Biofuels are receiving an everincreasing amount of attention from both commercial refiners and the general public, as they are considered to be new and alternative energy resources, and will contribute to secure energy on the earth.

These alternative products are manufactured from biomass, which is organic matter such as wood, plants, and organic wastes. Unlike other renewable energy sources, biomass can be converted directly into liquid fuels. These biofuels are being researched and developed as direct replacements for petroleum-based fuels and as additive partial replacements (admix) to “stretch” existing petroleum reserves and reduce overall dependence on fossil fuels.

At this time the leading biofuels are bioethanol added to or substituting gasoline, and biodiesel fuels substituting light oils.

"Bioethanol" is the ethanol (ethyl alcohol) produced by fermentation of the sugar contained in, for example, sugarcane, or of the starch in, for example, corn, or of cellulose from, for example, rice straws or woods.

"Biodiesel" is the fatty acid methyl ester (FAME) or other compounds similar to light oil, produced by chemical treatment to, for example, rapeseed oils, waste food oils, palm oils and sunflower oils.

Bioethanol has two types when it is mixed with gasoline for transportation purposes; direct mixing with gasoline, and addition to gasoline as ETBE (Ethyl Tertiary-Butyl Ether) produced from ethanol and iso-buthene.

In the U.S. and Brazil, which produce large amounts of corn and sugarcane, two of the raw materials widely used to produce bioethanol, the use of bioethanol fuel is, in line with policies related to energy and exhaust emission, becoming increasingly widespread. In recent years, the use of biodiesel has been promoted in EU countries, which are the main producers of rapeseed oil, one of the raw materials used to produce biodiesel. Moves aimed at promoting the widespread use of these biofuels are gaining pace all over the world.

The real key to getting the accuracy desired in biofuel production is proper analytical instrument configuration as well as the training and support for the personnel who will use it.

Shimadzu offers application supports responding customers’ demands in different regions by application chemists working at customer support centers of the regional headquarters in the USA, Germany, Turkey, Brazil, India, China, Singapore, and Japan.

This brochure will provide an overview of biofuel development, and Shimadzu analytical instruments used in quality control and general research.
Bioethanol and Biodiesel (BDF) used in the world

Shimadzu Products responding to Biofuel Specifications and Specified Test Methods

**Bioethanol**

<table>
<thead>
<tr>
<th></th>
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</thead>
<tbody>
<tr>
<td>Inorganic Chloride</td>
<td>(Potentiometric)</td>
<td>(Potentiometric)</td>
<td>NBR10894 (IC), (Potentiometric)</td>
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<td>Ethanol</td>
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<td>EC/2870/2000 (GC)</td>
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<td>Methanol</td>
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<td>NBR10894 (IC) (Potentiometric)</td>
<td>JAAS*001, 6.4 (GC)</td>
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<td>Sulfate</td>
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<td>NBR11331 (AA)</td>
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<td>Iron (Fe)</td>
<td>-</td>
<td>-</td>
<td>NBR10893 (AA)</td>
<td>JIS K0101 51.2 or 51.2 (AA)</td>
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<td>Copper (Cu)</td>
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**Biodiesel**

<table>
<thead>
<tr>
<th>Country/Area and Specification</th>
<th>USA ASTM D6751 (FAME)</th>
<th>EU EN14214 (B100) FAME</th>
<th>Brazil ANP 42/2004 (B100)</th>
<th>Japan JASO M360 for NEAT 2007 (FAME to blend)</th>
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<tbody>
<tr>
<td>Ester</td>
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<td>EN14103 (GC)</td>
<td>EN14103 (GC)</td>
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<td>Linolic acid methyl ester</td>
<td>-</td>
<td>EN14103 (GC)</td>
<td>-</td>
<td>EN14103 (GC)</td>
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<td>Methanol/Ethanol</td>
<td>-</td>
<td>EN14110 (GC)</td>
<td>EN14110 (GC)</td>
<td>JIS K2536, EN14110 (GC)</td>
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<tr>
<td>Mono-, Di-, Tri-glycerides</td>
<td>ASTM D6584 (GC)</td>
<td>EN14105 (GC)</td>
<td>ASTM D6584 (GC)</td>
<td>EN14105 (GC)</td>
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<tr>
<td>Free glycerin</td>
<td>ASTM D6584 (GC)</td>
<td>EN14105/14106 (GC)</td>
<td>ASTM D6584 (GC)</td>
<td>EN14105/14106 (GC)</td>
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<tr>
<td>Total glycerin</td>
<td>ASTM D6584 (GC)</td>
<td>EN14105/14106 (GC)</td>
<td>ASTM D6584 (GC)</td>
<td>EN14105/14106 (GC)</td>
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<td>Na + K</td>
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<td>EN14108/14109 (AA)</td>
<td>EN14108/14109 (AA)</td>
<td>EN14108/14109 (AA)</td>
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<td>Ca + Mg</td>
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<td>Phosphorous</td>
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<td>EN14107 (ICP)</td>
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</tr>
</tbody>
</table>

*Japan Alcohol Association Standard*
Bio-Ethanol Applications

From Feedstocks to Freeways - Overview
Ethanol, or ethyl alcohol, is a high-octane fuel produced from the fermentation of plant sugars. Corn is the primary feedstock for ethanol production in the United States. Ethanol is also produced from other organic sources such as barley, wheat, rice, sorghum, sunflower, potatoes, cassava and molasses. Outside North America, sugar cane and sugar beets are the most common feedstocks. It can also be produced from wild grasses, wheat straw and other organic matter currently considered wastes, such as rice straw, timbering waste, and plant leaves and stalks. E-5 (5 percent ethanol/95 percent gasoline) and E-10 are the most widely available ethanol blended gasoline for retail purchase for transportation, but auto fuel blends up to E-85 are produced. (Operating on E-85 requires a specially manufactured “flexible fuel vehicle” (FFV).)

Manufacture and Analysis
Quality control testing via laboratory analysis is typically conducted on feedstocks, inprocess materials, and end products. High-performance liquid chromatography (HPLC) is commonly used to analyze materials during the fermentation process to monitor the breakdown of starch molecules in glucose, then the conversion to ethanol.

One of typical methods for certifying the quality of fuel ethanol is ASTM D5501 covering the determination of the ethanol content of denatured fuel ethanol by gas chromatography (GC). This test method does identify and quantify methanol but does not purport to identify all individual components that make up the denaturant.

The quality of the gas chromatograph is determined by the consistency of its temperature programming and its ability to accurately control the carrier gas flow. The data determines three critical values: the methanol peak, the ethanol peak and the sum of all other peak areas (the denaturant). From these areas it is possible to calculate the mass response corrected area percentage of these components.

For the production of mainstream passenger car fuels, such as E-10, ASTM method D4806 specifies Standard Specification for Denatured Fuel Ethanol for Blending with Gasolines for Use as Automotive Spark-Ignition Engine Fuels. This specification covers nominally anhydrous denatured fuel ethanol intended to be blended with unleaded or leaded gasolines at 1 to 10 volume percent.

Flow of Bio-ethanol Production

Quantitative analysis of heavy metal components such as iron (Fe) and copper (Cu) can be conducted by Atomic Absorption spectrophotometer.

AA-6300 Atomic Absorption Spectrophotometer
Quantitative analysis of heavy metal components such as iron (Fe) and copper (Cu) can be conducted by Atomic Absorption spectrophotometer.

MOC-120H
Electronic Moisture Balance
Moisture content of dry distiller grain, a bi-product of bio-ethanol can be measured.
Typical chromatogram of denatured ethanol finished product (fuel-grade) for GC analysis
(Data prepared by Shimadzu Scientific Instruments, USA)

Gas Chromatograph is used for the quantitative analysis of methanol, ethanol, and denaturant based on ASTM D5501/D4805 and other standard test methods.

HPLC is commonly used to analyze materials during the fermentation process to monitor the breakdown of starch molecules in glucose, then the conversion to ethanol. Shimadzu HPLC is used in more than 100 bioethanol plants in the U.S.A.

Chromatogram of standard mixtures for maltose, succinic acid, lactic acid, glycerol, acetic acid, and ethanol, used for fermentation monitoring by HPLC
(Data prepared by Shimadzu Scientific Instruments, USA)

Chromatograms of denatured ethanol (red) and the same sample spiked with 1ppm chloride and sulfate.
(Data prepared by Shimadzu Scientific Instruments, USA)

Ion Chromatograph is used to analyze chloride ion (0.5-50mg/kg) and sulphate ion (0.5-20mg/kg) in bioethanol for quality control.
Bio Diesel Applications

**Biodiesel Is Booming - Overview**
Produced by transesterification, biodiesel comprises mono-alkyl esters of long-chain fatty acids derived from vegetable oils or animal fats. It thus differs structurally from the 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 major modifications. In the retail consumer market it is typically blended at levels from 2 to 30 percent and named for that percentage (B5, for example, is 5 percent biodiesel/95 percent conventional diesel.) It can also be used in its pure form, referred to as B100.

**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. Rapeseed oil is preferred in Europe, while countries in Southeast Asia utilize abundant palm kernel and palm seed oils. India and China are developing jatropha (physic nut) plantations, and the use of 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 production. GC analysis of glycerin concentration yields an effective measure of fuel quality. 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.

**Synthetic reaction route**

![Synthetic reaction route diagram](image)

**Comparison of mineral oil against rapeseed biodiesel by FTIR spectra.**
(Data prepared by Shimadzu Europe, Germany)

IRPrestige-21 Fourier Transform Infrared Spectrophotometer
Shimadzu IRPrestige-21 and ATR attenuated total reflection measurement attachment provides simple and smart analyses of biodiesel components using optional PLS software.
GC-2010 Gas Chromatograph
GC-2010 is optimized for fast and efficient analysis in quality control and for process optimization as well as improved detection limits. More than 35% of quality control laboratories of biodiesel manufactures in Europe use Shimadzu GC, based on our survey.

ICPE-9000 Inductively Coupled Plasma Spectrometer
Quantitative Analysis of trace elements such as phosphorus (P), sulfur (S), sodium (Na), potassium (K), calcium (Ca), and magnesium (Mg) can be conducted by Inductively Coupled Plasma Spectrometer (ICP).

Prominence HPLC System with RID detector
HPLC is used for determination of fatty acid methyl esters and triglycerides in biodiesel blended fuel.

Typical biodiesel chromatogram pattern from DIN EN14105 by GC
(Data prepared by Shimadzu Europe, Germany)

<table>
<thead>
<tr>
<th>Element</th>
<th>EN14214 Specifications</th>
<th>ICPE-9000 Detection</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca</td>
<td>Ca+Mg ≤5mg/kg</td>
<td>0.00002 mg/kg</td>
</tr>
<tr>
<td>Mg</td>
<td>Na+K ≤10mg/kg</td>
<td>0.00002 mg/kg</td>
</tr>
<tr>
<td>Na</td>
<td>Na+K ≤10mg/kg</td>
<td>0.001 mg/kg</td>
</tr>
<tr>
<td>K</td>
<td>Na+K ≤10mg/kg</td>
<td>0.001 mg/kg</td>
</tr>
<tr>
<td>P</td>
<td>≤10mg/kg</td>
<td>0.02 mg/kg</td>
</tr>
<tr>
<td>S</td>
<td>≤10mg/kg</td>
<td>0.07 mg/kg</td>
</tr>
</tbody>
</table>

Spectra for Ca and Mg and level of quantification for heavy metal components in biodiesel by ICP (Data prepared by Shimadzu Corporation, Japan)

Chromatogram of standard mixture of Methyl stearate and Trilinolein by HPLC
(Data prepared by Shimadzu Corporation, Japan)
Shimadzu Overseas Customer Support

To support customers engaged in biofuels research and quality assurance, Shimadzu has established a global service network incorporating customer support, training and service centers in the USA, Germany, Turkey, Brazil, India, China and Singapore, as well as in Japan. Shimadzu provides comprehensive support services including instrument maintenance, training workshops and the provision of relevant information to meet customer needs regarding both software and hardware.

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