Biodiesel Samples Derived from Palm Oil and Jatropha Curcas Linn by GCxGC-FID

LECO Corporation; Saint Joseph, Michigan USA

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1. Introduction

The capabilities of the LECO comprehensive two-dimensional gas chromatography FID instrument (GCxGC-FID) were demonstrated by running two samples on the instrument at the National Metrology Institute of South Africa (NMISA). This report details the results obtained in this analysis. The instrument conditions are described in Section 2 and qualitative results are outlined fully in Section 3.

The experiment was run to demonstrate the ability of the instrument to analyze highly complex mixtures and to provide results not achievable with conventional one-dimensional GC systems. When the GCxGC system is used, two separation mechanisms are employed to aid in the separation of complex sample mixtures. Typically the first column in the system is a non-polar column that produces a boiling point separation. The second column is a much shorter column employing a polarity based separation mechanism.

This increased chromatographic resolution is extremely powerful when coupled to the Automated Peak Find algorithm unique to the LECO GC and GCxGC systems. This powerful software can locate the position of peaks in the chromatogram. The software uses parameters selected by the analyst to locate the peaks. These values can be selected depending on the degree of information required from the analysis, e.g. choosing high S/N ratios and high peak widths will decrease the number of peaks located by the software. Conversely if low S/Ns are chosen together with low peak widths the software will locate many more peaks. Even peaks which cannot be seen on the chromatographic display will be located by the software. This is a feature not available on other systems which means that many low level peaks will be missed using those systems.

2. Instrument Conditions

GCxGC-FID Acquisition Parameters

Detector: LECO GCxGC-FID System
Data Collection Rate: 50 Hz
GC: Modified Hewlett Packard 6890N*
Column 1:
    Rtx 5Sil MS, 30 m x 0.25 mm ID, 0.25 μm film thickness
Column 2:
    Rtx-50, 2 m x 0.18 mm ID, 0.20 μm film thickness
Column 1 Oven:
    40°C for 2 min, to 160°C at 30°C/min., to 300°C at 2°C/min., hold for 5 min.
Column 2 Oven:
    60°C for 2 min, to 180°C at 30°C/min., to 320°C at 2°C/min., hold for 5 min
Second Dimension Separation Time: 6 sec.

Inlet: Split at 250°C; split ratio 50:1
Carrier Gas:
    Helium, 1.0 mL/min. corrected constant flow
Injection: 0.01 μL
Detector Temperature: 280°C
Make Up Gas: Nitrogen
Make Up Flow + Column Flow: 50 ml/min.
Hydrogen Flow: 40 ml/min.
Air Flow: 450 ml/min.
*The HP6890N GC has a high pressure Electronic Pressure Control (EPC) module.
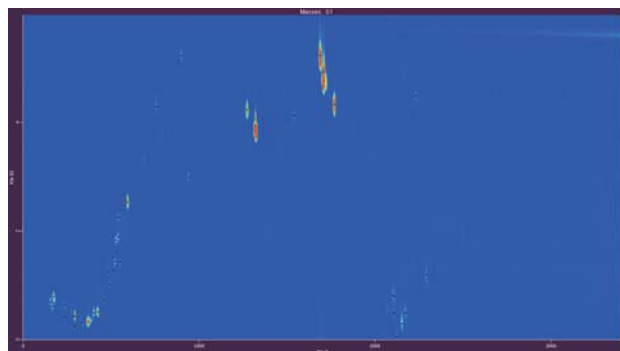
3. Results

Qualitative Analysis of the Jatropha Curcas Linn Sample

Once the data acquisition was complete, the data file for the Jatropha Curcas Linn sample was processed with the Automated Peak Find software. For Peak Find we used a second dimension peak width of 0.20 seconds and a signal-to-noise cut-off of 30:1. Only the peaks meeting these criteria were added to the peak table. The threshold values were set at these values to reduce the number of located peaks to a level which could be easily assimilated and to locate the important components in the sample. These values resulted in 38 located peaks in the Jatropha Curcas Linn sample. The data file can readily be reprocessed with different signal-to-noise and peak width cut-offs, if necessary, without sacrificing the results from previous data processing. This allows the analyst to adjust the number of located analytes in a given sample to a number that is most appropriate for the degree of information required from the analysis, without losing any previous information.

Contour Plots, showing the FID signal for the analysis, are included in this report. This information is contained in the pages subsequent to this. Peak intensity is color scaled in the figures from blue to red, with red representing the highest intensity. The positions of compounds in the Contour Plot are indicated by black dots.
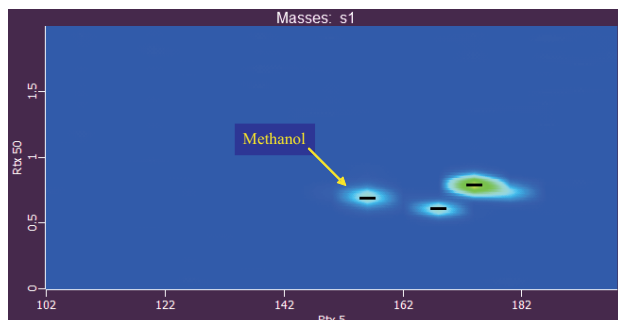
Peak Tables are also included in the report. The Peak Table contains first and second dimension retention times for each located peak in addition to values for the area and peak area %. One of the difficulties in calculating areas in GCxGC analyses is that broad peaks eluting from the long first dimension column can be split into several modulations. To obtain accurate area values, the software must recognize this, and recombine the fractions for each peak to obtain a total peak area. This function is performed automatically for the analyst by the LECO ChromaTOF software using retention time comparison and rise and fall logic. This is an extremely useful function and saves considerable time in the analysis of complex samples.

Contour Plot, showing the FID Signal, of the Jatropha Curcas Linn Sample.

Expanded Contour Plot, showing a methanol standard sample.
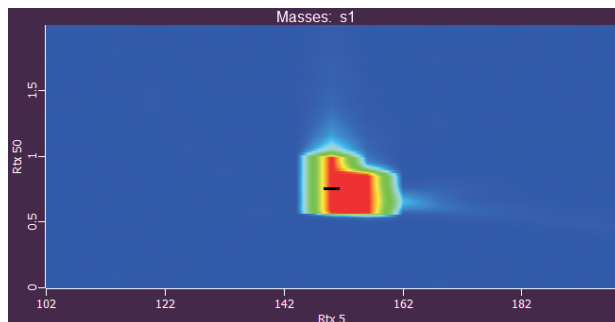
The above chromatogram demonstrates the complexity of the Jatropha Curcas Linn sample. The C16 and C18 fatty acid methyl esters occur as the most intense peaks. These compounds occur in the centre of the chromatogram in the upper half of the display.

Additional components, consisting of lower and higher molecular weight fatty acids and other components, are also present in the sample and occur before and after the main cluster at lower second dimension RT. It should be realized that the components occurring at higher first dimension RT than the main cluster have a lower second dimension RT because of the wrap around effect. They actually occur in the modulation subsequent to that in which they were injected, so their true second dimension RT is actually the measured RT plus 6 seconds. All components are well separated allowing easy quantitation of these components, which is not as simple with one dimensional GC, where all the compounds are translated down to the x-axis, and considerable coelution can occur.
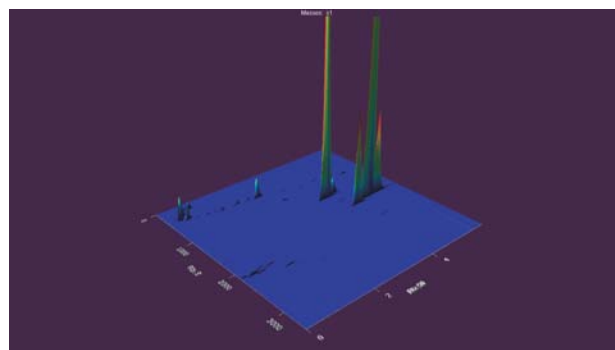

Surface Plot, showing the FID signal, of the Jatropha Curcas Linn Sample.

The surface plot above shows the data for the Jatropha Curcas Linn sample in a different format. This format gives a clearer picture of the relative intensity of the various components present in the sample. The plot may be rotated using the mouse to view the results from any angle. The ability to present data in different formats is a strong feature of the system, allowing different visual representations.

Expanded Contour Plot, showing the methanol region of the Jatropha Curcas Linn Sample.

The above contour plot shows an expansion of the main chromatogram, in which we are looking at the small area in the bottom left region (1st dim RT 100 to 200 sec, 2nd dim RT 0 to 2 sec). This region contains the methanol peak, which is indicated on the chromatogram. The component is easily located and can be accurately quantified. Confirmation of the identity of the methanol was obtained by running a standard methanol sample, shown in Table 1.

Table 1. Peak Table for the Jatropha Curcas Linn Sample.

| Peak #	Name	Ist Dim RT	2nd Dim RT	Area	Area %
1	Unknown 1	156	0.70	1028.1	0.187
2	Unknown 2	168	0.62	768.8	0.140
3	Unknown 3	174	0.80	2906.5	0.529
4	Unknown 4	240	0.44	201.0	0.037
5	Unknown 5	240	0.64	472.7	0.086
6	Unknown 6	294	0.26	215.0	0.039
7	Unknown 7	294	0.44	4962.2	0.904
8	Unknown 8	336	0.32	309.7	0.056
9	Unknown 9	372	0.34	8289.9	1.510
10	Unknown 10	402	0.50	1423.3	0.259
11	Unknown 11	426	0.52	4588.2	0.836
12	Unknown 12	462	0.74	340.5	0.062
13	Unknown 13	480	1.26	294.9	0.054
14	Unknown 14	492	1.02	430.2	0.078
15	Unknown 15	510	1.28	274.8	0.050
16	Unknown 16	522	1.44	751.5	0.137
17	Unknown 17	528	1.84	1034.2	0.188
18	Unknown 18	540	1.90	1225.3	0.223
19	Unknown 19	540	2.26	682.8	0.124
20	Unknown 20	552	1.44	411.5	0.075
21	Unknown 21	594	2.54	7335.7	1.336
22	Unknown 22	756	4.30	707.0	0.129
23	Unknown 23	900	5.24	925.6	0.169
24	Unknown 24	942	3.00	790.3	0.144
25	Unknown 25	1272	4.24	8353.1	1.521
26	Unknown 26	1320	3.96	156651.0	28.532
27	Unknown 27	1536	4.14	600.0	0.109
28	Unknown 28	1686	5.24	65624.0	11.953
29	Unknown 29	1710	4.94	217721.0	39.655
30	Unknown 30	1770	4.34	50721.0	9.238
31	Unknown 31	2100	0.82	857.0	0.156
32	Unknown 32	2106	0.50	588.1	0.107
33	Unknown 33	2112	0.80	814.7	0.148
34	Unknown 34	2124	0.06	741.4	0.135
35	Unknown 35	2154	0.30	3031.0	0.552
36	Unknown 36	2172	0.50	1300.9	0.237
37	Unknown 37	2232	4.50	686.4	0.125
38	Unknown 38	2292	1.20	980.4	0.179

The components present cannot be identified as no standard samples were available for the analysis, and MS data was not accumulated for this sample on this column set. The components are then identified only as Unknowns 1 through 38.

Qualitative Analysis of the Palm Oil Sample
Once the data acquisition was complete, the data file for the Palm Oil sample was processed with the Automated Peak Finding software. For Peak Find we used a second dimension peak width of 0.2 seconds and a signal-to-noise cut-off of 30:1. These values resulted in 21 located peaks in the Palm Oil sample.

Contour Plots, showing the FID signal for the analysis, are included in this report. Peak intensity is color scaled in the figures from blue to red, with red representing the highest intensity. The positions of compounds in the Contour Plot are indicated by black dots.

The Peak Table contains retention times for each located peak in addition to values for the peak area and peak area percentage.
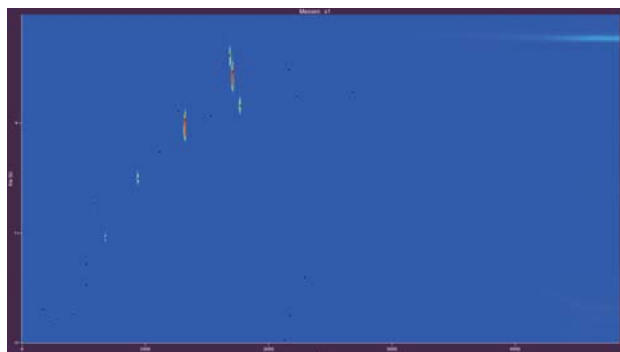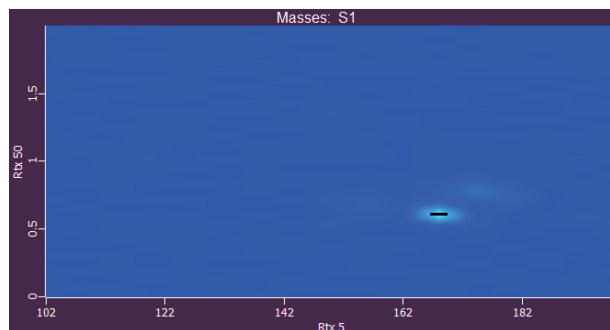

Contour Plot, showing the FID Signal, of the Palm Oil Sample.

The above chromatogram shows the results for the Palm Oil sample. The sample consisted primarily of the same components as were present in the Jatropha Curcas Linn sample. However, the Jatropha Curcas Linn sample contained small amounts of several different impurities which were not present in the Palm Oil sample. The Peak Table is shown below.

Table 2. Peak Table for the Palm Oil Sample Analysis

Peak #	Name	Ist Dim RT	2nd Dim RT	Area	Area %
1	Unknown 1	168	0.62	648.8	0.089
2	Unknown 2	294	0.44	1781.0	0.245
3	Unknown 3	426	0.52	1743.3	0.240
4	Unknown 4	522	1.06	566.1	0.078
5	Unknown 5	522	1.44	545.3	0.075
6	Unknown 6	594	2.54	2798.9	0.385
7	Unknown 7	678	1.92	8545.6	1.174
8	Unknown 8	942	3.00	17904.0	2.460
9	Unknown 9	1116	3.48	605.0	0.083
10	Unknown 10	1272	4.22	1588.8	0.218
11	Unknown 11	1326	4.06	353884.0	48.628
12	Unknown 12	1536	4.14	798.8	0.110
13	Unknown 13	1686	5.24	47585.0	6.539
14	Unknown 14	1710	4.94	245407.0	33.722
15	Unknown 15	1770	4.32	38994.0	5.358
16	Unknown 16	2124	0.06	494.9	0.068
17	Unknown 17	2166	4.98	603.7	0.083
18	Unknown 18	2172	0.50	589.7	0.081
19	Unknown 19	2232	4.50	1670.9	0.230
20	Unknown 20	2292	1.20	662.8	0.091
21	Unknown 21	2682	4.57	320.7	0.044

Expanded Contour Plot, showing the methanol region of the Palm Oil Sample.

As can be seen, no methanol can be detected in the Palm Oil sample. If the sample is taken, and methanol spiked into the sample, it can be clearly detected as shown in the contour plot below.

Thus any methanol present in the Palm Oil sample is at a lower concentration relative to the other components than in the Jatropha Curcas Linn sample.
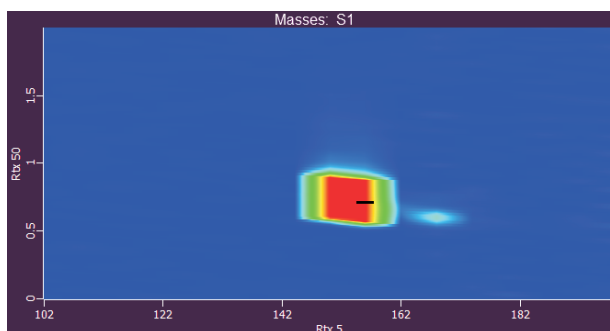
Expanded Contour Plot, showing the methanol region of the spiked Palm Oil Sample.

4. Additional Software Features
In addition to the software features outlined above, the GCxGC-FID instrument contains numerous other powerful and time-saving features. These include:
- Sample Comparison Software: this feature allows easy comparison of two samples and highlighting of the differences between them, which can be tremendously difficult and time-consuming to do manually.
- Classification of Analyte Classes: allows quick and easy classification of compound classes for total class area and area percentage measurements.
- Custom Report Software: creates custom reports by clicking and dragging the mouse.
- Total Automation: allows everything from data collection, data processing, report generation, and quality control management to be automated.
- Quality Control Management Software: easy and convenient to schedule QC tests
- Routine maintenance is also minimal, providing greater up-time and productivity.

5. Conclusions

The samples provided by the customer were analyzed on the LECO GCxGC-FID system. Unique software features, such as the Automated Peak Find algorithm, were used to locate and quantify individual components present in the sample.

The automated data processing algorithms available on the instrument reduce manual data analysis significantly. Low concentration peaks that are not visible in the FID chromatogram, or are heavily overlapped by much larger constituents, are automatically located with the Automated Peak Find algorithm. Without this algorithm, these peaks would have been missed entirely. In all other data systems, if the analyst cannot see a peak in the chromatogram, one does not know anything is there. These features, coupled with the increased resolving power of comprehensive two dimensional gas chromatography, make the LECO GCxGC-FID an extremely powerful instrument for the analysis of complex samples.

6. Appendix

The samples were provided by LECO Thailand, and analyses were run at the NMISA. We thank Ms. Jayne de Vos for the use of the instrument.