CDSolutions

APPLICATIONS INFORMATION USING ADVANCED SAMPLE HANDLING TECHNOLOGY

Cracking Products of Oleic Acid and Olive Oil

Unmodified vegetable oil can be used as fuel in adapted diesel engines, but because vegetable oil is more viscous than diesel fuel, it can cause problems in such engines over time. To create a fuel with a lower viscosity, oil can be modified. Thermal cracking, or controlled pyrolysis of oil decreases its molecular weight and is thereby effective in converting oil to a more useable fuel. Here, microscale pyrolysis is used to look at cracking products of supermarket bought olive oil, and a free fatty acid found abundantly in olive oil, oleic acid.

Each sample was heated inside a quartz tube using the platinum coil of the autosampler, to a setpoint 750°C for 15 seconds. The resulting pyrogram of oleic acid and olive oil are shown in Figures 1 and 2. Because oils and fatty acids are semivolatiles, it can be difficult to get them to pyrolyze before they evaporate. Oleic acid is particularly stable because it has only one double bond. The large peak at 30 minutes in Figure 1 is oleic acid that desorbed from the coil before it had a chance to pyrolyze.

Despite oleic acid's stability, we obtained abundant pyrolysis products; many of them were not well identified with the search engine. The few listed in Tables 1 and 2 had a library quality match of 80% or above. Oleic acid produced a few aromatics like benzene and toluene. Most products in the olive oil and oleic acid are long chain alkenes, alkanes, and alkynes.

Octane found in Oleic Acid (shown in Figure 3) may be from the cleavage of the weaker single bond next to oleic acid's double bond. Octane is found in olive oil too, and could be the directly related to its high oleic acid content.

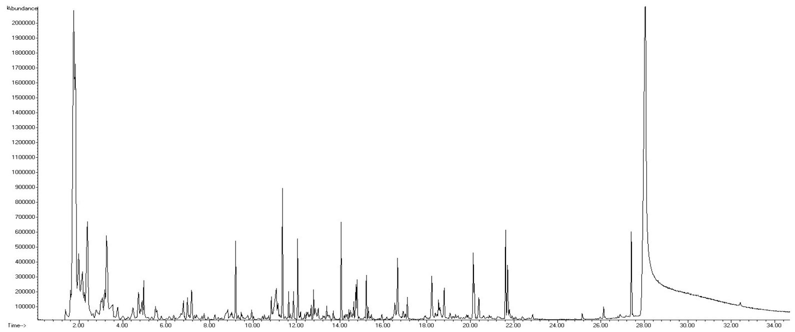

Figure 1: Oleic Acid 750°C for 15 seconds.

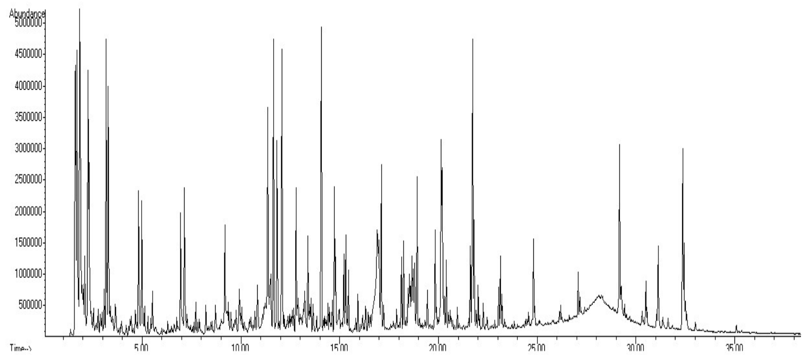

Figure 2: Olive Oil 750°C for 15 seconds.

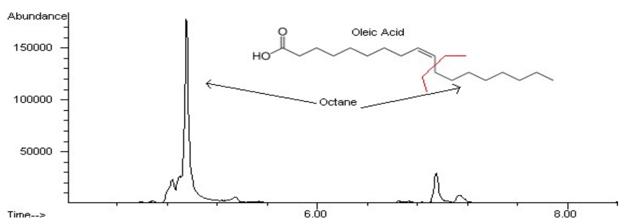

Figure 3: m/z 43 extracted to show Octane in Oleic Acid.

Table 1: Oleic Acid pyrolysis products, by retention time.

1.76	1,3-Butadiene	5.47	Cyclohexane, ethenyl-	12.91	Cyclodecene	18.53	Z-1,6-Tridecadiene
2.08	1,3-Cyclopentadiene	6.96	1-Nonene	13.38	1-Dodecene	19.43	1-Octadecyne
2.31	1-Hexene	7.72	Cyclopropane, 1,1'-(1,2-ethanediyl)bis-	14.05	5-Decyne	20.17	1-Hexadecyne
2.82	2,4-Hexadiene	8.23	Cyclopentene, 1-butyl-	14.72	2,4-Dodecadiene, (E,Z)-	20.59	cis-7-Tetradecen-1-ol
3.01	1,3-Cyclohexadiene	9.18	1-Decene	15.20	Cyclodecene	21.71	8-Heptadecene
3.72	Cyclopentane, ethenyl-	10.83	1,3-Nonadiene, (E)-	15.81	2,4-Decadienal, (E,E)-	22.38	9-Octadecyne
4.35	1,3,5-Hexatriene, 2-methyl-	11.35	1-Undecene	16.52	1,12-Tridecadiene	26.12	9-Octadecenal, (Z)-
4.68	1,7-Octadiene	12.05	1,3-Nonadiene, (E)-	17.10	1-Tetradecene	28.44	9-Octadecenoic acid, (E)-

Table 2: Olive Oil pyrolysis products, by retention time.

1.84	2-Propenal	8.23	Cyclopentene, 1-butyl-	17.23	Tetradecane	24.81	9-Octadecenal, (Z)-
2.02	1-Buten-3-yne, 2-methyl-	9.37	Decane	18.13	Cyclotetradecane	26.87	9,17-Octadecadienal, (Z)-
2.26	1-Hexene	9.93	1,3-Octadiene	18.54	Z-1,6-Tridecadiene	27.23	9,12-Octadecadienoic acid (Z,Z)-
2.42	1,4-Hexadiene, (Z)-	11.65	5-Undecene	18.67	Cyclododecane	27.68	Oleic Acid
2.77	1,3-Hexadiene,c&t	12.08	1,3-Nonadiene, (E)-	18.80	2-Tetradecene, (E)-	27.84	Z,E-2,13-Octadecadien-1-ol
2.97	1,3-Cyclohexadiene	12.91	trans-Bicyclo[5.1.0]octane	19.83	n-Nonylcyclohexane	28.04	2-Methyl-Z,Z-3,13-octadecadienol
3.18	1-Heptene	13.39	1-Dodecene	20.14	Cyclododecene, (E)-	28.14	11-Hexadecen-1-ol, acetate, (Z)-
3.39	2-Heptene	13.55	Dodecane	20.29	Cyclohexadecane	28.26	11-Hexadecen-1-ol, acetate, (Z)-
4.82	1-Octene	14.08	5-Decyne	20.51	Hexadecane	29.26	E,Z-2,13-Octadecadien-1-ol
5.12	2-Octene, (Z)-	15.21	Cyclodecene, (Z)-	21.74	8-Heptadecene	29.68	Oleic Acid
6.95	1-Nonene	15.45	Tridecane	22.28	Cyclododecene, 1-methyl-	31.13	9-Octadecenal, (Z)-
		16.99	n-Decanoic acid	23.14	5-Octadecene, (E)-	32.43	13-Docosen-1-ol, (Z)-

Equipment

These samples were analyzed using a CDS Model 5250 Pyroprobe, interfaced to an Agilent 6890/5975 gas chromatograph/mass spectrometer.

Model 5250 Conditions

Valve Oven: 225°C
Transfer Line: 300°C
Temperature: 750°C
Time: 15 seconds

GC Conditions

Carrier: Helium
Column: 5% phenyl, methyl silicone (30m X 0.25mm)
Detector: Agilent 5975 MSD
Scan: 25 to 550 amu
GC Program:
Initial: 40°C for 2 minutes
Ramp: 8°C/min.
Final: 300°C for 5 minutes

FOR MORE INFORMATION CONCERNING THIS APPLICATION, WE RECOMMEND THE FOLLOWING READING:

D. G. Lima et al., Diesel-like fuel obtained by pyrolysis of vegetable oils., J. Anal. Appl. Pyrolysis 71 (2004) 987-996.

Additional literature on this and related applications may be obtained by contacting your local CDS Analytical representative, or directly from CDS at the address below.

CDS Analytical, Inc. 465 Limestone Road, P.O. Box 277, Oxford, PA USA 19363-0277 PH: 610 932 3636 FX: 610 932 4158