Semi-Volatile and Volatile Compounds Formed by Degradation of Triglycerides in a Pressurized Reactor[1]

G. Knothe[a,*], M.O. Bagby[a], T.W. Ryan, III[b], H.G. Wheeler[b] and T.J. Callahan[b]
[a]Oil Chemical Research, National Center for Agricultural Utilization Research, Agricultural Research Service, U.S. Department of Agriculture, Peoria, Illinois 61604 and [b]Southwest Research Institute, San Antonio, Texas 78284

The products formed during precombustion reactions of several saturated and unsaturated triglycerides upon their injection into a reactor, simulating conditions that exist in a diesel engine, were collected. Two traps were employed in order to distinguish between volatile and semi-volatile components. The resulting samples were analyzed with gas chromatography-mass spectrometry techniques. Various aliphatic and aromatic hydrocarbons were detected as major degradation products. Oxygenated degradation products were found in smaller numbers. Differences observed in the samples compared to previous work are attributed to the higher temperature used in the present study (450°C *vs.* 400°C). The environment (air or nitrogen) had considerable influence on product formation. The number of components was less for samples of tripalmitin, tristearin and triolein reacted under nitrogen than under air; but more components were formed from trilinolein and trilinolenin under nitrogen atmosphere than under air.

KEY WORDS: **Alternative diesel fuel, degradation, GC-MS, precombustion chemistry, semi-volatiles, triglycerides, volatiles.**

The precombustion chemistry of unsaturated triglycerides injected into a pressurized reactor was recently studied (1). Because vegetable oils have been suggested as possible replacements for diesel fuel (2–4), that investigation was undertaken to study the precombustion chemistry of triglycerides when they were subjected to conditions simulating those that exist in a diesel engine. From a clear understanding of the precombustion chemistry of triglycerides, problems such as incomplete combustion, nozzle-coking, engine deposits, dilution of lubricating oil and deposit-related ring sticking (1–3,5), associated with the use of vegetable oils as alternative diesel fuels, can be effectively addressed. Knowledge about the nature of the products formed or persisting during the injection of the vegetable oils, and thus the reactions leading to them, can be used to help solve or at least reduce the problems involved.

In the previous study (1), fatty acids, various aliphatic hydrocarbons and other materials, such as aldehydes, were found as degradation products. Investigations conducted on the degradation of triglycerides and vegetable oils under varying conditions (*e.g.*, pyrolysis, radiolysis or frying) have shown that aliphatic and aromatic hydrocarbons, fatty acids, aldehydes, ketones, etc., are usually the major degradation products (1 and references therein, 6).

In the previous study (1) on unsaturated triglycerides, the collected degradation products were not distinguished by volatility. In fact, some products may have been lost. Now, improvements in the sample collection system permitted the separate trapping of volatile and semi-volatile components. Furthermore, two saturated triglycerides, tripalmitin and tristearin, were investigated in the present study in addition to the unsaturated triglycerides triolein, trilinolein and trilinolenin. The reaction temperature was increased from 400°C in the previous study to 450°C in the present work.

EXPERIMENTAL PROCEDURES

Materials. Triglycerides were obtained from Nu Chek Prep, Inc. (Elysian, MN). Purities were >99% as determined by the manufacturer.

Analyses. Gas chromatography-mass spectrometry (GC-MS) analyses of the volatile samples were performed on a Finnigan 3000 (Finnigan Corp., Sunnyvale, CA) mass spectrometer equipped with a Model 9500 gas chromatograph and a Tekmar Model 4000 (Tekmar, Cincinnati, OH) thermal desorption module. The components were separated on a Vocol column (Supelco, Inc., Bellefonte, PA) subjected to a temperature program of 25–180°C at 6°C/min.

Semi-volatile samples were analyzed on a Finnigan 3000 quadrupole mass spectrometer equipped with a Tracor 560 (Tracor Instruments, Austin, TX) gas chromatograph. The components were separated on a DB-5 capillary column (0.25 mm ID × 30 m, 0.25 micron film thickness; J&W Scientific, Folsom, CA) subjected to a temperature program of 40°C for 2 min, rising to 295°C at 10°C/min. Injection temperature was 265°C, helium flow rate was 1 mL/min. The traps of the volatile samples were spiked with 250 ng 1,4-difluoro-benzene as internal standard for quantitation (in a GC standards mixture obtained from Supelco). d8-Naphthalene was added to the semi-volatile samples as internal standard (in a GC standards mixture obtained from Supelco) at an extract concentration of 40 ng/μL.

Reactor, sample collection and preparation. The reactor used in this work has been described previously (1,7). Samples were collected for the test materials injected into both air and nitrogen at gas temperatures of 450°C and pressures of 4.1 MPa (600 psi). The maximum gas temperature in the experiments reported previously (1) was 400°C.

Changes were made on the sample collection system. The present trap system consisted of two traps in series (Fig. 1). The first trap was designed to collect the semi-volatile components and the second to trap the volatile components.

The semi-volatiles trap consisted of two sections. The first section was a coil of 0.635-cm (1/4-inch) stainless steel tubing, 81 cm (32 inch) long and immersed in a dry ice/methanol bath. This section was designed to condense and trap the heavier molecular weight components. The second section of the semi-volatiles trap was a 10-cm (4-in) section of 1.27-cm (1/2-inch) tubing that contained a polyurethane foam (PUF) plug, which trapped any liquid droplets that did not collect on the wall of the 0.635-cm (1/4-inch) tubing. For preparing a semi-volatile sample for GC-MS analysis, the 0.635-cm (1/4-inch) coiled stainless

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*To whom correspondence should be addressed at NCAUR/ARS/USDA, 1815 N. University St., Peoria, IL 61604.

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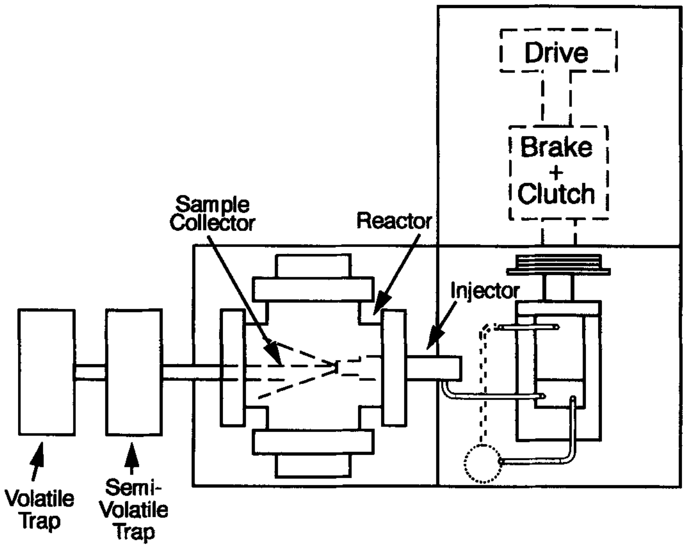

FIG. 1. Reactor for studying precombustion chemistry of triglycerides under conditions that exist in a diesel engine.

steel tubing was concentrated as mentioned above. The PUF was Soxhlet-extracted with 90:10 methylene chloride:acetone for 16 hr. Then the extracts were concentrated as mentioned above. Before being concentrated, extracts were passed through anhydrous sodium sulfate to remove moisture. Extracts were reduced to a final volume of 1 mL for GC-MS analysis with a Kuderna-Danish concentrator and dry nitrogen.

The volatiles trap was downstream of the PUF plug. It consisted of a 20-cm (8-inch) section of 0.635-cm (1/4-inch) O.D. stainless-steel tubing containing 180 mg of Tenax TA 60:80 mesh (Enka Research Institute, Arnhem, Netherlands) and 100 mg of Carbosieve S-11 (Supelco).

RESULTS AND DISCUSSION

The physical phenomena occurring upon injection of triglycerides into a pressurized reactor simulating the conditions that exist in a diesel engine have been discussed (1,5,8). Although temperatures higher than 450°C can be reached during combustion in a diesel engine, it is significant to study the reactions occurring at these temperatures because the precombustion products formed will influence the combustion process and may well endure the combustion process and contribute to problems associated with the use of vegetable oils as alternative diesel fuels.

Sample evaluation. The samples were evaluated by GC-MS methods similar to those of the previous report (1). The samples' spectra were checked against those of the background as it arises from the materials used in the analytical procedure. Compounds that obviously were present in the background were not considered for evaluation. When the amount of a compound present in the samples and in the background was significantly greater in the samples, it was considered as also arising during the reaction.

The component patterns of the various samples were similar, regardless of the atmosphere into which the triglycerides were injected, as had been observed in the earlier study (1). However, in the present experiments, the number of components was considerably less for samples of tripalmitin, tristearin and triolein injected into a nitrogen atmosphere as compared to an air atmosphere; while for trilinolein and trilinolenin, the number of components formed in nitrogen atmosphere was equivalent or even greater (Tables 1 and 2). Furthermore, there were differences in the nature of compounds formed during degradation compared to those of the previous study (1). While carboxylic acids and aliphatic hydrocarbons (among them a significant number of saturated ones) were the major components found earlier (1), the present samples contained large amounts of unsaturated aliphatic hydrocarbons, aromatics with aliphatic side chains, polycyclic compounds and aldehydes. Furthermore, the present samples were far more complex than those obtained earlier (1) in terms of the numbers of components eluting within a given retention time (overlapping of components). Major components detected in the present samples are listed in Tables 3 and 4, and approximate amounts of classes of compounds for semi-volatile samples are given in Table 5.

The complexity of the samples with considerable overlapping of fractions rendered precise quantitation impossible, analogous to results of the previous study (1). Many samples also contained continuous background flows of hydrocarbons, which were present in virtually all scans and interfered with quantitation. This hydrocarbon background presumably consists of a wide variety of isomers of unsaturated aliphatic hydrocarbons, aldehydes

TABLE 1

Approximate Number of Semi-Volatile Components in a Given Reaction Sample

		Classes of compounds				
Sample	Total number of compounds	Aliphatic hydrocarbons	Aliphatic-aromatic hydrocarbons	Aliphatic aldehydes	Aromatic carbonyl compounds	Others
C 16:0 Air	230	58	19	4	1	8
C 16:0 N_2	20	7	1			1
C 18:0 Air	180	40	16	3	1	8
C 18:0 N_2	45	8	2			1
C 18:1 Air	175	37	18	4	1	1
C 18:1 N_2	45	17	3			1
C 18:2 Air	40	7	4			1
C 18:2 N_2	40	4				1
C 18:3 Air	60	2	17		2	1
C 18:3 N_2	120	6	6		1	

TABLE 2

Approximate Number of Volatile Components in a Given Reaction Sample

		Classes of compounds				
Sample	Total number of compounds	Aliphatic hydrocarbons	Aliphatic-aromatic hydrocarbons	Aliphatic aldehydes	Aromatic carbonyl compounds	Others
C 16:0 Air	165	43	10	1	2	1
C 16:0 N_2	100	25	11	1		
C 18:0 Air	190	42	9		1	
C 18:0 N_2	41	3	1			
C 18:1 Air	42	12	4			1
C 18:1 N_2	21	10	1			
C 18:2 Air	25	4	3	2		
C 18:2 N_2	105	25	17	3		
C 18:3 Air	95	31	5		2	
C 18:3 N_2	170	64	23		1	

TABLE 3

Major Semi-Volatile Fractions Observed[a]

Evaluation[b]	160A[c]	160N	180A	180N	181A	181N	182A	182N	183A	183N
Phenylacetylene	c		b		c				b	
Styrene	d		c		c				b	
Ethylbenzene	b		b	b	c				b	b
Arom 91:120[d]	b		b		c				b	b
Benzaldehyde	c		b		c				b	
Phenol	b		b,		c		b		b	
Decene	e		c							
Methylstyrene	b		b		c					
Propylbenzene[e]	b		b		c				b	
Indene	b		c		d				b	
Undecene	e		d							
Undecane	b	b	b							
Nonanal	c		c		d					
Decanal	b		b		c					
Tridecene	e		d		c					
Tridecane	c	a	b		c					
Me naphthalene	c		b		c	b	b		b	
Me naphthalene	c		b	b	c		b		b	b
Biphenyl	b	a	b		c	b			b	
Tetradecene	e		d		c	b				
Acenaphthene	b		b		c	b				a
Pentadecene	c	b	b							
Hexadecene	b		d	b						
Hexadecane	c	b	c	c	h	h	b	c	c	d
Heptadecene		a	c	b		b				b
Tridecanal	c		b		c					
Anthracene	c		b		c					
Octadecane	c		b							
Unknown arom[e]	b		b		c					
Fluoranthene	b		b		c		b		b	b
Pyrene	c		b		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 d8-naphthalene as internal standard (see Experimental Section). The ranges are coded as follows: a, <1%, b, 1–10%; c, 10–50%; d, 50–100%; e, 100–200%; f, 200–500%; g, 500–1000%; h, >1000%. Blank areas indicate that this fraction was not observed in the sample.

[b] Abbreviations used in this column of Tables 3 and 4: arom, aromatic, b, base peak; hc, hydrocarbon; me, methyl; ovl, overlap; unsat, unsaturated.

[c] The first two digits refer to the number of carbons in the parent acid of the triglyceride, the second to the number of double bonds, and the letter to the atmosphere (A, air; N, nitrogen). Thus, 160A stands for the reaction of tripalmitin under air.

[d] The first number (91) indicates the base peak, the second number (120) refers to the molecular weight of the compound.

[e] Tentative identification.

TABLE 4

Major Volatile Components[a]

Evaluation	160A[b]	160N	180A	180N	181A	181N	182A	182N	183A	183N
Cyclic or unsat. C5; b=67	f									
Cyclic or unsat. C5; b=66	e		c						h	
Unknown hc		e	f				c	d	f	g
Hexene		f						f		f
Benzene	h	e	g	d	h	d	b	f	h	f
Heptene	g	f	g					d		f
Toluene	g	h	f		g	d		g	f	f
Hexanal	d		f					h		
Nonene	g	f	g		c			d		d
Phenylacetylene	c		e		b					
Arom 91:106 ethylbenzene[c]	c	c	d				b	f	c	c
Styrene	e	c	f	c	d			e	c	c
Arom 105:120	c		c					c		
Arom 91:120								d		c
Decene/decane ovl	f	f	g							
Benzaldehyde	c	b	d						d	
Undecane	f	d	f	c			b	c		
Dodecane	e	d	e	b						
Tridecane	c	d	c	c				c		c

[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 1,4-difluorobenzene as internal standard (see Experimental Section). For definition of ranges and explanation of abbreviations see Table 3.

[b] See footnote [c] in Table 3.

[c] Tentative identification.

TABLE 5

Approximate Amounts of Classes of Compounds in Semi-Volatile Samples[a]

	Classes of compounds				
Sample[b]	Aliphatic hydrocarbons	Aliphatic-aromatic hydrocarbons	Aliphatic aldehydes	Aromatic carbonyl compounds	Others
160A	g	f	c	c	d
160N	c	a			a
180A	g	e	c	b	d
180N	d	b			b
181A	h	g	e	c	d
182A	c	b			b
183A	c	d		b	
183N	d	b		b	

[a] For definition of ranges see Table 3.

[b] See footnote [c] in Table 3.

and other classes of compounds and may be partly due to the sample-independent background. The materials causing this hydrocarbon background were not evaluated, and only fractions which obviously contained more prominent compounds are reported. Thus, the amounts of compounds are reported by range values, as was done previously (1). These values are related to the selected internal standards (see Experimental Section), which were d8-naphthalene for the semi-volatile samples and 1,4-difluorobenzene for volatile samples. The standards were assigned the value of 100%.

Semi-volatiles. The major classes of compounds detected in the semi-volatile samples were unsaturated aliphatic hydrocarbons of chain length greater than C8, as well as various aromatic compounds with aliphatic substituents and certain polycyclic compounds. Aldehydes were present in smaller amounts and had chain lengths greater than C6. The samples derived from tripalmitin, tristearin and triolein in air atmosphere had considerably larger numbers of components than those obtained in nitrogen atmosphere. For trilinolein the numbers of components are roughly equal in the two atmospheres, while the number of components from trilinolenin is greater for the nitrogen atmosphere.

The most prominent unsaturated aliphatic compounds are alkenes of the C10-C14 series. They were present in amounts greater than the internal standard. Alkenes of greater chain length were present in amounts less than that of the internal standard. Alkenes with shorter chains than approximately C8 were identified in the volatile samples.

Alkanes were also identified, although their amounts and the numbers of components are much lower than those of the unsaturated compounds. Hexadecane was the most prominent alkane and was identified in every semi-volatile sample.

Aromatic compounds with side chains varying in their degrees of unsaturation were observed as shown by the presence of phenylacetylene, styrene and ethylbenzene. Also, there were aromatic compounds with saturated aliphatic side chains present. Numerous fractions were observed that contained typically aromatic base peak/molecular weight combinations, such as 91:106, 91:120, 105:120, etc. These compounds would include xylenes, propylbenzene, etc. Most of these compounds are not listed in Table 3 because of their relatively low concentrations. There was little evidence of aromatics with longer, unsaturated side chains. However, indene, an aromatic compound with a fused aliphatic ring, appeared in some samples.

The semi-volatiles contained an interesting array of polyaromatic compounds, including those with a hydrocarbon substituent, such as methylnaphthalene (presumably both the 1- and 2-isomers), those with rings connected by a single bond like biphenyl, and larger annulated species, such as anthracene and pyrene. Presumably, an annulated aromatic compound with a fused aliphatic moiety, acenaphthene, was also present. The corresponding compound with an attached benzene ring, fluoranthene, was also found. The abundance of these compounds is low compared to the most prominent alkenes. The existence of other polyaromatic compounds in the present samples is likely but could not be conclusively proven. The existence of polycyclic aromatic hydrocarbons identical or similar to those found here has been reported recently in the emissions of vegetable oil-based alternative fuels (9). The present study shows that these materials can already be formed during the precombustion phase when using vegetable oils as alternative diesel fuel. In addition to these aromatic compounds, several oxygenated aromatic species were detected. These included phenol and benzaldehyde. Both were detected only in samples injected into air.

Prominent aliphatic aldehydes were present in smaller numbers than aliphatic and aromatic hydrocarbons, although they might have been present in greater numbers in the hydrocarbon background. Only a few aldehydes are shown in Table 3.

The general lack of oxygenated compounds is also shown by the absence of other classes of compounds containing oxygen. Only few fractions of low intensity were identified as alcohols.

Estimated total amounts of classes of compounds from the semi-volatile samples are given in Table 5.

Volatiles. Generally, the same classes of components were found in the volatile samples as in the semi-volatile samples, but, as expected, the amounts of low molecular weight compounds observed here were much greater than in the semi-volatile samples. Correspondingly, virtually no polyaromatic compounds were detected among the volatiles. From the more saturated triglycerides, the number of components obtained in air atmosphere were significantly larger than in nitrogen. However, trilinolein and trilinolenin yielded greater numbers of components in nitrogen than in air.

Unsaturated aliphatic hydrocarbons were the most numerous compounds in volatiles samples. Especially from tripalmitin and tristearin, a vast number of low molecular compounds eluted within the first few minutes of the GC run. These compounds are unsaturated hydrocarbons with chain lengths up to about C5. Unsaturated cycloaliphatic hydrocarbons were also presumably present. Due to the complexity of the mixture, individual components could not be identified. Aliphatic hydrocarbons were identified beginning at chain lengths of about C6. Some major compounds are listed in Table 4.

As in the case of the semi-volatiles, aromatic compounds were the other most prominent class of compounds present. Benzene and toluene were the most abundant. Various other aromatics with aliphatic side chains, including phenylacetylene, styrene and ethylbenzene, were found in the volatile as well as in the semi-volatile samples. Their abundance in both cases was generally comparable. Again, many minor fractions with base peak/molecular weight combinations, such as 91:106, 91:120 and 105:120, were observed, thus showing the existence of aromatics with aliphatic side chains in the volatile samples. Benzaldehyde was identified in some samples.

Low molecular weight aldehydes were presumed to be present in the complex mixture that was eluted in the first several minutes. Unsaturated aldehydes are predominant breakdown products of unsaturated fatty acids, as shown recently for a study in which UV-irradiation was used (6). Other oxygenated compounds, like alcohols, were not present in the volatile samples. Due to the complexity of some volatile samples, no attempt was made to quantitate the classes of compounds.

The results of the present experiments differ from those of the previous study (1). The differences must be the result of raising the temperature from 400°C to 450°C. Neither fatty acids nor glycerol or its breakdown product, acrolein (10–12), were found. A great variety of aromatic and polycyclic compounds not observed previously was formed. As noted in the previous study, the nature of many compounds in the samples could not be positively established. However, most unidentified components probably belong to the classes of compounds identified. In addition to extensive overlapping of components, these uncertainties were often due to fragmentary spectra lacking less intensive, but significant, peaks.

The present study, which included two saturated triglycerides besides the unsaturated ones, confirmed that the component pattern does not change significantly with different degrees of unsaturation in the starting materials; although the numbers of components collected in the traps did vary.

Mechanism. As previously discussed (1), the main reaction of a triglyceride upon injection into a pressurized bomb is chain degradation to shorter-chain compounds. In contrast to the previous study (1), in which benzoic acid was identified as the sole aromatic compound, extensive aromatization took place. These reactions were accompanied by nearly complete decarboxylation of the fatty acids. Thus, fatty acids found previously were absent in this study. The findings for aldehydes and other oxygenated compounds roughly correspond to previous observations.

Despite the experimental changes and differences in composition of collected reaction samples compared to the previous investigation (1), the results of the present work generally coincide with prior literature (1 and references therein) on the degradation of triglycerides and related materials. The results confirm that triglycerides are extensively degraded prior to combustion in a diesel engine as has been reported (1). The nature of the products depends on the temperature as shown by the contrasting results obtained at 400 and 450°C (1). Means to diminish undesired reactions, such as aromatization and polymerization, are being investigated.

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