

Degradation of Unsaturated Triglycerides Injected into a Pressurized Reactor¹

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To evaluate the precombustion chemistry of vegetable oils under conditions that exist in a diesel engine, several pure unsaturated triglycerides (triolein, trilinolein, trilinolenin) were injected into a pressurized reactor where they were subjected to thermal and oxidative degradation under varying conditions of atmosphere (air or nitrogen), temperature and pressure. Vapor samples were collected and then analyzed by gas chromatography/mass spectrometry techniques. In general, the samples consisted of similar mixtures regardless of the reaction conditions or triglyceride used as starting material. The most prominent compounds identified in these samples were fatty acids of different chain lengths and a variety of aliphatic hydrocarbons. Smaller numbers of other classes of compounds, such as aldehydes, were also detected.

KEY WORDS: Alternative diesel fuel, degradation, GC/MS, precombustion chemistry, unsaturated triglycerides.

Recurring concerns about the availability and economic aspects of petroleum-based fuels have inspired the investigation of alternative materials for utilization as fuels. Among the candidates considered as replacements for diesel fuel are various vegetable oils (1-3). These materials possess approximately 90% of the heat content of diesel fuel but differ from diesel fuel in their spray, ignition and combustion characteristics. Experiments have also demonstrated that durability problems arise when vegetable oils are used as fuels in diesel engines (1,2). Among the severest problems are nozzle-coking, engine deposits, dilution of lubricating oil and ring sticking related to deposits (4). Other operational problems of lesser significance include degraded thermal efficiency, starting problems, unreliable ignition and misfire. All of these problems are related to the reactions that occur during fuel injection into the engine and during the ignition and combustion events.

Various fatty esters have been explored regarding their use as diesel fuels (5). The cetane numbers of fatty esters, fatty alcohols and triglyceride have been determined (6). The suitability of a given material as diesel fuel depends not only on the cetane number but also on other properties such as melting point, viscosity and volatility. Analysis of intermediate or final reaction products has not been performed. The degradation of triglycerides under varying conditions (e.g., pyrolysis, radiolysis or frying) has

been studied by many authors (7-21). Similar investigations have been conducted for vegetable oils (22-29) and for fatty acids in presence of sodium carbonate (30) or lignin (31). In cases in which the resulting materials were analyzed, carboxylic acids and various aliphatic hydrocarbons usually constituted major portions. However, aromatic hydrocarbons, ketones, aldehydes, etc., were also found.

Objectives of this work were to identify the extent to which preignition chemical reactions may occur in the engine and to identify the major products of preignition events. To simplify the analyses, pure triglycerides, i.e., triolein, trilinolein and trilinolenin were injected separately into a pressurized reactor. This reactor simulated conditions that exist in a diesel engine prior to combustion. Analyses of the resulting precombustion samples provided information on the types of reaction occurring under these conditions. Ultimately, these data will help define and diminish the combustion problems arising from the use of vegetable oils as alternative diesel fuels.

EXPERIMENTAL PROCEDURES

Materials. Triolein, trilinolein and trilinolenin were obtained from Nu Chek Prep, Inc. (Elysian, MN). Purity was >99%. The samples collected from the reactor were transesterified with a 0.2N solution of (m-trifluoromethylphenyl)-trimethylammonium hydroxide in methanol (Meth-Prep II; Applied Science State College, PA).

Analyses. Gas chromatographic/mass spectrometry (GC/MS) analyses of the collected samples were performed with a Hewlett-Packard 5890/5970 GC/MS system (Hewlett-Packard, Palo Alto, CA) equipped with a DB1701 capillary column (30 m × 0.25 mm ID, J&W Scientific, Folsom, CA). The injection temperature was 265°C and 1 μL was injected with a split ratio of 100:1. For triglyceride detection, a Hewlett-Packard 5890A gas chromatograph was used with a 2.5 m × 0.32 mm HT 5 Al-clad NP capillary column (temp. 170-350°C, 10°C per min, He 113 mL/min) obtained from Scientific Glass Engineering (Ringwood, Australia).

Reactor and sample collection. The reactor apparatus with the attached sample collection system is depicted in Figure 1.

The apparatus consists of a pressurized reactor with an injection nozzle and a sample probe opposite the nozzle. Parallel to the injection direction, quartz windows were positioned for viewing and acquisition of high-speed motion pictures of the injected fuels. Two different lighting techniques were employed. Back-lighting was used for movies taken at 25,000 quarter-frames per second. These movies were used for positioning the sample probe. Front-lighting was used to film the combustion process.

Prior to each set of experiments, the injector was removed from the reactor, taken apart and rinsed with heptane and acetone to prevent contamination from

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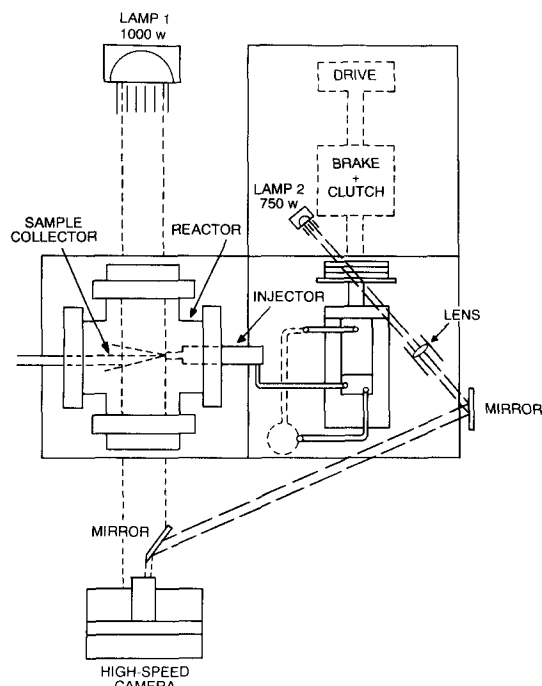


FIG. 1. Reactor for studying the precombustion chemistry of triglycerides under conditions that exist in a diesel engine. The diagram shows the essential features as described in the text with the sample collector opposite the injector.

previous test materials. The fuel system and sample collector were also flushed with heptane and acetone. Then the injector was assembled and reinstalled in a

reproducible manner (with the aid of a fixture), and the sample probe and line were purged with nitrogen. Then the fuel system was filled with the test fuel and purged of air. Two clean sample bottles were attached in series to the sample line. The first bottle was immersed in an ice/water bath and the latter in a dry-ice/acetone bath. Depending upon desired test conditions, the reactor was pressurized with air or nitrogen and equilibrated to the test temperature. Reactor gas temperature was controlled by using electrical heaters. Fuel temperature was controlled by the temperature and flow rate of the cooling water surrounding the injector. After achieving the test conditions, the drive system was engaged for one injection. The electronic controls synchronized the sampling event with the first few milliseconds of the injection to ensure collection of samples in a reproducible manner. After injection and sampling, the reactor was purged, and then the process was restarted. Ten injections were sampled individually in this manner to collect one test sample for analysis. Samples were collected at various reactor pressures, temperatures and atmospheres before the injector was removed and the fuel was changed. The atmosphere was either air or nitrogen, and the temperature of the fuel (T_f) was varied between 26 and 140°C. Gas temperature in the reactor (T_g) was between 26 and 400°C, and gas pressure (P_g) was either 300 or 600 psig. Exact conditions for each sample run and reaction numbers are given in Table 1. Reproducibility was checked by conducting several experiments under the same conditions. Samples were stored under refrigeration until analyzed.

TABLE 1

Reaction Conditions^a

Reaction number	Atmosphere	Reactor pressure (P_g , psig)	Reactor temperature (T_g , °C)	Fuel temperature (T_f , °C)
1) Triolein				
1A-1	Air	300	400	40
1A-2	Air	600	26	26
1A-4	Air	600	210	140
1A-5a	Air	600	400	40
1A-5b	Air	600	400	40
1A-5c	Air	600	400	40
1N-4a	Nitrogen	600	210	140
1N-4b	Nitrogen	600	210	140
1N-5a	Nitrogen	600	400	40
1N-5b	Nitrogen	600	400	40
1N-5c	Nitrogen	600	400	40
2) Trilinolein				
2A-3	Air	600	210	40
2A-4	Air	600	210	140
2A-5	Air	600	400	40
2A-6	Air	600	400	140
2N-2a	Nitrogen	600	26	26
2N-2b	Nitrogen	600	26	26
2N-4	Nitrogen	600	210	140
2N-5	Nitrogen	600	400	40
2N-6	Nitrogen	600	400	140
3) Trilinolenin				
3A-5	Air	600	400	40
3N-5	Nitrogen	600	400	40

^a The first digit of the reaction number indicates the triglyceride (by number of double bonds in the parent acid), the capital letter denotes the atmosphere, the second digit refers to the reaction conditions, and the small letter points out repeated reactions.

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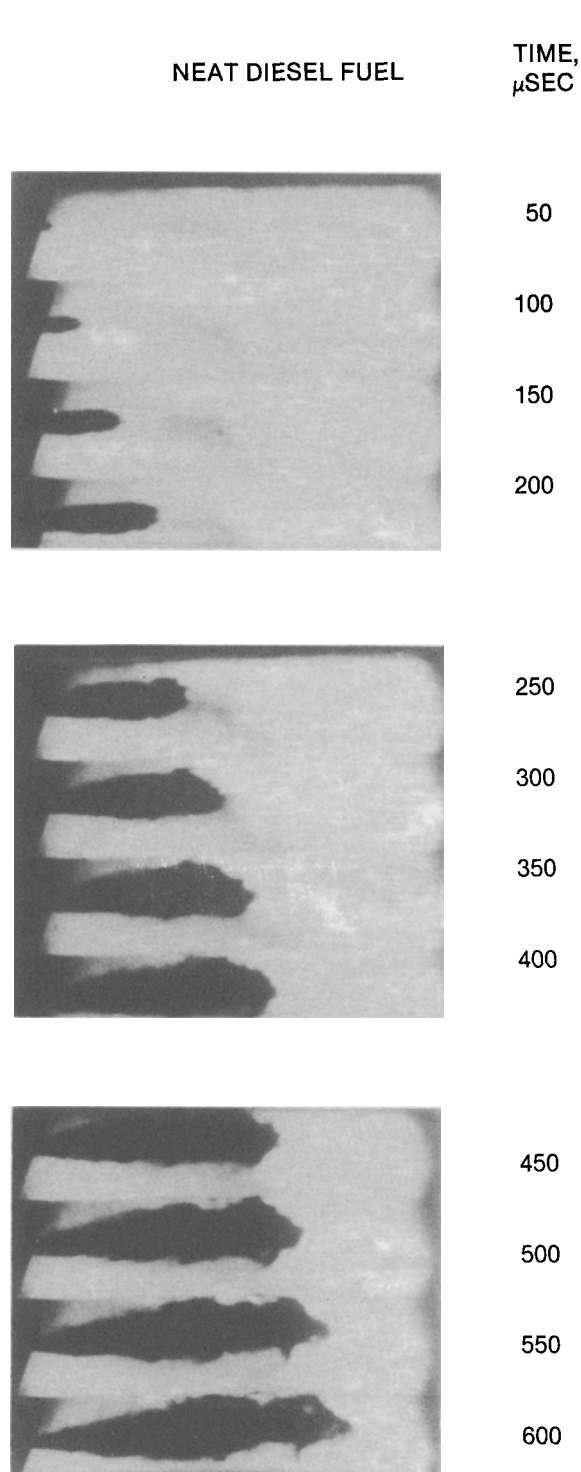


FIG. 2. Photograph showing the injection of triglyceride into the reactor depicted in Figure 1. The volume of the injected fuel cloud increases with time. At approximately 500 μ sec, the cloud shows stronger dissipation.

RESULTS AND DISCUSSION

Injection event. In a typical injection, the fuel appeared as

a cloud within the reactor. Figure 2 shows a typical injection event in nitrogen and without the sample probe. In air, ignition occurred at many points initially within the fuel cloud, thus resembling a sparking before the flame developed. Fuels ignited more rapidly as the number of injections increased. Likely, shorter ignition delay was observed because the temperature of metal surfaces within the reactor increased. The combustion of all fuels appeared similar. Motion pictures of the injection event gave visual evidence that sampling was occurring, and confirmed that only a small portion of the injected fuel was collected. Most of the material remained in the reactor.

Motion pictures have revealed some other interesting phenomena in the spray characteristics of vegetable oils (4,32). The penetration rate, defined as the time rate at which the leading edge of the spray advances away from the nozzle, was lower for a number of vegetable oils than for diesel fuels. The cone angle, defined as the solid angle encompassing the spray with the apex of the angle located upstream of the nozzle discharge, was larger for vegetable oils than for diesel fuels. In these experiments (4,32), both the vegetable oils and diesel fuel were injected at 40°C through the same injection system into identical atmospheric conditions (4.1 MPa and 480°C) and under the same operating conditions for the injection system (same plunger velocity). Heating the vegetable oils to reduce their viscosity from 40 cSt to 4 cSt resulted in increased penetration rates and decreased cone angles. These results were similar to those obtained with diesel fuel at 2.5 cSt and 40°C. Experiences with petroleum-derived fuel (33,34) and other fuels (35) indicate the increased fuel viscosity typically results in increased penetration rate and decreased cone angle of the visible spray of such fuels. A possible explanation for the unexpected performance of the vegetable oils was the occurrence of chemical reactions during the injection of the oils at decreased viscosity. These reactions result in the formation of low molecular weight gases and very dense inner core of high molecular weight liquids. Rapid gasification of the oil fragments in the fringes of the spray could account for an apparent contraction of the visible core and an increase in the penetration rate.

Another interesting phenomenon observed with vegetable oil fuels for diesel engines is the discrepancy between the measured cetane rating of the oils and their observed ignition quality in other engines and at elevated fuel temperatures (4,32). Vegetable oils apparently possess better ignition qualities than their cetane numbers indicate. As with spray phenomena, the ignition qualities could be related to chemical changes occurring during the ignition delay period of the combustion process. The chemical processes that occur during the atomization of fuels in engines are numerous and complex. The various possibilities include pyrolysis, polymerization and partial oxidation. In addition, the fuel is subjected to extreme physical and thermodynamic forces such as high shear rate, high temperature gradients, high velocity gradients and vaporization. The investigation of such complex systems is greatly facilitated by simplifying the system and/or reducing the number of possible processes occurring during the experiment. In the experiments described above (4,32), the process was simplified by injecting the fuels into a quiescent nitrogen environment, thus limiting the complex flow field and restricting the chemical

reactions to pyrolysis and polymerization. A previous report (36) showed that oils undergo significant chemical change during the injection process (residence times in the order of 400 microseconds). These chemical changes may be causing the observed spray characteristics, possibly due to rapid gasification or unknown variations in viscosity and surface tension resulting from changes in composition.

On a fundamental level, an understanding of the processes occurring during the injection of vegetable oils will come only with identification of the important species, definition of the reaction mechanisms, and determination of the relationships between the physical and thermodynamic conditions and the chemical reactions.

Sample evaluation. The collected samples were evaluated by GC-MS methods. Every scan of each sample for a retention time up to 60 min was viewed for evaluation. Of the two sample traps employed, only the data for the reaction products collected in the dry ice-cooled trap are discussed. This trap contained a significant number of fractions which the other did not. The samples were transesterified before the GC-MS studies (see Experimental Section).

All samples generally exhibited the same component pattern regardless of starting material and reaction conditions. Replicated experiments, however, exhibited different intensities of the same components, and not all components are present in all such samples. Tables 2-4

TABLE 2

Major Fractions in Samples Derived from Triolein^a

Evaluation ^b	1A-1	1A-2	1A-4	1A-5a	1A-5b	1A-5c	1N-4a	1N-4b	1N-5a	1N-5b	1N-5c
Ethanedial	h	e	d	h	— ^c		e	e	ovl ^d		
C3 sc fame			b	e	b	b					b
C4 sc fame			b	d	b	b	b	b	c		b
Pentanol										b	
Hexanal										d	
C5 sc fame	b	b	c	e	b	c	b	b	d		c
C6 sc fame	b	c	c	e	c	d	b	c	d	e	d
C11 alkene?	— ^e		b	d	b	b	a	b	c	b	b
C7 sc fame	b	ovl	c	e	d	d	b	c	c	d	d
Undecane	b				b	a				b	b
Succinic acid dime	b		c	f	c	d	b	b	c	c	c
Unknown; b: 113	a		b	c	b	b					
C12 alkene?	b		c	e	b	c	b	b	b	b	b
C8 sc fame	b	b	c	e	d	d	c	c	c	e	e
Dodecane	b		b	c	ovl	ovl	b	b		ovl	ovl
Benzoic acid me	a		b	d	b	b			b	b	b
Glycerol	b	f	f	e	d	d	e	e	d	e	c
Unknown; b: 174	a	b	b	b	b	b	b	b	b		
C9 sc fame	c	a	d	f	d	d	c	c	d	d	c
Tridecane	c	b	b				a	b	b		
C10 sc fame	b	a	b	d	b	c	b	a	b	b	c
Tetradecane	c	a	b	ovl	b	b	b	a	b	b	b
Fame + br. alkane	b		b	c			—	a	a	b	
C11 sc fame				b		b					
Pentadecane	c	a	a		b	b	b	b	b	b	b
C12 sc fame	b	b	a	c		a		b	b		
Ovl hydrocarbons C12-13			b	b	a	c		a		b	b
C13 alkene?	c				c	c			b	c	c
C13 fame + heptadecane		b	b	c	b	c	b	b		f	c
Unsat. C14-fame?	b	b	ovl	b		b	b			c	
C16-fame	d	g	e	e	b	b	d	e	d	b	b
Oleic fame	100	100	100	100	100	100	100	100	100	100	100
Linoleic fame		h	g	f	ovl	ovl	ovl	g	g	ovl	ovl
C18 sc fame	e	ovl	ovl	e	b	c	d	d	d	c	c
C20 sc fame	b	c	b				a	b	d		
Unsat. fame?			a		b	c		a		d	c
Unsat. fame?			b		b	b		b		d	b
C24 alkene?					b	b				b	b
C22 sc fame	b	e	b	b			b	b	b		
C24 sc fame	a	c	b				b	b			

^a Compounds are listed in the order in which they elute from the column. The amounts are given as approximate range values (in %) relative to the parent acid methyl ester (= 100%). The ranges are coded as follows: a = <0.1%, b = 0.1-0.5%, c = 0.5-1%, d = 1-2%, e = 2-5%, f = 5-10%, g = 10-20%, h = >20%.

^b Abbreviations used in this column: fame = fatty acid methyl ester, dime = dimethyl ester, me = methyl ester, sc = straight chain, b = base peak, br. = branched, ovl = overlap or overlapping.

^c Blank areas indicate that this fraction was not observed in the sample.

^d Overlap. Indicates that the integration could not be unambiguously determined because the peak was overlapped by that of another fraction.

^e Indicates that no integration value was obtained at the selected threshold value of the computer software.

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TABLE 3

Major Fractions in Samples Derived from Trilinolein^a

Evaluation	2A-3	2A-4	2A-5	2A-6	2N-2a	2N-2b	2N-4	2N-5	2N6
C3 sc fame	a	a	b	ovl		a	a		ovl
Pentanal	b	a	b				a		
C4 sc fame	b	b	b		a	a	a		
Toluene	b	a	ovl	b	a	a	a	b	a
Unknown	ovl		b	ovl	a	a	a	c	a
Unknown		a	b	b	a		a		b
Unknown	a	a	b	c	a	a	a	c	b
Pentanol	b	b	b		a		a		—
Hexanal	b	b			b	a	b		
C5 sc fame	b	c	b	c	b	a	b		a
Unknown; b = 45	a	a	a	b	a	—	a		
C6 sc fame	d	e	c	d	c	b	d	c	b
C7 sc fame	ovl	b	b	c	ovl	ovl	ovl	c	b
Alkene?	b	b	b	b		a	a		a
Succinic acid dime	b	c	c	d	b	c	b	c	c
Unknwon; b = 113	b	a	b		—		a		
C8 sc fame	b	b	b	c	b	b	b	c	b
Dodecane	a	a			a	a	a		
Benzoic acid me	a	a	a	b	a	a	a		b
C13 alkene?	a	a			a	a	a		
Glycerol	e	f	—		e	e	f		
Unknown; b = 174	a	a	a	b	a	a	—		—
C9 sc fame	b	b	a	b	b	b	b	b	b
Tridecane	a	a	a		b	a	b		a
C10 sc fame	a	b			a	a	b		a
Tetradecane	a	b	b	b	a	a	b		b
C11 sc fame		ovl				a	a		
Pentadecane	b	b	a	b	a	a	b	c	b
Unknown; b = 43	b	b	b	b	b	b	b		a
Unsat. C12 fame?	a	ovl			—		a		
Alkane	a	b	b	c	a	b	b	c	b
C12 sc fame	a	b			a	a	b		
C17 alkene?		a			b	b	a	—	b
Br. C17 alkane?		ovl			ovl	—	ovl	b	
Unsat. C13-fame?	b	b		d	b	b	b		b
Heptadecane	a	a	a		a		b		
C16-fame	b	b	b	c	c	b	b	c	b
Oleic fame	ovl	ovl	ovl	e	ovl	ovl	ovl	d	ovl
Linoleic fame	100	100	100	100	100	100	100	100	100
C18-fame	ovl	ovl		c					
Linoleic isomer?	b	b	ovl			b	b	d	d
Linoleic isomer?	a	b	b	c	b	ovl		d	c
Linoleic isomer?	b	a	b	c	b	b	b	c	b
Linoleic isomer?	b	b	b		b	c	b	b	c
C20-fame	a					a	a		

^a Compounds are given in the order in which they elute from the column. The amounts are given as approximate range values (in %) relative to the parent acid methyl ester (= 100%). For definition of ranges and explanation of abbreviations see Table 2.

contain information on some significant compounds detected in various samples. Table 5 summarizes information on various classes of compounds observed in the samples. Table 6 gives approximate numbers of components in the samples with retention times up to 60 min, at which time methyl tetracosanoate has eluted. No other compounds were eluted after this time.

The major classes of compounds identified in the various samples are fatty acids (detected as the corresponding methyl esters) and aliphatic hydrocarbons. Other compounds detected but in lesser amounts included aldehydes, alcohols, glycerol, succinic acid and benzoic acid. The various compounds were identified by their mass spectra and GC retention times by comparison with known compounds. The fact that these compounds were formed in the reactor was established by transesterifying

known triglycerides with the same reagent and noting that these compounds were absent during GC-MS analyses. These comparison samples will be referred to as base spectra in the following discussion.

Many, usually minor, components in the samples were not unambiguously identifiable even with respect to the class of compound. In part, this uncertainty was the result of low intensities for the mass spectra of many minor fractions. On the other hand, many components, especially straight-chain alkanes, were classified by fragmentary mass spectra. For almost all alkanes, the mass spectra terminated at low m/z values (71, 85, 99 etc.) of the well-known C_nH_{2n+1} peak series. In these cases, several factors led to the structure assignment. These were: i) comparison of GC retention times with those of known samples; ii) a straight-chain alkane eluted from the

column several tenths of a minute later than a straight-chain ester with four carbon atoms less in the chain; and iii) the linear relationship between chain length and retention time for homologous compounds (37,38).

Clear assignments were also difficult because GC peaks containing apparently different classes of compounds overlap. The overlapping of different fractions usually did not allow unambiguous assignments, because many compounds of different classes often have intense peaks at the same m/z . Overlapping of components also interfered with quantitation.

The quantities of all fractions were low compared to the parent acid (defined as the starting triglyceride fatty acid). For quantitation purposes, the starting fatty acid was set at 100%, and all other integration values were calculated relative to that value.

Triglycerides have been degraded to a certain extent under GC conditions when using a persilanized glass capillary column coated with SE-52 (39). Degradation products were mainly the corresponding parent acid and, for triolein, unidentified products of diolein-like structure. Therefore, a contribution of column-degraded triglyceride to the integration value of the parent acid cannot be excluded. However, in this study we found no evidence of degradation of known triglyceride samples. Under the conditions used here, base-line separation is not attained for 18-carbon fatty acid methyl ester. Due to these various uncertainties, integration values were considered approximations and are reported by ranges relative to the value of 100 for the parent acid (Tables 2-5).

Fatty acids. Fatty acids were the most prominent class of compounds present in the samples. Further, the parent acids gave the most intense peak in the GC. However, all samples contained analogues of the parent acid with varying degree of saturation, e.g., samples derived from triolein contained mono-, di- and triunsaturated acids as well as stearic acid.

Saturated straight-chain fatty acids were detected from C_3 upwards. Especially prominent were those in the range C_3 - C_{10} . The C_{11} - C_{14} were less abundant, while C_{16} was always present. C_{15} and C_{17} were not observed. Also, C_{20} , C_{22} and C_{24} acids were detected, especially from triolein-derived samples. The relative intensities of the saturated straight-chain fatty acids were usually 0.1-5% of that for the parent acid.

Presumably, branched saturated acids were present. In most samples, a few minor components showing m/z values typical for saturated fatty acids (m/z 74, 87) were found without clear indication of structure or molecular weight. If these compounds were present, their approximate molecular weights can be deduced only from GC retention times.

Unsaturated fatty acids shorter than C_{18} were present in significant quantities only for trilinolenin and, to a lesser extent, trilinolein-derived species. However, various isomers of di- and triunsaturated C_{18} fatty acids were detected in all samples, and unsaturated acids longer than C_{18} were also present in most samples. The geometric isomers of oleic and linoleic acid have been separated by GC, but most peaks were not assigned to specific isomers (40). That the isomers were formed during the injection event and not by isomerization in the GC column was shown by comparison with the base spectra in which hardly any isomers appeared to be present.

Acids of chain lengths other than that of the parent

TABLE 4

Major Fractions in Samples Derived from Trilinolenin^a

Evaluation	3A-5	3N-5
C3 sc fame	d	e
C4 sc fame	c	—
Unknown; b = 45	b	b
C5 sc fame	c	b
C6 sc fame	c	d
C7 sc fame	c	d
Succinic acid dime	d	
C8 sc fame	d	d
Benzoic acid me	b	
Glycerol	e	
Unknown; b = 174	c	c
C10 sc fame	b	c
Tetradecane	b	b
C11 sc fame	b	
Pentadecane	b	
Unsat. C12 fame?	ovl	
Hexadecane	c	c
Ovl C13 sc fame/tridecane	c	c
C16 sc fame	b	b
C18:3 fame isomer	b	b
Oleic fame	h	g
Linoleic fame	ovl	
Linolenic fame	100	100
C18:3 fame isomer	b	d
C18:3 fame isomer	c	e
Unsat. C20 fame?	b	
Unsat. C20 fame?	b	

^a Compounds are given in the order in which they elute from the column. The amounts are given as approximate range values (in %) relative to the parent acid methyl ester (= 100%). For definition of ranges and explanation of abbreviations see Table 2.

acids in the known triglycerides made only a minute contribution to the detection of shorter chain acids. Only the saturated acids C_6 and C_{16} were found in amounts <0.1% relative to the parent acid in some base spectra.

Hydrocarbons. Various aliphatic hydrocarbons comprised the second most prominent class of compounds detected (Tables 2-5). Triolein and trilinolein provided alkanes as the major class; while trilinolenin yielded unsaturated (or alicyclic) compounds as the major representatives.

The C_{12} to C_{18} hydrocarbons were dominant, however, also present were homologues containing either more or fewer carbon atoms. In almost all samples, considerably greater numbers of aliphatic hydrocarbons were found than would be anticipated from direct cleavage of straight-chain parent acids. The presence of excess hydrocarbons suggests branched species, such as was assumed for some fatty acids. Again the increasing number of possible isomers for longer chains makes exact assignments difficult. The approximate number of carbon atoms was determined from GC retention times.

Other compounds. Besides fatty acids and aliphatic hydrocarbons, several other compounds were identified in the sample mixtures, and their approximate ratios relative to the parent acid are also given in Tables 2-5.

The most prominent compound among these was glycerol, which can arise either during the injection into the reactor or during transesterification from unreacted triglyceride in the collected sample. However, the amount of glycerol detected was considerably less than that

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TABLE 5

Approximate Amounts of Classes of Compounds Relative to the Parent Acid (= 100)^a

A) Triolein	1A-1	1A-2	1A-4	1A-5a	1A-5b	1A-5c	1N-4a	1N-4b	1N-5a	1N-5b	1N-5c
Parent acid	100	100	100	100	100	100	100	100	100	100	100
Sat. straight-chain acids	e	h	f	h	f	f	f	f	f	g	f
Other acids	c	d	c	f	c	e	b	b	—	f	e
Straight-chain alkanes	e	c	c	e	d	e	c	c	c	e	d
Other hydrocarbons	f	b	d	f	e	f	d	d	d	f	e
Glycerol	b	f	f	e	d	d	e	e	d	e	c
Aldehydes	h	e	d	h	—	—	e	e		d	—
Alcohols										b	
Diacids	b	—	c	f	c	d	b	b	d	c	c
Aromatic acids	a		b	d	b	b	—	—	b	b	b
B) Trilinolein		2A-3	2A-4	2A-5		2A-6	2N-2a	2N-2b	2N-4	2N-5	2N-6
Parent acid		100	100	100		100	100	100	100	100	100
Sat. straight-chain acids		f	f	e		f	f	e	f	e	d
Other acids		b	d	b		—	b	b	e	—	—
Straight-chain alkanes		b	c	c		d	a	b	c	e	c
Other hydrocarbons		c	e	b		d	d	c	d	d	c
Glycerol		e	f	—			e		f		
Aldehydes		b	b	b			b	a	b		
Alcohols		b	b	b			a		b		—
Diacids		b	c	c		d	b	c	b	c	c
Aromatic acids		a	a	a		a	a	a	a		b
C) Trilinolenin				3A-5						3N-5	
Parent acid				100						100	
Sat. straight-chain acids				f						g	
Other acids				e						d	
Straight-chain alkanes				c						b	
Other hydrocarbons				e						d	
Glycerol				e							
Diacids				d							
Aromatic acids				b							

^a The letter code for the amount ranges is defined in Table 2.

expected to accumulate from a triglyceride. This observation led to the conclusion that most of the parent acid was liberated during the injection into the reactor and not by transesterification of unreacted triglyceride. As can be seen from Tables 2-5, some samples did not contain glycerol even after transesterification. This observation would imply that glycerol was, at best, only formed as an intermediate during the injection event and was subsequently degraded. Acrolein as a degradation product of glycerol has been reported (13,22,41) from triglyceride decomposition, but it was not detected here. It should be noted that unreacted triglyceride was found in some exemplary samples examined under other conditions (see Experimental Section).

Aldehydes were also detected. The few components identified from this class were pentanal, hexanal and a dialdehyde, presumably ethanedial, which appeared to be present in significant amounts relative to the parent acid. The presence of these oxygenated compounds did not depend on the environment (air or nitrogen) used in the reactor.

As the sole alcohol, pentanol was observed irrespective of the environment. Methanol was present in high abundance but probably remained from solvent in the transesterification reagent. Other components detected in the sample mixtures included succinic acid and benzoic acid. No other components were definitively detected.

The nature of approximately 50% of all components in the samples could not be established for reasons given above. These components were, as already mentioned, of

low abundance and did not constitute more than 10-20% of the sample relative to the parent acid. The observed ions for these compounds indicated a wide variety of materials. It was nearly certain that additional hydrocarbons and other previously mentioned classes of compounds were present. However, clear assignments were not possible because fragmentary spectra of the various classes of compounds often exhibit peaks at nearly identical *m/z*. Approximate numbers of components in the various samples are given in Table 6.

Mechanism. Besides decomposition of the triglyceride into glycerol and the parent acid, the predominant reaction of a triglyceride when injected into a pressurized reactor under the conditions applied here appeared to be chain degradation. This conclusion was supported by the preponderance of data for shorter-chain acids and hydrocarbons. Intermediates were presumably radicals, which readily combine to form the compounds observed. The presence of branched-chain compounds were anticipated from such reactions. The presence of benzoic acid demonstrated that aromatization occurred; however, other aromatic compounds were not positively identified. Aspects of chain degradation by a radical mechanism together with aromatization have been discussed (22). Aldehydes and other oxygenated compounds are typical products for such reactions (9-13,16,17,21). Ketones could not be positively identified. The large numbers of unidentified minor components suggest that there were probably other significant reactions occurring during the injection event. However, their nature cannot be unam-

TABLE 6

Approximate Number of Components in a Given Reaction Sample^a

Components	Approximate total in sample											
	1A-1	1A-2	1A-4	1A-5a	1A-5b	1A-5c	1N-4a	1N-4b	1N-5a	1N-5b	1N-5c	
Triolein												
Overall	165	75	90	65	80	120	50	60	40	145	85	
Unbranched, saturated acids	13	11	14	12	10	12	12	12	10	9	10	
Other acids	2	8	9	5	4	8	4	6	1	13	5	
Straight-chain alkanes	10	8	7	4	4	6	6	6	5	6	4	
Other aliphatic hydrocarbons	30	1	10	10	8	10	7	6	8	14	8	
Trilinolein			2A-3	2A-4	2A-5		2A-6	2N-2a	2N-2b	2N-4	2N-5	2N-6
Overall			125	175	80		55	85	115	185	45	80
Unbranched, saturated acids			13	15	8		9	11	15	15	5	10
Other fatty acids			6	15	1		0	4	4	14	0	0
Straight-chain alkanes			6	7	5		3	6	5	7	3	5
Other aliphatic hydrocarbons			10	27	2		3	11	13	25	3	6
Trilinolenin					3A-5						3N-5	
Overall					100						45	
Unbranched, saturated fatty acids					11						9	
Other fatty acids											2	
Straight-chain alkanes											1	
Other aliphatic hydrocarbons											2	

^a These values do not contain unidentified components.

biguously determined with the present data. As the data from Tables 2–6 demonstrate, relationships between the reaction parameters and the degradation products of the unsaturated triglycerides could not be established. The relative abundance of single components as well as classes of compounds and the approximate numbers of compounds showed that deviations were considerable, even for replicated reactions. The component patterns, however, remained consistent regardless of starting material or reaction conditions and generally coincide with prior literature (7–31).

The results showed that triglycerides (and thus vegetable oils) are degraded prior to combustion under conditions that exist in a diesel engine. It is therefore likely that reactions leading to products known to impart poor fuel quality (low cetane numbers) at least partially occur during this time. The undesired reactions, for example, polymerization and aromatization, can be initiated by the radical species formed during atomization. Evidence for the occurrence of these reactions and products prior to combustion in the diesel engine has been lacking. The results showed that the undesired products formed by the use of vegetable oil in diesel engines arise prior to, as well as during, the combustion event.

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