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# biofuels
## plant & technology



*Cover:* The BP Rotterdam refinery's (BPRR) ETBE unit revamped, with only minor changes to existing equipment, to produce ETBE based on etherification of isobutylene and bio-ethanol. BPRR is the first refinery in The Netherlands to produce biofuels with this revamped unit.

*Photo courtesy of BP and CDTech*

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# PTQ Biofuels roundtable

**The biofuels industry continues to expand as a result of government regulations and high crude oil prices compelling the need for a wider variety of fuel and energy sources. Rapid developments in biofuel technology are needed to achieve capacity targets and quality specifications, as discussed by several industry experts who responded to the following questions developed by PTQ. Details of recently posted biofuels and clean fuels Q&A dialogue are posted on PTQ's website (www.eptq.com)**

*In the area of biofuels production, what are some of the most important developments that will increase capacity of biofuels (e.g. catalysts, reactor technology, improved pre-treatment stages, etc.)?*

**Paul O'Connor, director science & technology, BIOeCON, paul.oconnor@bio-e-con.com:** The most important factors hindering a significant increase in the amount of biofuels produced are economical: the availability and costs of raw biomass, which can be processed to renewable fuels.

The first generation of biofuels (biodiesel from vegetable oils and ethanol from sugar, starch or corn) are rather limited in supply, and costly, and one may ask the question if it really makes sense to 'downgrade' these scarce and high-value edible materials to transportation fuels. The story is different for the second generation of biofuels, which makes use of the more abundantly available cellulosic biomass waste. Several new technologies are being developed to unlock these large and low-cost sources of biomass energy.

Cellulosic ethanol can be produced via enzymatic conversion once the solid cellulose is separated from lignin and opened up and made more accessible to the enzymes. There are several ongoing projects to develop pre-treatment processes in this area. Unfortunately the separation of ethanol from water remains a costly factor, while ethanol volatility may limit the quantity that can be blended into the gasoline.

An alternative is to convert the solid biomass into a gas and produce a synthesis gas ($CO + H_2$), which can then be converted to a liquid via the Fischer-Tropsch process. This is often called biomass-to-liquid (BTL) via gas-to-liquid (GTL). Although this can work, it requires several complex process steps and is quite expensive in investment and energy.

A more simple and robust approach (in terms of feedstock flexibility) is to convert the solid biomass into a liquid (BTL) by direct liquefaction. Several thermal and thermo-catalytic processes are under development in this area. A drawback is that the quality of the biocrude produced is often rather poor, and extensive (hydro) treatment and upgrading is required in order to produce the right components for transportation fuels and/or chemicals.

An interesting new approach in this respect is catalytic pyrolysis of biomass, whereby catalytic technology is used to achieve the liquefaction of the solid biomass under milder conditions and at a lower cost. The technology is similar to fluid catalytic cracking (FCC) and therefore will require less time to commercialise than most other schemes. An economical comparison of the various routes is provided in the attached table (Table 1).

**Economic comparison of various first- and second-generation biofuels process routes, including catalytic pyrolysis of biomass**

| | $/Boe | $/GJ |
|---|---|---|
| **Crude Oil** | 60 | 10 |
| **Ethanol** | | |
| Sugarcane (Energy = biowaste) | 54 | 9 |
| Sugarcane (Energy = fossil) | 90 | 15 |
| Cellulose | 120 | 20 |
| **Diesel** | | |
| Biodiesel from Jatropha | 156 | 26 |
| BTL via GTL | 110 | 18 |
| **Bio-Crude (via direct BTL)** | | |
| Pyrolysis or Hydrothermal (HTU) | 72 | 12 |
| Catalytic Pyrolysis | 60 | 10 |

Boe: Barrel of Oil equivalents GJ: Giga Joules

**Table 1**

*What instrumentation and analytical systems are available to ensure that high-volume biofuels production conforms to regulatory specifications in markets such as Europe and North America?*

**Oliver Sauer, director marketing & sales, Grabner Instruments Messtechnik GmbH, oliver.sauer@ametek.at:** As the content of biofuels within gasoline and diesel is on the rise, manufacturers of analytical instrumentation are striving to meet the standards for analysing biofuels. Biofuels used for combustion engines are biodiesel and bioethanol. The following discussion lists some of the instruments amenable to ensure regulatory specifications and new standards evolving around the new applications.

**Biodiesel**

ASTM D6751-07a is the standard specification for biodiesel fuel blendstock (B100) for middle distillate fuels in the USA. The Grabner Instruments IROX-Diesel can determine the concentration of biodiesel according to D6751-07a in diesel fuel from 0 to 40 volume per cent (0-40 vol%) using FT-IR spectroscopy. The measurement method is under evaluation within the ASTM committee and will become a standard method within the year 2008 (new standard test method for determination of biodiesel [fatty acid methyl esters: FAME] in diesel fuel oil using mid-infrared spectroscopy). The actual draft is available within the ASTM (WK10753).

In addition to the determination of total biodiesel, the IROX uses a math model to separate overlapping peaks for deriving the content of FAME, FAEE and even higher alcohol esters within the biodiesel fuel blend.

While the vapour pressure of biodiesel blends is not significantly influenced, even by small amounts of free alcohols, the flash point of biodiesel drops dramatically from 120°C down to 60°C with only some tenth of weight per cent (0.10 wt%) of free methanol. With a new standard method currently worked on for available instruments, the flash point of pure biodiesel can be controlled.

Distillation is a common quality check for fuel distillates.

Biodiesel tends to push up the distillation curve towards higher boiling points, especially in the T50 region. This can be verified with the MiniDIS in a fast, D86-compliant, true atmospheric distillation. The MiniVis VIS445, a viscometer applying the rolling ball principle, automatically monitors the viscosity of fuels and its temperature dependence in a wide range. Viscosity measurements will always complement routine quality checks of fuels.

**Bioethanol**

For bioethanol in gasoline the following standards apply: ASTM D4806-06c is the standard specification for denatured fuel ethanol for blending with gasoline for use as automotive spark-ignition engine fuel. ASTM D5798 is the standard specification for fuel ethanol for automotive spark-ignition engines. ASTM D5798 covers standards E75 to E85.

The IROX 2000 can determine the concentration of ethanol in gasoline fuel up to 20 vol%, improving continuously. The second derivative of the peaks at 1091 per centimeter (1091/cm) and 1050/cm are used for the calculation. The use of the second derivative ensures the elimination of offsets and drifts in the IR spectrum of the ethanol blended gasoline. With dilutions, which factors that can be automatically accounted for by the instrument, it is possible to assess higher concentration ranges.

It is known that ethanol blending affects the vapour pressure behaviour of gasoline. While actually the vapour pressure of pure ethanol is much lower than that of gasoline, molecular effects are increasing the vapour pressure of the gasoline in blends up to 25%. Therefore, vapour pressure needs to be thoroughly checked and reported for ethanol-blended gasoline. Almost 50% of such fuels around the world are tested with the MiniVAP VPS. The ASTM method D6378 is especially suitable as no air saturation and chilling is required, that interfere with these molecular effects.

Distillation curves of ethanol-blended fuels tend to show a plateau around the azeotropic boiling point of 78°C. The plateau extends to the point where all of the azeotropic mixture, consisting mostly of ethanol, is distilled over. It is virtually consistent with the alcohol content. Then the distillation curve increases sharply towards the end boiling point of gasoline determined by its heavier components. The MiniDIS allows for a good resolution of this distillation behaviour.

**Analytical instrumentation outlook**

We expect a shift in the analytical instruments market. With the worldwide push for more environmentally friendly fuels and mandates to blend biofuels into regular petrofuels, there is an ever-increasing demand for checking the quality of the biofuel subjected to blending and also the blends, especially with regard to monitoring the concentration. Companies are now beginning to adapt and extend their standard instruments for such new applications. Specific new standards will soon be released to the market.

**Olaf Schulz, product manager, ICP Spectrometers, Spectro Analytical Instruments GmbH & Co. KG, olaf.shulz@amatech.com:** To allow precise, and accurate measurement of elemental species in bio-extenders and final blended biofuels, the use of Spectro XRF and ICP-OES technology has been developed to meet the current and future needs of the petroleum industry for alternative fuels such as biofuels.

The polarised ED-XRF analysers include an excitation and detection system, comprising a low-power x-ray tube, combined with a C-force polarisation optical system, ensuring optimal excitation of the elements in the sample. The limit of detection exceeds below 1.0mg/kg for sulphur level for

biofuels and extenders using Spectro iQ II. In addition, the instrument is able to provide measurement of phosphorous at the sub-10mg/kg in petroleum and biofuel matrices. Spectro Phoenix II exhibits a limit of detection for sulphur of 1.5mg/kg, used for screening in the range of 10-15mg/kg and when blending biofuels at higher levels.

However, to fully enable the lab to measure at the precision and accuracy for the key Group I & II metal elements such as Ca, Mg, K & Na, along with phosphorous, the only solution is the use of inductively coupled plasma optical emission spectrometry (ICP-OES).

In order to further enhance detection limits for Na and K, an application incorporating addition of oxygen and argon to the ICP gases has been developed. This reduces spectral interferences by the removal of carbon and carbon compounds by oxidation and enhances the signal-to-background ratio (SBR) by creating excitation conditions, particularly favourable for these elements. With Spectro Arcos, limit of detection (LOD) for the spectral lines of Ca, K, Na, Mg and P in the µg/kg range are achieved.

The use of XRF and ICP-OES allows the biodiesel producer to utilise a time- and cost-effective analytical tool to ensure optimum process conditions and control levels of undesirable levels of key elements that are specified in EN 14141 and other global standards for biofuel extenders.

*Can you comment on process technology developments that will make ethanol production more competitive?*

**Katharina Harlander, marketing manager, Vogelbusch GmbH, hak@vienna.vogelbusch.com:** Bioethanol is a price-sensitive product that has to compete with gasoline. Consequently, the industry is keen to bring down production cost. There are a number of technology trends focusing on the main impacts on production cost: the raw material and the energy cost.

One evident target is the broadening of the raw material basis. Additional grain types like rye and barley as well as waste starch and residues from gluten extraction are taken into account and research advances are made for the use of cellulosic materials as a carbohydrate source in a number of pilot applications around the globe.

Further improvements include process simplification by integration of process steps (e.g. integration of saccharification and fermentation) and combining bioethanol production with processes for further byproducts from grains (e.g. gluten from wheat).

A reduction of energy cost can be gained by process optimisation and circulation of process streams (stillage recirculation and increase of alcohol concentration in fermentation). On the engineering side, a considerable reduction of thermal energy consumption can be obtained from thermal (heat) integration on the level of single process steps and on the plant as a whole, including:

- Multi-effect evaporation units for stillage concentration
- Evaporation units with mechanical vapour compression
- Thermal integration of distillation and dehydration thermal integration of distillation and evaporation
- Multi-pressure systems with split mash and rectification column
- Thermal integration of stillage drying with evaporation.

Other aspects of process development include:

- More complex distillation systems for separation of fermentation byproducts owing to high quality criteria, especially in Europe
- Alternative methods for stillage processing, such as incineration and anaerobic gasification
- Waste water reduction by using stillage recirculation and the use of treated waste water in utilities (cooling towers) and even process purposes.

*What fuel additives are being developed as the industry seeks to maintain stability in hydrocarbon fuels blended with various percentages of biofuels?*

**Rob Davidson, global business manager, fuel additives, Afton Chemical, rob.davidson@aftonchemical.com:** Two different classes of additives are needed to maintain stability of biodiesel fuels. The first class is additives that prevent decomposition of the biodiesel fuels. These additives include antioxidants, stabilisers, metal deactivators and biocides. In most cases, these additives are used in the neat biodiesel fuel and often must be added shortly after the neat biodiesel is produced to provide maximum efficacy. The second class of additives is used to mitigate potential problems resulting from decomposition of the biofuel. These additives typically are multifunctional packages containing a diesel dispersant, and are added to the blended fuel. The multifunctional package can provide a wide variety of performance benefits including water shedding, foam reduction and fuel injector cleanliness.

**Malcom Rose, worldwide marketing communications manager, Infineum UK Ltd, malcom.rose@infineum.com:** The fuels industry is currently in a period of tremendous change, with the introduction of low-sulphur fuels as well as biofuels. With the changes also come a lot of challenges in uncharted territories. On top of the large variety of petroleum crudes, in come a large variety of biofuel streams, particularly in the area of biodiesel.

The source of biodiesel feedstock expanded rapidly, due to supply-demand balance and cost, from the originally widely used rapeseed oil to palm oil, soy oil, sunflower oil, used kitchen oil, animal fats and their blends. Jatropha and algae have now also attracted commercial interests. This diversity created many potential challenges in the manufacturing of quality fuels, such as:

- Introduction of highly saturated FAME into diesel fuels that have stretched CFPP targets, requiring highly advanced novel cold flow additive technologies
- Putting highly unsaturated FAME into diesel fuels could lead to higher levels of injector deposits, particularly in EURO V engines, which require advanced new detergent additive technologies to minimise the impact of deposits
- The unsaturation present in FAME, especially those that contain significant percentage of polyunsaturated esters, could give rise to issues related to oxidation, such as filter blocking, sediments and deposits. Specialised new stability improvers are designed to alleviate these problems
- A number of FAMEs could also lead to filterability problems, at well above cloud point temperatures, when blended into diesel, due to the presence of impurities in the natural products. Development of specialised additives could help to bring biodiesel quality in line with that of ULSD
- FAME, with higher saturations, increases difficulty in handling, storage and transport. Advanced biodiesel flow improvers can help to reduce the constraints and cost of handling these materials.

*Prediction of blending indices and characterisation of fuel components has increased in complexity with the blending of biofuels and certain additives (e.g. cetan improvers). How can blending indices be accurately computed to improve fuel recipe quality while reducing re-blends?*

**Dirk Schmalzried, product manager, OR Soft Jänicke GmbH, dirk.schmalzried@orsoft.de:** The task consists of the following six aspects:

**1.** Creation of a reliable model on behaviour of considered quality indices of a blend: If nothing is known about the

non-linear mathematical correlations, those models could be created, such as by means of neural networks (especially radial basis function networks). Those neural networks will be trained with collected values of the past and could be used to complete the model with so-far unknown combinations. Besides neural networks, mathematical interpolation methods can also be used. This will result in a reliable model and recipes for blending with non-linear components.

**2.** Linearising of models: Functions and recipes can nevertheless be – at least partially – linearised by using mathematical methods. This offers the advantage that linear optimisation can be additionally utilised to help solve (optimise) the blending task. Now, margin maximisation with respect to cost reduction as the objective function can be pursued in addition to the objective recipe quality during daily operative planning. The rule to linearise the function is described by less than 10 parameters in applications known to OR Soft and therefore has little complexity in practice.

**3.** Identification of cost-optimal blends: Blending optimisation is used to ascertain cost-optimal blending recipes with regard to all orders known of different target products. Available intermediate product batches will be used at their optimal quantity, so that the margin overall target products to be produced will be maximised. All hard constraints, such as restricted percentages of components in the target product, will be considered. For instance, conventional diesel in the European Union must currently contain a minimum of two per cent (2.0%) and a maximum of five per cent (5.0%) of biodiesel (fatty acid methyl ester- FAME). Further constraints relate to the maximum marketable quantity in the rough-cut planning or to the facility's capacity limit in the detailed planning. Permissible intervals for every single type of fuel are determined as part of the quality specifications. Threshold for incoming batches (i.e. minimum quantities per blend) will be introduced into the model if parts of the blending facility are not connected via pipelines to storage tanks, but are supplied by tank trucks.

**4.** Capacity reliable schedules: Advanced planning and scheduling software such as OR Soft's Manufacturing Workbench allows scheduling in terms of reliable capacity consumption of additionally computed blends with regard to available resources, throughputs and tank storage.

**5.** Achieve robustness with respect to analysis deviation: So-called robust optimisation can help to avoid additional re-blending cycles, because data uncertainty (lab analysis result of a sample) will be integrated into the optimisation method. The robust optimisation approach allows for several uncertainties of sample quality indices and determines a blending recipe that is robust against such perturbations. Practical tests show that results of robust optimisation are only slightly worse, while the probability of necessary re-blending considerably declines.

**6.** Ascertain variants of the optimisation results (what if): Besides the optimisation of recipes against an objective function (profit maximisation, cost-reduction), further sub-optimal recipes with certain soft constraints are of interest in practice. Such soft constraints are, for example, a high number of completely emptied tanks (i.e. bought flexibility) or a low number of utilised components (i.e. saving of resources). Therefore, a comparison of several recipe variants with comparable target products is desired at decision-making. Software systems offer the opportunity to quickly visually compare several blending recipes in terms of their objective function and certain soft constraints of interest.

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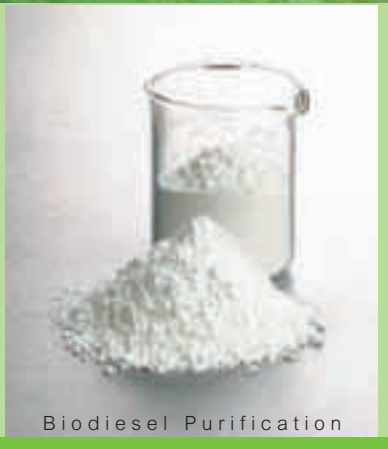

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# Biofuel feedstock: is there enough?

**A wider variety of feedstocks needs to be considered for biodiesel production. Processing costs and undesirable byproduct formation are the reasons for considering entirely new technical routes**

Rene Gonzalez
*PTQ*

The future availability of biomass feedstock for renewable fuel processes is currently the most significant issue in the biofuels industry. The agri-energy industry is bumping up against limits to the amount of ethanol (for gasoline) and FAME (for biodiesel) that can be produced with first-generation biofuels technology. This is not because governments and industry groups are unwilling to support expansion of these 'green fuels'; there is simply a finite supply of corn and sugar cane (for ethanol production) and vegetable oils (for FAME biodiesel production).

In addition to government incentives promoting biofuels expansion worldwide, free market incentives are developing for scale-up of technology that can process other types of bio-organic feedstocks, such as lignocellulose and algae. At this stage in the development of these second-generation biofuel processes, the ability to process a wider diversity of bio-organic feedstocks into fuels will play a key role in determining which technology will succeed, as will be discussed in more detail in the following articles.

The various biomass feedstocks used for producing biofuels can be grouped into two basic categories. The first is the currently available first-generation feedstock, which comprises various grain and vegetable crops. These are harvested for their sugar, starch or oil content and can be converted into liquid fuels using conventional technology. By contrast, the next-generation (or second-generation) biofuel feedstock comprises cellulose-rich organic material, which is harvested for its total biomass. These fibres can be converted into liquid biofuels only by advanced technical processes, many of which are still under development. Promising energy crops include fast-growing woody crops.

Research into the conversion of cellulosic-based feedstock into fuels via gasification and other processing routes are evolving out of academia and into venture capitalist- and corporate-funded scale-up and pilot plant projects. The stakes are very high, but the potential rewards are even higher. Scepticism remains among many in the industry as to whether second-generation biofuels can ever be produced without government subsidies and high energy and resource consumption, as has been experienced with first-generation biofuels processes for ethanol production.

In the refining industry clean fuels evolution, there were doubts up until the late 1990s that zero-sulphur gasoline and diesel could ever be produced cost-effectively. Similar doubts have emerged concerning the viability of second-generation biofuels technology. In comparing the biofuels evolution with the clean fuels evolution, both "parallel" events have converged. More importantly, the next two or three years are critical for demonstrating the cost-effectiveness of second generation-based biodiesel technology.

## Challenges

Generally speaking, a commercial biofuels plant requires large amounts of biomass to exploit the advantages of economy of scale. The available biomass potential and cost is therefore a prerequisite for economic evaluation of a biofuel plant location. Take, for example, the cost to build a biodiesel plant in the USA, where 250 million gallons of biodiesel were produced in 2006. With a long-term goal set by the Bush administration to produce 1.4 billion gallons per year (gpy) of biodiesel, it stands to reason that high levels of plant investment are to be expected. Most likely, these new facilities would have a nameplate capacity in excess of 20 million gpy to achieve economies of scale, employing a continuous production process over a batch process.

These new facilities would be located in areas where they are well integrated into the current fuel supply and distribution network (e.g. close to rail and barge facilities). But there is concern about the availability of feedstock at this level of production (1.4 billion gpy). Also important to consider is that since the biodiesel industry is relatively new, there really are few, if any, long-term feedstock supplier agreements that have been put into place.

It is interesting to note that total 2006 diesel consumption (i.e. conventional diesel and biodiesel combined) in the USA market was 40 billion gallons. Therefore, the previously mentioned 250 million gallons of biodiesel consumption in 2006 represents only 0.625% of the total diesel volume – obviously a small, if only symbolic, contribution to the fuel matrix. The compelling argument is that this small contribution from biodiesel to the total overall diesel pool lowers emissions of unburned hydrocarbons, CO and zero-sulphur. In spite of processing costs and certain biodiesel quality concerns (e.g. cloud point and cold weather properties), proponents point to the increasing amount of research for mitigating these issues and developing alternative feedstocks such as algae, as opposed to fatty acid-based feedstocks (e.g. vegetable oil and animal fat oils). For example, FAME biodiesel processing costs increase with higher levels of free fatty acid (FFA).

Another very important cost consideration with regard to biodiesel production is the dispensation of glycerin byproduct. In the transesterification process for the production of biodiesel, oils and/or fats rich in triglycerides are mixed with an alcohol such as methanol and base such as potassium or sodium hydroxide, resulting in a methyl ester biodiesel stream and a glycerine side stream. This glycerine side stream typically contains a mixture of glycerine, methanol, water, inorganic salts (catalyst residue) free fatty acids, unreacted mono-, di-, and

triglycerides, methyl esters and a variety of other matter organic non-glycerol (MONG) in varying quantities. The methanol is typically stripped from this stream and reused, leaving behind, after neutralisation, what is known as crude glycerine. In raw form, this crude glycerine has high salt and free fatty acid content.

Consequently, crude glycerine has few direct uses due to the presence of the salts and other species, and its fuel value is also marginal. The industry generates millions of gallons of crude glycerin waste each year, and the amount produced is growing rapidly along with the dramatic growth of biodiesel production. Much has been said about upgrading glycerin for use in the cosmetics and pharmaceutical industry. In addition, other potential routes for adding value to glycerine are being considered, such as for use as cattle feed. With glycerine byproduct currently valued at $0.04 per pound in the USA market, as opposed to $0.08 per pound for corn-based feed, it would appear to be a viable alternative.

## Feedstock diversity and quality

Along with the previously noted shortages in certain types of biofuel feedstocks, variations in feedstock quality are apparent processing challenges. This will become even more exacerbated as other biomass sources are exploited. This is why gasification of biomass into synthesis gas, followed by Fishcer-Tropsch gas-to-liquids (GTL) technology is being considered as one of the most important processing routes for future expansion of biofuels production if the costs can be reduced. The conversion of biomass, such as lignocellulosic material (i.e. wood) into biofuels is complicated and not yet a commercial business, but the trends towards commercialisation are evident.

One major advantage with gasification is the wide range of biomass resources available, ranging from agricultural crops, dedicated energy crops to residues and organic wastes. While all of these types of feedstocks surely have a wide variation in quality, their gasification is quite standardised and yields a homogeneous product. This makes it possible to choose the feedstock that is the most available and economic at all times. While a detailed review of the gasification process is beyond the scope of this discussion, gasification is basically the process of gaseous fuel production by partial oxidation of a solid fuel, such as cellulosic biomass.

## Biofuels politics and trends

From Canada to South Africa, government announcements on renewable fuels regulations are a significant global trend. For example, South Africa's cabinet approved a biofuels industry strategy that proposes an average biofuels market penetration of 4.5% of the liquid road transport fuels by 2013. It would require nationwide blending of 8% ethanol and 2% biodiesel. This would allow the country to domestically produce approximately 40% of its fuel supply through renewables, coal, synfuels and crude oil production.

The Philippines is moving towards implementing renewable fuels in the nation's fuel supply. The bicameral Congress of the Philippines recently passed a bill that will require ethanol and biodiesel. Within two years of becoming effective, the bill requires at least 5% ethanol shall comprise the total annual volume of gasoline sold and distributed in the country. Within three months of becoming effective, a minimum 1% by volume biodiesel shall be blended into all diesel engine fuels sold in the country. That volume could be increased to 2% within two years.

The Canadian federal government will require 5% renewable content in gasoline by 2010 and a 2% content in diesel fuel and home heating oil by no later than 2012.

The United States' current renewable fuels standard was set at 7.5 billion gallons by 2012 in the Energy Policy Act of 2005. European Union biofuel standards and regulations have been well discussed over the past few years in the trade press, and will be further discussed in several of the articles to follow in this issue of *Biofuels*. The most important piece of legislation for biofuels in Europe is the Biofuels Directive (Directive 2003/30/EC). It aims to promote the use in transport of fuels made from biomass, as well as other renewable fuels. The directive sets a reference value of 5.75% for the market share of biofuels in 2010, measured in terms of energy content.

## Opportunities

The recent pace of advancement in technology, policy and investment suggest that the rapid growth of biofuel use could continue for decades to come and that these fuels have the potential to displace a significant share of the oil now consumed in many countries. A recent study found that advanced biofuel technologies could allow biofuels to substitute for 37% of USA gasoline within the next 25 years. The biofuel potential of EU countries is said to be in the range of 20-25%. Other regions, such as in the tropics, show promising opportunities for exploiting of their biomass resources into fuel and energy products.


## Biomass conversion – a key technology of the future

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# Agri-energy: the new technology frontier

**Supply chain complexities and technology for managing risk in biofuels production and trading. Systems deployed to manage risk in agri-energy should aggregate risk factors across multiple commodities from the agriculture and energy side of the equation**

Michael Schwartz
*Triple Point Technology*

In the wake of the various UN publications on the impact of climate change, the subject of biofuels has entered public debate. The terms of that debate have largely been confined to impact on climate change and food production, but the new alliance of agriculture and energy ushered in by the new emphasis on biofuels will also have a serious impact on participants in the commodities and energy markets.

When the International Energy Agency (IEA) announced last June that it predicted an oil crunch in five years' time it was yet another boost to the biofuels industry. It may not be known when fossil fuel supply will reach its peak, or indeed, if it has already done so, but it is known that biofuels will form a large part of the world's energy mix in the future.

## Estimating the global biofuels market

The world's biggest energy consumers have given strong indications on how seriously they take moves to wean us from our addiction to fossil fuels. The 2007 State of the Union address saw President Bush call for a 20% reduction in the USA's use of gasoline in the coming decade, with renewable and alternative fuels to account for three quarters of that reduction.

The Chinese government has pledged $200 billion to be spent on renewable energy over the next 15 years, while the EU has committed to a 20% boost in renewable fuel use by 2020.

The actions of governments have been reflected by the financial markets, which have experienced a rapid response to the new political and economic realities. Nearly nine billion dollars was invested in clean energy by venture capitalists and private equity firms in 2006.

These political and financial statements confirm that the old order is changing. But that is about all that can be confirmed. The precise form of the biofuels industry, the agriculture sectors that will support it, and the markets in which the commodities and their derivatives will be traded are far less clear-cut. While traders are happy to predict that carbon is destined to become one of the biggest markets in the world, when it comes to the new agri-energy business, the predominant sentiment among market participants is more akin to 'suck it and see'.

## Winners, losers or equal partners in fledgling industry?

To talk about the biofuels industry is to give it a heterogeneous, monolithic status that does not accurately convey the current fractured nature of the sector. This fledgling business raises many questions, not least of which is what the main refined fuels and raw materials are likely to be.

Brazil, where cars powered by bioethanol have been seen on the crowded streets of Sao Paulo for decades, is pushing sugar as a prime raw material for its production. This is unsurprising, since it is an abundant and easily grown native crop, whose properties are proven in this field.

The USA, on the other hand, is likely to see a market that is dominated by bioethanol derived from corn, if only for political reasons and the strength of the corn-growing lobby.

These two countries are the behemoths of biofuel manufacture. Between them they represent more than two-thirds of the world's ethanol production. As a result they are likely to dominate the space, at least in the short term. But other parts of the globe are looking to their own indigenous crops and are catching up with the lead taken in the Americas. In Malaysia, palm oil is being used to create biodiesel, while European nations are investigating the possibilities of their wheat crops as potential sources of fuel. Even forestry, a prime candidate for the manufacture of solid biomass, can be converted to ethanol through secondary processing.

Biodiesel itself, derived from animal or vegetable oils, is an attractive proposition for investors since it is something of a known quantity: the first-ever diesel engine was designed to run on peanut oil. On the other hand, cellulosic biofuel, manufactured from prairie grasses, among other crops, is being produced only at pilot and commercial demonstration scale and is therefore still too much of a leap in the dark for many.

Although it is in the manufacturers' interest to present a Manichean choice, it is far more likely that there will be a diverse mix, protected by government policy, rather than one dominant fuel or fuel source, particularly given the sensitivity of the market.

## New players and strange bed fellows

However the complexity of the market, in terms of inputs and end product, is almost overshadowed by the pattern of interrelated competitive and collaborative partnerships that characterise this emerging sector.

Unsurprisingly, familiar names from more traditional energy sectors appear with some frequency. Among those trying to gain a leadership role are the USA's ConocoPhillips, the Chinese CNOOC and Brazil's Petrobras, all of which are taking advantage of existing and potential natural, infrastructure and economic resources available to them. BP and Royal Dutch Shell have long promoted their own development of renewable alternatives to their staple petroleum products, and it can be expected that most major fossil energy companies will follow suit.

But these energy giants are likely to be joined by businesses whose background is in agricultural, rather than hydrocarbons, and who have identified significant expansion opportunities in growing energy crops.

Investment has begun, and has attracted some eyebrow-raising partners. Monsanto and BASF are working

together and jointly funding a $1.5 billion genetic seeds venture, to develop traits that increase yields and hardiness from corn, soybean, cotton and canola.

Meat producer, Tyson Foods Inc, is joining forces with ConocoPhillips to make biodiesel for transportation from beef, pork and poultry byproduct fat. Other companies getting into the game include chemicals giant Dupont, while agricultural processor Archer Daniels Midland continues to hold its central position in the US biofuels sector.

Financial institutions with commodity desks are also joining the fray, adding their particular ingredients to an already complex mix. That's the old school. But the sector will also see a number of completely new startups dedicated to producing bio-ethanol and biodiesel and hoping to take advantage of a move away from oil, gas and coal.

## Key trading technology requirements

Ethanol is already traded on the Chicago Board of Trade, and it's safe to say that the number of exchanges accepting biofuel derivatives is set to grow.

However, prices of these commodities will inevitably correlate with the price of fossil fuels. Biofuels become less financially viable when the price of fossil fuels drops. In addition, the price of food crops and their derivatives will be pegged to those of energy equivalents. The tight demand and supply situation, and ongoing tensions between food crops and energy crops also means that market volatility – already approaching 35% for both corn and wheat – can be expected to increase.

Any technology deployed to manage risk in this field therefore needs to be able to aggregate that risk across multiple commodities from both the agriculture and energy side of the equation. Functionality that can provide views of both physical and financial portfolios is a pre-requisite, as is the ability to drill down to the trade level in real time.

Traders should also be given the ability to calculate, view and analyse option sensitivities and VaR – or any other chosen risk measurement technique – as well as the option to conduct stress testing that will simulate shocks to the market.

As well as these basic risk management features, any trading desk entering the agri-energy arena needs a system that can easily and accurately model new complex trade types and structured products with agricultural feedstocks and biofuel outputs.

It needs to provide energy yield equivalent curves that offer precise hedge quantities for spot and forward markets, allowing traders, for example, to manage the relationships between agriculture, crude oil and biofuel products. Other attributes, such as complex pricing, unpricing and rollover, volume/mass conversions, qualities, crop year, tolerances, foreign exchange exposure and repurchase contracts need to be included.

## Biofuel supply chain complexities

The new supply chain complexities of renewable fuels include attributes from agriculture and energy. Farm procurement, modes of transport including vessel, rail, truck, blending and processing at the plant all need to be factored in, as do marketing and any additional logistical requirements.

The technology to be used also needs to have an advanced architecture with the capacity to accommodate the inevitable change of an emerging market with many unknowns, and to adapt to responding shifts in business strategy – without taking up time and resources to do so.

There are exciting opportunities ahead as the focus on renewable fuel sources intensifies, and a new agriculture-energy complex emerges. But accompanying these opportunities are new forms of risk to be managed, new inputs and outputs to be analysed and new market patterns to be managed. Standard systems that have been patched up to do the job will not cut it in this brave new world. In this game, it is advanced, sophisticated enterprise systems that will maximise returns.

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# Catalytic conversion of cellulosic biomass

**Future process routes based on heterogeneous catalysis will enable effective and economical conversion of solid biomass into sustainable fuels, chemicals and energy. This conversion is based on the effective opening or unlocking of solid biomass**

Paul O'Connor and Rob van der Meij
*BIOeCON BV*

The first generation of biofuels (biodiesel from vegetable oils and ethanol from sugar and starch) are rather limited in supply and it is questionable if it really makes sense to 'downgrade' these valuable edible feedstocks to transportation fuels. The story is different for the second generation of biofuels (i.e. biofuels 2.0), which is based on using abundantly available lignocellulosic biomass wastes.

Cellulosic ethanol can be produced via enzymatic conversion of lignocellulosic biomass. Unfortunately, the conversion and separation of ethanol and water remains difficult and costly, while ethanol volatility may eventually limit the quantity that can be blended into the fuel pool. An alternative route is to gasify the solid biomass and reform this into synthesis gas, which can then be converted into a liquid fuel. This route requires several complex process steps and is rather expensive in investment as well as energy consumption.

A simpler and more robust approach is to convert the solid biomass into a bio-oil by direct thermal liquefaction. The bio-oil can then be transported (by pipeline) to existing refineries for further upgrading. Unfortunately, the quality of the bio-oil produced is poor and extensive further treatment is required in order to produce the right quality for transportation fuels.

Interesting new developments have emerged from the field of heterogeneous catalysis, which will enable the effective and economical conversion of the solid biomass into sustainable fuels, chemicals and energy. We foresee that these processes can be applied industrially rather soon by making use of, and building on, existing technologies and infrastructure.

## Current energy sources face serious challenges

The world is facing serious challenges in the future. The shortage of low-cost energy is strongly influencing the world economy and shifting political power. It is becoming evident that while fossil fuels are not yet running out, the costs of recovering the newer sources of fossil energy are increasing rapidly. An added complication is that the increasing use of fossil energy leads to higher $CO_2$ emissions into the atmosphere, leading to a greenhouse kind of effect, which is suspected to be the main cause of global warming. At present, most leading scientists support this theory, and the United States government is now also seriously contemplating the impact of ever-increasing $CO_2$ and global warming.

The fundamental answer to this challenge is to tap solar energy. Each year the sun radiates 5.5 million ExaJoules (EJ) to the earth. The earth absorbs about 3.7 million EJ (Table 1). This is a huge quantity compared to our energy consumption, which is about 430 EJ today and is expected to be in the order of 1500-1800 EJ in 2050. There is enough solar energy; the question is how to capture, store and distribute this energy in the most cost-effective way.

Nature has been storing the energy (and capturing $CO_2$) via photosynthesis in the form of biomass. At present only about 1% of the 3.7 million EJ is converted to terrestrial biomass, of which about one-third is available for conversion to energy. This comes down to about 1400 EJ. Research in biomass growth and photosynthesis suggests that the efficiency can be improved up to 10%, while farming of the oceans (e.g. algae) can increase the total source of biomass even further in the future.

The use of biomass can be considered as an intermediate solution to the time when we can directly farm the energy of the sun via (for instance) artificial photosynthesis and/or a strongly improved science of photovoltaic technology. However, for the next 50 years, biomass is the only practical way towards replacing a substantial part of the fossil fuels, making use of most of the energy storage and distribution structure we already have in place for fossil fuels. Eventually, when the direct capture of solar energy becomes more competitive, biomass fuels may still remain the preferred way of storing this energy in its hydrogenated form, without requiring a complete redesign of the energy distribution infrastructure (Figure 1).

**Supply of biomass today versus the total global energy requirement**

| Yearly energy | TW yr | EJ |
|---|---|---|
| Solar energy to earth | 178000 | 5500000 |
| Adsorbed by atmosphere | 120000 | |
| Adsorbed by earth | 53000 | 3700000 |
| Adsorbed by terrestrial | 16000 | |
| Terrestrial photosynthesis (<1%) | 128 | ~ 4000 |
| Available for biomass conversion | 46 | ~ 1426 |
| Energy demand today | 14 | ~ 430 |
| Energy demand in 2050 | >30 | 600-1800 |
| Estimates biomass in 2050 | | 100-350 |

*TW = Tatra Watts year/year*
*EJ = Exa Joules (= $10^{18}$ Joules)*

***Table 1***

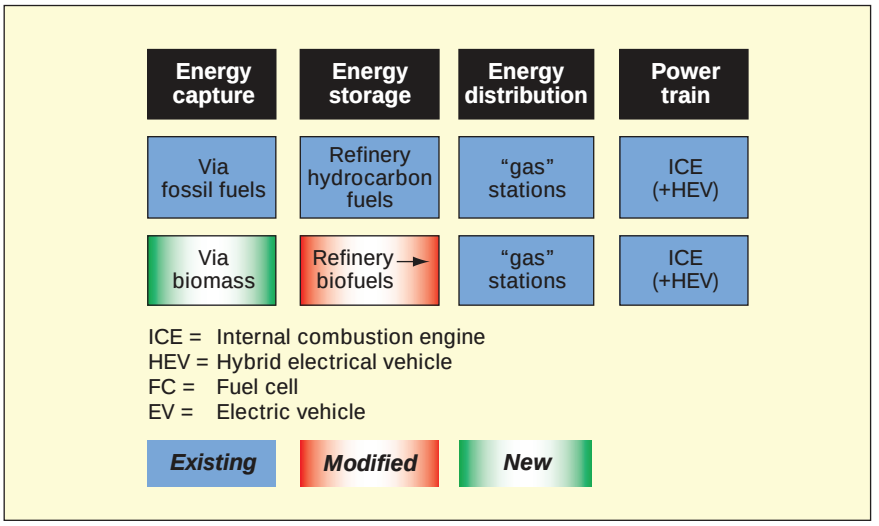


***Figure 1*** *Biomass can 'blend' into existing fossil fuels infrastructure*

## Biomass conversion poised to make a big entry in the next few years

At present, only a small part of the available biomass is effectively used, and a lot of biomass residue or waste is produced, which can at best be utilised at its low heating fuel value. More effective conversion of biomass waste into higher-value transportation fuels and chemicals is a must in order to make biomass an economical route for renewable fuels (Figure 2).

What is required are low-cost, large-scale robust ecological biomass refining processes, which can produce the right building blocks for the production of transportation fuels, polymers and/or other speciality chemicals. Furthermore, it is essential that the technology fits into the existing infrastructure of oil refining, fuel distribution and/or chemical industry to avoid excessive investments and create faster acceptance.

## Biofuels face serious constraints and limitations

There is a strong and heated debate concerning the possible negative aspects of the increasing use of bio-energy and biofuels. Different aspects have come to the attention, such as concerns about the fact that the use of biomass for bio-energy may increase the food shortage. Even the advantages of biofuels for $CO_2$ reduction are disputed. Biomass by itself creates no additional $CO_2$ emission and this is a positive point, but if we produce fuel out of biomass and need a lot of energy in the overall process (like in the case of the conversion of vegetable oils to diesel), then these fuels are not economically or ecologically an improvement in respect to the fossil fuels we are already using today.

There is also the question of if it is ethical to use high-quality foods, such as sugar and corn, to convert into fuels, while in some parts of the world people still starve from malnutrition. Even more shocking is the deliberate cultivation of non-edible plants at the expense of food crops, so that this ethical point of view can be circumvented.

We share the foregoing concerns. The fact is, however, that less than 30% of the world's cultivated biomass is fit for human consumption. The non-digestible, low- value component of the biomass, often more than 70%, is usually not used and/or simply burned. Bio-energy from biomass will become really interesting when we are able to convert this difficult-to-digest cellulose part (agrarian waste, wood, fibres, etc.) into a useful energy source:

**Ethical:**
Bio-energy from biomass waste doesn't compete with the normal food supply.

**Ecological:**
If produced with minimal energy consumption, the net $CO_2$ generation of these fuels will indeed be lower than with current fossil fuels.

**Economical:**
The world has enough biomass waste to supply a big part of the planet with energy. Energy scenarios from MIT indicate the potential to collect 30-40% of the energy from biomass in the 21st century.

Bioenergy from biomass waste can compete with crude oil and coals if the process to convert biomass waste into useful biofuels is not too energy intensive. There are already several processes that convert biomass waste into fuels. Usually they apply gasification and gas-to-liquid (GTL) technology to convert biomass waste flows into liquid fuels. An alternative route is to make use of enzymes. Special enzymes (biocatalysts) are being developed that are also capable of digesting wood-based biomass waste.

## Guiding principles for developing biofuels 2.0

The most important factors hindering the growth of biofuels are economical: the availability and costs of raw biomass, which can be processed to renewable fuels. Guiding principles for the development of second-generation biofuels (biofuels 2.0) are:

No competition with food crops → Use of abundant cellulosic material

Competitive with fossil fuels → Improve energy efficiency

The first generation of biofuels (biodiesel from vegetable oils and ethanol from

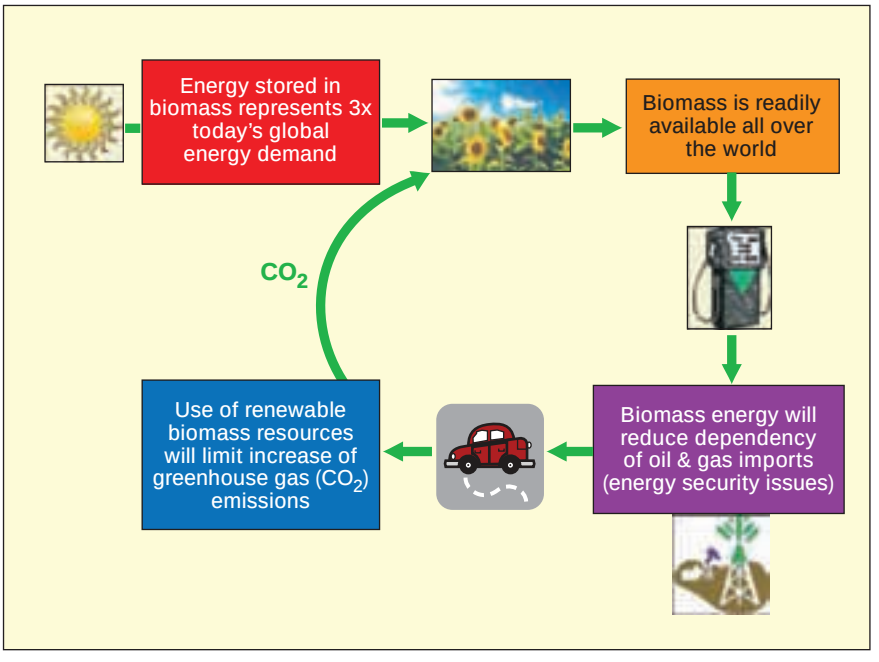


***Figure 2*** *Biomass as a sustainable energy-generation cycle*

sugar, starch or corn) make use of raw materials, which are rather limited in supply and therefore costly. Furthermore, as discussed in the previous section, one may raise the question if it really makes sense to 'downgrade' these scarce and high-value edible materials into transportation fuels.

The story is different for second-generation biofuels (biofuels 2.0), which make use of the more abundantly available cellulosic biomass waste. Several new technologies are being developed to unlock these large, low-cost sources of biomass energy.

Cellulosic ethanol can be produced via enzymatic conversion once the solid cellulose is separated from lignin (the structure) and opened up, and hence made more accessible to the enzymes. There are several developments pertaining to pre-treatment processes, such as acid and/or steam heat treatments. Unfortunately, the separation of ethanol from water still remains a costly factor, while ethanol volatility may limit the quantity, which can be blended into the gasoline.

An alternative route is to convert the solid biomass into a gas and produce a synthesis gas (CO + $H_2$), which can then be converted to a liquid via the Fischer-Tropsch process. This route is often called BTL (biomass-to-liquid) via GTL (gas-to-liquid). While this technology is proven, it does require several complex process steps and is quite capital and energy intensive.

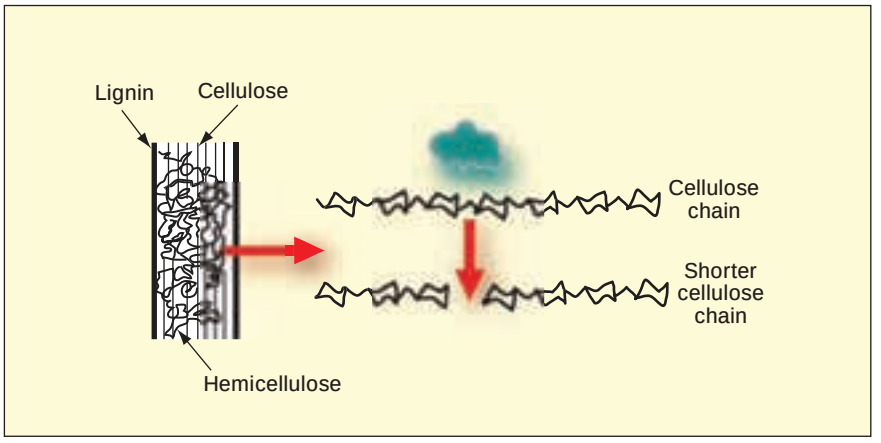


***Figure 3*** *Unlocking the cellulose from the woody structure enables the conversion*

A more simple and robust (in terms of feedstock flexibility) approach is to convert the solid biomass into a liquid (BTL) by direct liquefaction. Several thermal and thermo-catalytic processes are under development in this area. A drawback is that the quality of the bio-oil produced is often rather poor, and extensive treatment and upgrading is required in order to produce the right components for transportation fuels and/or chemicals.

An interesting new approach in this respect is catalytic pyrolysis of biomass, whereby catalytic technology is used to achieve the liquefaction of the solid biomass under milder conditions and at a lower cost. The technology is similar to FCC (fluid catalytic cracking) and therefore requires less time to commercialise than most other schemes. This opens the way for an ethically and ecologically justified raw material, ready for further processing in existing petrochemical refineries instead of fossil-based crude oil. Economically, this is an interesting development because it uses a major part of the existing infrastructure from oil and/or petrochemical refineries. This means that a limited investment will be required for the production of durable fuels and biological degradable polymers from biomass.

## Making biomass accessible for conversion

The key technical problem to solve for the conversion of the non-edible cellulosic biomass is how to open up

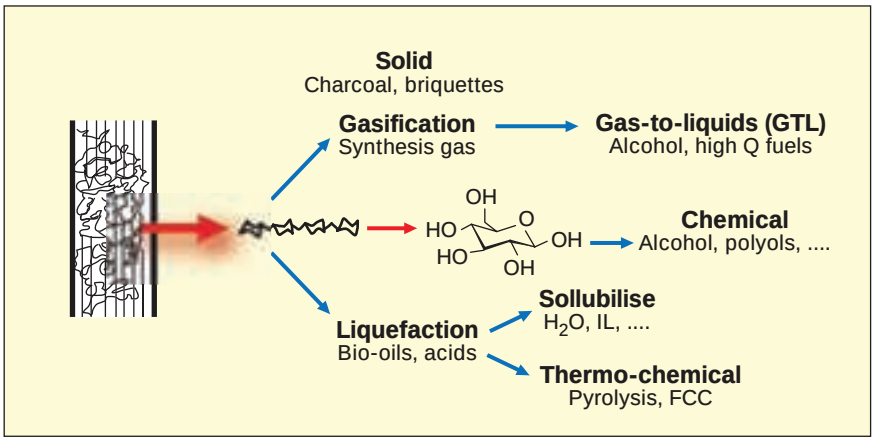


***Figure 4*** *Conversion of accessible biomass molecules*

the inaccessible solid fibrous 'woody' material so that it can be effectively transformed by chemicals, enzymes or catalysts. Cellulose, the main component of wood, is a very pure polymer of glucose (sugar); once we 'unlock' the woody structure and 'unzip' this natural polymer, we can obtain excellent base chemicals, which may be further converted into several products (bioethanol, biobutanol, bio-oils, etc.).

Unfortunately most of the existing processes to unlock the woody structures are quite costly and need either a lot of energy and/or chemicals. The challenge is to find a simple non-energy-intensive way to make the woody biomass accessible to reactive media, catalysts and/or enzymes. Making use of the extensive knowledge, experience and creativity of our international research network, a radical, novel approach was discovered.

## Applying catalysis to break the fibrous cellulosic structures

The goal principle of the new technology is to make the solid biomass susceptible to conversion at milder conditions (lower temperatures and pressures). This leads to improved product quality and improved economics (capital costs + energy costs) of the subsequent processes involved. The underlying principle is that by adding a catalyst, the biomass structure is destabilised (or in other terms: activated). The resultant transition structure can then be converted into a liquid at much milder conditions than with the traditional state-of-the-art methods. The explanation for this is that there is a close (electronic, electro-chemical) interaction between organic (bio) materials and certain inorganic materials. It is claimed, for instance, that the first organic molecules on earth were formed by clays, which functioned as 'templates' for the more complex molecules to grow on. The presence of the charged inorganic structures seems to activate the organics. This principle is used in many processes, such as with the catalytic cracking of heavy oils, and in the synthesis of speciality chemicals. In the new technology, the same concept ('templating') is being exploited, but upside down (i.e. deconstructing the biomass structure instead of constructing complex structures).

The catalytic route is more robust and more suitable for the primary conversion of solid biomass than the enzymatic route. An interesting example of the power of catalysis versus enzymes is given by Atsush Fukuoka and Paresh Dhepe of Hokkaido University, Japan[1], who developed metal catalysts that can outperform enzymes. They used platinum and ruthenium, supported on silica or alumina, to convert an aqueous mixture of cellulose and hydrogen gas into glucose. This sugar was then reduced to sorbitol and mannitol, which were easily separated from the reaction. Sorbitol can be used to make fuel-type hydrocarbons, as demonstrated by George Huber[2], while both alcohols are useful chemical feedstock compounds. Although the foregoing is an elegant example, we expect that an approach that avoids the use of expensive noble metals will be more effective at a much lower cost.

## Biomass conversion technologies

Once it becomes possible to unlock the solid biomass structure, the biomass molecules will become more reactive and accessible to catalysts, enzymes and/or other chemicals.

Making use of this breakthrough, several processing routes can be pursued. At present we are focusing on developing several biomass conversion technologies based on the effective opening (accessibility) or unlocking (depolymerisation) of solid biomass. The four most important routes are:

- Biomass catalytic conversion (BCC)
- Biomass pretreated for enzymatic conversion (BIPEC)
- Biomass to electrical power (BICEPS)
- Biomass to speciality chemicals (BICHEMS)

BCC is an improvement to classical biomass pyrolysis and is known as catalytic pyrolysis (or biomass catalytic cracking), whereby catalytically accessible biomass is converted into a biocrude suitable for transport to existing refineries and for further processing in new or existing (bio) oil refineries.

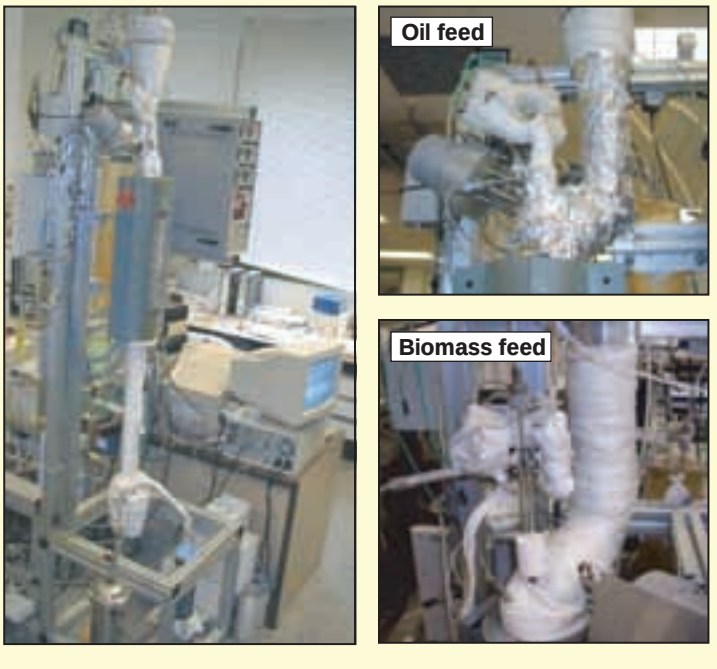


***Figure 5*** *Testing biomass in a Micro Inverse Riser FCC*[3]

The BIPEC technology opens up the biomass to the enzymes for enzymatic conversion and can become the low-cost alternative to existing pre-treat processes (such as steam explosion and acid digestion) for the production of cellulosic ethanol.

Efficiently producing electrical power from biomass can be an important alternative to coal-fired power stations, and crucial to reduce the strong growth in $CO_2$ expected from new power stations in the developing world. BIOeCON is exploring a technology in this field known as biocatalytic electrochemical power systems (BICEPS).

In BICHEMS, after unlocking and de-polymerising cellulosic biomass, interesting chemical building blocks can be obtained, which can be further transformed into speciality chemical molecules.

We envisage that BCC will be the first technology to be implemented on a large scale. BCC builds on fluid catalytic cracking (FCC) technology, which has been the low-cost conversion workhorse in the oil industry since the Second World War.

**Editor's note**
BIOeCON (the 'e' for: economic, ecologic and ethical energy) was formed as a think-tank bringing together an international network of creative scientists to develop a third way to produce biofuels out of biomass waste: the biomass waste is directly converted into a liquid phase with the use of selective catalysis.

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# Quality control of biofuels

**For quality control of biofuels, determination of oxidation stability, iodine and acid number as well as water, alkali metal and alkaline earth metal content are important. Titrimetric and ion chromatographic analyses are also addressed**

A. Steinbach, U. Loyall, B. Zumbrägel, C. Haider, G. Spinnler, R. Schlink and A. Wille
*Metrohm AG*

The four primary driving forces behind biofuels are the world's increasing gluttony for petroleum (80 million bpd), the diminishing supply of fossil fuels, global warming and the imperative to reduce dependence on fuel imports. Additionally, most biofuels are produced by straightforward manufacturing processes, are readily biodegradable and non-toxic, have low emission profiles and can be used as is or blended with conventional fuels. Biodiesel and bioethanol are currently the leading fuel alternatives, driven by recent regulations such as the EU Directive 2003/30/EC or the United States (US) Department of Energy's Federal Bio-based Products Preferred Procurement Program (FB4P).

The concept of using liquid biofuel dates back to 1895, when German engineer Rudolf Diesel (1858-1913) developed the first engine running on vegetable oil. At that time, existing motors with their large injectors could easily cope with viscous vegetable fuels. However, due to low petroleum prices, engine technology was increasingly tailored to consume low-viscosity conventional fuel. Consequently, vegetable oils were only sought after in times of high oil prices.

Not until vegetable oils were 'derivatised' was low-viscosity biofuel available. In a so-called transesterification reaction that is catalysed by a base, acid or enzyme, a vegetable oil or animal fat is reacted with methanol to yield fatty acid methyl esters (FAME, biodiesel) and glycerin as co-product. The latter, if produced in high quality, finds use as a valuable feedstock in the cosmetic and pharmaceutical industry. The base-catalysed transesterification is considered to be the most promising production process (Figure 1)[1]. Due to the reversible character of the reaction, a large excess of alcohol shifts the equilibrium to the products side and thus ensures total conversion to the esters. After completion of the transesterification reaction, the biodiesel phase is separated from the more dense glycerin phase by gravitational settling or centrifugation. Subsequently, the methyl esters, which still contain large amounts of residual alcohol, traces of dispersed glycerin and unreacted sodium hydroxide or soaps, are cleaned by a water-wash. Remaining water and poorly water-soluble impurities, such as unreacted feedstock or the mono- and di-glycerides, are removed by further steps such as distillation or stripping.

> "While the standardisation of biodiesel in Europe has been well established by the EN 14214 since 2003, the European standard for bioethanol, the prEN 15376 is currently under approval"

In 1908, some years after the development of the diesel engine, Henry Ford designed the Ford Model-T to run on ethanol. However, the low petroleum prices and the seemingly inexhaustible fossil fuel reserves also displaced ethanol. Not until the worldwide oil crisis in 1973 did Brazil and the USA launch their first ethanol programmes, paving the way for their leadership position in the production and utilisation of bioethanol.

Bioethanol is generally made from products containing sugar, starch or lignocellulosic biomass. The microbial fermentation of biomass-sourced sugars via yeast is a well-established technology, applied commercially on a large scale. In contrast, starch biomass, with its larger carbohydrates, is not directly fermentable. Prior to yeast-induced fermentation, starch-containing feedstock has to be converted to sugars. Fermentation yields relatively dilute aqueous solutions of ethanol, which, for their later use as a fuel, are distilled to provide 95% ethanol. The (anhydrous) 99% ethanol is mainly produced via physical water absorption using molecular sieve technology.

Despite all the previously mentioned advantages, biofuels had to struggle for acceptance. Reports highlighting engine problems due to poor-quality biofuel discredited the promising biogenic route. Low-quality biodiesel, often produced from crude feedstocks in uncontrolled home-brewing plants, contained detrimental contaminants, resulting in injector fouling, enhanced corrosion and clogging of the fuel system. Not until reliable quality standards were defined did the quality of biofuels, and thus the confidence of the consumer and the automobile industry, improve. The major biodiesel standards, which commonly serve as reference for other standards, are the ASTM D 6751 from the American Society for Testing and Materials (ASTM) and the European EN 14214 (Table 1a). Additionally, there exists the separate

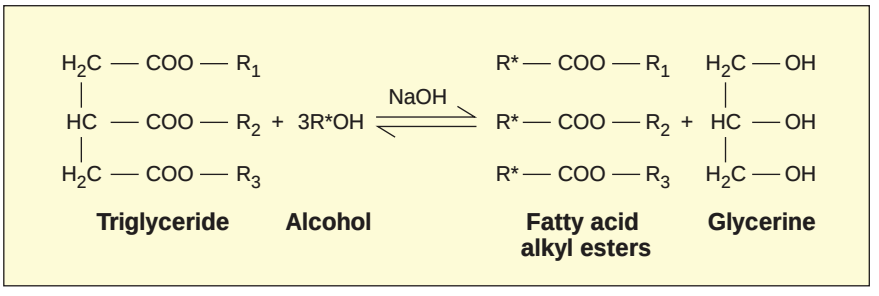



***Figure 1*** *Base-catalysed transesterification of a triacylglyceride with alcohol*

**European and US biodiesel standards (selection)**

| BIODIESEL | EN 14214/14213 | EN 14214 | EN 14213 | ASTM D 6751 | |
|---|---|---|---|---|---|
| **Property** | **Test method** | **Limits** | | **Test method** | **Limits** |
| **Oxidative stability** [h] | EN 14112 | > 6 | > 4 | EN 14112 | > 3 |
| Iodine value [g I2/100 g] | EN 14111 | < 120 | < 130 | - | - |
| Acid number [mg KOH/g] | EN 14104 | < 0.5 | | ASTM D 664 | < 0.5 |
| Water content [mg/kg] | EN ISO 12937 | < 500 | | ASTM D 2709 | < 500 |
| Group I metals (Na + K) [mg/kg] | EN 14108 EN 14109 | < 5.0 | - | EN 14538 | < 5.0 |
| Group II metals (Ca + Mg) [mg/kg] | EN 14538 | < 5.0 | - | EN 14538 | < 5.0 |
| Total glycerin [% mass] | EN 14105 | < 0.25 | | ASTM D 6584 | < 0.24 |

*Table 1a*

**Temperature dependence of the induction time (mean of two determinations)**

| Temperature | Induction time |
|---|---|
| [°C] | [h] |
| 120 | 3.3 |
| 110 | 6.3 |
| 100 | 11.6 |

*Table 2*

standard EN 14213 defining the minimal requirements for biodiesel used as heating oil or as a blending component for heating oil.

## Structure indices/quality indices

These standards include fuel-inherent properties such as the oxidation stability or the iodine value. These so-called structure indices originally served to exclude the use of certain vegetable oils or animal fats as feedstocks[2]. On the other hand, there are properties that are basically related to the production process. These parameters, also called quality indices, indicate the content of unreacted starting material in the biodiesel. Process-related parameters include the acid number and the glycerin, methanol, water and sodium hydroxide content. As will be discussed, determination of both water content and acid number is crucial for feedstock quality control and for optimising the production process[3-5].

While the standardisation of biodiesel in Europe has been well established by the EN 14214 since 2003, the European standard for bioethanol, the prEN 15376 is currently under approval. In contrast, the leading ethanol producers

**US and European bioethanol standards (selection)**

| BIOETHANOL | ASTM D 4806 ASTM D 5798 | | prEN 15376 | |
|---|---|---|---|---|
| **Property** | **Test method** | **Limits** | **Test method** | **Limits** |
| Acidity as acetic acid [% m/m] | ASTM D 1613 | < 0.007 < 0.005 | prEN 15491 | < 0.007 |
| Water content [%] [m/m] | ASTM E 1064$_{coul}$ ASTM E 203$_{vol}$ | < 1 [v/v] | prEN 15489 | < 0.3% |
| Inorganic chloride [mg/L] | ASTM D 512 | < 40 < 1 | prEN 15484 prEN 15492 | < 20 |
| Inorganic sulphate [mg/L] | ASTM D 7318$_{pot}$ ASTM D 7319$_{IC}$ | < 4 | - | - |
| pH | ASTM D 6423 | 6.5 - 9.0 | prEN 15490 | 6.5 - 9.0 |
| Copper content [mg/kg] | ASTM D 1688 | < 0.10 < 0.07 | prEN 15488 | < 0.1 |

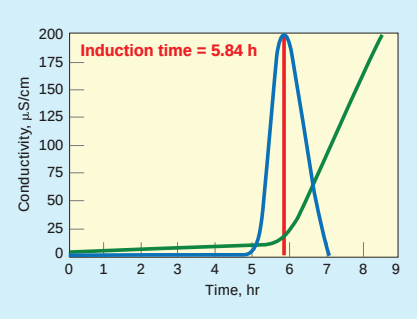
*Table 1b*

– the US and Brazil – dispose of two well-established standards, the ASTM D 4806 and the ASTM D 5798 for denatured fuel ethanol only and for mixtures of bioethanol and gasoline (Ed75-Ed85), respectively (Table 1b).

In view of the fact that the quality control of biodiesel begins with the refining of the vegetable oil feed, this discussion stresses the importance of feedstock acid number and water content. However, emphasis is on specifications and test methods prescribed by the two biodiesel standards, namely determination of oxidation stability, iodine and acid number as well as water, alkali metal and alkaline earth metal content. Titrimetric and ion chromatographic analyses referred to in the ASTM D 4806 bioethanol standard are addressed as well.

## Oxidation stability of biodiesel

As mentioned earlier, biodiesel is readily biodegradable, allowing its use in environmentally sensitive areas.



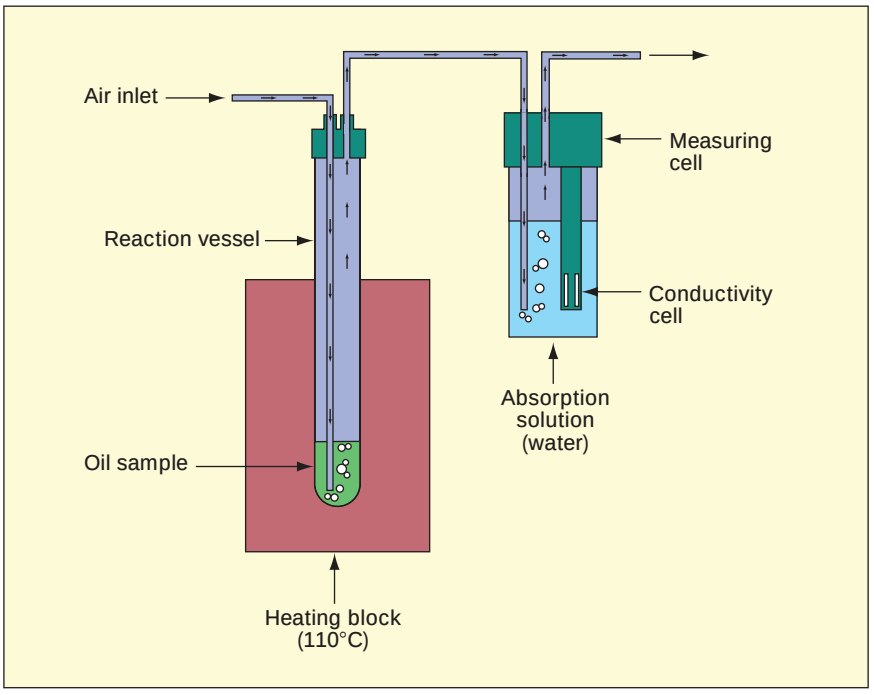




***Figure 2*** *Schematic of the 873 Biodiesel Rancimat's setup (right) and output (above)*

However, this environmental advantage also means that the fuel is less stable, which affects storage behaviour. In particular, those derivatives of polyunsaturated fatty acids, such as linoleic (C18, two double bonds) and linolenic acid (C18, three double bonds) with one or two bis-allylic methylene positions, are highly susceptible to oxidation. During the first step of fuel oxidation (hydro)peroxides form through a free-radical chain mechanism. In the second step the radicals produce short-chain aldehydes, ketones and carboxylic acids (acid number increases). Under certain conditions, a radical-initiated polymerisation can form insoluble polymers, which in turn can clog fuel lines, filters and pumps. These drawbacks are less pronounced in

**Iodine value (IV) of the investigated biodiesel sample**

| BIODIESEL | Blank | Biodiesel |
|---|---|---|
| Number of determinations n | 3 | 7 |
| Mean value thiosulphate consumption [ml] | 47.71 | 33.79 |
| Iodine number [g iodine/100g sample] | – | 114.40 |
| Standard deviation | – | 0.50 |
| Relative standard deviation [%] | – | 0.44 |

***Table 3***

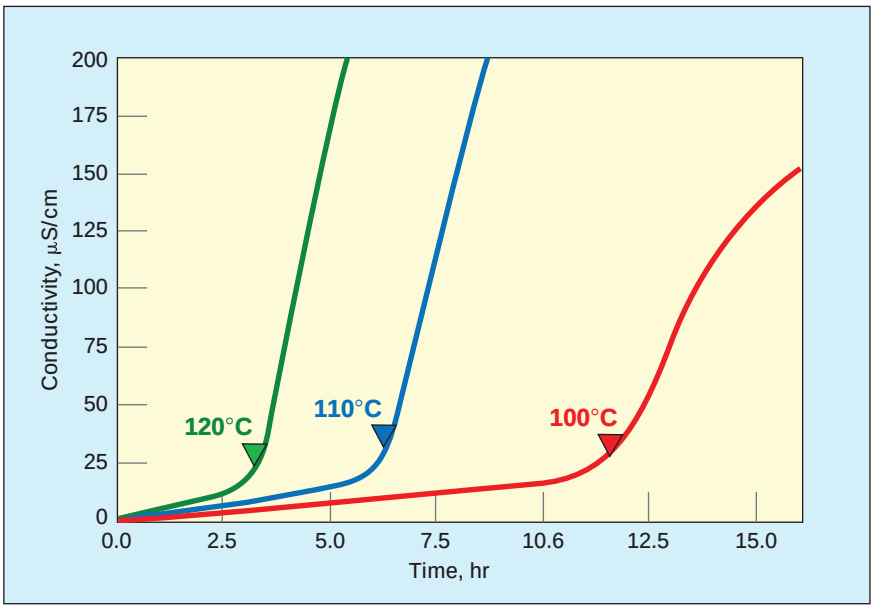



***Figure 3*** *Plots of conductivity (µS/cm) versus time (h) obtained at 100, 110 and 120°C*

unrefined vegetable oils containing natural antioxidants. During refining, these antioxidants get partly lost and oxidation stability decreases. However, premature degradation can be overcome by the addition of synthetic antioxidants. Their effectiveness can accurately be investigated with the so-called Rancimat method.

The Rancimat method mimics oxidation of a biodiesel sample at a fixed temperature, usually far above ambient. The result is then extrapolated to the stability under real-world conditions. In practice, a stream of purified air is passed through the heated sample (usually 110°C) and is subsequently bubbled through a vessel containing deionised water (Figure 2). The resulting oxidation products – volatile organic acids (predominantly formic acid) – are swept from the sample into the water, thus increasing its continually monitored conductivity. The point at which the maximum change of oxidation rate occurs is the so-called induction time. The PC software evaluates induction time automatically from the maximum of the second derivative of the conductivity with respect to time.

### Experimental

In order to determine the temperature dependence of the induction time, sample amounts between 3.0 and 6.0 g biodiesel were analysed at 100, 110 and 120°C (Figure 3).

**Determination of the titer and the acid number (AN) of the biodiesel sample**

| BIODIESEL | Titer | Acid number |
|---|---|---|
| Number of determinations n | 3 | 9 |
| Mean value | 0.987 | 0.202 mg/g |
| Relative standard deviation | 0.34% | 0.94% |

***Table 4***

The results (Table 2) agree with the Arrhenius equation, according to which a temperature reduction of 10°C should result in an approximate doubling of the induction time. At 110°C the investigated biodiesel sample has an induction time of 6.3 h. It thus complies with the minimal requirements of EN 14112 in EN 14214 (6 h) and ASTM 6751 (3 h).

## Iodine value in biodiesel

The iodine value (IV) or iodine number is another stability index and measures unsaturation in organic compounds. It is the amount of iodine (in grams) that can be added to 100g of the sample and is used as an indicator of the number of double bonds. The higher the IV, the higher the number of double bonds. Originally, the IV in EN 14214 had the function of excluding certain feedstocks for biodiesel production. However, since the IV does not consider the positions of the double bonds within the compound, it does not correlate well with the oxidation stability. Knothe et al showed that different fatty acid structures can give the same IV[6]. Consequently, the IV is increasingly understood as a rough indicator. Stability specifications known as APE (allylic position equivalents), BAPE (bis-allylic position equivalents) and, above all, the previously described Rancimat test characterise the oxidation stability of diodiesel much more accurately.

### Experimental

After the titer determination, 0.15g biodiesel sample is dissolved in 20ml glacial acetic acid and treated with 25ml Wijs solution as iodinating reagent, consisting of iodine monochloride in glacial acetic acid. After five minutes, 15ml potassium iodide solution is added. As in classical iodometry, the excess of iodine is titrated with standardised 0.01mol/l sodium thiosulphate solution. A Pt Titrode is used for endpoint indication.

The investigated biodiesel sample has an IV of 114.4 and thus meets the requirements of EN 14214 with a

**Results of the determination of the water content in biodiesel**

| KF reagent | Water content | | | | | |
|---|---|---|---|---|---|---|
| | Minimum value $x_{min}$ | Maximum value $x_{max}$ [ppm] | Mean value $x^1$ | RSD [%] | Difference $x_{max}$-$x_{min}$ [ppm] | Repeatability r • 100 |
| Coulomat AG (without solubiliser) | 184.9 | 189.6 | 187.7 | 0.8 | 4.7 | 25.7 |
| Coulomat AG + Xylene | 192.8 | 199.5 | 196.6 | 1.1 | 6.7 | 26.3 |
| Coulomat AG Oil ($CHCl_3$ + Xylene) | 179.4 | 183.0 | 181.3 | 0.7 | 3.6 | 25.2 |
| Coulomat A ($CHCl_3$) | 188.9 | 194.3 | 191.7 | 1.0 | 5.4 | 25.9 |
| Coulomat AG-H (long-chain alcohol) | 186.1 | 191.5 | 189.1 | 0.9 | 5.4 | 25.8 |

[1] Mean of 10 determinations

***Table 5***

permitted maximal value of 120g iodine per 100g sample (Table 3).

## Acid number in biodiesel and acidity in bioethanol

High fuel acidity is associated with corrosion and engine deposits, particularly in the fuel injectors. The acid number (AN) or acid value of edible oils or their corresponding esters indicates the quantity of fatty acids and mineral acids (negligible) present in the sample. According to ASTM D 664 and EN 14104, the AN is expressed in mg KOH required to neutralise 1.0g of FAME. The acidity of bioethanol is contained in both ASTM D 4806 and ASTM D 5798 using the method ASTM D 1613. It covers the determination of total acidity as acetic acid.

The AN is included in EN 14214 and ASTM D 6751, which suggests the methods EN 14104 and ASTM D 664, respectively. Both standards stipulate a non-aqueous potentiometric acid-base titration and limit the acid content to 0.5mg KOH per g sample. Alternatively, ASTM D 974 can be used for coloured samples; it involves the non-aqueous colourimetric titration using KOH in isopropanol as the titrant and p-naphtholbenzein as the indicator.

Besides the quality control of biodiesel, the AN plays a significant role in the quality control of feedstocks. Generally, the glycerides should have an AN below 1.0mg KOH/g[3,7]. Higher ANs lower the ester yields and increase NaOH consumption for neutralisation. Feedstocks containing high levels of fatty acids should therefore preferably be processed to biodiesel via an acid-catalysed transesterification. Additionally, increasing ANs, when compared to the initial AN of the biodiesel, can point to ongoing fuel degradation or the intrusion of water (hydrolysis of the FFAs). The determination of the AN of a biodiesel sample is illustrated using method EN 14104.

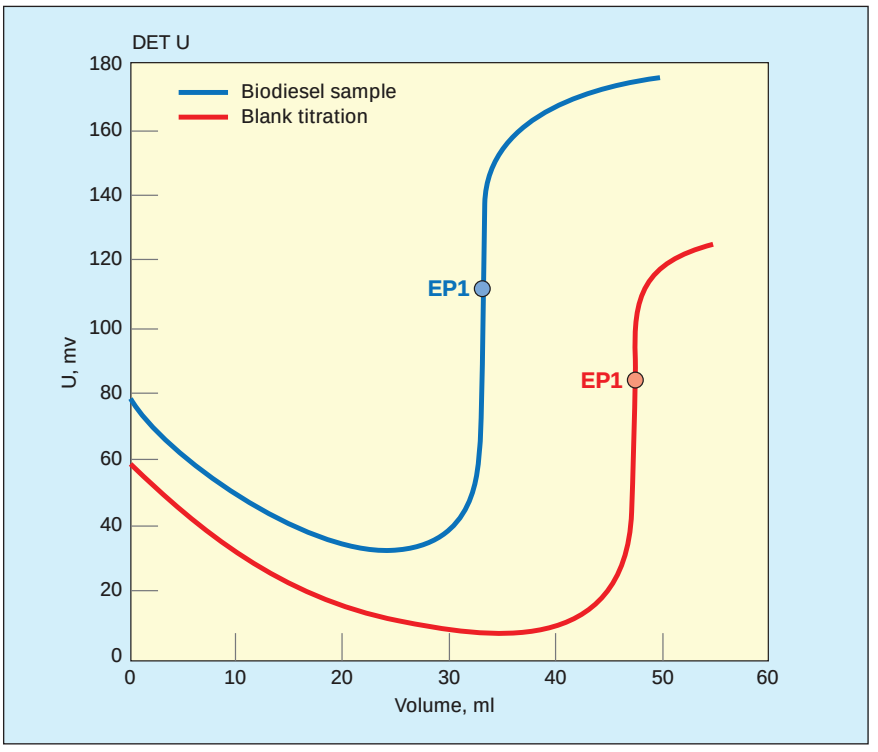



***Figure 4*** *Titration curves for liberated iodine, titrated with sodium thiosulphate solution*

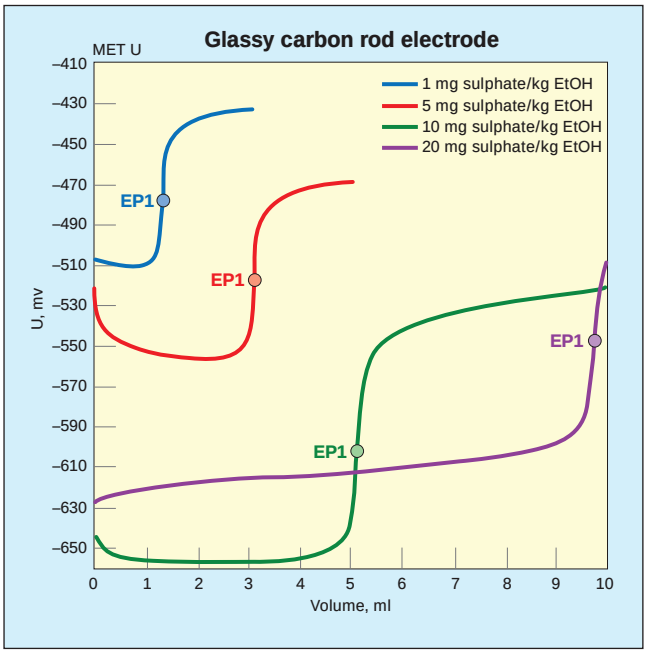
### Experimental

Between 14 and 15g biodiesel sample is dissolved in 50ml bioethanol/diethyl ether mixture (1:1, v/v). The sample is titrated potentiometrically with alcoholic potassium hydroxide (KOH). After each titration the Solvotrode, a pH glass electrode that has been especially developed for non-aqueous acid-base titrations, is thoroughly rinsed with isopropyl alcohol. The regeneration of the membrane is achieved by immersing the electrode in water for at least three minutes.

The determined AN of the biodiesel sample is 0.202mg KOH/g. This value complies with the requirements of ASTM D 6751 and EN 14214, which both stipulate a maximum AN of 0.5mg KOH/g (Table 4).

## Water determination in biodiesel and ethanol

In the biodiesel production process, water contamination of biodiesel plays a significant role in both the quality



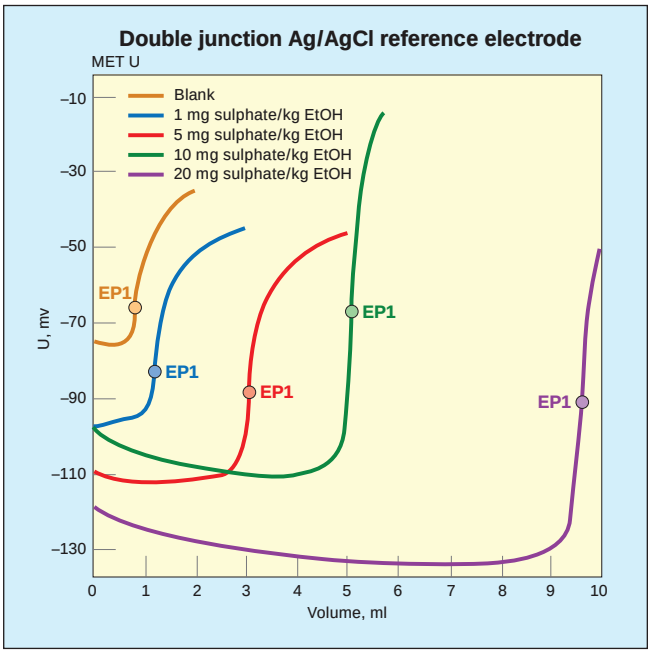




***Figure 5a & b*** *Titration curves of sulphate determinations in ethanol with a lead nitrate solution*

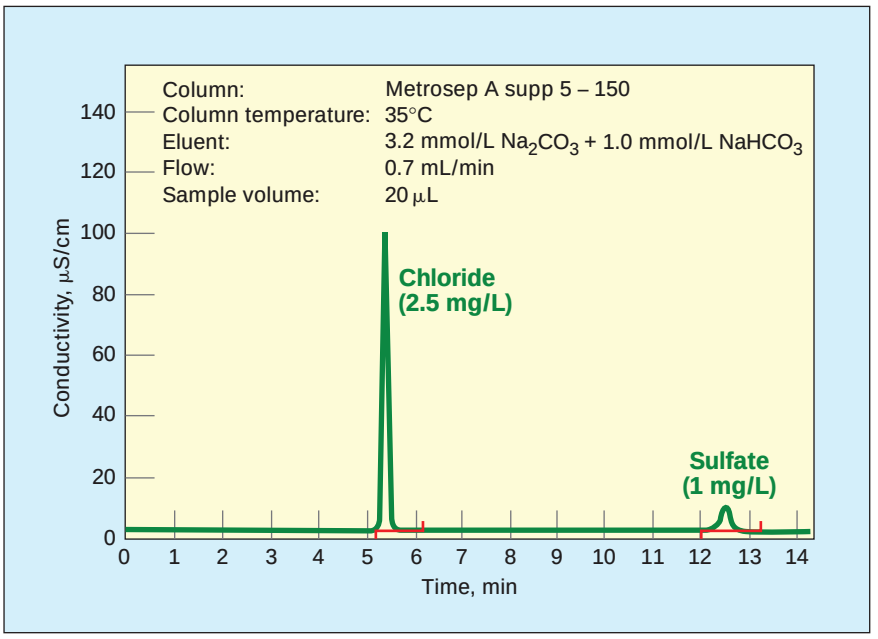



***Figure 6*** *Chromatogram of a denatured ethanol sample spiked with 2.5ppm chloride and 1ppm sulphate*

control of the feedstock and the end product. Biodiesel, although considered to be hydrophobic, can contain as much as 1500ppm of dissolved water, excluding suspended water droplets. The presence of water in biofuels reduces the calorific value, enhances corrosion, promotes growth of microorganisms and increases the probability that oxidation products are formed during long-term storage. Additionally, water cleaves the ester bond of the FAMEs via hydrolytic degradation. The same applies for glycerides in the feedstock. The liberated FFAs consume the added NaOH, forming soaps and emulsions that increase viscosity and seriously hinder the phase separation of glycerin. Because of this, all materials used in the biodiesel production process should be essentially anhydrous.

Several methods exist for the determination of water: loss on drying, reaction with calcium hydride, Karl Fischer titration (KFT), Fourier transform infrared (FTIR) and Raman spectroscopy as well as dielectric measurements. Among these, KFT is certainly the method of choice when trace amounts of free, emulsified or dissolved water have to be accurately determined in a reasonable time.

KFT is based on the stoichiometric reaction of water with iodine and sulphur dioxide in the presence of a short-chain alcohol (R` = $CH_3$, C2H5) and an organic base (RN), according to the following equation:

$$R`OH + SO_2 + 3\,RN + I_2 + H_2O \rightarrow 3\,RNH^+ + R`OSO3^- + 2\,I^-$$

Whereas volumetric KFT is applied to samples with water contents ranging from approximately 1.0 up to 100%, the coulometric technique is ideally suited for low water contents in the range of a few µg/g. In the volumetric KF technique, a titrant containing iodine is directly added to the sample via a buret. In contrast, in coulometric KFT, iodine is generated electrochemically from iodide directly in the titration cell. In both cases iodine reacts with the water in the sample.

ISO 12937 in EN 14214 prescribes coulometric KFT for the determination of the water content. According to EN ISO 12937, the test results must meet the following requirements regarding repeatability:

> The difference between two test results, obtained by the same person under identical test conditions, may exceed the following value *(r)* for the repeatability only once in 20 cases:
>
> $$r=0.01874\sqrt{x}$$
>
> where (x) is the mean value of all test results given as a mass fraction in per cent rounded off to 0.001%.

By means of direct coulometric titration using different commercially available KF reagents, the water content of a biodiesel sample is determined and the repeatability (r) calculated.

**Experimental**

Between 0.9 and 3.0g biodiesel sample is directly injected into the reaction solution with a syringe. Once all the available water has reacted (equivalence point), the indicator electrode detects the first excess of iodine and the KFT stops. The amount of water is calculated by measuring the electric charge needed for iodine generation.

Irrespective of the KF reagent used, all results are in the same ppm range (Table 5). The differences ($x_{max}$-$x_{min}$) are much smaller than the repeatabilities (r) defined by EN ISO 12937. This clearly shows that direct KFT provides a far better repeatability than is required by EN ISO 12937. The same applies for the automated pipetting system of Metrohm, which has been especially developed for high sample throughputs[8].

Accordingly, for ethanol the ASTM standard E 1064 in ASTM D 4806 prescribes the coulometric KFT of low water contents. For water contents greater than 2%, the recommended test method is volumetric titration as per ASTM E 203 in ASTM D 4806.

## Chloride and sulphate in ethanol

Contamination of ethanol with inorganic anions such as chlorides and

**Sulphate concentrations and recovery rates determined by potentiometric titration**

| Conc. | Double junction Ag/AgCl reference electrode | | | | Glassy-carbon rod electrode | | | |
|---|---|---|---|---|---|---|---|---|
| [ppm] | $SO_4^{2-}$ conc. [ppm] | RSD[a] [%] | n[b] | Recovery rate [%] | $SO_4^{2-}$ conc. [ppm] | RSD[a] [%] | n[b] | Recovery rate [%] |
| 0.998 | 0.978 | 0.81 | 3 | 98 | 1.063 | 1.46 | 3 | 106.5 |
| 4.989 | 5.229 | 0.41 | 4 | 104.8 | 5.268 | 0.23 | 3 | 105.6 |
| 9.978 | 10.047 | 0.52 | 4 | 100.7 | 10.063 | 0.24 | 3 | 100.9 |
| 19.965 | 21.627 | 1.08 | 5 | 108.3 | 21.735 | 0.75 | 4 | 108.9 |

[a]relative standard deviation, [b]number of determinations

***Table 6***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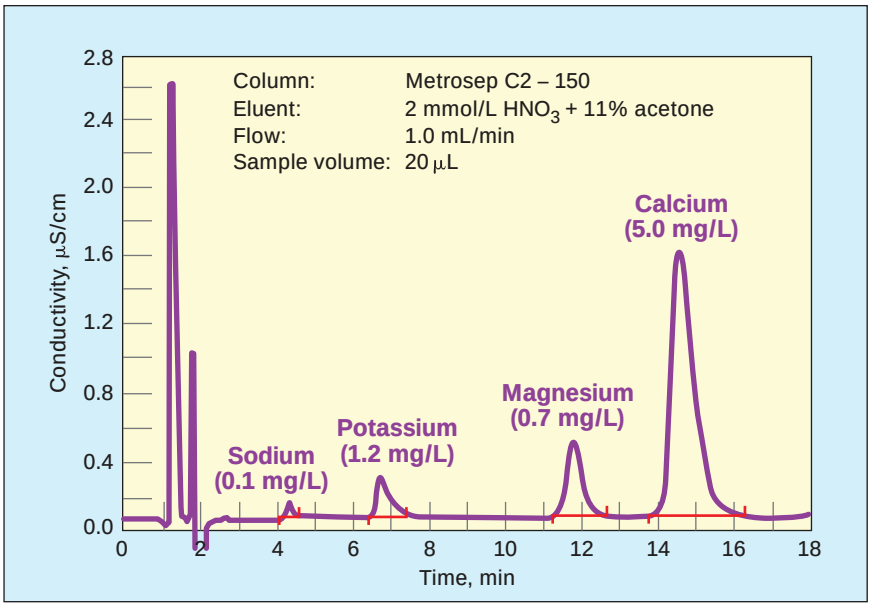


***Figure 7*** *Separation and detection of alkali metals and alkaline earth metals*

sulphates can affect the engine performance because precipitating salts clog filters and fuel injector nozzles. Furthermore, these salts induce corrosion in the vehicle components in contact with the fuel. Against this background, the ethanol specification ASTM D 4806 limits the sulphate and chloride content to 4.0 and 40ppm, respectively. ASTM D 512 and ASTM D 318 prescribe the use of potentiometric titration for chloride and sulphate, respectively. ASTM D 7319 presents a direct-injection suppressed ion chromatographic method for the determination of both anions.

**a) Titration**

As an example for potentiometric biofuel titrations, the determination of sulphate in ethanol according to ASTM D 7318 is presented. The determination of chloride, which can be carried out by mercurimetric or argentometric titration or with a Cl-selective electrode, is beyond the scope of this article.

A 100g bioethanol sample is spiked with known amounts of a sulphate standard. After the addition of 1.0mL 0.1 mol/l perchloric acid, the sulphate is precipitated with a lead nitrate solution. The Pb-selective electrode detects the first excess of lead ions at the equivalence point. A double junction Ag/AgCl (Figure 5a) or a glassy-carbon rod electrode (Figure 5b) are used as reference electrode.

While sulphate concentrations between 5 and 10ppm result in recovery rates of 100.7…105.6%, sulphate contents of 1 and 20ppm provide recovery rates of 98.0…106.5% and 108.3…108.9%, respectively (Table 6). Correlation coefficients of real concentrations versus determined concentrations for the double junction Ag/AgCl and the glassy carbon rod electrode are 0.9993 and 0.9991, respectively (Table 6).

**b) Ion chromatography**

After direct injection, chloride and sulphate are separated on an anion exchange column and then determined quantitatively by suppressed conductivity detection.

The limits of detection for chloride and sulphate are 0.6 and 0.2ppm, respectively. Even after 1500 ethanol injections containing denaturants and hydrogen peroxide, the analytical unit still provides stable retention times, repeatable peak areas and consistent concentration values[9]. This highlights the extraordinary ruggedness of the applied micro packed tri-chamber suppressor (MSM II) in long-term use. The presented direct injection IC system is 100% solvent compatible and ensures the accurate and precise determination of sulphate, chloride and other anions in full compliance with ASTM D 4806.

## Alkali metals and alkaline earth metals in biodiesel

After esterification and subsequent treatment, alkali metals and alkaline earth metals may be present in biodiesel as unwanted residues. Standard DIN EN 14214 permits a cumulative concentration of 5.0mg/kg for both the alkali metals sodium and potassium and also for the alkaline earth metals magnesium and calcium. Both groups of cations can be determined rapidly and accurately in a single ion chromatographic run (Figure 7).

**Experimental**

The samples are extracted with dilute nitric acid, dialysed and then injected directly into the IC system. The complete sample preparation procedure and analysis takes place fully automatically. The setup consists of the proprietary 861 Advanced Compact IC with Metrohm inline extraction and dialysis.

## Antioxidants in biodiesel

As already mentioned, the oxidation stability of biodiesel can be improved by the addition of antioxidants. The addition of Baynox® to the biodiesel sample inhibits both the oxidation to corrosive acids and the formation of insoluble polymers. Although not regulated by standards, these substances are determined within the context of

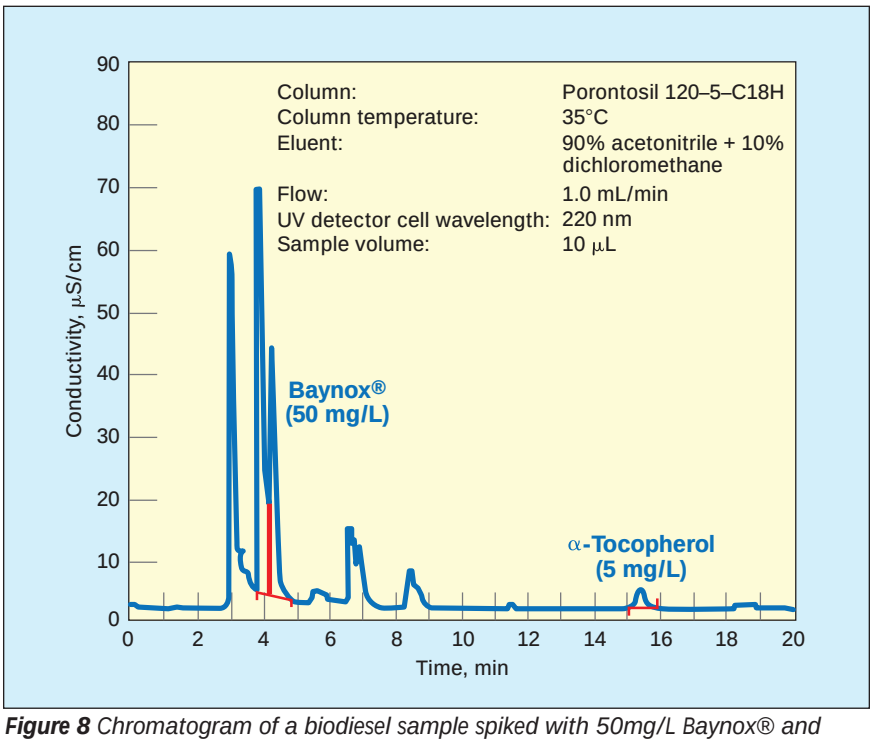


***Figure 8*** *Chromatogram of a biodiesel sample spiked with 50mg/L Baynox® and 5mg/L tocopherol*

quality monitoring and for determining the amounts of additives to be added.

### Experimental

Because of their structural similarities, vitamin E (∝-tocopherol and Baynox can be determined together in a single analysis (Figure 8). To improve solubility, dichloromethane is added to the eluent and analyte solutions. The biodiesel samples should be diluted 1:1000. The analytes are separated at 35°C and then determined quantitatively using UV detection.

## Implications

This paper presents several established and straightforward biofuel and feedstock test methods. However, several analysis techniques have not been addressed, for example the ion chromatographic detection of glycerin. Other promising techniques, such as the voltammetric determination of copper in ethanol or the measurement of the pH in ethanol, will probably emerge with the adoption of the European ethanol standard prEN 15376.

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# New standards of efficiency for biogas installations

**Case studies show that benefits from automation and control of biogas installations are being realised at facilities of various capacities. For these facilities, plant operation was made substantially easier, and availability and reliability were considerably improved**

Alexandre Bouriant
*Siemens AG*

The latest process controlequipment and systems create a solid basis for greater efficiency in biogas installations. The overall stability of such systems is what convinced biogas plant operator Bio Power e.K. According to a recommendation of system integrator Sigma Engineering, the use of such systems has substantial benefits and makes sense, even for smaller-scale biogas installations. The investment is also worthwhile because of the problem-free process operation possible in such plants. For example, the biogas plant of Bio Power e.K., Weyberhöfe, Germany, initially with an output of about 0.5MW, can now be increased to around 1MW on the solid and scalable basis of the process control system.

Since the Renewable Energy Sources Act (Erneuerbare Energien Gesetzes (EEG)) was amended in 2004, the number of new biogas installations has increased dramatically. The technology for biogas extraction, however, is still in the early stages of development in spite of the approximately 3,500 biogas plants already operating in Germany. Processes are continually being tested and analysed in the context of various projects and the results are being used to design more effective processes. However, in such projects it is rare that automation is regarded as an essential or important factor, even though the corresponding costs are only a fraction of the total investment. Consequently, relatively simple control methods involving different degrees of professionalism and different technical functions are often employed.

***Figure 1*** *Improving reliability of rotating equipment in biodiesel facilities with PCS systems has substantial benefits, even for small plants*

## Biogas plant automation challenges

But it is in this automation and control area, where there is a lack of experience, that particular attention should be paid to expanded functionality. Without a record of operating parameters and without daily checks, lasting and effective optimisation of the processes is not possible. Detailed visualisation and logging of the process values as well as an easy-to-use sequence control system help to improve the whole biogas process.

Equipment failures (Figure 1) due to unreliable control electronics or resulting from necessary changes are usually associated with high loss of earnings and maintenance costs. In view of the pressure being exerted on biogas plant operators owing to the rising price of grain, such plant outages can ultimately lead to financial emergencies.

Today's state-of-the-art process automation systems can make a considerable contribution towards efficient production and optimisation of biogas installations. If a well thought-out operator control and visualisation concept is applied, it is possible to achieve a more favourable ratio between the amount of material used and the resulting energy yield through maximum utilisation of the installation in question.

## Provision of electricity and heat at Sailauf

Since fossil fuel sources are finite and a substitute form of energy is therefore

needed, the use of biogas for producing energy is becoming more important. In 2006, biogas plants in Germany produced more than 5 billion kWh of electricity (Figure 2). For example, the Weyberhöfen installation makes use of direct power conversion (locally), which is the method usually adopted throughout Germany.

The input comes in the form of renewable raw materials, which are grown in an area of 220ha around the plant, as well as manure (liquid) from local farmers. Specially prepared straw is added to the liquid manure stored in the mixing pit (120m³) and the mixture is then pumped into a hydrolysis tank (120m³). Here, hydrolysis or acidification takes place, whereby the pH value is 4.5 to 6.3. In the two-grain silos (each 496m³), preliminary fermentation also takes place. Here, the long-chain polymers of the wheat and maize are split up into simpler organic compounds (i.e. they dissolve). Hydrolysis and the grain silo supply the fermenter (1000m³) with biomass via pipes. In order to know what masses are moved between the individual stages of the process, flow meters measure the flow rate at different points. On average, over 650 litres of substrate per hour are pumped.

In the fermenter, acetic acids, which are formed, are converted by micro-organisms mainly into methane and carbon dioxide. The process takes place in the mesophilic[1] temperature range (32-42°C) and at a pH value of 6.8 to 7.5. Combustible $CH_4$ is the main component of biogas, accounting for 50 to 55% of the total volume. A gas analyser with automatic measured-value acquisition ($CH_4$, $CO_2$, $H_2$, $O_2$...) breaks the gas down into its constituents and stores them. A measurement of the gas bubble by means of the Siemens PROBE LU in the fermenter provides information on the fill level (Figure 3).

After being vacuum-removed from the fermenter, the gas that has accumulated in the biogas collector is cleansed of hydrogen sulphide ($H_2S$) in a downstream desulphurisation unit, dried by means of condensation pipes and then converted into electricity in the engine-based cogeneration plant. A spark-ignition gas engine burns the biogas thus obtained to convert it into force (movement), which in turn drives a generator. The electricity thus produced is fed into the power grid by a transformer substation and upgraded in accordance with the EEG. At present, the engine-based cogeneration plant outputs 320kW. The heat resulting from combustion is used for drying the stored wood cuttings and for ensuring the correct process temperature in the fermenter. Even more efficiently, the heat is used in the district heating network supplying the nearby industrial district. The substrate from the fermenter is kept in the fermentation-residue storage tank (1900m³). The fermentation residue is a high-quality fertiliser and is reused in the fields of the manure suppliers.

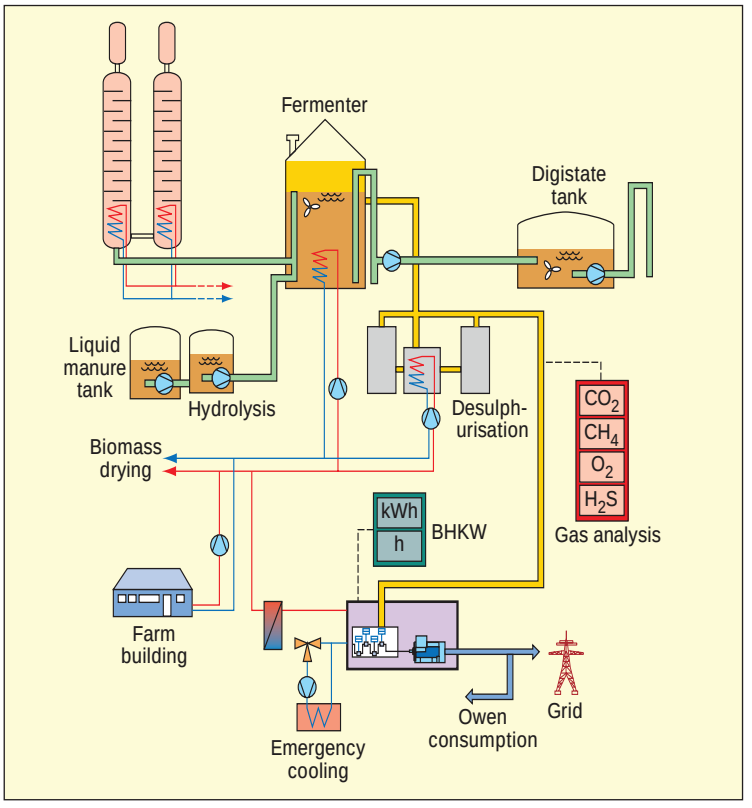


***Figure 2*** *A typical biogas process as used in the first phase of expansion*

## Changeover to the new process control system

In March 2007, the engineering office of Sigma in Goldbach received an order to re-equip an existing biogas plant. The plant in question was built 1½ years ago near the Weyberhöfe/Sailauf industrial estate in the Aschaffenburg district. The owner had been forced to put up with repeated faults and outages since the plant had started operating. This made him finally decide to bring about a change in the situation.

Between January and April, the owner suffered recorded losses of 9,000 Euros due to misinformation and malfunctioning of the original control solution. The costs of service and personnel were incurred by the owner for all times of the day and night. The combination of high susceptibility to faults and low availability caused total losses amounting to about 20,000 Euros.

A solution in line with the existing industrial standard promised improvement. After an inspection of the biogas plant, Martin Spinnler, managing director of Sigma, decided to make this 'emergency situation' into a pilot project for his company. The challenge was not only to considerably improve the functionality of the biogas plant but also to smoothly change over from the old open-loop control method to the new process control system. According to Spinnler, "The decision in favour of a process control system has proved right. The additional cost of the system has already been regained since commissioning."

Considerations of how to solve the automation problem initially envisaged a PLC-based solution (PLC = programmable logic controller with SCADA programming), a method frequently adopted in similar situations. In spite of the somewhat more favourable acquisition costs, however, this notion soon faded into the background as the solution with the all-round process control system (i.e. SIMATIC PCS 7 with PCS 7 Box) entailed considerably less expenditure for engineering and commissioning and was therefore more than able to make up for its higher costs of purchase.

## Plant equipment scope

In the old system, the gas analysis and gas bubble measurement readings had to be taken by an operator and then entered into the control system by hand. Now the plant was equipped with extensive measuring technology, which made for an increase in the quality of process monitoring and optimisation. The process control system proved very flexible when it came to the connection of non-Siemens products. The biogas plant now has the following process control measuring systems, which are used for the following purposes:

- One weighing system: For recording the amount of supplied biomass
- Four flow meters: For measurement of substrate amounts
- Three fill level indicators: In grain silos and for fermentation
- Two pH value detectors: For the

hydrolysis section and in the fermenter
- One gas bubble measuring instrument: For measurement of the amount of gas produced in the fermenter
- One gas content analyser with automatic measured-value acquisition of the four main components: methane, carbon dioxide, oxygen and hydrogen sulphide.

On the actuator side, four drives are controlled:
- Four frequency converters for the agitators
- One frequency converter for the pumps.

Power and heat supply:
- One controlled heat supply unit for the district heating network and for drying biomass
- One engine-based cogeneration plant control unit activated by the process control system.

The instrumentation with analogue outputs is connected to the system via the peripheral Simatic ET200M unit. This unit was fitted with the appropriate modules:
- Two modules each with 32 digital inputs (24V)
- Three modules each with 8 analogue inputs (4mA to 20mA)
- One module with 32 digital outputs (24 V)
- One module with 2 analogue outputs (4mA to 20mA).

The ET200M unit itself is connected to the process control system via Profibus DP. This type of peripheral setup enables simple expansion with additional field instruments/actuators and also has integrated diagnostic capabilities. The uncomplicated setup based on a field bus reduces cabling costs and saves time at the commissioning stage. In particular, configuration and assembly errors are detected and tracked down more quickly during commissioning.

The engineering was carried out by Sigma with Simatic PCS 7. The 110 project objects (PO) provided in the starting software package were sufficient to meet all automation requirements. Moreover, the number of POs can easily be increased as with the scalable PCS 7 licence.

At the owner's request, a user-friendly step-sequence visualisation system was implemented, with which the operating personnel can obtain a clear picture of the overall process and, in the event of a fault, can react quickly and flexibly. In addition, all the brought-in amounts of material can be continually shown on a balance sheet together with a monthly log.

***Figure 3*** *Gas bubble measurement equipment*

## Operator control of the plant

The reaction of the plant operating personnel to the process control solution was very good. They became familiar with the new control system and learned how to use it in less than two days. It is very easy for the personnel to control the plant due to the clear and uncomplicated operator station. With the basic functions provided by the PCS, production reports can also be written with little effort and complexity. The indication lists generated in the process can also be used as the basis for logs.

With the sequential function chart (SFC), operating personnel can now visualise the process sequence step-by-step. As a result, any faults that occur can be quickly detected and optimally responded to.

The recorded process data can be shown in a clear layout on the screen and can be archived at the same time. The display of curves based on operating parameters enables efficient online analysis of the process. Consideration of these curves over the long term makes it possible to better analyse process sequences. This provides a good basis for optimisation.

## Engineering

With the module libraries provided in PCS 7, it was possible to cover all the automation functions of the biogas plant. The development office was able to test almost all aspects of the biogas plant application on the basis of the standard process-simulation functions, test functions and self-created testing methods in PCS 7. The commissioning time needed for such a plant was therefore reduced considerably.

The high degree of integration of the process control system saves a lot of time in comparison with conventional PLC engineering. Sequence control, for example, is reduced to definition of the steps and the transition conditions. Programming of visualisation and operator control is normally necessary for the later operating mode and is generated by the system itself.

Integration of the existing instrumentation, which came from different manufacturers, proved straightforward.

The changes and improvements in the application, which were necessary to lend the finishing touches to the control system, were carried out precisely, easily and quickly during commissioning. It will also be possible to integrate later additions.

Due to the possibility of online alteration, which is a typical characteristic of such process control systems, the changes can be carried out in the application quickly, without having to shut down the biogas plant (stop state).

The changeover from the old control system to the new system proceeded smoothly within four days.

Field bus technology is one of the advantages of the system. Modern field bus devices perform additional diagnostic and asset management functions, which facilitate maintenance of the plant and increase its availability. But in the plant under consideration, the traditional analogue instrumentation was already incorporated. If a changeover were to be made to field bus instrumentation, many disconnecting, terminal and distribution devices would be replaced by the field bus system. In addition, considerable savings and reductions in terms of the material expended and the commissioning time would be achieved.

## Future additions

Operation of the plant was made substantially easier, and availability and reliability were considerably improved as well. Moreover, the intention was to be able to operate the plant without extensive supervision. The system includes the possibility of reporting any process problems and fault messages to the plant manager or operating personnel by SMS. With remote control access, it is even possible to control and visualise the plant from a PC at home. To this end, PCS 7 can be configured in different ways, which must be adapted to the necessary network security measures in order to ensure that the system works without any risks. Reducing the amount of necessary effort by making appropriate extensions can contribute substantially towards improving plant efficiency.

Another measure is the plan to expand the biogas plant. The former mesophilic system with preliminary

hydrolysis and a fermenter will be changed over to a combined mesophilic and thermophilic system with two fermenters (without preliminary hydrolysis) plus all the necessary equipment. The storage tank for fermentation residue will also play the role of an additional after-fermenter.

For the planned increase in capacity, an additional cogeneration plant will be installed, allowing the Bio Power e.K. installation to achieve an output of approximately 1MW.

## Preferences over SCADA system

Sigma's previously mentioned managing director does not regret his preference for a PCS 7 Box solution instead of the usual SCADA program. The hardware costs for the SCADA solution would have been lower but it would have meant considerably more expenditure for engineering and commissioning. Since the biogas sector is no doubt due to undergo transformation in many respects, the possibility of implementing changes with only minimal effort when additions and improvements have to be made is an enormous advantage.

Reconnection of the control equipment to an ET 200 M module and commissioning of the PCS 7 software was successfully completed within four days. All the software changes during commissioning were carried out without any interruption to plant operation and, as there were no problems, the customer did not have to put up with any notable stoppages.

## Control system performance

Ever since PCS 7 started to control the plant, not one system-related fault or malfunction has occurred, even though the biogas plant has been continually expanded or modified. According to M. Fleckenstein, managing director of Bio Power e.K., Sailauf, "The system has considerably increased the availability of our plant. Migration from the earlier control system was carried out without problems or production losses. We now have a control system basis that makes us more efficient." The plant owner also stated that he was very pleased with the system's reliability and resistance to faults. In his opinion, other plants that have control problems could also benefit. Unfortunately, he is not aware of any other company that has adopted such a comparable professional approach.

For him personally, the plant is now very easy to control, while his personnel continue to find ways of improving his processes. Visualisation, logging and the indication system simplify operator control and are very user-friendly. The process control system with the functions of online changeability, the speed with which special requirements can be implemented and the system's constant stability have convinced the owner of the system's effectiveness.

**Acknowledgement**
The author extends special recognition to Mathias Fleckenstein, managing director of Bio Power e.K., in Sailauf, Germany, and Martin Spinnler, managing director of Sigma Engineering in Goldbach, Germany, for their feedback concerning the results of this control system implementation.

1 Mesophilic: Temperature range in the biogas process between 32 and 42 °C. Most of the known methane bacteria experience their optimum growth in the mesophilic temperature range. Mesophilically operated installations are currently the most widespread types.
2 Thermophilic: Temperature range in the biogas process between 50 and 57 °C. Due to the higher process temperature, a higher gas yield is achieved. However, more energy has to be used to reach the corresponding temperature range. Faults have a greater effect on the process in the thermophilic temperature range.

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# Biodiesel concentration measurements

**Methods providing greater accuracy over the AFNOR method for determining biodiesel concentration in fuel blends are discussed. Principal component regression is explored as a means of alleviating errors when FAME is produced from varying feedstocks**

David Wooton and David Armstrong
*Wooton Consulting and Perkin Elmer*

Biodiesel is most often delivered to the end-user in the form of a blend in which the biodiesel is mixed with a petroleum-based diesel fuel. These blends are identified by the percentage of biodiesel contained in the final blend – B20 contains 20% biodiesel blended with 80% petroleum diesel. Recent investigations have shown that the accuracy of such blends is often very low, with some reports showing that more than one-third of B20 blends sold to the consumer are not B20 at all.

## Measurement inconsistencies

There are several methods designed to measure the fatty acid methyl ester (FAME) content in diesel fuels. The most common methods include AFNOR NF EN 14078 – 'Determining of fatty acid methyl esters (FAME) in middle distillates – infrared spectroscopy method' – and a newly approved ASTM method – 'Determination of biodiesel (fatty acid methyl esters) content in diesel fuel oil using mid infrared spectroscopy'. The AFNOR method is developed around a flow cell measurement, while the ASTM method is developed around an attenuated total reflectance (ATR) cell. The ATR method does not lend itself to use in a laboratory that has numerous samples to analyse, since it requires operator loading of every sample.

While the AFNOR NF EN 14078 method serves as one of the standards in the industry for measuring the biodiesel content in a blend such as B20, the method does have some limitations. Two methods that provide greater accuracy and utility over the AFNOR method are considered. While still using the technology of infrared spectroscopy, the advantages of using peak area measurements over peak height measurements, as specified in the AFNOR method, are explored. Additionally, the use of principal component regression (PCR) is explored as a means of alleviating errors that are introduced when the FAME used in the biodiesel blend is produced from varying feedstocks. All methods use the time-proven technology of mid-range FTIR spectroscopy.

***Figure 1*** *Typical instrumentation for determination of FAME in middle distillates*

## Instrumentation

In this study a PerkinElmer Spectrum OilExpress was used, which consists of Spectrum 100 Fourier transform infrared (FTIR) spectrometer, a transmission cell with zinc selenide (ZnSe) windows with a 0.1mm path length, an autosampler and software (Figure 1). The system used for the work described in this article was equipped with a KBr beamsplitter, which provides coverage of the spectral range from 7,800-350cm$^{-1}$, which is in the mid-infrared range. The system can be provided either with or without an autosampler to best suit the sample load of any given laboratory.

## Beer's Law

Beer's Law, which is sometimes associated with the name Lambert, correlates the concentration of a substance to the amount of light that is absorbed by that material. This correlation is readily expressed with the equation $A = \alpha\ l\ c$ where $A$ is the absorbance of the light passed through the material measured, $\alpha$ is the absorption coefficient of the absorbing material, $l$ is the distance that the light travels through the material (path length), and $c$ is the concentration of the absorbing species. Absorbance may be a value determined from simply measuring the height of an absorbance peak, or it may be determined by measuring the area of an absorbance peak. The value of $l$ will be stated in this document as the path length of the cell used in the infrared instrument.

## Pearson's correlation

The most common correlation between two variables is Pearson's correlation. This correlation reflects the degree of linear relationship between two variables with a perfect positive correlation identified with a +1.

## Principal component regression (PCR)

A mathematical function that is based on the best summary of the relationship between the variables. In practice, it involves the calibration of an analytical instrument, such as an FTIR, with a

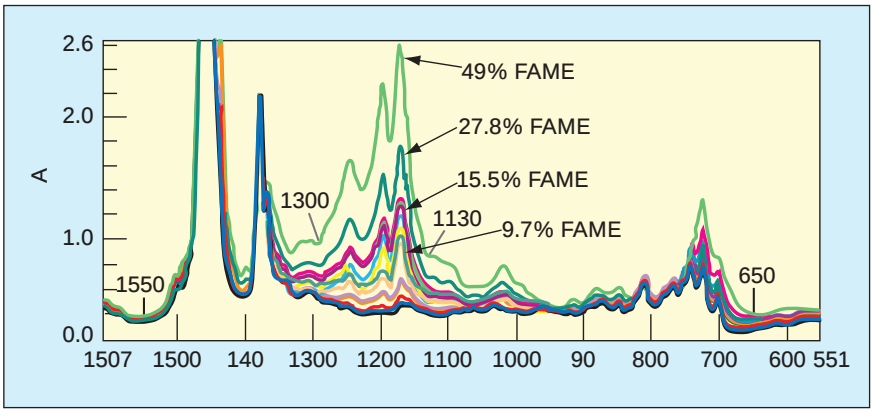


*Figure 2*

relatively large sampling of standards. The data from this large sampling is then processed by a software package that will identify the relationship between the variables of absorbance and concentration. While an initial investment in calibration time is required before the first sample can be analysed, the data generated through the use of PCR is typically more robust than data determined through the use of simpler peak height or peak area measurements.

## ANFOR method

Association Francaise de Normalisation (ANFOR) has developed a method for determining fatty acid methyl esters (FAME) in middle distillates using infrared spectroscopy that will serve as the starting point for the following discussion. The method uses a cell of 0.5mm path length and measures the height of a carbonyl band at or near 1745cm$^{-1}$. The baseline used for this measurement is drawn from 1820 to 1670cm$^{-1}$ (Figure 2). This method is based on sound scientific principals. However, it does invoke some practical concerns. Because the path length of the cell is relatively long, it is easy for measurements to exceed the working range of the technique, thus invoking the need for sample dilutions. Additionally, experimentation has shown that the measurements made with this method may be skewed by variances in the feedstock used to produce the biodiesel. If the biodiesel to be measured contains product made both from soybean oil and used cooking oil, for example, the measured result will likely be biased in one direction or another.

## Modifications

Two major modifications have improved the AFNOR method. So that the need for dilutions can be eliminated, the path length of the cell used is 0.1mm rather than the 0.5mm recommended in the AFNOR method. Additionally, the measurement of the peak has been changed from peak height to peak area with a range of 1820-1670cm$^{-1}$. It has been found that this spectral range is well suited for blends in the range of B0 to B16. If a higher concentration of biodiesel is to be measured, the peak in the range of 1300-1130cm$^{-1}$ works well for measurements up to and including B49 (Figure 3). Measurements made at either of these spectral ranges yielded a Pearson's correlation that was greater than or equal to 0.9990 (> 0.9990). This better method is capable of measuring biodiesel blends over the broad range of B0 to B49.

## Best method

If even higher Pearson's correlation values or wider biodiesel blend ratios are desired, principal component regression (PCR) is the method of choice. This method uses nearly all of the information available in the full spectral region of mid-infrared range. For this study, biodiesel blends between B0 and B20 were used. However, the range could be extended to accommodate higher concentrations of biodiesel in the blend. By using the entire spectral region, a more robust model has been generated, which is shown in the improved Pearson's correlation of 0.9997. It has been found that the PCR model is best able to handle variables brought about when different feedstocks have been used to produce the biodiesel. This PCR model has also shown greater freedom from errors brought about by noise and interferents.

## Conclusion

FTIR spectroscopy is a technology that is very well suited to the analysis of biodiesel content in blends. The technology used is rugged, time proven and moderately easy. Each of the methods discussed is appropriate for the measurement of biodiesel blends, depending on the demands placed on the laboratory by the sample type and the level of accuracy required.

Note: Spectrum Oil Express is a mark of Perkin Elmer.

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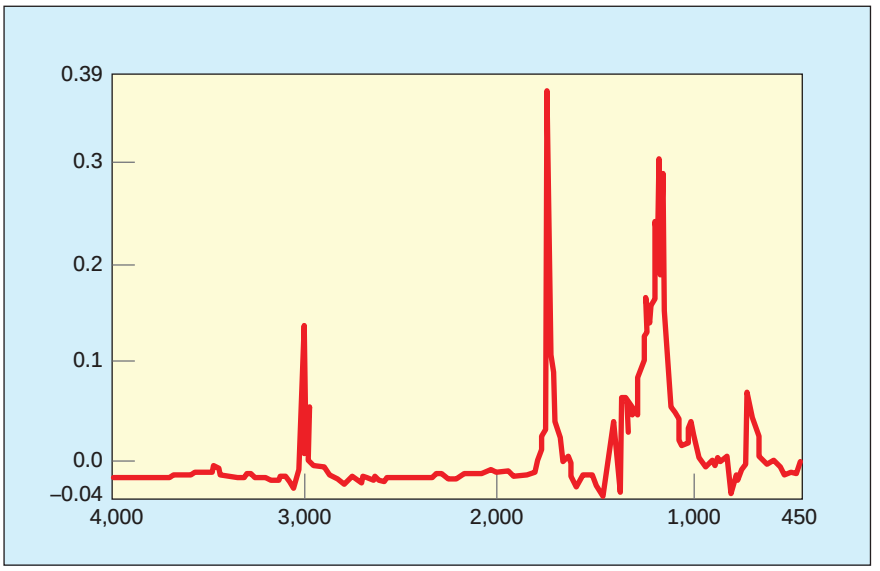


*Figure 3*

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