	—	—	a/a
Nonane	b/—	b/—	—	—	b/—	—	—	—	c/a	—	c/—	e/—
Decane	a/—	b/—	—	—	a/a	a/—	—	a/—	b/—	—	d/—	e/—
Undecane	a/—	—	c/—	—	a/—	a/—	b/—	a/—	b/—	a/—	b/—	c/—
Dodecane	—	—/a	c/a	—	—/a	—	—	a/a	—/a	—	—	—

^aThe starting materials are coded as described in the following example: 18:1 Me = methyl oleate. First the fatty acid chain is given (18:0 = stearate, 18:1 = oleate, 18:1 Δ11 = vaccenate, 18:2 = linoleate, 18:3 = linolenate) and then the functional group at C1 (Ac = acid, me = methyl ester, et = ethyl ester, pr = propyl ester, bu = butyl ester)

^bQuantitation results from both runs (see text) are given. For example, a/c denotes that a compound was detected in range a in the first run and range c in the second run; a hyphen denotes a compound was not detected (if a compound was not detected in either run, this is denoted by one hyphen). Quantitation ranges are as follows (relative to the most intense peak): a = <1%, b = 1–2%, c = 2–5%, d = 5–10%, e = 10–25%, f = 25–50%, g = 50–75%, h = 75–100%.

^c400°C, 2.3 MPa.

^dStandard conditions.

^eSubstitution pattern of trimethylcyclohexanes could not be established.

showed some of these aromatics, they were not observed for methyl *cis*-vaccenate. Therefore, the position of the double bond can play a role in the formation of precombustion species. For oleate and methyl petroselinate, the species formed by cleavage of the fatty acid chain depends on the position of the double bond. The cleavage of oleate leads to a fragment that can easily cyclize to an aromatic species; the cleavage of petroselinate would not cause such a fragment. In this connection, the trimethyl-substituted cyclohexanes (see Table 2) were found predominantly for linolenates (C_{18:3}).

The greater content of aromatics in the precombustion samples of more highly unsaturated fatty compounds may coincide with their low CN. Cetane testing on a CVCA has shown that methyl oleate had a lower CN (47.2) than its isomers methyl vaccenate (methyl *cis*-11-octadecenoate; CN = 49.5) and methyl petroselinate (CN 55.4) in one series of CN determinations (5,17). A generalized interpretation of this finding is that the CN of a certain fatty compound (as well as the CN of nonfatty compounds) is, at least partially, determined by the intermediate species formed during the precombustion phase. Other factors may also play a role. For exam-

ple, there is a positive correlation between CN and boiling point of a fatty compound (18). Another work, in which regression analyses were conducted, showed that boiling point was the most reliable property for predicting the CN of fatty compounds (19). It was more reliable than heat of combustion, carbon number, and melting point.

That small amounts of low-cetane compounds may have significant effects on the overall CN of the tested compound is clarified by the following equation for a simple two-component system:

$$\text{CN} = \frac{[a (\text{high CN component}) + b (\text{low CN component})]}{100} \quad [1]$$

with *a* and *b* being the amounts of the two components in volume-%. For example, a system that consists of 95% of a compound with CN 60 and 5% of a compound with CN 10 (a very low CN, but it is that of xylene, see Ref. 16) would have a CN of 56.5. This equation implies a linear relationship; however, usually the overall CN is nonlinear (20).

Other compounds, for example short-chain and branched hydrocarbons, may have similar effects on the overall CN of

TABLE 3
Shorter-Chain Esters Identified^a

Compound	18:1 Ac	18:1 Me	18:1 Et	18:1 Pr	18:1 Bu	18:2 Ac	18:2 Me ^c	18:2 Et	18:2 Pr	18:2 Bu
Methyl acetate	f/—	f/g	—	—	—	—	g/g	g/f	—	—
Propyl formate	—	—	—	f/g	—/a	—	—	—	—	—
Methyl 2-propenoate	—	f/—	—	—	—	—	g/—	—	—	—
Ethyl 2-propenoate	—	—	—/f	—	—	—	—	a/—	—	—
Ethyl propanoate ^b	—	—	—	—	—	—	—	—	—	—
Propyl acetate	—	—	—	f/a	—	—	—	—	a/—	—
Butyl formate	—	—	—	—	—/e	—	—	—	—	f/—
Methyl 4-Pentenoate	—	b/—	—	—	—	—	d/a	—	—	—
Butyl acetate	—	—	—	—	f/f	—	—	—	—	f/e

^aFor explanatory remarks on the tables, see footnotes for Table 2.

^bDetected only in 18:0 Et and 18:3 Et at c/—.

^cStandard conditions.

TABLE 4
Aromatic Compounds^a

Compound	18:0 Ac	18:0 Et	18:1 Ac	18:1 Me	18:1 Et	18:1 Δ11 Me	18:2 Ac	18:2 Me ^b	18:2 Me ^c	18:2 Et	18:3 Me	18:3 Et
Benzene	—	—/a	—	—	—/a	—	b/c	b/b	—	—	—/d	—
Toluene	e/c	e/e	a/b	a/—	e/e	d/a	b/a	g/f	f/f	f/e	f/b	f/b
Ethylbenzene	a/	a/	—/a	—	a/a	—	—	b/a	b/a	e/a	b/a	b/a
1,4-Dimethylbenzene	—	—	a/a	—	—/a	—	—	b/—	f/a	a/a	e/a	d/—
1,3-Dimethylbenzene	a/—	a/—	—	—	a/—	—	—	f/—	e/—	b/—	—	—
1,2-Dimethylbenzene	—	—	a/—	—	—	—	—	f/—	e/—	a/—	b/—	b/—

^aFor explanatory remarks on the tables, see footnotes for Table 2.^b400°C, 2.3 MPa.^cStandard conditions.

fatty compounds and contribute to lower CN of more unsaturated species. The aromatics, however, are particularly good examples for discussing this effect because of their facile identification in GC-MS, as discussed above.

Oxygenated species (aldehydes and ketones) were also detected and are given in Table 5. Aldehydes are known to form in hydrocarbon combustion (13,14) because they are combustible intermediates and can lead to chain branching. On the other hand, many compounds will have only slight or no effects on the CN of fatty compounds. This holds, for example, for the furans. Furan has only a small decreasing effect on the CN of conventional diesel fuel at levels of 1–1000 ppm, as some CN determinations conducted within the framework of this project showed. Alkylated furans (2-ethylfuran and 2-pentylfuran), as detected here, will likely have slightly higher CN than the unsubstituted parent compound. It therefore appears unlikely that furans contribute in any significant fashion to CN variations of fatty compounds, also because of the small amounts in which they were detected.

In conclusion, this work has shown that numerous classes of compounds, including alkanes, alkenes, cycloaliphatics, and aromatics, and oxygenated species, such as aldehydes, shorter-chain esters, and furans, arise during the precombustion phase of fatty compounds in a diesel engine. No significant dependence on the conditions employed here was observed. The formation of low-CN compounds during precombustion may contribute to the lower CN of some fatty compounds, especially more highly unsaturated ones. This was demonstrated most conspicuously for aromatics. Ulti-

mately, enhanced understanding of precombustion of fatty compounds will aid in the development of techniques, such as cetane improvement, for reducing emissions, especially NO_x, when biodiesel is used as a fuel. In general, decreasing the ignition delay time (precombustion phase) of a fuel can raise the CN because less CN-decreasing intermediates are formed.

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REFERENCES

1. Knothe, G., R.O. Dunn, and M.O. Bagby, Biodiesel: The Use of Vegetable Oils and Their Derivatives as Alternative Diesel Fuels, in *ACS Symposium Series 666 (Fuels and Chemicals from Biomass)*, American Chemical Society, 1997, pp. 172–208.
2. Anon., Biodiesel ASTM Standard Under Consideration, *Biodiesel Report*, National Biodiesel Board, Jefferson City, March 1996.
3. *Book of ASTM Standards*, Standard Test Method for Ignition Quality of Diesel Fuels by the Cetane Method, American Society for Testing and Materials, Philadelphia, ASTM D-613, 1987, 5 pp.
4. *Ibid.*, Standard Specification for Diesel Fuel Oils, ASTM D-975, 1995, 12 pp.
5. Knothe, G., M.O. Bagby, and T.W. Ryan, III, Cetane Numbers of Fatty Compounds: Influence of Compound Structure and of

TABLE 5
Aldehydes and Ketones^a

Compound	18:0 Ac	18:0 Et	18:1 Ac	18:1 Me	18:1 Et	18:1 Δ11 Me	18:2 Ac	18:2 Me ^b	18:2 Me ^c	18:2 Et	18:3 Me	18:3 Et
Acetaldehyde	h/d	h/d	h/a	h/b	h/e	h/a	h/f	h/f	h/f	h/f	h/f	h/g
Acetone	h/h	h/h	h/h	h/h	h/h	h/h	h/h	h/h	h/h	h/h	h/h	h/h
2-Butanone	f/g	g/a	—/g	—/g	f/g	—/f	—/g	—	—	f/f	—	—
Dimethyl-2-butanone	—/a	—	f/a	—	—	—	—	a/a	—	—	—	—/a
2-Hexanone	f/e	—	f/c	f/b	—/c	b/b	—	—	—	—	a/a	—
Hexanal	—	—	—	—	—/e	—	g/g	f/c	f/b	f/f	c/—	—
Benzaldehyde	—	—	b/a	b/—	—	—	—	—	—/a	—	—	—

^aFor explanatory remarks on the tables, see footnotes for Table 2.^b400°C, 2.3 MPa.^cStandard conditions.

- Various Potential Cetane Improvers, in *State of Alternative Fuel Technologies*, SAE (Society of Automotive Engineers) Publication SP-1274, Warrendale, 1997, pp. 127–132.
- Harrington, K.J., Chemical and Physical Properties of Vegetable Oil Esters and Their Effect on Diesel Fuel Performance, *Bio-mass* 9:1–17 (1986).
 - Ladommatos, N., M. Parsi, and A. Knowles, The Effect of Fuel Cetane Improver on Diesel Pollutant Emissions, *Fuel* 75:8–14 (1996).
 - Lilly, L.R.C., *Diesel Engine Reference Book*, Butterworths, London, 1985, pp. 18/9–18/10.
 - Knothe, G., M.O. Bagby, T.W. Ryan, III, and T.J. Callahan, Degradation of Unsaturated Triglycerides Injected into a Pressurized Reactor, *J. Am. Oil Chem. Soc.* 68:259–267 (1991).
 - Knothe, G., M.O. Bagby, T.W. Ryan, III, H.G. Wheeler, and T.J. Callahan, Semi-Volatile and Volatile Compounds Formed by Degradation of Triglycerides in a Pressurized Reactor, *Ibid.* 69:341–346 (1992).
 - Knothe, G., M.O. Bagby, T.W. Ryan, III, T.J. Callahan, and T.J. Callahan, Vegetable Oils as Alternative Diesel Fuels: Degradation of Pure Triglycerides During the Precombustion Phase in a Reactor Simulating a Diesel Engine, in *Alternative Fuels for CI and SI Engines*, SAE (Society of Automotive Engineers) Publication SP-900, Warrendale, 1992, pp. 37–63.
 - Ryan, T.W., III, and B. Stapper, Diesel Fuel Ignition Quality as Determined in a Constant Volume Combustion Bomb, *Soc. Automot. Eng. Techn. Pap. Ser.* 870586, 1987.
 - Hucknall, D.J., *Chemistry of Hydrocarbon Combustion*, Chapman and Hall, London and New York, 1985.
 - Glassman, I., *Combustion*, Academic Press, Orlando, 1987.
 - Berndt, T., O. Boege, and W. Rolle, Products of the Gas-Phase Reactions of NO₃ Radicals with Furan and Tetramethylfuran, *Environ. Sci. Technol.* 31:1157–1162 (1997).
 - Clothier, P.Q.E., B.D. Aguda, A. Moise, and H.O. Pritchard, How Do Diesel-Fuel Ignition Improvers Work?, *Chem. Soc. Rev.* 22:101–108 (1993).
 - Bagby, M.O., Inks, Biofuels and Other Emerging Industrial Products from Vegetable Oils, *Proceedings of the Ninth International Conference on Jojoba and Its Uses, Third International Conference on New Industrial Crops Products*, edited by L.H. Princen and C. Rossi, Association for the Advancement of Industrial Crops, Phoenix, 1996, pp. 220–224.
 - Klopfenstein, W.E., Effect of Molecular Weights of Fatty Acid Esters on Cetane Numbers as Diesel Fuels, *J. Am. Oil Chem. Soc.* 62:1029–1031 (1985).
 - Freedman, B., and M.O. Bagby, Predicting Cetane Numbers of *n*-Alcohols and Methyl Esters from Their Physical Properties, *Ibid.* 67:565–571 (1990).
 - Aradi, A.J., and T.W. Ryan, III, Cetane Effect on Diesel Engine Ignition Delay Times Measured in a Constant Volume Combustion Apparatus, *Soc. Automot. Eng. Techn. Pap. Ser.* 952352, 1995.

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