NREL Advances in Technology at the National Renewable Energy Laboratory

Technology Brief

TMBMS Beams Up Instant Analysis

NREL Takes Sophisticated Research Tool on the Road

In Colorado, researchers used it to compare emissions from a diesel engine burning biodiesel (diesel substitute made from oils derived from plants such as soybeans and rapeseeds) to the same engine burning conventional diesel fuel.

In Ohio, and again in Illinois, researchers used it to continuously monitor the chemical species produced by the gasification of plant materials to make fuels such as methanol or to generate electric power.

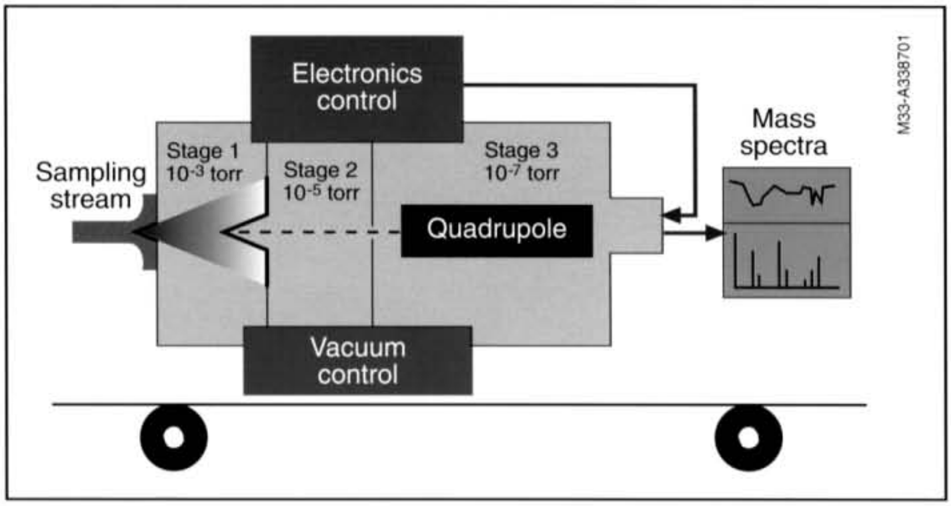
The innovative technology that was so helpful to these research projects is the prototype transportable molecular beam mass spectrometer (TMBMS) developed by the National Renewable Energy Laboratory (NREL). Without it, each of these research projects would have had to rely on batch sampling—in which analysis is done after the fact and there is risk of altering samples in the process of collecting them—or settle for monitoring only certain chemicals. In explaining the capabilities of TMBMS, NREL researcher Matt Ratcliff uses the analogy that gas chromatography of batch samples is like a color photograph and a single-gas continuous emission monitor is like a black-and-white video, but molecular beam mass spectrometry is like a full-color video.

PIX #1387, Mike Linenberger, NREL

The transportable molecular beam mass spectrometer connected to a diesel engine to determine the composition of exhaust gases. The main vacuum chambers and pumps are in the center. The sampling orifice is connected to the engine by the silver sampling line at top, right of center. Further right are the computer and data acquisition system.

NREL scientists developed the TMBMS because molecular beam mass spectrometry is such an integral part of the development of several highly promising thermochemical conversion technologies at this U.S. Department of Energy research facility, and they saw the tremendous potential value of a portable version. One of NREL's conversion technologies is selective pyrolysis, which recovers individual original building block chemicals from mixtures of waste plastics. Another is vortex-reactor fast pyrolysis, which turns wood or other biomass into an oil from which adhesives, fuel oil, refinery feedstocks, or fuel additive ethers can be made. These process development projects rely on the instantaneous, complete, and precise identification of reaction products, and molecular beam mass spectrometry effectively provides this information so researchers can set conditions and select catalysts to obtain the desired products.

Now, with the TMBMS, NREL is able to share this capability with other researchers such as those at the Colorado Institute for Fuels and High Altitude Engine Research (CIFER) in Denver, Colorado; the Battelle Laboratory in Columbus, Ohio; and the Institute of Gas Technology (IGT) in Chicago, Illinois. Using the TMBMS for continuous emission monitoring, the CIFER research team found that biodiesel emissions have



Schematic of the transportable molecular beam mass spectrometer system. In stage 1, the pressure of the sample vapor stream drops dramatically, causing it to undergo free-jet expansion and adiabatic cooling. In stage 2, the core of the expanded sample is collimated by an orifice of 1.0–1.2 mm to form the molecular beam. In the mass spectrometer, the molecules of the beam are ionized and mass analyzed.

significantly lower levels of a variety of complex and troublesome hydrocarbons, confirming some of the air quality benefits of this promising alternative fuel.

In the arena of thermochemical conversion processes, the TMBMS is playing a key role in developing biomass gasification technologies that convert plant material to synthesis gas, which can then be burned to generate power or be transformed to liquid fuels such as methanol. Battelle and NREL researchers were able to rapidly identify exactly which tars (undesired larger hydrocarbon molecules) were being produced by the gasification process and develop catalysts to destroy those tars. IGT tested synthesis gas cleanup technology for biomass gasification at the scale of 10 tons of feedstock per day.

For both thermochemical conversion research and continuous emission monitoring, a key advantage of molecular beam mass spectrometry is that it detects the chemical effects of short-duration events such as the rapid acceleration of an engine or a momentary upset in the feed rate of a chemical process. It can also identify intermediary compounds before they change to the final product. NREL uses molecular beam mass spectrometry in its solar detoxification research. Future continuous emission monitoring uses might include industrial stacks and hazardous waste incineration. The prototype TMBMS can be used now under cooperative arrangements, and, in the future, NREL will be seeking an industrial partner to develop the TMBMS for production.

Instantaneous, Full Spectrum Analysis

Molecular beam mass spectrometry works by continuously measuring the mass of molecules in a gas stream. To do this, the TMBMS uses a three-stage vacuum system. The TMBMS extracts the sampled gases and vapors through a small nozzle into the first chamber, expanding and cooling them in the process. These expanded gases and vapors are collimated (caused to flow in a straight molecular beam) as they pass through a second nozzle into the second vacuum chamber. Entering the third chamber, the molecules pass through an electron cloud and

Same Charge, Different Masses

How do you tell the chemical composition of gaseous molecules in a high-temperature, high-pressure gas? You (1) keep the molecules from reacting with each other by expanding them into a vacuum and cooling them rapidly, (2) put an electrical charge on the molecules by knocking an electron off each molecule, (3) take advantage of the distinct mass-to-charge ratios that the different ions now have to either screen out one ratio at a time or distinguish them on the basis of their speed, (4) count the number of ions with various masses, and (5) match the various masses to the appropriate chemical compounds.

Because the molecules each have a charge of one (under normal operating conditions, after having an average of one electron knocked off), but their masses vary by compound, their mass-to-charge ratios also vary by compound. The different mass-to-charge ratios make it possible for the different compounds to be separated and distinguished by mass spectrometry. Of NREL's two prototype transportable molecular beam mass spectrometers, one uses a quadrupole mass spectrometer and one a time-of-flight mass spectrometer. The quadrupole uses radio frequency and electrical fields that are electronically controlled to sweep the fields one mass-to-charge ratio at a time, excluding all but molecules of a particular mass that pass through to be counted. The time-of-flight spectrometer distinguishes among different mass-to-charge ratios by pulsing the generation of ions and measuring how long it takes them to reach the detector.

Comparison of TMBMS with other Analyzers

	TMBMS	Gas Chromatography/ Mass Spectrometry	Gas Analyzer
Continuous On-Line Monitoring	**Yes**	**No,** takes batch samples that are analyzed in minutes.	**Yes**
Multiple Component Analysis	**Yes**	**Yes**	**No,** requires a specific analyzer for each species.*
Detection of High-Molecular-Weight Vapors	**Yes**, detects species up to 750 amu with quadrupole mass spectrometer, 2000 amu with time-of-flight spectrometer.	**Yes,** but only those species that separate within the temperature limits of the given column, generally <350 amu.	**No,** limited to permanent gases and light vapors.
Direct Sampling from High-Temperature, Particulate-Laden Gas Streams	**Yes,** up to at least 2000°C.	**Yes,** but limited by seals in sampling system; filtering required; get condensation in the gas chromatograph.	**No,** sample needs to be cooled to less than 150°C and filtered to protect analyzer.
Fast Response Time (<10 seconds to enable detection of transient events)	**Yes,** 0.1–1.0 seconds, depending on scan range.	**No,** requires 2–20 minutes for sampling and analysis.	**Yes**

* A few newer instruments can analyze multiple species, but only if all the species have low mass.

are ionized (charged) before entering the mass spectrometer. The ionized molecules of the various compounds in the beam now have distinct mass-to-charge ratios, allowing them to be distinguished and counted by either of two mass spectrometer technologies (see sidebar on previous page for basic explanation).

By sampling the emissions or product vapors directly from an engine, an incinerator, or a thermochemical process, as they are produced, molecular beam mass spectrometry examines the actual chemicals generated. There is little time for those chemicals to degrade, react with each other, or react with whatever sampling device might be used to capture them. Short-term phenomena are captured, and analysis is nearly instantaneous—no waiting for samples to come back from the lab.

Molecular beam mass spectrometry also identifies the full spectrum of compounds from simple hydrogen gas to complex polynuclear aromatics (molecular weights of 2 to 750 with the quadrupole spectrometer, 2 to 2000 with the time-of-flight spectrometer). Other analytical devices can have lower limits of detection or perhaps measure more precisely, but only if they are limited to a few predetermined chemical compounds. Molecular beam mass spectrometry can identify many chemical compounds at the same time. It can also handle high-temperature, high-pressure, moist, or particulate-laden emissions or product streams. It is ideal for investigating processes such as thermochemical conversion and incineration, for which it is important to know all the compounds being generated, as they are generated.

Similar Performance and Cost—One Fifth the Size

There are, however, only 20 or 30 molecular beam mass spectrometers in the world. These each required permanent, custom installation of \$300,000 to \$500,000 worth of equipment, plus liquid nitrogen, chilled water, and three-phase electrical connections. Molecular beam mass spectrometry has—until now—been a major investment that was not practical for short-term projects nor movable from one project to another.

To make this powerful analytical technology more accessible, NREL scientists reduced the size and weight of the equipment to about one-fifth of that previously required. Power consumption was also cut in half. NREL's prototype TMBMS weighs only about 500 kg (1100 pounds) and requires only an electrical connection. Most of the TMBMS equipment fits on a 1-meter by 1.6-meter (39" by 63") rolling cart, so it can be readily transported by truck or moving van and set up at a new location.

To reduce the size of the TMBMS—without sacrificing quality—NREL scientists developed an innovative layout for the vacuum chambers and took advantage of a newly available, compact, molecular drag pump developed for the semiconductor industry. The TMBMS has custom-built vacuum chambers, but most of the other equipment used, including the mass spectrometer itself, is available commercially. If it is necessary to distinguish between two chemical species with the same molecular weight, two additional quadrupole mass spectrometers are needed, but otherwise the TMBMS performs equally well as a permanent installation in all aspects.

TMBMS Specifications

Response Time	1 second (less if scan range is limited)	
Mass Range	2–750 atomic mass units (quadrupole) 2–2000 atomic mass units (time-of-flight)	
Dynamic Range	1 million	
Sample Stream Range:		
Pressure	Subambient to 30 psig	
Temperature	To 2000°C (with cooling of sampling nozzle)	
Representative Detection Limits		
Phenol	3.1 ppmv	11.2 ppmv quantification
Napthalene	0.6 ppmv	2.6 ppmv quantification
Phenanthrene	1.3 ppmv	4.5 ppmv quantification
Pyrene	0.6 ppmv	2.8 ppmv quantification
Weight	500 kg	
Equipment Cost	$300,000	

The Door is Open

NREL scientists are continuing to improve and test the TMBMS with an eye toward working with an equipment manufacturer for commercial production. They also continue to find valuable new uses for it. In the meantime, NREL will make the two prototypes available to other researchers under cooperative agreements. Molecular beam mass spectrometry is a powerful analytical tool that creates new opportunities for research on thermochemical conversion and emissions monitoring. By making this powerful analytical tool portable, TMBMS makes a highly valuable resource available to a wide range of researchers.

Publications

Dayton, D.C.; French, R.J.; Milne, T.A. (1994). "Identification of Gas-Phase Alkali Species Released During Biomass Combustion." *Proceedings of the Sixth National Bioenergy Conference, Sparks/Reno, NV, October 1994.* Golden, CO: Western Regional Biomass Energy Program; pp. 607–614.

Ratcliff, M.A.; Milne, T.A.; Graboski, M.S. (1993). "On-Line Hydrocarbon Emissions Speciation by Molecular Beam Mass Spectrometry." *Proceedings of the 1993 Diesel Emission Reduction Workshop, University of California, San Diego, CA, July 1993.* U.S. Department of Energy, Office of Transportation Technologies; pp. V:11–V:31.

Nimlos, M.R.; Jacoby, W.A.; Blake, D.M.; Milne, T.A. (1993). "Direct Mass Spectrometric Studies of the Destruction of Hazardous Wastes 2: Gas Phase Photocatalytic Oxidation of Trichloroethylene Over TiO_2: Products and Mechanisms." *Environmental Science and Technology.* (27:4); pp. 732–740 .

Agblevor, F.A.; Rejai, B.; Evans, R.J.; Johnson, K.D. (1992). "Pyrolytic Analysis and Catalytic Upgrading of Lignocellulosic Materials by Molecular Beam Mass Spectrometry." *Proceedings of the 16th Conference on Energy from Biomass and Wastes, Orlando, Florida, March 1992.* Chicago, IL: Institute of Gas Technology.

Evans, R.J.; Milne, T.A. (1987). "Molecular Characterization of the Pyrolysis of Biomass: 1. Fundamentals." *Energy and Fuels.* (1:2); pp. 123–137.

Evans, R.J.; Milne, T.A. (1987). "Molecular Characterization of the Pyrolysis of Biomass: 2. Applications." *Energy and Fuels.* (1:2); pp. 311–319.

For More Information

General Information and other NREL Technology Briefs:
Technical Inquiry Service
(303) 275-4099
rubin@tcplink.nrel.gov

Technical Information on this NREL Project:
Matt Ratcliff (303) 384–6129
ratclifm@tcplink.nrel.gov

NREL Business Information:
Technology Transfer Office
(303) 275-3008
technology_transfer@nrel.gov

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