



Analytical Quantification of Deoxygenated Compounds in Catalytic Reaction Samples as an Evaluation Technique to Determine Reaction Conversion from a Bioderived Oil in Novel Biofuel Testing

Application Note

Energy & Chemicals, Biofuels & Alternative Energy

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Abstract

This Application Note describes an HPLC method to simultaneously separate and identify deoxygenated compounds from a guaiacol catalytic reaction to evaluate the conversion rate under varied reaction conditions, as part of the novel catalysis processes to obtain renewable biofuels from bioderived oils. The proposed methodology was applied to two different reaction batches, 13 samples were collected to quantify the efficiency of the catalyst proposed. A comparison between a GC method and the one proposed in this Application Note demonstrates time savings with the LC technique as a quality control measurement that could be implemented in biofuel manufacturing process stages.



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Introduction

Dwindling crude oil reserves, accompanied by rising prices and environmental concerns, have led to increased interest in the use of renewable fuels. Biofuels produced from waste agricultural or forestry material are desirable because they avoid diverting resources from the production of food crops. Oils produced by high-temperature treatment of these waste materials, however, contain a large number of oxygenated compounds that result in undesirable properties such as high viscosity and corrosiveness. New approaches describe a series of catalysts that might be used to upgrade these oils by removing the undesirable oxygen-containing functional groups. The compound guaiacol is being used as a model for oxygenated bioderived oils. Guaiacol provides, in a single and easily available compound, the types of oxygen-containing functional groups that typically need to be removed. Depending on the catalyst used, varied rate conversions of guaiacol can be obtained. The one proposed in this methodology is rhodium supported in HY zeolite. Chromatographic techniques have been used effectively to identify and quantify this type of compound. Although GC has always been considered as the primary technique, long run times are common, in addition to the equilibration time needed. Alternatively, an LC technique can be used to reduce run times by half, while being able to identify some of the compounds of interest with excellent reproducibility, using solvents more friendly to the environment.

Experimental

Equipment

The Agilent 1260 Infinity II LC system used for the experiments comprised the following modules:

- Agilent 1260 Infinity II Quaternary Pump (G7104A)
- Agilent 1260 Infinity II Vialsampler (G7167B)
- Agilent 1260 Infinity II Multicolumn Thermostat (G7116B)
- Agilent 1260 Infinity II Variable Wavelength Detector (G4212B)

Software

Agilent OpenLAB CDS ChemStation Edition, version C.01.07

Column

Agilent ZORBAX Eclipse Plus C18, 4.6 × 100 mm, 3.5 μm (p/n 959961-902)

Chemicals

All solvents were LC grade. Acetonitrile was purchased from J.T. Baker, USA. Ultrapure water was LC-grade purchased from J.T. Baker, USA.

Samples and sample preparation

Six compounds were obtained as individual standards from Sigma-Aldrich: anisole, benzene, toluene, *o*-xylene, *m*-xylene, and guaiacol. Each compound was mixed to reach a final concentration of 2,000 ppm, and labeled as the standard mix solution. From this standard mixture, three dilutions in hexane were performed to obtain a four-level calibration curve, including the stock solution, with the concentrations 1,000, 500, and 100 ppm. Reaction samples were placed into a vial for HPLC injection after being collected under varied reaction conditions such as temperature (°C) and flow of reactive (mL/min). Table 1 shows the detailed list of conditions for the 13 total reaction samples.

Table 1. Catalytic reaction conditions for each sample.

Sample	Temperature (°C)	Reaction time (hours)
RXN_01	150	0.5
RXN_02	150	2.0
RXN_03	150	5.0
RXN_01	200	6.0
RXN_02	200	6.3
RXN_03	200	7.5
RXN_04	200	10.3
RXN_01	250	11.3
RXN_02	250	11.9
RXN_03	250	12.9
RXN_04	250	16.3
RXN_01	250	17.0
RXN_02	250	18.0

Chromatographic conditions

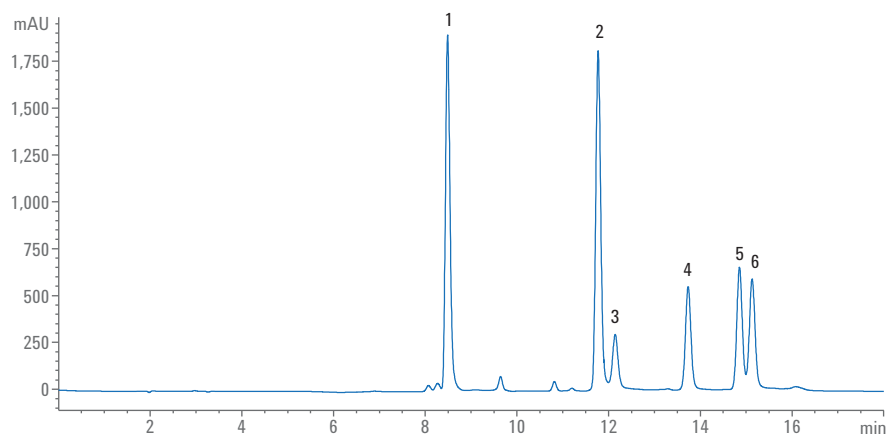
The separation was achieved using a binary linear elution gradient with (A) water and (B) acetonitrile. Table 2 shows the chromatographic conditions for the HPLC gradient.

Results and Discussion

A mix of six standard compounds was separated using an HPLC binary gradient. The relative standard deviation (RSD) of retention time (RT) and area were evaluated over seven subsequent runs. Figure 1 shows the results of the separation. The analysis showed excellent precision of RT and area. The RSD for RT was <0.2, and the area RSD was <2.0 for all standard compounds.

Table 2. Chromatographic conditions, HPLC gradient.

Parameter	Value
Binary gradient	Time (min)
	A: Water
	B: Acetonitrile
	0.00
	95.00
1.00	
77.00	
23.00	
11.00	
20.00	
80.00	
13.50	
20.00	
80.00	
14.00	
95.00	
5.00	
Stop time	17.00 minutes
Post time	2.00 minutes
Flow rate	0.600 mL/min
Injection volume	10 µL
Sample temperature	Ambient
Column temperature	60 °C
Detection	270 nm, peak width > 0.1 minutes (2 second response time), 5 Hz



Peak no.	Compound	% RSD RT	% RSD area
1	Guaiacol	0.052	1.7325
2	Anisole	0.052	0.5634
3	Benzene	0.284	0.7262
4	Toluene	0.060	1.3988
5	<i>o</i> -xylene	0.057	0.3721
6	<i>m</i> -xylene	0.054	0.8718

Figure 1. Chromatogram obtained by HPLC gradient for the Standard Mix sample where the six compounds are separated.

The Standard mix solution was diluted from 2,000 ppm down to 50 ppm to obtain the calibration curve. Table 3 shows the results of the evaluation for the HPLC method.

The 13 samples collected at varied reaction conditions were analyzed. The deoxygenated compound content was quantified by external standard method. Comparison with the results previously obtained by a GC method was performed.

Some of the samples, which showed a high conversion, occurred under high temperature and longtime reaction, such as the RXN02_250C, RXN04_250C, and RXN07_250C. Consistently, two compounds apart from guaiacol were quantified in these samples: *m*-xylene with a total quantification range from 335 to 355 ppm, and *o*-xylene from 280 to 300 ppm. Figure 2 shows the chromatograms corresponding to these samples.

Table 3. Linearity results for HPLC conditions.

Compound	Correlation coefficient UHPLC
Guaiacol	0.98929
Anisole	0.98996
Benzene	0.97918
Toluene	0.98651
<i>o</i> -xylene	0.99028
<i>m</i> -xylene	0.98686

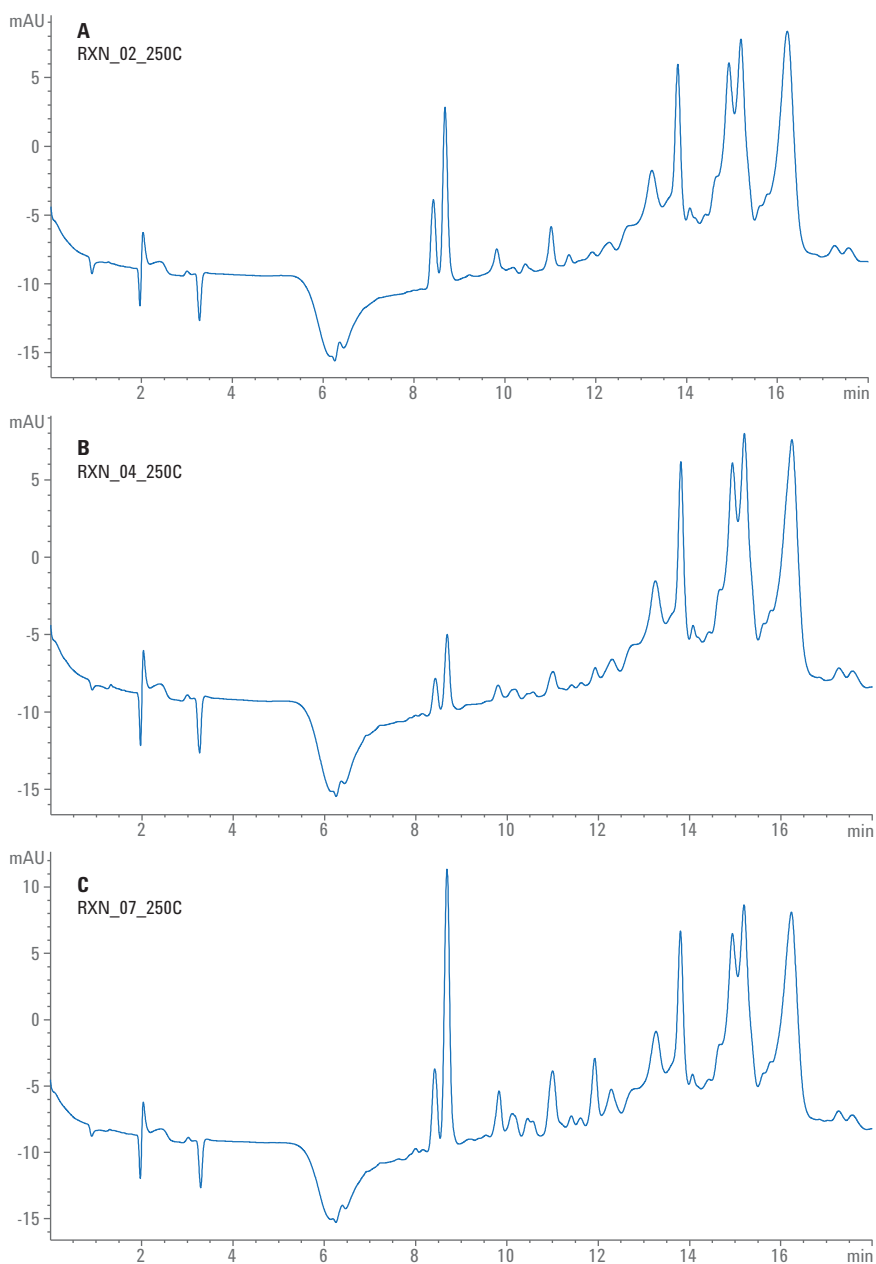


Figure 2. Chromatograms of three different reaction samples collected at the same temperature (250 °C).

Toluene and anisole were only identified under lower temperature conditions (150 °C) and shorter reaction times; however, conversion kept decreasing until the temperature was raised again. Quantification for these two compounds ranged from 850 to 1,100 ppm for toluene, and approximately 250 ppm for anisole. Figure 3 presents an example of one sample reaction at this temperature condition.

After quantification, results were obtained and analyzed for every sample, and compared with the results obtained with the implemented GC method. Results were consistent with the GC technique. This was confirmed by reaction conversion calculation, and compared with the LC results obtained in this analysis for the evaluation of conversion of guaiacol. Figure 4 shows the final comparison between the two chromatographic techniques monitoring the conversion of guaiacol.

Although both methods are comparable, the analysis time of the HPLC method was considerably shorter. With only 18 minutes run time, the separation and quantification was performed precisely, whereas the GC method took approximately 45 minutes to accomplish the same goal.

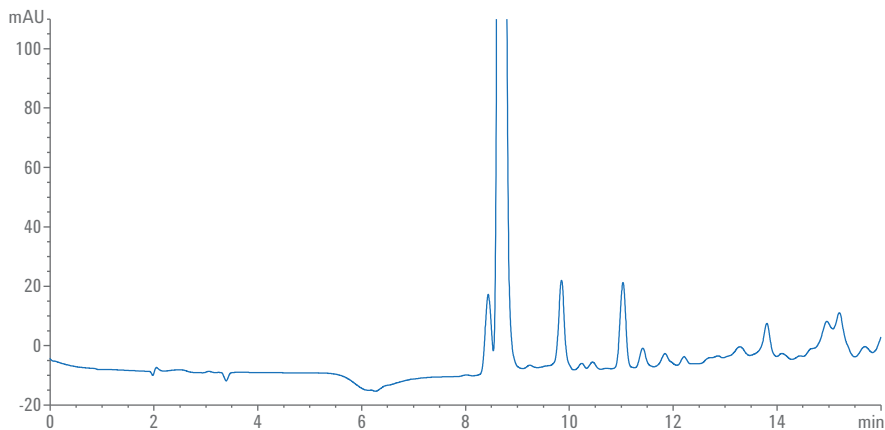


Figure 3. Magnification of the chromatogram for the RXN_07_150C sample reaction, collected at 150 °C.

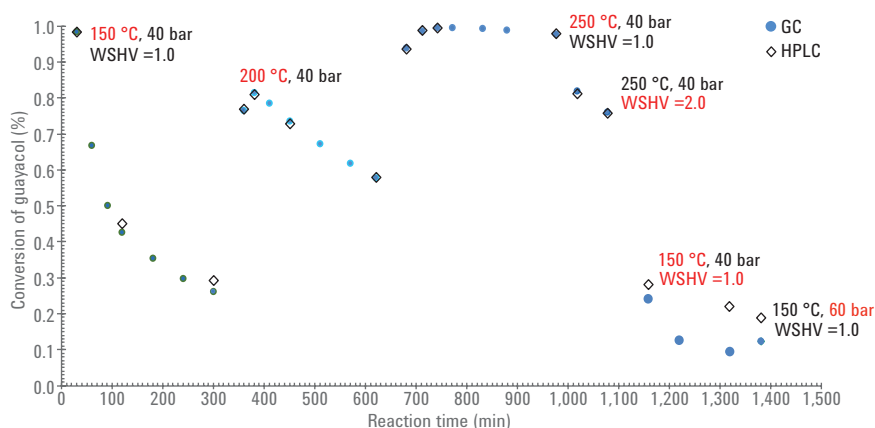


Figure 4. Comparison between LC and GC methods to monitor the conversion of guaiacol.

Conclusion

An analytical methodology for the analysis of deoxygenated compounds was developed for HPLC using a binary gradient with the Agilent 1260 Infinity II LC.

Thirteen reaction samples were collected and analyzed under the described analytical conditions to demonstrate that LC is an effective chromatographic technique for the identification and quantification of compounds involved in biofuel production. This could help increase laboratory productivity with shorter analysis times in comparison with available GC methods.

The results obtained with the LC methodology agreed with the ones obtained by traditional GC methods, confirming the variation of guaiacol conversion according to the different reaction conditions tested by researchers so far. The LC technique reduces run times, with excellent reproducibility, and uses environmentally friendly solvents. The technique can be considered an alternative approach to the identification of some of the compounds of interest currently involved in novel approaches developing alternative fuels to overcome the huge day-to-day demand on crude oil reserves.

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