Excellence in Science

Analytical and Testing Instruments for Renewable Fuels

Shimadzu's Analytical Solutions for the Renewable Fuels Industry

Biofuels from Ancient History to Today

Biofuels and bioenergy are as old as civilization itself. Solid biofuels like wood, dung and charcoal have been used ever since man discovered fire, and are still used today for cooking and heating in many communities in developing countries.

Even liquid biofuels such as olive oil and whale oil have been used at least since early antiquity. Whale oil was extensively used in the mid-1700s and early 1800s and was the fuel of choice for lighting houses.

The first cars ever built were made to function on biofuels, rather than fossil fuels. The first internal combustion engine to be patented in the US in 1826 was designed to run on a blend of ethanol and turpentine (derived from pine trees). Henry Ford designed his original 1908 Model T to run on ethanol and Rudolph Diesel intended to power his engine with vegetable oil

During World War I, there were (fossil) oil shortages, and therefore ethanol was in high demand, as it became known that ethanol could be blended with gasoline for a suitable motor fuel.

Because fossil fuels are finite, many countries are part of a global movement to produce more alternative or renewable fuels. Not to mention, they are used to reduce harmful gas emissions. From bioethanol to biodiesel, these fuels are becoming more ubiquitous at the gas stations and airport fuel facilities of the world due to governmental mandates. Producing biofuels from natural plant sources (typically corn or sugar cane based) creates production and analytical challenges.

Analytical tools such as GC, HPLC, TOC, UV/VIS, FTIR, moisture balances, and balances are necessary to research & develop new biofuels, monitor biofuel production, and determine impurities affecting the fuel's performance.

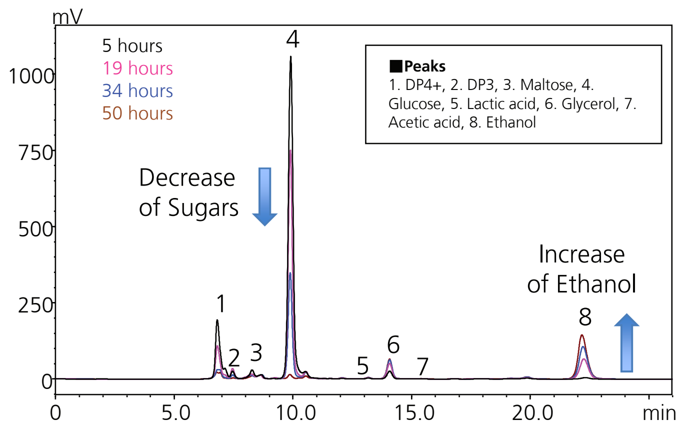
Automobile and airplane manufacturers are also researching the efficacy of these fuels. As demand for higher percentages of ethanol and biodiesel increase in the fuel supply, do these higher levels have deleterious effects on automobile and airplane engines? Material testing techniques are used to analyze and monitor for these affects.

Further complicating this situation is the argument that making fuel from corn depletes the valuable food supply for developing countries. Non-corn-based ethanol products, such as Algae, are also being researched, creating new analytical challenges.

Contents

Monitoring the Fermentation Process in Bioethanol Production

In a bioethanol production facility, High Performance Liquid Chromatography (HPLC) is typically used to profile the carbohydrate, alcohol, and organic acid contents of the fermentation broth. These aliphatic compounds display almost no ultraviolet absorbtion and therefore are detected by using a differential refractive index detector.



Checking the amount of ethanol produced by the passage of fermentation time via HPLC

Shimadzu BioEthanol Analyzer System Features

Bio Ethanol Analyzer

- Complete turnkey startup package to hit the ground running
- Ease of access integrated system
- Quick batch function simplifies batch file creation for simplified use
- Space-saving small footprint to free up bench space
- Based on the award-winning Shimadzu Prominence-i series HPLC
- Open rack access to the autosampler for convenient sample loading
- Remote monitoring for quick response to a production problem
- Closed system with back flushing capability eliminates system contamination
- Shimadzu quality hardware, software and service support, adding value to your operation

Introducing the Shimadzu BioEthanol Analyzer with the RID-20A Refractive Index Detector

Shimadzu's new BioEthanol Analyzer includes a complete turnkey system to analyze your important compounds of interest. The system includes the newest generation Shimadzu HPLC: the Prominence-i isocratic quaternary pumping system with the RID-20A Refractive Index Detector and Shimadzu's liquid autosampler. Shimadzu also includes the latest column technology with the CHATA™ solvent system.

Pumping System

The Prominence-i enjoys the flexibility of a quaternary pumping system, giving the analyst additional solvent selection capability. A valve option provides up to seven solvents for method development or system flush at shutdown, saving valuable time.

Autosampler

The i-Series autosampler features an ultra-fast (14 sec) injection cycle with ultra-low carryover (less than 0.0025%). C models have 4-45°C temperature control

Refractive Index Detector

Inheriting the stability and extensibility that are the strengths of the Prominence series, the new RID-20A reduces the time to stabilization after power-on dramatically by utilizing dual temperature control for the optical system

Column Oven

The column oven uses forced air circulation for (ambient -10) to 85°C temperature control. Ideal for bioethanol applications with a refractive index detector.

Display

Full-color LED touchscreen for front panel control with real-time chromatogram display. Remote monitoring capability from a smartphone or tablet.

Biodiesel Quality Control (FTIR)

When vegetable oil is used as the fuel for diesel cars, use of the raw fats and oils directly as the fuel causes engine problems due to high viscosity and the occurrence of deposits. Therefore, the raw fats and oils are normally converted to fatty acid methyl esters (FAME) for use as automotive fuel in an ester replacement reaction. The figure below shows overlaid spectra of FAME (derived from copra oil) and petroleum diesel measured using a horizontal ATR attachment. In the FAME spectrum, absorption due to the ester carbonyl group is clearly evident in the vicinity of 1750 cm^{-1}. Because this absorption is absent in the diesel oil, this peak can be used for quantitation of FAME in diesel oil.

Shimadzu IRAffinity-1S FTIR Spectrophotometer Features

Airtight Interferometer

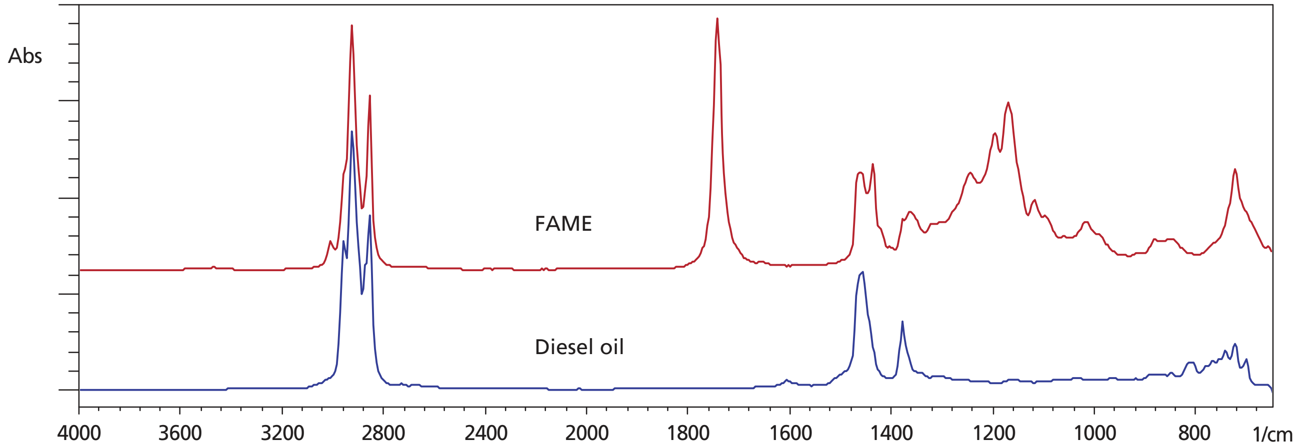
In the IRAffinity-1S, the interferometer is airtight and incorporates a unique internal auto dryer.

Dynamic Light source

Through the incorporation of a high-energy ceramic light source, a temperature-controlled, high-sensitivity DLATGS detector, a high-throughput optical element, and the optimization of the electrical system and optical system, the IRAffinity-1S achieves an outstanding S/N ratio.

Versatile FTIR

Despite its compact design, it offers full functionality for all FTIR techniques, including transmission, diffuse reflection, and attenuated total reflection (ATR). The full-sized sample compartment accommodates a wide variety of accessories to meet a diverse range of application requirements.



Infrared Spectra of FAME and Petroleum Diesel Measured with a Horizontal ATR Attachment

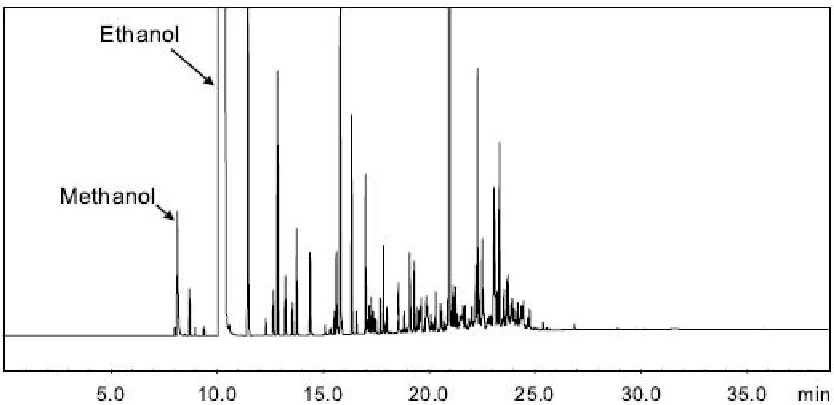
Analyzing Denaturant in Ethanol

With rising concern over the need to reduce carbon dioxide emissions as one measure for controlling global warming, bioethanol is receiving greater attention as an alternative fuel for gasoline.

In the United States, a denaturant is added to fuel grade ethanol, and the quality standard for this denatured fuel ethanol is specified in ASTM Method D4806. As part of this specification, D5501-04 specifies the measurement method and allowable concentrations of methanol as an impurity and ethanol as the principle ingredient. Furthermore, it also stipulates that gas chromatography be used for this determination of the methanol and ethanol content in denatured fuel ethanol.

Shimadzu Analysis of Ethanol, Methanol, and Denaturants Features

- Adheres to ASTM methods D4806 and D5501-04
- GC is an excellent quantitative tool for quality control
- Improved analysis times



GC Chromatogram of Denatured Fuel Ethanol Column: Rtx-1 PONA (100 m, 0.25 mm I.D. df = 0.5 um)

Shimadzu Gas Chromatograph (GC) Features

Large display
Shows most analysis details at a glance. Intelligent self-diagnostics validate the instrument before injection, which reduces unexpected downtime

Split/Splitless Injection Unit
Standard unit for high-speed analysis with a narrow bore column. The gas saver function restricts the total gas used. High-pressure injection standard.

Flame Ionization Detector
Automatic ignition and re-ignition functions are standard. By mounting an APC or solenoid valve unit, a feedback function cuts off gas supply when the hydrogen flame is extinguished. Generally used for detection of organic compounds with a hydrogen carbon bond. An optional flame monitor is available. Single and dual FIDs are available

AOC-20 Series Auto Injector
The AOC-20i auto injector and AOC-20s auto sampler are used with the GC-2014. Varying the parameters of sample injection sets the optimal injection mode. This high level of precision and repeatability is not possible with manual injection.

Monitoring Biodiesel Production

Produced by transesterification, biodiesel is comprised of mono-alkyl esters of long chain fatty acids derived from vegetable oils or animal fats. It thus differs differently from alkanes and aromatic hydrocarbons found in petroleum derived diesel. But because it is miscible with traditional diesel in all proportions, biodiesel is compatible with all existing fuel infrastructures without modifications.

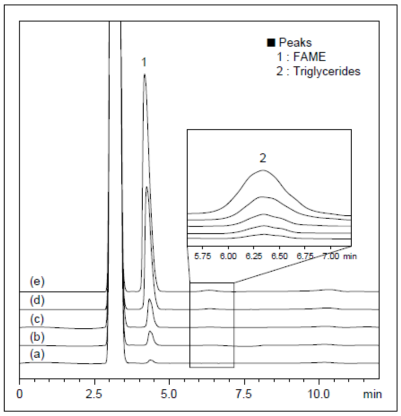
Manufacture and Analysis

The choice of feedstocks for biodiesel manufacture depends on local availability and affordability. It can be produced from waste vegetable oils, such as those used in cooking, but most commercial refiners currently consume unused oils. Refined soybean oil is the most commonly used material in the United States and Brazil. The use of other feedstocks, such as rapeseed oil, kernel and palm seed oils, and cottonseed oil, is rapidly increasing.

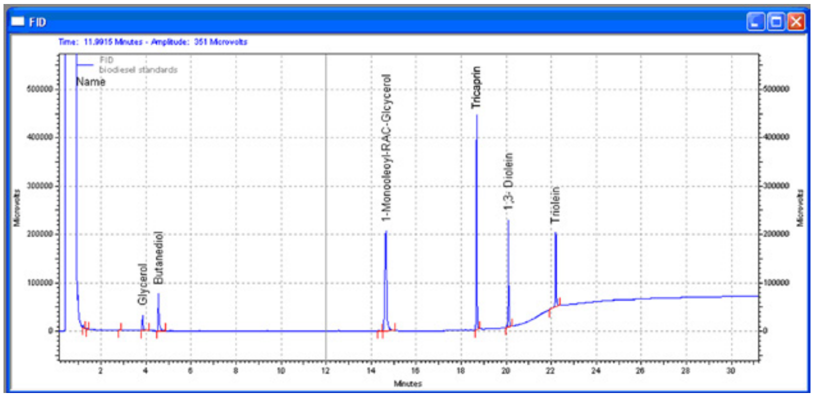
The transesterification reaction of triacylglycerols (TAGs) in oils is most commonly done by reacting TAGs with methanol in the presence of a catalyst yielding the fatty acid methyl ester (FAME). During the process, monoacylglycerols (MAGs), diacylglycerols (DAGs) and other intermediate glycerols are formed. These, along with unreacted TAGs, can remain in and contaminate the final product, and potentially cause severe engine problems.

Free glycerin, along with water, is a byproduct of fatty acid methyl ester (FAME) production. GC analysis of glycerin concentration yields an effective measure of fuel quality. Diesel fuel made from plants has the potential to contain glycerols in the form of free glycerin, mono, di and tri glycerides. These compounds have been found to be detrimental to diesel engines so must be removed prior to use.

ASTM method D6584 provides standard test method for the quantitative determination of free and total glycerin in B-100 methyl esters by gas chromatography. Also, EN14105 specifies test method for determination of free and total glycerol and mono-, di-, triglyceride contents by gas chromatography.



Biodiesel Standard Chromatogram: 1ul injection of the Supelco Free, mono, di and Triglycerides standard, level 4 concentration



Chromatograms of Biodiesel-Blended Fuel (10 uL Injected)

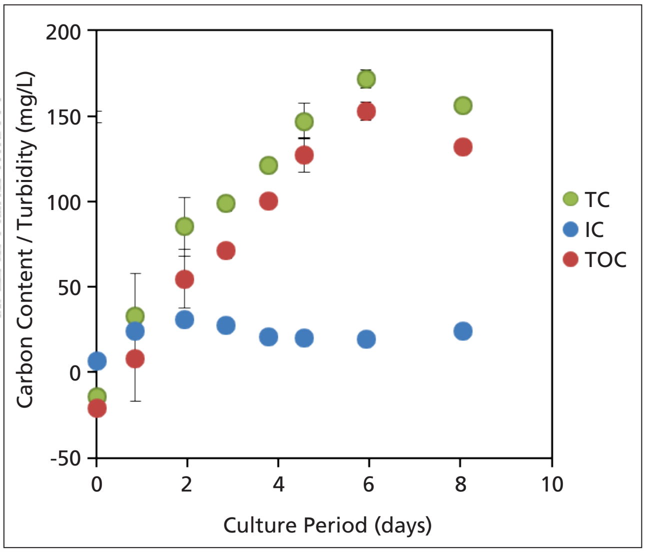
Biodiesel Quality Control Features (GC)

- Conforms to ASTM method 6584 and DIN EN 14110
- Automated reporting of free and total glycerines in biodiesel fuel
- The injection technique uses Cool on column injection (OCI) to avoid discrimination effects.

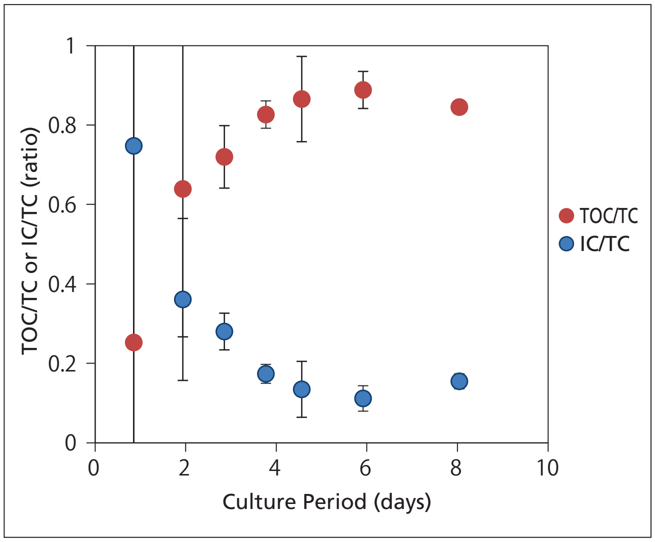
Algae as a Renewable Fuel Source

The key to algae's potential as a renewable fuel source lies in the high productivities of algal biomass that can be grown in a given area; some researchers say algae could be 10 or even 100 times more productive than traditional bioenergy feedstocks. Achieving the potential for these high productivities in real-world systems is a key challenge to realizing the promise of sustainable and affordable algal biofuels. Once harvested, algae can be readily processed into the raw material to make fuel for cars, trucks, trains, and planes.

Global warming due to the excessive use of fossil fuels is becoming a problem that has prompted and accelerated the search for alternative fuels. Among the more attractive alternatives is biomass fuel, which is attracting considerable attention. Microalgae can be used for the production of oil without competing with food production, and to a greater extent than other biofuels, its productivity per unit time and area is high, while arable land selection possibilities are great. As for the practical use of microalgal biomass, various studies have been conducted at each stage of its production, including stock selection and breeding, cultivation, harvesting, oil extraction, and purification.



Changes in TC, IC, TOC Quantity in Microalgae Cells
(Conversion value per turbidity unit)



Changes in TOC/TC and IC/TC in Microalgae Cells

The figure on the left shows the measurement results for the total carbon (TC), total organic carbon (TOC) and inorganic carbon (IC) associated with the cell mass during the culture period. The ratios of TOC to IC in the microalgae cells are shown in the figure on the right. From these results, it was possible to obtain information regarding the increase and decrease of TC, IC and TOC values associated with the microalgae cells throughout the culture process.

One essential element in the practical realization of microalgal biomass is establishment of the culture conditions, and it is clear from this study that information regarding the carbon balance can be obtained using a TOC analyzer.

Algae Application Features

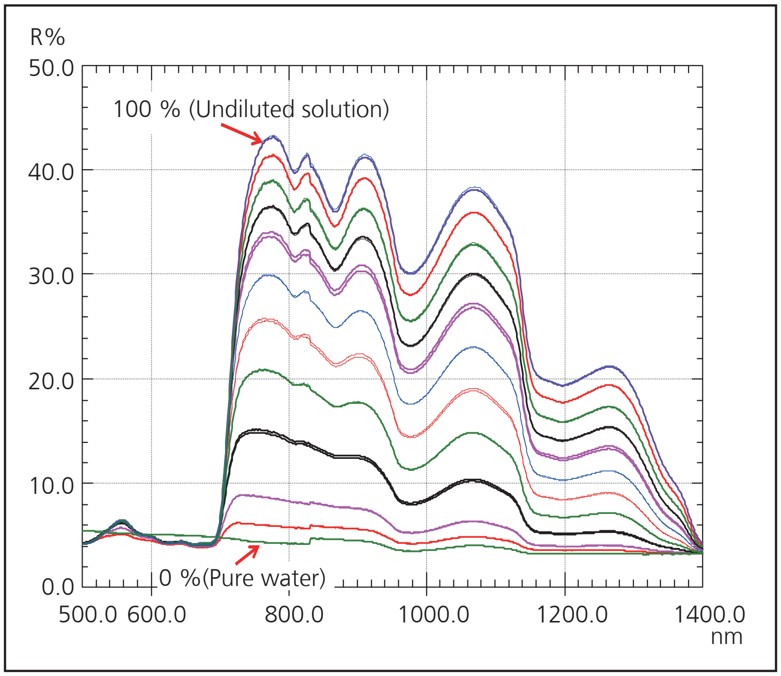
- The Shimadzu TOC-L Series Total Organic Carbon Analyzer can be used to conduct measurement of total carbon and nitrogen content in water, quantity dissolved, quantity suspended.
- Measurement of total carbon, organic carbon, inorganic carbon in water.
- Measurement of dissolved CO2 in water; thus, the TOC-L series can be utilized for such applications as the following types of microalgae research:
    - Obtain information related to the physiological state and the properties of microalgae.
    - Understand the changes in cell material with respect to changes over time in the culture and changes due to light and dark environment.
    - Understand quantitatively the carbon and nitrogen balance in the culture system.

Shimadzu TOC-L Series Total Organic Carbon Analyzer Features

- Extremely wide measurement range from 4 µg/L to 30,000 mg/L, applicable to everything from ultrapure water to highly contaminated water (TOC-LCSH/CPH)
- Reliable sample injection system
- Select from 4 models to suit your application
- Suitable for aqueous samples, as well as gas and solid samples
- Compressed air can be used as the carrier gas (with carrier gas purification kit)
- Compatible with small sample volumes (with optional kit)
- Sea water samples can be continuously measured with minimal maintenance (with combustion tubes for high salt samples)

Simple Quantitative Measurement of Micro Algae in Water

In studying micro algae, measurement of the daily growth (concentration) is important. Currently, this measurement is conducted by the dry weight method, in which the sample is filtered using filter paper, and then dried prior to weighing. However, a simpler, faster method is being sought to replace this time-consuming dry weight method. Introduced here is Shimadzu's newly developed UV micro algae analysis system, which permits simple measurement of the micro algae concentration using a spectrophotometer. Measurement of a single sample can be accomplished very quickly in about one minute using a disposable screw-cap vial (or disposable cell).



Reflection Spectra of Micro Algae in Disposable Vials

Shimadzu UV-2600 Spectrophotometer Features

- High precision spectrophotometer capable of measuring reflectance, transmittance, and so on, for a wide variety of samples - not only liquids, but also solid samples.
- High cost performance and can be used for a wide variety of analyses, including organic and inorganic compounds, measuring optical material characteristics
- Though the exterior is compact, it offers a large sample compartment able to easily accommodate a wide range of sample shapes.
- Attaching an optional integrating sphere extends the UV-2600 wavelength measurement range to include the near infrared region, from 220 nm to 1400 nm.

Table of Analytical Instruments for Renewable Fuels

	Monitor Fermetation Process	Monitor Fermetation Process	Monitor Fermetation Process	Monitor Fermetation Process	Monitor Fermetation Process	Analyzing Denaturant in Ethanol	Monitoring Bio-Diesel Production	Monitoring Bio-Diesel Production
	Sugars	Organic acids	Methanol	Ethanol	Glycerols	Methanol	Biodiesel	Glycerides, Mono, di, & tri
Gas Chromatograph (GC)		✦	✦		✦	✦	✦	✦
Liquid Chromatograph (LC)	✦	✦		✦				
UV-VIS Spectrophotometer								
Total Organic Carbon Analyzer (TOC)								
FTIR Spectrometer					✦			

	Monitoring Bio-Diesel Production	Monitoring Bio-Diesel Production	Algae as a renewable fuel source	Algae as a renewable fuel source	Algae as a renewable fuel source	Algae as a renewable fuel source	Algae as a renewable fuel source
	Faty Acid Methyl Esters (FAME)	Free Glycerin	Organic carbon	Inorganic carbon	Micro algae	Algae biomass	FAME
Gas Chromatograph (GC)	✦	✦					✦
Liquid Chromatograph (LC)							
UV-VIS Spectrophotometer					✦		
Total Organic Carbon Analyzer (TOC)			✦	✦			
FTIR Spectrometer	✦					✦	✦

UniBloc Family of Balances




Shimadzu Corporation
www.shimadzu.com/an/

Shimadzu Scientific Instruments
7102 Riverwood Drive, Columbia, Maryland 21046, U.S.A.
Phone: 800-477-1227/410-381-1227, Fax: 410-381-1222
www.ssi.shimadzu.com