

A Practical Applications Guide for Analytical Pyrolysis -GC/MS

Energy



Thermal Cracking of Olive Oil

Thermal cracking through a Fluid Catalytic Cracking Unit (FCCU, shown in Figure 1) of oil decreases its molecular weight of vegetable oils and so is effective in converting it to a more usable 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 to a setpoint 750°C for 15 seconds. The resulting pyrogram of oleic acid and olive oil are shown in Figures 2 and 3. 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. Pyrolysis products are shown in Tables 1 and 2.

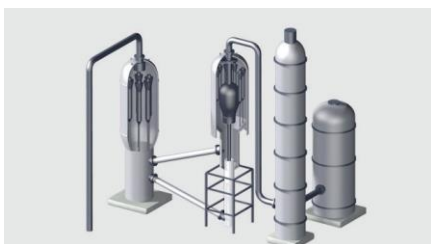


Figure 1. FCCU Diagram

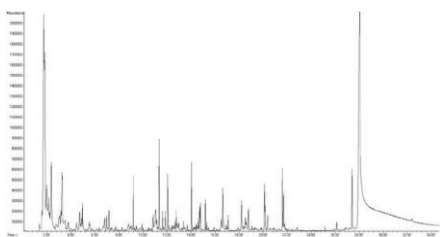


Figure 2. Oleic Acid, 750°C.

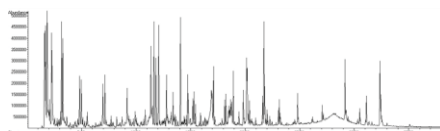


Figure 3 Olive Oil, 750°C

Pyroprobe Setting

Set-point: 700°C 15 sec
 Valve Oven: 300°C
 Transfer Line: 325°C

GC/MS Setting

Column: 5% phenyl
 Carrier: Helium, 50:1 split
 Injector: 300°C
 Oven: 40°C for 2 minutes
 8°C/min to 300°C
 hold 5 min
 Mass Range: 25-550

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

1.76	1,3-Butadiene	5.47	Cyclohexane, ethenyl-	12.91	Cyclododecane	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-ethanedithyl)bis-	14.05	5-Decyne	20.17	1-Hexacosyne
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	Cyclododecane	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-	11.05	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)-
2.25	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-2,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	28.25	11-Hexadecen-1-ol, acetate, (Z)-
4.42	1-Octene	14.08	5-Decyne	20.51	Hexadecane	29.25	E,Z-2,13-Octadecadien-1-ol
5.12	2-Octene, (Z)-	15.21	Cyclododecene, (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)-
		16.59	n-Decanoic acid	23.14	5-Octadecene, (E)-	32.43	19-Docosen-1-ol, (Z)-

High Pressure Pyrolysis of Switchgrass

Elevated pressure and temperature conditions of biomass feedstock can be studied on a microscale level, prior to building a pilot reactor. Figure 1 shows pyrograms of switchgrass at atmospheric pressure and elevated pressure (400 psi, 27atm). Each run contains typical components like levoglucosan (shown in lower run) from cellulose, and vinyl methoxyphenol (shown in the upper run) from lignin. The run performed at elevated pressure reveals more aromatic structures, including phenol and the methyl phenols shown in Figure 2.

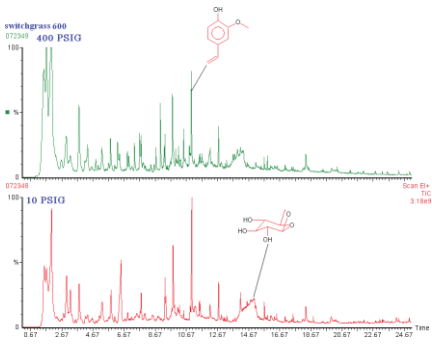


Figure 1: Pyrograms of Switchgrass

Pyroprobe HPR Setting

Interface:	300°C 5 minutes
Pyrolysis:	600°C
Valve Oven:	300°C
Transfer Line:	325°C
Trap Desorb:	300°C 5 minutes
Back Press:	400psi, 27atm

GC/MS Setting

Column:	5% phenyl
Carrier:	Helium, 50:1 split
Injector:	300°C
Oven:	40°C for 2 minutes 10°C/min to 300°C
Mass Range:	35-600amu

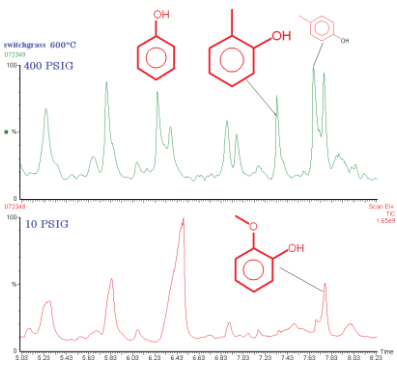
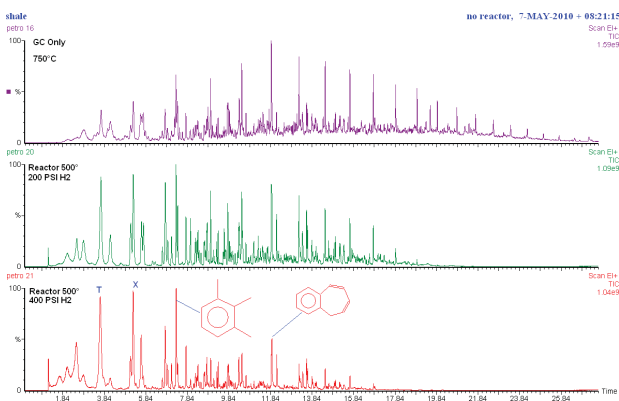


Figure 2: Zoom-in of Pyrograms



Pyrolysis of Oil Shale Under Various Conditions

Behavior of oil shale was studied at different pressure, temperature and reactive conditions can studied on a microscale level. Typical pyrolysis results of oil shale look like the top chromatogram in the figure below, showing a series of long chain aliphatic interspersed with aromatics and branched compounds. In the middle chromatogram, the same shale has again been pyrolysed, but this time in hydrogen at 200 PSI (14 atm). The pyrolysis products are then carried through a platinum reactor where double bonds are reduced. In addition, further cracking takes place in the reactor, and there is some conversion to aromatics. This is mainly caused by the elevated pressure, as seen in the lower chromatogram, in which the hydrogen pressure is 400 PSI (27 atm) and the production of aromatics is further increased.



Pyrolysis of shale under 3 different conditions

Pyroprobe HPR Setting	Flow:	40 ml/minute
Interface: 325°C for 4 min	Trap:	325°C for 4 min
Pyrolysis: 750°C for 15 sec	GC/MS Setting	
Valve oven: 325°C	Column:	5% phenyl
Transfer line: 325°C	Carrier:	Helium, 50:1 split
Reactor: 500°C, Platinum	Injector:	300°C
Pressure: 200 PSI (14atm)	Oven:	40°C for 2 min
400 PSI (27atm)		10°C/min to 300°C
Carrier: Hydrogen	Mass Range:	35-600amu

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