Biofuels and their Precursors – A Challenge for Common Elemental Analyzers

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In times of steadily increasing prices for the decreasing oil resources, alternative strategies for the production of liquid fuels become more and more of interest. Since fossil fuels are evolved by transformation of different organic materials under high pressure and temperature, in oxygen-free atmosphere, scientists decided to use this matter too as starting point. While technologies based on fermentation of starch and sugar, and transesterification or hydrocracking of plant and animal oil – 1st generation biofuels – are not yet able to satisfy the enormous needs of high-performance fuels, other approaches, based on the conversion of cellulose-rich biomass and waste, seem to be more promising – 2nd generation biofuels. With the use of biogenic materials for fuel production, their inherently high content of harmful nitrogen, sulfur and chlorine-containing hydrocarbons has to be monitored. This is not only due to the adherence of given legal limits, but also to avoid negative effects on the production process and environment. Because of this, a strict checking of the feed stocks, intermediates, and final products is inevitable. As different as the origins of such matrices are, as different is their digestion behavior. To ensure the quantitative combustion of all sample components is the precondition for a correct elemental analysis. In the past this was a real time-consuming challenge, requiring experienced operators to develop for each sample matrix a specific boat program. And still then there was frequent need for maintenance interventions and repeated measurements.

The innovative flame sensor technology makes all this redundant. For each matrix, the most sufficient digestion program is fully automatically generated and applied to receive trustable results as fast as possible.

There is more than Bio Ethanol

For nearly a century, mankind has dealt with the development of economic alternatives to liquid mineral fuels. The first stage was applying materials, which were different from classic fuels but with comparable properties.

Untreated refined vegetable oils behave like diesel, but their use requires an adaptation of the engine. Biodiesel (FAME) is gained by transesterification, Green diesel by hydrocracking of vegetable oil or animal fat. Their properties are equivalent to the common diesel fuel, which makes them quite suitable as blend components. Bio ethanol is a product of fermentation of sugar- or cellulose-rich plants. It is either used as additive for gasoline up to 85 % or pure, as fuel for special FFV – flexible fuel vehicles. Today a demand covering production of these 1st generation biofuels is not possible due to the limited sources for feed materials.

Besides that other attempts, which try to convert solid cellulose-rich biomass directly by fermentation, pyrolysis, or use of special catalysts into bio crude oil (BCO), a mix of liquid hydrocarbons, are promising. The BCO is nearly similar to the mineral crude oil, which allows processing it in common refineries. The resulting fuels can be used directly in normal cars without risk of damages. The required feed materials are available everywhere. These 2 advantages make the biofuels of the 2nd generation, so attractive.

But independent of which feed material a biofuel was made of, there is always the need for checking for undesired pollutants. Compounds containing sulfur, nitrogen and chlorine can lead to catalyst poisoning, rapid corrosion of extraction, transportation and storage equipment, and low quality fuels. Production processes are monitored and controlled by means of the analysis of raw materials, intermediates and final products. As diverse as the digestion behavior of these matrices is, as diverse are their element contents. They vary between a few ppb and mass percent.

In quality assurance every minute counts. This is why an elemental analyzer that delivers fast reliable results, independent of concentration and matrix properties, is essential.

Therefore, the analysis technique used, should not only provide an adjustment-free wide linear operation range, but also allow for fully automatic optimization of the combustion process for a safe and complete digestion.

Flame Sensor Technology

Without an optimal digestion, the quality of results may vary widely depending on method settings and sample quantity introduced. This effect is caused by the complexity and composition of the matrix.

Conventional elemental analysis systems require exact prior knowledge of each samples digestion behavior to enable a time consuming, empiric method development. A slight change of sample composition resp. the introduced sample quantity will affect the completeness of the combustion process remarkably. That results in untrustworthy, in a wide range scattering, usually too low analysis results.

Unlike this the multi EA® 5000 enables the operator to run samples immediately, without prior knowledge of their composition, boiling points etc.. The quality of results achieved is independent of matrix properties. The secret behind this is the innovative flame sensor technology, which is ensuring the fully automatic process optimization. Thus saving valuable operation time and allowing a far higher sample throughput.

Quantitative Combustion is not a dream anymore

The function of the flame sensor creates ideal digestion conditions for any organic sample matrix. Just one single method for solids or liquids is enough to analyze the full spectrum of sample matrices, independent of their viscosity, volatility, and combustibility.

The different biofuels and precursors were analyzed for their nitrogen, sulfur and chlorine content by means of an elemental analyzer of the type multi EA® 5000. Thanks to modern HiPerSens detection, it combines an unattained wide and linear operation range with unique sensitivity and robustness.

Fig. 1: multi EA® 5000 – analysis system with flame sensor technology

The analyses have been run in horizontal operation mode. The samples were dosed into boats fully automatically by means of a multi matrix sampler. Transfer into the furnace was done with the aid of an automatic boat drive. The samples were digested in a catalyst-free, biphasic process at 1050°C. Thereby the flame sensor technology ensures a trouble-free and matrix-optimized transfer and combustion of the different materials.

In the first phase, the evaporation of volatile sample components in inert gas stream followed by the combustion of the formed gaseous products in an oxygen rich atmosphere, takes place. In the second phase the remaining none volatile components are quantitatively oxidized in pure oxygen. Thereby the flame sensor ensures a uniform evaporation of exactly the sample quantity, which can be oxidized completely by the available O_2 molecules. For this purpose the formed combustion flame is monitored. The registered flame values are used to calculate an optimum digestion program for each matrix, including a sufficient number of waiting points, minimized waiting times, and maximized speed. That is used to adjust the process fully automatically to the specific requirements of each individual component. So not only the quality of analysis is optimized, but also its duration.

The dried gaseous reaction products were transferred into the relevant detection systems, for sulfur – UV fluorescence, respectively for nitrogen – chemoluminescence. Chlorine determination was carried out by means of micro coulometric titration.

Measurement of Biofuels and Selected Precursors

For the determination of sulfur, nitrogen, and chlorine the analyzer was calibrated with certified standard kits on basis of isooctane. Thanks to the multi element mode, all parameters were determined in just one single analysis cycle.

The examined samples are a representative spectrum from the field of biofuel production. Because of the matrix-optimized combustion, a threefold determination is normally sufficient.

Table 1: Results of elemental analysis

No.	Sample	TS ± RSD	TN ± RSD	TCl ± RSD
1	BCO* (crop plants)	0.40 wt-% ± 0.42 %	0.41 wt-% ± 0.62 %	23.4 ppm ± 3,32 %
2	Corn oil	20.3 ppm ± 1.92 %	54.2 ppm ± 0.18 %	8.82 ppm ± 1,10 %
3	BCO* (wood)	0.22 wt-% ± 3.15 %	0.21 wt-% ± 0.65 %	38.4 ppm ± 0.88 %
4	Crude tall oil	0.36 wt-% ± 0.61 %	99.91 ppm ± 2.89 %	8.36 ppm ± 0.97 %
5	B-t-L** Diesel (wood)	5.33 ppm ± 1.57 %	0.38 ppm ± 2.57 %	< 0.10 ppm
6	Diesel (tall oil)	6.60 ppm ± 1.64 %	0.12 ppm ± 8.60 %	< 0.10 ppm
7	Bio Diesel (corn oil)	0.87 ppm ± 2.83 %	2.00 mg/kg ± 2.30 %	< 0.10 ppm
8	Bio ethanol (cellulose)	0.73 ppm ± 1.83 %	0.06 ppm ± 11.2 %	0.56 ppm ± 11.2 %

* BCO = bio crude oil, ** B-t-L = bio mass to liquid

Samples 1 – 4 are highly viscose and polluted feed stock and process materials. The samples 5 – 8, pure biofuels, are volatile liquids with low viscosity. As final products their content is naturally in trace level. Figure 2a – 2c show the measuring curves for the crude tall oil (CTO).
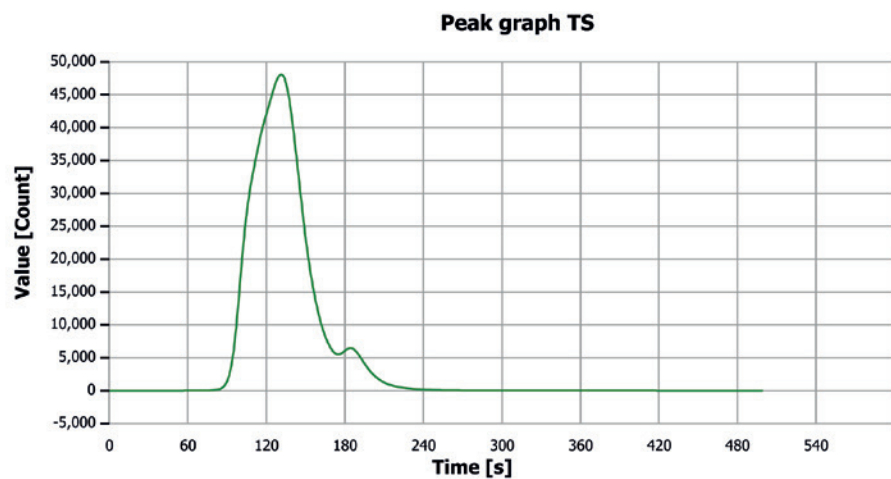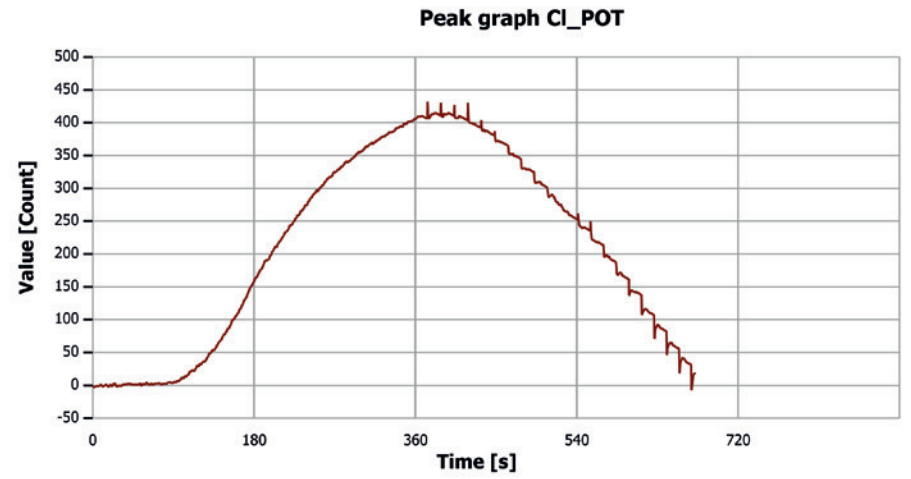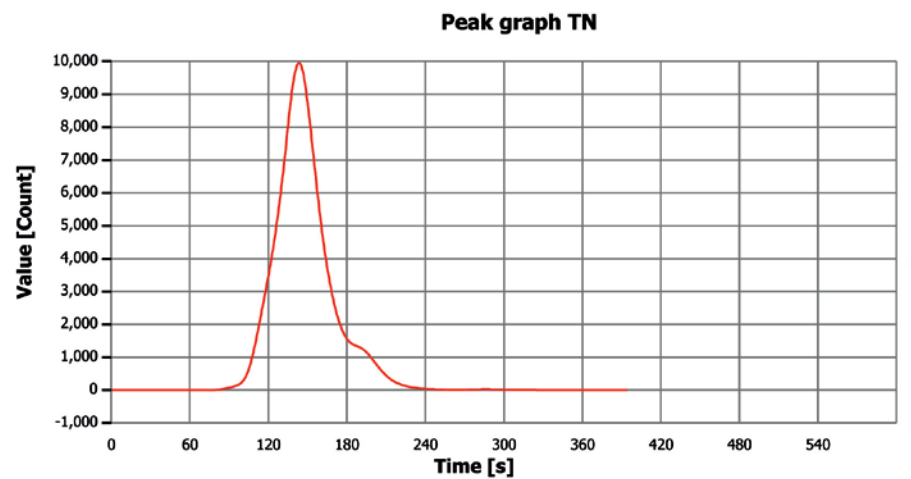

Fig. 2a

Fig. 2b

Fig. 2c; 2a-2c show Elemental analysis curves for CTO

The analysis results proof, that the applied technique offers an excellent degree of precision, independent of matrix properties.

New Matrices – New Challenge

Quality assurance is constantly striving to achieve maximum efficiency with lowest possible effort. In case of biogenic materials, this requires elemental analyzers which can ensure sufficient digestion of all sample components. In the past this was a real time-consuming challenge, requiring experienced operators to develop a specific boat program for each sample matrix. And still then there was frequent need for maintenance interventions and repeated measurements.

Now flame sensor technology makes all this redundant. For each matrix, the most sufficient digestion program is generated fully automatically.

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