White Paper

Endress+Hauser
People for Process Automation

Craig McIntyre
Chemical Industry Manager

April 12, 2007

Measurement solutions for biodiesel renewable fuels industry

Overview

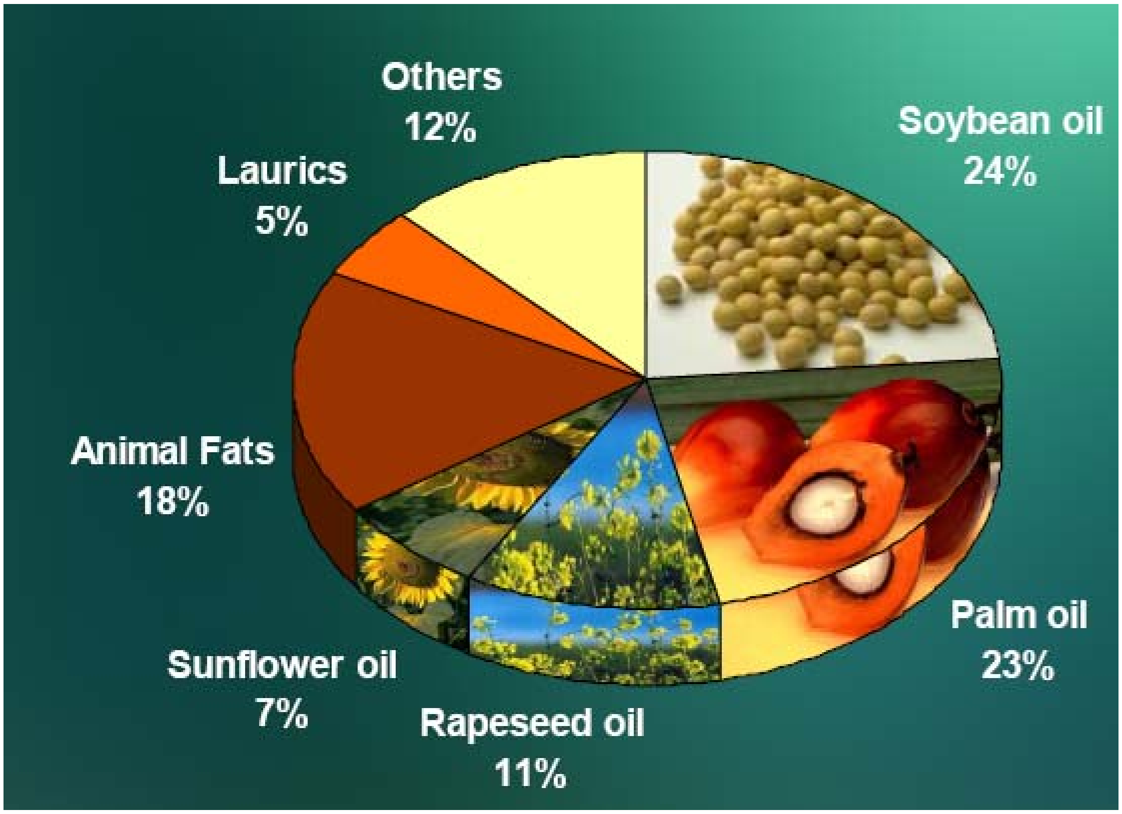
Endress+Hauser is one of the leading supporters of the growing ethanol and biodiesel renewable fuels industry. Many engineering/construction firms and production operations around the world rely on Endress+Hauser instrumentation, application engineering and operations support to achieve their operational and financial goals.

This paper describes some of the market drivers that are contributing to the strong global expansion of biodiesel production. A typical continuous biodiesel production process is described and typical non proprietary biodiesel process measurement applications of Endress+Hauser temperature, pressure, flow, density, level and analytical measurement systems are listed. Examples of the benefits gained from implementation of Endress+Hauser measurement solutions in process, utilities, safety and supply chain operations are described.

What is Biodiesel?

Vegetable oils have long been promoted as possible substitutes for diesel fuel. In fact, Rudolph Diesel, the inventor of the diesel engine, reportedly used peanut oil in his original engine designs around the turn of the last century.
Biodiesel is a renewable, environmentally friendly substitute for or value added additive to petroleum-based diesel fuel. It is produced from vegetable oils (i.e. palm, soybean, and rapeseed), animal fats, or waste cooking oils and fats, and can be used in existing diesel engines without any expensive modifications. Biodiesel can be added to petroleum diesel to create a biodiesel blend with favorable performance attributes and environmental benefits roughly proportional to the biodiesel fraction. Biodiesel is safe, nontoxic, biodegradable, and reduces the emissions of many harmful compounds associated with the combustion of petroleum-based diesel. Because biodiesel is produced from domestically produced plant oils or waste fats, switching from petroleum-based diesel to biodiesel decreases dependence on foreign petroleum, reduces net greenhouse gas emissions, and provides tangible benefits for the domestic economy.

The US produces over 3.8 billion gallons a year of fats and oils which can be tapped for biodiesel and glycerin conversion. Although each region in the world generally has a predominate source of oils used in biodiesel operations, some facilities can accommodate several types of oil feedstocks.



Drivers for the growth in Biodiesel production

The potential benefits associated with biodiesel have driven many national, state, and local governments to adopt policies that mandate or make it financially beneficial to produce and use biodiesel. The uncertain supply of fossil fuels and the increasing level of global environmental consciousness suggest that additional incentives and mandates are likely in the future. The most important US federal mandates affecting biodiesel demand are the Energy Policy Act (EPAct), which requires specific levels of alternative fuel usage in federal fleets, and the Clean Air Act, which will require all diesel fuel sold for on-road use to be ultra-low sulfur by 2006. In large metropolitan areas, more strength air quality standards are helping increase the demand for biodiesel. Biodiesel incentive programs can be delineated into two main categories—production and consumption. Both types of incentives lower the cost of biodiesel, eroding any price differentials that prevent its widespread adoption.

The market size for biodiesel in the US reached 150 MGY in 2006; double the 75 MGY produced in 2005. Emerging US legislation is expected to establish a biodiesel standard of 250 million gallons per year in 2008 to 2 billion gallons per year by 2015.

For comparison, Europe currently consumes over a quarter billion gallons of biodiesel fuel annually. Several companies in China are already producing large quantities of biodiesel from virgin rapeseed oil. The climate of India might be favorable for producing substantial quantities of biodiesel from a native tree that produces large quantities of inedible oil. Palm Oil operations in Asia are building biodiesel operations to convert their palm oil feedstocks.

Biodiesel blended with petroleum diesel can significantly help address emerging and current emissions targets. When biodiesel is blended with conventional petroleum-based diesel in any fraction; the resulting blend is referred to as "BXX", where "XX" is the percentage biodiesel.

In the United States, fuel-grade biodiesel conforms to ASTM D6751 and is registered with the Environmental Protection Agency as a legal motor fuel. This standard defines pure biodiesel (B100) for blending with petrodiesel in levels up to 20% by volume.

As an additive, Biodiesel improves the "lubricity" of the fuel. Even B2 (2 % biodiesel) biodiesel offers 66% higher lubricity than No 2 diesel alone. This extends engine life and improves cold flow without giving up horsepower, torque and mileage. There is some evidence that the addition of biodiesel may allow diesel engines to burn cooler as well as improve engine cleaning.

Oils/fats to biodiesel and glycerin/glycerol conversion processes

The high viscosity of natural vegetable oils and animal fats generally results in poor diesel engine fuel atomization and fuel injector blockage especially in lower temperature climates. These oils need to be converted into mono-alkyl esters of long chain fatty acids commonly referred to as methyl esters or biodiesel. Transesterification is the process of transforming one ester into another ester. Esters are chains of hydrocarbons that will bond with other molecules. Molecules of vegetable oil are composed of three esters bonded to a molecule of glycerin. This type of molecule is called a triglyceride. Vegetable oil is relatively thick and sticky because the legs of the molecules get tangled up with each other. To reduce the viscosity of the oil we need to break the molecule apart, remove the glycerin molecule, and bond each individual ester with a molecule of alcohol.

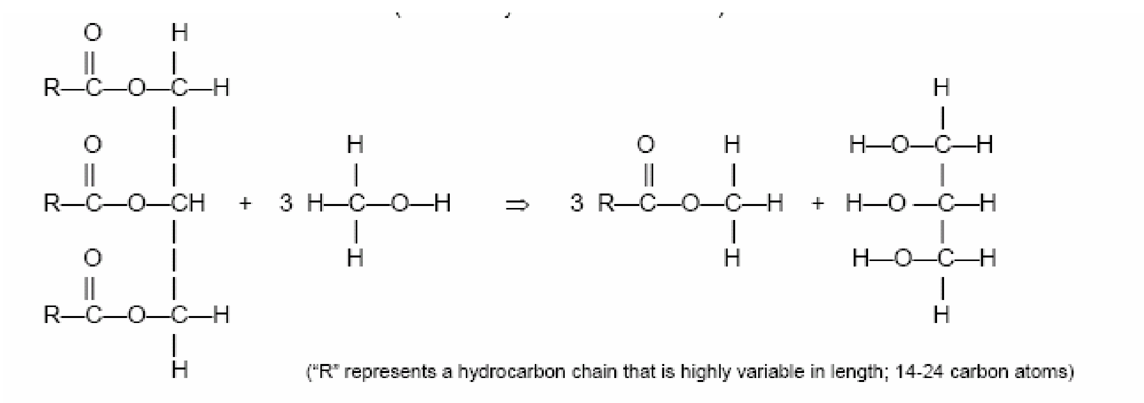
A catalyst (i.e. sodium hydroxide, NaOH; potassium hydroxide, KOH, or sodium methylate) is used to break the vegetable oil molecule apart; and then the free esters, otherwise known as fatty acids because they are acidic, will rapidly bond with the alcohol, because it is basic, to produce biodiesel esters. A catalyst is a substance that is required for a reaction to happen between other substances but itself is unchanged in the reaction.

Alkyl ester is a generic technical term that refers to any combination of vegetable oil ester and alcohol, but each different combination of oil and alcohol has a different name. When methanol is used, the resulting esters are called methyl esters. Methanol is the alcohol that is used most often by people producing biodiesel because it produces the most reliable reaction. Some people use ethanol because it is less toxic and is made from biomass; using ethanol creates ethyl esters. However, ethanol is more difficult to extract and recycle than methanol reducing its usage.

The type of vegetable oil used can also contribute to the name of the finished product; for example, soy methyl esters (SME) are the most common type of esters sold as biodiesel in the United States because most of it is made from soybean oil and methanol. In Europe, biodiesel is usually made from rapeseed (canola) and methanol, and thus it is called rapeseed methyl esters (RME).
Whichever type of vegetable oil and alcohol are used, the transesterification reaction breaks the triglyceride vegetable oil molecule into three esters and one glycerin molecule. An alcohol molecule attaches to the end of each free ester to form three alkyl esters and one glycerin molecule from each vegetable oil molecule.

Transesterification Reaction

Vegetable Oil + Alcohol (Methanol) ⇒ **Alkyl Esters (Biodiesel) + Glycerin (Soap)**
(with catalyst – NaOH or KOH)



(Picture courtesy of Campa® – Biodiesel GmbH & Co. KG/ Ltd.)

A deeper look at transesterification

It is extremely important to realize that vegetable oils are mixtures of triglycerides from various fatty acids. The composition of vegetable oils varies with the plant source. Often the terms fatty acid profile or fatty acid composition are used to describe the specific nature of fatty acids occurring in fats and oils. The chemical and physical properties of fats and oils and the esters derived from them vary with the fatty acid profile. For example, mixtures containing larger amounts of methyl palmitate or methyl stearate will solidify at higher temperatures than those containing lesser amounts. The corresponding esters of those fatty acids with glycerol are known as tripalmitin, tristearin, triolein, trilinolein and trilinolenin.

In a variation of the formation of esters from acids and alcohols, an ester can react with another alcohol. In that case, the new alcohol is derived from the original ester is formed and the new ester is derived from the original alcohol. Thus, an ethyl ester can react with methanol to form a methyl ester and ethanol. This process is called transesterification. Transesterification is extremely important for biodiesel. Biodiesel as it is defined today is obtained by transesterifying the triglycerides with methanol. Methanol is the preferred alcohol for obtaining biodiesel because it is the cheapest (and most available) alcohol. However, for the reaction to occur in a reasonable time, a substance called a catalyst (catalysts are substances that often present in small amounts, accelerate the speed of a reaction; in many cases virtually no reaction would occur without a catalyst), must be added to the mixture of the vegetable oil and methanol.

For the transesterification to occur, usually 6 moles of alcohol are used for every mole of triglyceride. As the term "equilibrium" indicates, not all reactions easily proceed to completion and after some time the starting materials and reaction products are present in constant amounts (the equilibrium has been attained). In many cases, the fact that a reaction can proceed in the reverse fashion (from right to left in the equation) also plays a role in formation of the equilibrium. To force the equilibrium in the direction of the products (as is almost always desired), one or more parameter(s) of the reaction may need to be changed. Such parameters include the molar ratio as well as others such as temperature, pressure and use of a catalyst.

In accordance with the names of fatty acids and their esters, the methyl ester of soybean oil is often called methyl soyate. The term soybean oil methyl ester (SME) is also very common. The same holds for the esters of other vegetable oils. Another common abbreviation that is commonly used is FAME (fatty acid methyl ester).

Besides triglycerides, mono- and diglycerides can also exist. They are formed as intermediates during the transesterification reaction. This is one of the problems when conducting chemical reactions in general, not only the transesterification reaction. It is almost always the goal of chemical reactions to obtain products that are as pure as possible. However, hardly any chemical reaction proceeds to full completion. Therefore, often intermediates (in the case of transesterification the intermediates are partially reacted triglycerides, i.e., the mono- and diglycerides) can contaminate the final product. Other materials that can contaminate biodiesel are residual methanol (or other alcohol), glycerol, and catalyst.

When the transesterification reaction is conducted, you can visually observe that not all materials can be readily mixed with each other. A term often used for this phenomenon is that there are two phases. At the start of the reaction, you can notice that methanol and vegetable oil do not readily mix. At the end of the reaction, you can notice that there are two layers (phases), one consisting mainly of glycerol, the other of the methyl esters. Obviously, glycerol and methyl esters do not mix readily. How readily one compound will dissolve in another depends on the structural features of the compounds, for example the existence of OH groups. Thus, compounds containing OH groups and those not containing OH groups often will not readily mix.

The most commonly used catalyst materials for converting triglycerides to biodiesel are sodium hydroxide, potassium hydroxide, and sodium methoxide. Most base catalyst systems use vegetable oils as a feedstock. If the vegetable oil is crude, it contains small amounts (<2%) of free fatty acids that will form soaps that will end up in the crude glycerin. Refined feedstocks, such as refined soy oil can also be used with base catalysts. The base catalysts are highly hygroscopic and they form chemical water when dissolved in the alcohol reactant. They also absorb water from the air during storage. If too much water has been adsorbed the catalyst will perform poorly and the biodiesel may not meet the total glycerin standard.
Base catalyzed reactions are relatively fast, with residence times from about 5 minutes to about 1 hour, depending on temperature, concentration, mixing and alcohol-triglyceride ratio. Many (especially in Europe) use sodium hydroxide (NaOH) or potassium hydroxide (KOH) as catalysts, although glycerol refiners prefer NaOH. KOH has a higher cost but the potassium can be precipitated as potassium phosphate (K3PO4), a fertilizer, when the products are neutralized using phosphoric acid. Sodium methoxide, usually as a 25 % solution in methanol, is a more powerful catalyst on a weight basis than the mixture of NaOH and methanol. This appears to be, in part, the result of the negative effect of the chemical water produced in situ when NaOH and methanol react to form sodium methoxide. Sodium Methylate seems to becoming the base catalyst of choice.

The counterparts of bases are known as acids. Many acids can also be used as catalysts in the transesterification reaction. The base-catalyzed reaction has advantages such as a higher reaction rate although acid-catalyzed reactions employing advanced mixing technologies (i.e. ultrasonic) to increase reaction rates are emerging.

A deeper look at biodiesel/glycerin separation

The biodiesel/glycerin separation is typically the first step of product recovery in most biodiesel processes. The separation process is based on the facts that fatty acid alcohol esters and glycerol are sparingly mutually soluble, and that there is a significant difference in density between the ester and glycerol phases. The presence of methanol in one or both phases affects the solubility of ester in glycerol and glycerol in ester. The ester washing step is used to neutralize any residual catalyst, to remove any soaps formed during the etherification reaction, and to remove residual free glycerol and methanol. Ester drying is required to meet the stringent limits on the amount of water present in the final biodiesel product. In addition, there may be other treatments used to reduce color bodies in the fuel, remove sulfur and/or phosphorus from the fuel, or to remove glycerides. Additization is the addition of materials that have a specific functionality that modifies one or more fuel properties. Examples include cloud point/pour point additives, antioxidants, or other stability enhancing agents.

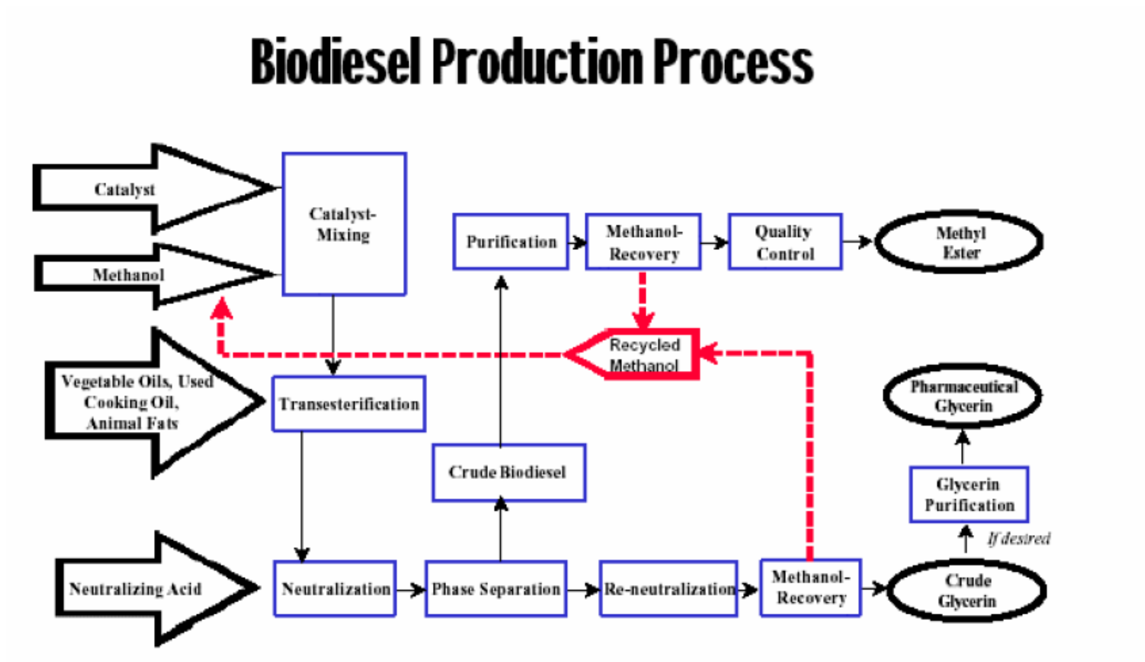
Fatty acid alcohol esters have a density of about 0.88 gm/cc, while the glycerol phase has a density on the order of 1.05 gm/cc, or more. The glycerol density depends on the amount of methanol, water, and catalyst in the glycerol. This density difference is sufficient for the use of simple gravity separation techniques for the two phases. However, the rate of separation is affected by several factors. Most biodiesel processes use relatively intense mixing, at least at the beginning of the reaction, to incorporate the sparingly soluble alcohol into the oil phase. If this mixing continues for the entire reaction, the glycerol can be dispersed in very fine droplets throughout the mixture. This dispersion requires from one hour to several hours to allow the droplets to coalesce into a distinct glycerol phase. For this reason, mixing is generally slowed as the reaction begins to progress, to reduce the time required for phase separation. The more nearly neutral the pH, the quicker the glycerol phase will coalesce. This is one reason to minimize the total catalyst use. The presence of significant quantities of mono-, di-, and triglycerides in the final mixture can lead to the formation of an emulsion layer at the ester – glycerol interface. At best, this layer represents a net loss of product, unless it is recovered and separated. At worst, the ester phase will not meet the biodiesel specification and will have to be re-run. If problems with mono, di, and triglycerides occur, one should reevaluate the entire reaction to see where improvements can be made to improve process yields in the preceding steps. The esterification process is run with an excess of alcohol to ensure complete reaction and to attain higher reaction rates. The residual alcohol is distributed between the ester and glycerol phases. The alcohol can act as a dispersant for the ester into the glycerol phase and for the glycerol into the ester phase. The result can be a need for additional processing of the products to meet specifications. Other people claim that methanol aids in phase separation, which is one reason that product is generally phase separated before methanol recovery.

There are two main types of equipment used to separate the ester and glycerol phases. One of the most common is the decanter or gravity separator. Decanter systems rely solely on the density difference and residence time to achieve the separation. For relatively small throughput, or batch processes, the 1 to 8 hours required for complete separation of the phases may be acceptable. However, a separation that requires a residence time of 1 hour requires a decanter with a volume of at least 700 gallons to affect separation for a 5,000,000 gallon per year, continuous plant. For lower extent of reaction, the separation is slower, and the decanter will have to be much larger. The primary determinant for designing a decanter for biodiesel production is the desired residence time. This, plus the product mixture flow rate determines the size of the unit. Decanter units should be rather tall and narrow to allow physical separation between the ester and the glycerol withdrawal points. L/D ratios of 5 to 10 can work well. The temperature in the decanter affects the solubility of the alcohol in both phases, and the viscosity of the two liquids. Too high a temperature in the decanter can cause residual alcohol to flash, potentially restricting the flow of the ester phase out of the tank. On the other hand, too low a temperature increases the viscosity in both phases. The increased viscosity will slow the coalescence rate in the system. The presence of an emulsion layer is indicative of mono- and di-glycerides. The emulsion layer will form between the phases. In continuous operation, there must be a provision for removing the emulsion, so it does not fill the decanter.

Another approach to separate the phases in continuous plants is to use a centrifuge. The centrifuge creates an artificial, high gravity field by spinning at very high speeds accomplishing separation quite quickly. The disadvantage of the centrifuge is its initial cost, and the need for considerable and careful maintenance. Centrifuges are used extensively in the several biodiesel process designs. Centrifuges are high-speed, rotating devices. The artificial gravity of the centrifuge results from the rotation. Speeds of 2000 to 5000 rpm are not uncommon. A batch or a continuous centrifuge can be used with smaller throughput facilities. Multiple centrifuges are often used. The use of a batch centrifuge in a continuous process requires a surge tank to match the batch cycle time with the continuous processing rate.

Biodiesel production

There are a number of batch and continuous biodiesel production processes using a variety of feedstocks. Engineering groups throughout the world engage in designing the most efficient and cost productive means to convert the chosen feedstock(s) into the quality and quantity of biodiesel and glycerin required. Although the general conversion processes may have underlying similarities, the equipment and techniques these engineering groups choose to accomplish these conversions and associated processes can be quite different. Some units may be very modular while other may consist of several built in place units.



Some of the process steps in biodiesel production are defined below as well as the range of measurement requirements addressed by Endress+Hauser instrumentation. Keep in mind that there are variations in measurement requirements as defined by the designs from several engineering groups. It is also important to note that the technologies employed in biodiesel conversion are not static. Improved processing and associated measurement techniques are continually being developed and proven in commercial operations.

In general one can group the process steps as follows:

- **Feedstock handling and preparation**
- **Pretreatment**
- **Reaction**
- **Separation/Washing/Purification**
- **Supply chain management (i.e. load-in, storage and load-out)**

Utilities are also required to provide power, steam, water, gases and depending on the process water treatment. One also must manage the Safety, Health and Environmental aspects surrounding the operation and movement of the chemicals and products in a biodiesel facility.

Feedstock handling and preparation

The feedstocks commonly used for biodiesel production include several different oilseed crops, rendered animal fats, recycled cooking oils and fats.

Most of the biodiesel produced in the United States and Brazil is made from soybean oil. Soybean crush and refinery operations extract the crude soybean oil and prepare it for further processing. Some Biodiesel facilities store and crush process their own soybeans to crude oil and refined oil; others receive crude or refined oil from other soybean processing facilities.

Rapeseeds which dominate the biodiesel industry in Europe and Canada are processed to obtain Rapeseed oil, a close cousin of canola oil.

Palm oil producing countries such as Malaysia and Indonesia process the palm fruit bunches from palm trees to get palm/palm nut oils. Jatropha plants are being cultivated in India as a source of Jatropha oil for biodiesel production.

Other virgin oil sources include sunflower and cotton seeds. More exotic oil sources include high oil content algaes which are “fed” CO2 laden gases from power production facilities.

A growing amount of biodiesel is produced using waste cooking fats and oils. Many rendering companies and state and foreign governments have recently started investigating biodiesel production from yellow grease and animal tallow.

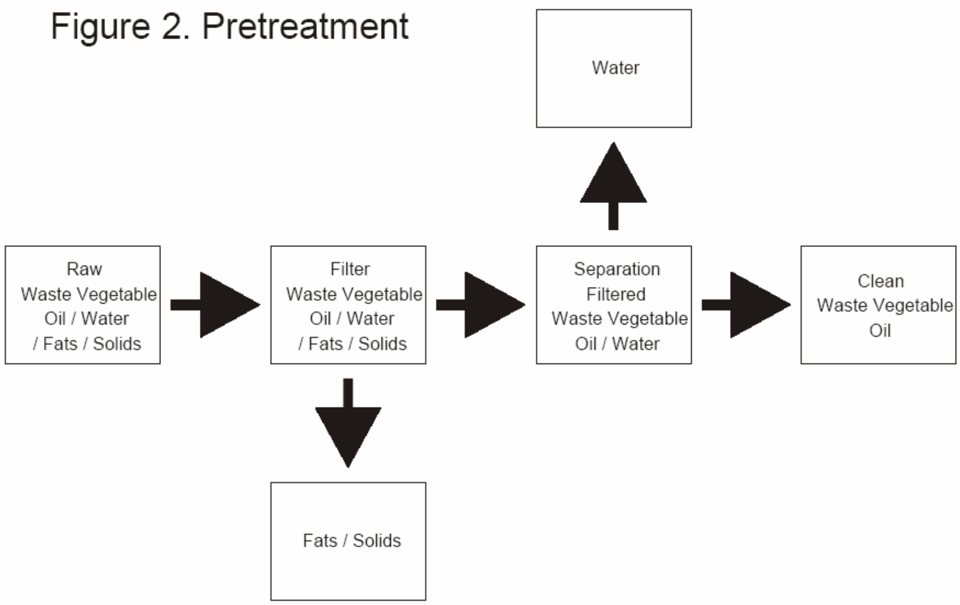
The process steps to prepare feedstocks for a biodiesel operation are quite varied.

Endress+Hauser provides measurement instrumentation throughout these steps beginning with the feedstock handling and processing.

Pretreatment

The crude or waste oil must first be pretreated (filtered, refined, degummed, bleached and filtered again) to create finished refined oil suitable for conversion to biodiesel. Examples of some of the process measurements are given below.

Figure 2. Pretreatment

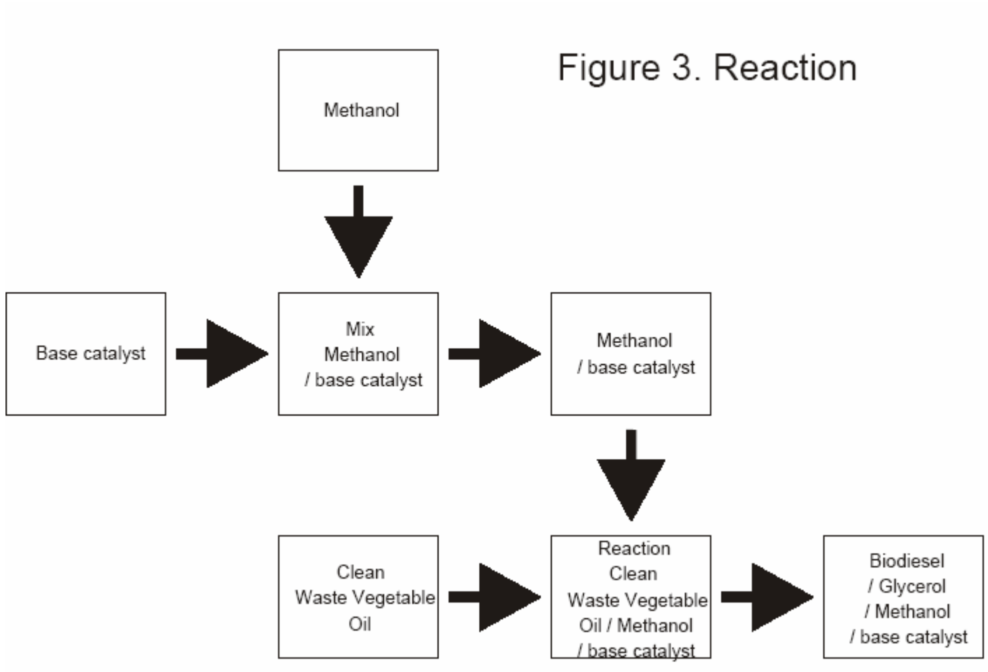


Process Measurement	Parameter	Endress+Hauser
Soap Stock Storage Tank	Temperature	i-Temp
Soap Stock Storage Tank	Radar level	Micropilot
Steamings Tank Pressure	Pressure	Cerabar
Vacuum Bleacher Tank Vacuum	Pressure	Cerabar
Bleach Clay Filter Aerator	Pressure	Cerabar
Compressed Air Header	Pressure	Cerabar
N2 Header	Pressure	Cerabar
High Pressure Steam Header	Pressure	Cerabar
Condensed Wet Steam Header	Pressure	Cerabar
Crude Oil Heater Outlet	Temperature	i-Temp
Phosphoric Acid Tank	Temperature	i-Temp
Retention Tank	Temperature	I-Temp
NaOH Tank	Temperature	I-Temp
Centrifuge Trim Heater Outlet	Temperature	I-Temp
Silica Slurry Tank	Temperature	I-Temp
Clay Slurry Tank	Temperature	I-Temp

Vacuum Bleacher Trim Heater Outlet	Temperature	I-Temp
Vacuum Bleacher	Temperature	I-Temp
Finished/Bleached Oil Trim Cooler Outlet	Temperature	I-Temp
Finished/Bleached Oil Storage Tank	Temperature	I-Temp
Wet Soap Tank	Temperature	I-Temp
Crude Oil Outlet	Temperature	I-Temp
Phosphoric Acid Tank	Radar level	Micropilot
Retention Tank	Radar level	Micropilot
NaOH Tank	Radar level	Micropilot
Dilute Caustic Tank	Differential Pressure	Deltabar
Silica Slurry Tank	Differential Pressure	Deltabar
Clay Slurry Tank	Differential Pressure	Deltabar
Vacuum Bleacher Tank	Differential Pressure	Deltabar
Precoat/Slurry Tank	Differential Pressure	Deltabar
Steamings Tank	Differential Pressure	Deltabar
Filtrate Receiver	Differential Pressure	Deltabar
Finished/Bleached Oil Storage Tank	Radar level	Micropilot
Refined Bleach Oil Storage Tank	Radar level	Micropilot
Wet Soap Tank	Differential Pressure	Deltabar
Condensate Tank	Differential Pressure	Deltabar
Phosphoric Acid Metering Pump Mixer	Magnetic flowmeter	Promag
Phosphoric Acid Metering Pump Trim Heater	Coriolis mass flowmeter	Promass
Caustic Metering System	Magnetic flowmeter	Promag
NaOH Inlet	Magnetic flowmeter	Promag
Soft Water Inlet	Magnetic flowmeter	Promag
Dose Metering Pump Outlet	Magnetic flowmeter	Promag
High Shear Mixer Inlet	Coriolis mass flowmeter	Promass
Refining Centrifuge Outlet	Coriolis mass flowmeter	Promass
Clay Slurry Tank Inlet	Coriolis mass flowmeter	Promass
Vacuum Bleacher Trim Heater Inlet	Coriolis mass flowmeter	Promass
Bleach Clay Outlet	Coriolis mass flowmeter	Promass
Refined Bleach Oil Loadout Pump Outlet	Coriolis mass flowmeter	Promass
Soy Oil Absorber	Absolute pressure	Cerabar
Soy Oil Absorber Sump Tank	Guided Wave Radar Level	Levelflex

Reaction

As described earlier, biodiesel can be produced using several well-known industrial processes, the most common of which is base catalyzed transesterification with alcohol. The transesterification process begins when precise amounts of properly prepared oil are mixed with controlled amounts of methanol/ethanol in the presence of a suitable catalyst in a reactor. The output is a 10 parts biodiesel to 1 part glycerin mixture with leftover alcohol, catalyst and (if managed well) little else. Glycerin is a valuable by-product and can be sold as a chemical or pharmaceutical feedstock. The catalyst and any excess methanol can be recovered for reuse, so that nothing is wasted in the production process. The base catalyzed reaction is more economical than other production methods because the reaction has a very high conversion rate (98%), generally requires only a single production step, and proceeds quickly at a relatively low pressure (20 psi) and temperature (150 F). Some of the process measurements related to this step are given below.



Methanol to Mixer	Coriolis mass flowmeter	Promass
Base Catalyst to Mixer	Magnetic flowmeter	Promag
Base Catalyst to Mixer	pH	Liquidize
Prepared Catalyst to Reactor	Coriolis mass flowmeter	Promass
Methanol to Reactor	Coriolis mass flowmeter	Promass
Refined Oil to Reactor	Coriolis mass flowmeter	Promass
Reactor Temperature	Temperature	I-Temp
Reactor Temperature	Absolute pressure	Cerabar
Reactor Level	Guided Wave Radar Level	Levelflex

Separation/Wash/Purification

The reacted mixture moves into a series of process steps to separate the biodiesel from the glycerin, reclaim the alcohol and catalyst that remains and purify the biodiesel and glycerin to meet required quality standards.

Different techniques are used to accomplish separations of the reactants and achieve the degree of purity and chemical recovery required. At first gravity based separators may be used or some kind of mechanical separation may be employed. Depending on the design different approaches to wash the biodiesel and glycerin are used.

One should not automatically assume that a particular instrument used successfully in one engineered process will by itself always work the same way in a differently engineered process.

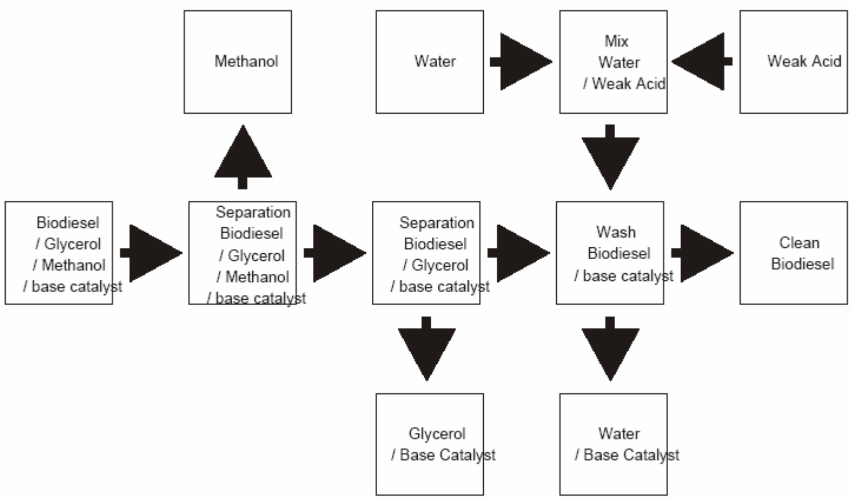
This is especially true when it comes to the gravity separation process after the reaction of methanol, catalyst and oil feedstock (transesterification). Dealing with upsets, feedstock variations, throughput variations and retention times may create conditions where a particular technology or a form of that technology may provide the desired information less than 100% of the time. Endress+Hauser have worked with a number of biodiesel designers/builders to determine measurement solutions to help solve gravity separation control issues. There may be as many as three stages of separators. Combinations of gravity settlers (decanters) and/or mechanical (centrifuges) separators may be used in series. Each of these stages has different conditions. Some solutions involve specific forms of Endress+Hauser measurement technologies which are engineered process specific. Sometimes there are changing measurement requirements when scaling up from pilot to larger scale.

Another critical measurement at different points of the biodiesel process is pH. Good pH measurement and control of reactants or neutralization can have a great impact on product quality and plant financial performance. As discussed before the chemistry is not the same with different design/build plants. Endress+Hauser has field proven pH electrodes that address biodiesel process conditions and provide long operation life.

Some processes at the point of online pH measurement will promote build-up on pH electrodes. In this case Endress+Hauser provides a pH package that provides periodic automatic electrode cleaning. Some processes do not produce these conditions so a periodic cleaning solution is not required. Some points in the process may have conditions where there is little water resulting in dehydration of the electrode. If this occurs frequently enough to make manual maintenance an issue an automatic cleaning system can be used to keep the electrode hydrated.

The examples below illustrate some of the separation, washing and purification process measurements

Figure 4. Separation and Wash



Centrifugal separator	Coriolis mass flowmeter	Promass
Decanter separator interface	Supplier Specific	Various
Decanter separator	Gauge pressure	Cerabar
Process fluid from Bottom of Decanter	pH	Liquiline
Process Fluid from Bottom of Decanter	Magnetic flowmeter	Promag
Reactor Effluent to Decanter	pH	Liquiline
Glycerin Layer from Decanter	Magnetic flowmeter	Promag
Vacuum Pump	Absolute pressure	Cerabar
Acidulated Glycerin to Neutralized Glycerin Cooler	pH	Liquiline
Neutralized Glycerin to Methanol Recovery	pH	Liquiline
Neutralized Glycerin Surge Tank	Ultrasonic Level	Prosonic
Wash Water to Acid Dilution Tank	Magnetic flowmeter	Promag
Water to Acid Dilution Static Mixer	Magnetic flowmeter	Promag
Acid to Acidulation Reactor	Magnetic flowmeter	Promag
Caustic Soda to Glycerin Neutralizer	Magnetic flowmeter	Promag
Acid to Dilution Tank	Magnetic flowmeter	Promag
Acid Dilution Tank	Guided Wave Radar Level	Levelflex
Feed to Methanol Rectification Column	Vortex flowmeter	Prowers
Reflux to Methanol Rectification Column	Vortex flowmeter	Prowirl
Feed to Glycerin Methanol Stripper	Magnetic flowmeter	Promag
Glycerin Methanol Stripper	Absolute pressure	Cerabar
Glycerin Methanol Stripper	Guided Wave Radar Level	Levelflex
Sparge Steam to Glycerin Methanol Stripper	Vortex flowmeter	Prowirl
Rectification Reflux Condenser	Gauge pressure	Cerabar

Rectification Vent Condenser	Gauge pressure	Cerabar
Methanol Rectification Column	Guided Wave Radar Level	Levelflex
Methanol Rectification Column	Gauge pressure	Cerabar
Dry Methanol to Storage	Coriolis mass flowmeter	Promass
Dry Methanol Receiver	Guided Wave Radar Level	Levelflex
Water Absorbers Sump Tank	Guided Wave Radar Level	Levelflex
Wet Methanol Receiver	Guided Wave Radar Level	Levelflex
Feed to Biodiesel Methanol Stripper	Vortex flowmeter	Prowirl
Biodiesel Methanol Stripper	Absolute pressure	Cerabar
Biodiesel Methanol Stripper	Guided Wave Radar Level	Levelflex
Biodiesel Product Filter	Differential pressure	Deltabar
Wash Water to Wash Biodiesel Wash Tank	Magnetic flowmeter	Promag
Methanol to Biodiesel Wash Tank	Vortex flowmeter	Prowirl
Water to Vapor Inlet	Magnetic flowmeter	Promag
Crude Glycerin Product to Storage	Coriolis mass flowmeter	Promass
Washed Biodiesel Receiver	Guided Wave Radar Level	Levelflex

Supply chain management (i.e. storage, load-in and load-out)

Following separation and purification, the biodiesel, glycerin and reclaimed chemicals are directed to storage. At various times biodiesel and glycerin are loaded into rail cars or tank trucks for transportation. The influx of chemicals required to run the biodiesel process also must be managed and replenished from time to time. Some of the process measurements related to this step are given below.

Biodiesel Product to Storage	Coriolis mass flowmeter	Promass
Glycerin Product to Storage	Coriolis mass flowmeter	Promass
Glycerin Storage Tank Temperature Transmitter	Temperature	I-Temp
Fatty Acid Storage Tank Temperature Transmitter	Temperature	I-Temp
Biodiesel Tank Temperature Transmitter	Temperature	I-Temp
Biodiesel Shift Tank Level Transmitter	Radar level	Micropilot
Glycerin Storage Tank Level Transmitter	Radar level	Micropilot
Fatty Acid Storage Tank Level Transmitter	Radar level	Micropilot
Biodiesel Storage Tank Level Transmitter	Radar level	Micropilot
Biodiesel Shift Tank Temperature Transmitter	Temperature	I-Temp
Biodiesel to Load-out	Coriolis mass flowmeter	Promass
Glycerin to Load-out	Coriolis mass flowmeter	Promass
Over spill prevention (all tanks)	Tuning fork switch	Liquiphant
Sodium Methylate Load-in	Coriolis massflow	Promass
Methanol Load-in	Coriolis massflow	Promass
Hydrochloric Acid Load-in	Magnetic flowmeter	Promag
Methanol Storage Tank Temperature Transmitter	Temperature	I-Temp
Sodium Methylate Storage Tank Temperature Transmitter	Temperature	I-Temp
Methanol Storage Tank Level Transmitter	Radar level	Micropilot
Methanol Storage Tank Level Transmitter	Radar level	Micropilot
Sodium Methylate Storage Tank Level Transmitter	Radar level	Micropilot

Hydrochloric Acid Storage Tank Level Transmitter	Ultrasonic level	Prosonic
Hydrochloric Acid Storage Tank Temperature Transmitter	Temperature	I-Temp
Over spill prevention (all tanks)	Tuning fork switch	Liquiphant
Refined Oil to Storage	Coriolis mass flowmeter	Promass
Refined Oil Storage Tank Level Transmitter	Radar level	Micropilot
Over spill prevention (all tanks)	Tuning fork switch	Liquiphant

Utilities

Surrounding the actual pretreatment, transesterification and separation/cleaning processes are support utilities. As in most processing operations, feedstock preparation/biodiesel facilities require power, steam, water, gases and (depending on the process) effluent treatment.

Building Main Steam Header	Gauge pressure	Cerabar
Building Main Cooling Water Header	Gauge pressure	Cerabar
Building Nitrogen Blanketing Header	Gauge pressure	Cerabar
Cooling Water Condenser	Absolute pressure	Cerabar
Chilled Fluid Condenser	Absolute pressure	Cerabar
Building Main Instrument Air Header	Gauge pressure	Cerabar
Chilled Fluid Supply Header	Gauge pressure	Cerabar
High Pressure Steam Header Flow Transmitter	Pitotube flowmeter	Deltabar
Boiler Drum	Guided Wave Radar Level	Levelflex
Boiler Gas Feed	Energy/Mass flowmeter	T-mass
Boiler	Temperature	I-Temp
Boiler	Pressure	Deltabar
CWS Header Flow Transmitter	Pitotube flowmeter	Deltabar
PW Header Flow Transmitter	Magnetic flowmeter	Promag

Safety, Health and Environmental

Biodiesel operations need to safely manage hazardous chemicals at every stage of use.

Alcohol:
- Methanol (most common)
- Ethanol

Catalyst:
- Sodium Hydroxide
- Potassium Hydroxide
- Sodium Methylate

Methanol is a poison. Personnel should avoid all contact with it, including getting it on skin or breathing the fumes. Contact with methanol can cause irreversible illness, blindness, and death. Methanol absorbs water, and so should not be stored in any open container where water can accumulate. Methanol is normally stored in appropriate sealed and marked vessels.

Methanol is also highly flammable. There are several documented cases of severe fire damage to biodiesel production plants caused by ignition of improperly managed methanol

Sodium hydroxide and other bases are caustic (a strong base). Caustics will absorb water (out of people) and are dangerous if not handled properly.

Feedstocks and finished biodiesel need to be properly stored. Oil feedstocks can go rancid (smell bad) or even be rancid when you get them. Used oil has to be turned into biodiesel as soon as possible, in order to keep it from going rancid and increasing the amount of free fatty acids. Rancid oil produces less biodiesel and may not even react to make it.

Finished biodiesel has a long shelf life and is a good solvent. It will dissolve rubber and some plastics, remove paint, oxidize aluminum and other metals, and has been reported to destroy asphalt and concrete if spills were not cleaned quickly. Measurement instruments need to be constructed out of appropriate materials or protected from damaging chemicals.

Overspill safety is addressed by Endress+Hauser though its Liquiphant line of level switches. These Safety Integrity Level (SIL) evaluated detectors have no calibration requirements and can provide a solid alarm base for safety systems. The same device can be used for both empty pipe and tank high and low level detection throughout a biodiesel facility.

A deeper look at some instrumentation practices

Following are some closer looks at instrumentation applications within Biodiesel operations.

Ceramic cell Differential Pressure level – abrasive conditions in Pretreatment/Preparation

- Coriolis massflow - Reactor feed control
- Tuning Fork Universal level-switch/overspill prevention
- Time Domain Radar level versus Differential Pressure level
- Decanter Separator (Interface measurement)
- Mechanical Separators (massflow and density measurement)

pH measurements differences in Biodiesel operations

- Neutralization pH measurement – static mixing vs retention tank
- Glycerin Purification - Interface Measurement

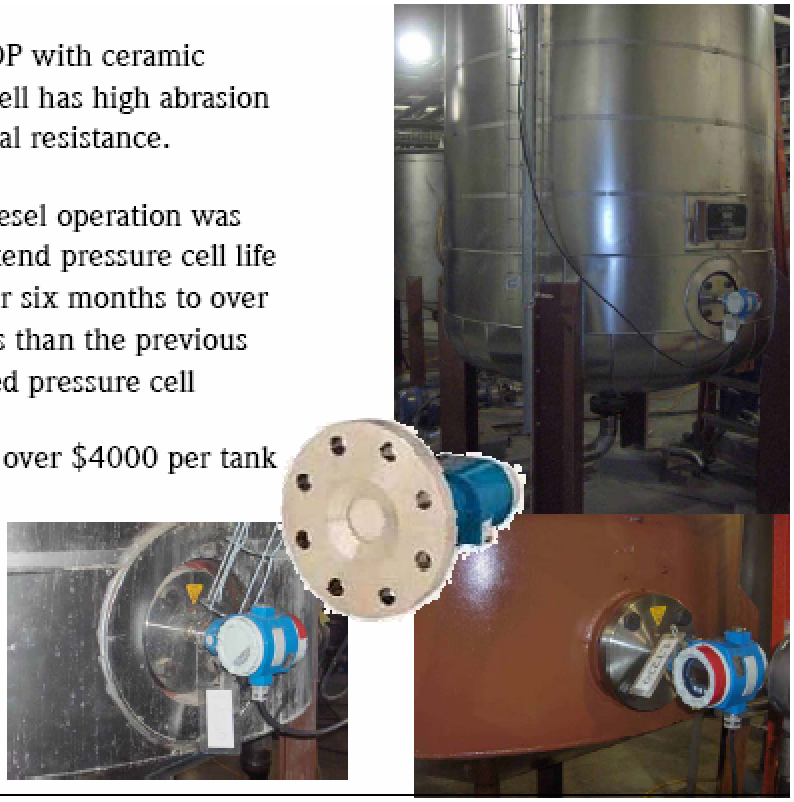
Load-in: Chemicals with Coriolis massflow meters

Load-out: Truck and Railcar with Coriolis massflow

- Inventory: (Chemicals and Biodiesel/Glycerin) with Tuning Fork level-switch and Radar level
- Utilities – fuel, boiler (water, steam generation)
- Utilities – Cooling Tower water flow
- Utilities - Natural Gas Energy measurement

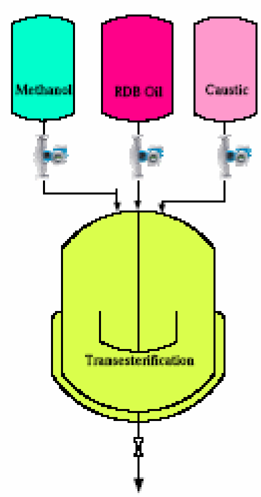
Ceramic cell Differential Pressure level – abrasive conditions in Pretreatment/Preparation

- Deltabar DP with ceramic pressure cell has high abrasion an chemical resistance.
- One Biodiesel operation was able to extend pressure cell life from under six months to over 18 months than the previous metal based pressure cell
- Savings of over $4000 per tank



Coriolis massflow - Reactor feed control

- Proper introduction of caustic solutions (Sodium Methylate, NaOH, KOH), Methanol and RDB oil are critical to management of continuous transesterification reactors
- Coriolis mass flowmeters monitor flow as well as density
- Promass Coriolis high zero stability and accuracy even without special mounting provides accurate addition information regardless of piping and flow implementations

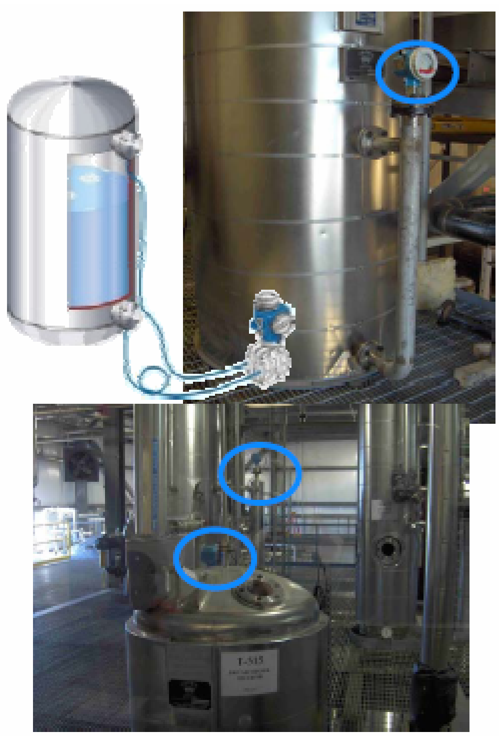


Tuning Fork Universal level-switch/overspill prevention

- Overspill Alarm or Empty pipe detection
- Process vessel "multipoint" level
- Typically 75 -150 per plant
- Benefits: spares reduction, install and "forget" maintenance
- No calibration requirements
- Measurement unaffected by most kinds of foam, buildup.
- Measurement unaffected by conductivity, capacitance

Time Domain Radar level versus Differential Pressure level

- Radar and Time Domain Radar is replacing many traditional DP level applications
- DP vulnerable to errors from capillary imbalances (i.e. temperature) density changes
- Installed cost can be 50% higher than Radar or TDR level installation.
- Radar or TDR have one flanged tank opening at top versus DP with two flange tank openings (top and bottom)

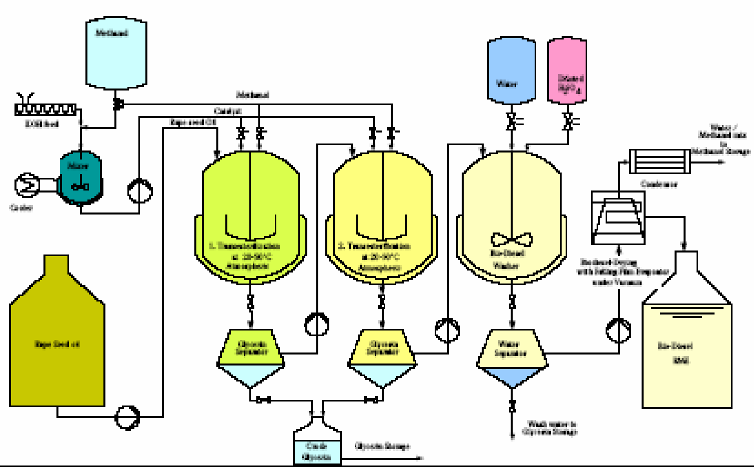


Decanter Separator (Interface measurement)
Mechanical Separators (massflow and density measurement)

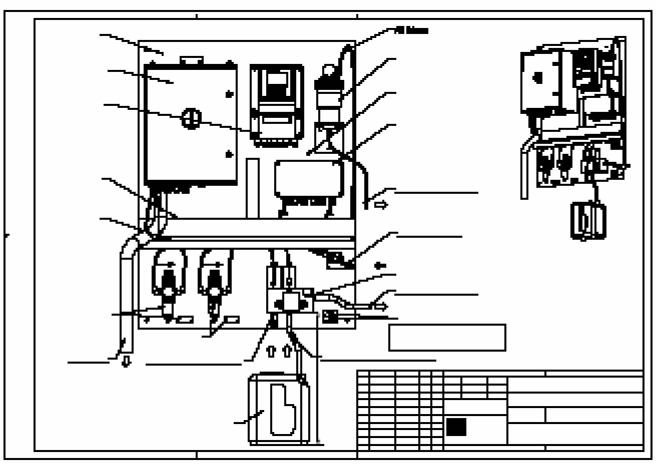
- Methyl Ester/Glycerin mechanical gravity separators largely use Coriolis massflow and density for control information.
- Promass coriolis provides stabile density information and massflow without zero shift from piping stresses or plant vibration
- Promass can be mounted in piping without any special considerations for flow profile/pipe diameters

pH measurements differences in Biodiesel operations

- pH values play central roles in the performance of a Biodiesel operation
- The conditions for pH measurements can be demanding especially when only little water is present
- Some processes tend to create high electrode contamination conditions, when this is at play measurement without automatic cleaning is not recommended. Otherwise a manual insertion solution can be used.



- Some process implementations do not promote buildup on pH electrodes. It seems in Europe neutralization with H_2SO_4 vs HCL in the US may contribute.
- Also the effort to precipitate fertilizer (i.e. K_3PO_4) means KOH may be used as the transesterification caustic.
- Kalrez sealing and Hastelloy is recommended to cover all applications in a Biodiesel plant. Although chemical corrosion demands are greater at the front of the plant, we typically recommend one system for all applications if reasonable.



- TopClean CPC30 pH measurement as a total auto cleaning package when required
- Everything from one hand to save time during engineering and initial start-up.

- The use of Digital electrode technology (Memosens) fully allows all calibration and conditioning to be done in a lab environment. Field calibration can be eliminated

- Promotes Safety: Since no calibration work is done at the measuring point, anyone can exchange preclalibrated electrodes in the filed.

- For example: Electrodes can recover in KCl solution and be recalibrated in the lab. If there is high organic buildup content you can rehydrate the electrode and precalibrate. If you don't do this (i.e. field calibration) you may calibrate with an offset if the electrode is not complete rehydrated.

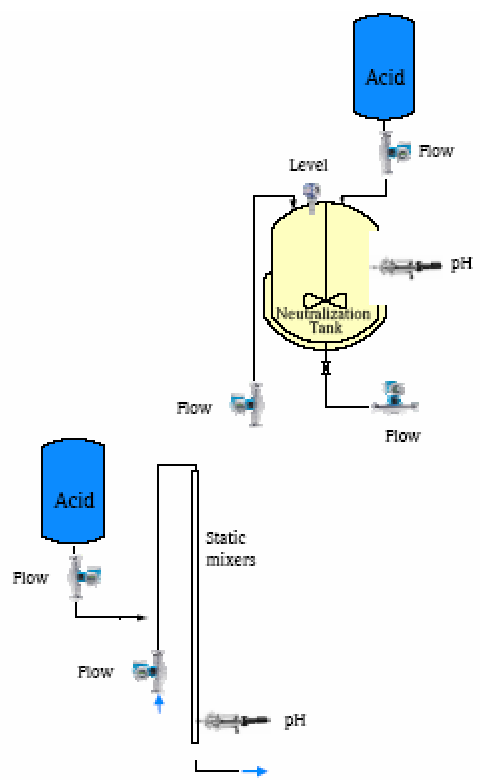
Neutralization pH measurement – static mixing vs retention tank

- Traditional neutralization requires a retention tank to manage proper conditions

- Several processors are employing static mixers for neutralization to save on equipment costs

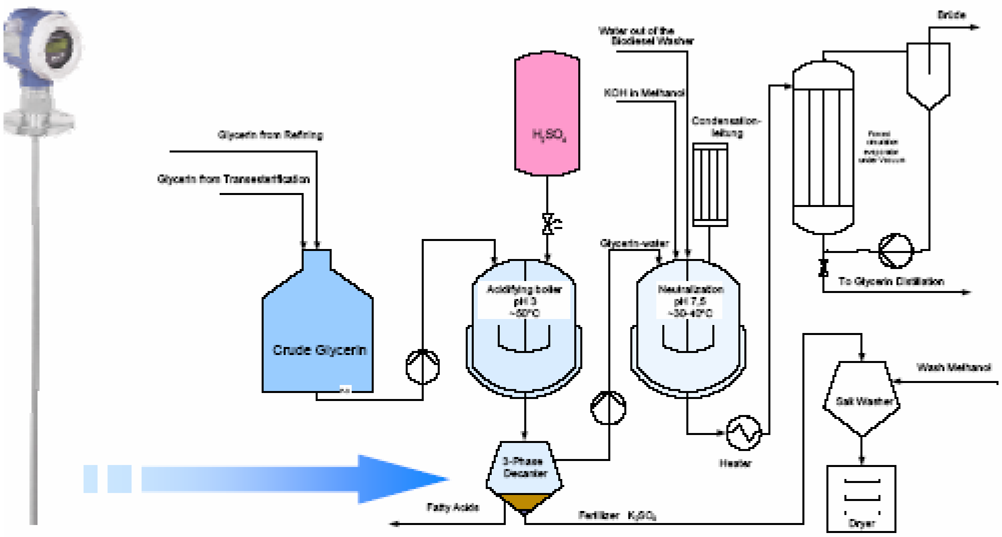
- Proprietary mixing arrangements are used to get get proper residence time

- pH response time and positioning is critical

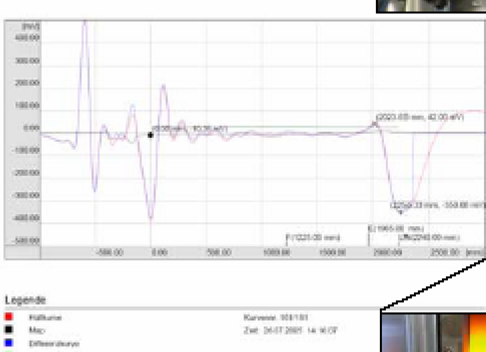


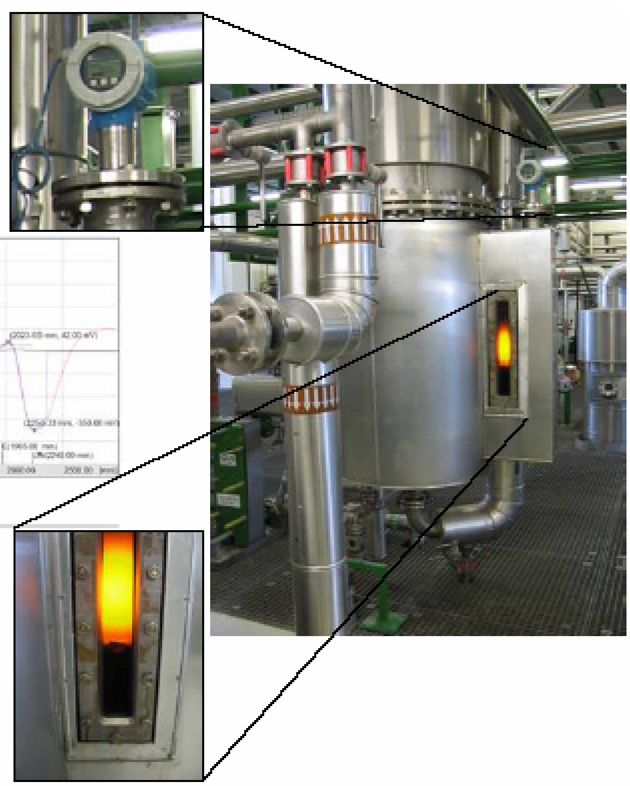
Glycerin Purification - Interface Measurement

- The crude Glycerin from Transesterification is reacted with sulfuric acid to pH 3. Fatty acid and K2SO4 is separated out.
- Levelflex M FMP 40 is used in the phase separator to measure the interface .



Separation from:
- Glycerin-water
- Fatty Acid





Load-in: Chemicals with Coriolis massflow meters

- Biodiesel operations need a continuous influx of chemicals. Larger operations receive chemicals in bulk.
- Sodium Methyl ate for example is accurately received at a rail car load – in rack
- Promass Coriolis high zero stability and accuracy even without special mounting provides accurate addition information regardless of piping and flow implementations

Load-out: Truck and Railcar with Coriolis massflow

Volumetric Custody Transfer to NIST Handbook 44

Process:

Biodiesel fuel producers transfer final product to truck or railcars using certified flow meters regulated by U.S. standards and State Weights and Measures Officials. This can require either mass or volume flow measurement certification depending on the application

Solution:

A biodiesel producer needed to track the sales of biodiesel and glycerin sold in compliance with NCWM custody transfer needing an NTEP approved flow meter

The Promass 83F was used for volumetric totalization of product and certified by State officials after verification by an independent contractor to meet U.S. NIST Handbook 44 requirements of repeatability of <0.2% on their biodiesel product.

Key Success Factors:

The Promass compliance testing done on site and confirmed 30 days later produced a repeatability result of 0.01% when compared against a Seraphin volume proving method – far exceeding the NTEP requirements. Tests were run on 1000 gallon proving runs.

Process Specs:

Fluid: Biodiesel B100 – ASTM D6751

Pressure: Varies in process points

Temperature: <200 degrees F

Flow Range: 0.3 to 20 GPM depending on flow loop

Instrument:

Model: Promass/Promag

Size/Lining: 3/8” to 3” line sizes

Software/Bus: 4-20mA HART, (2) 4-20mA out, relay flex I/O

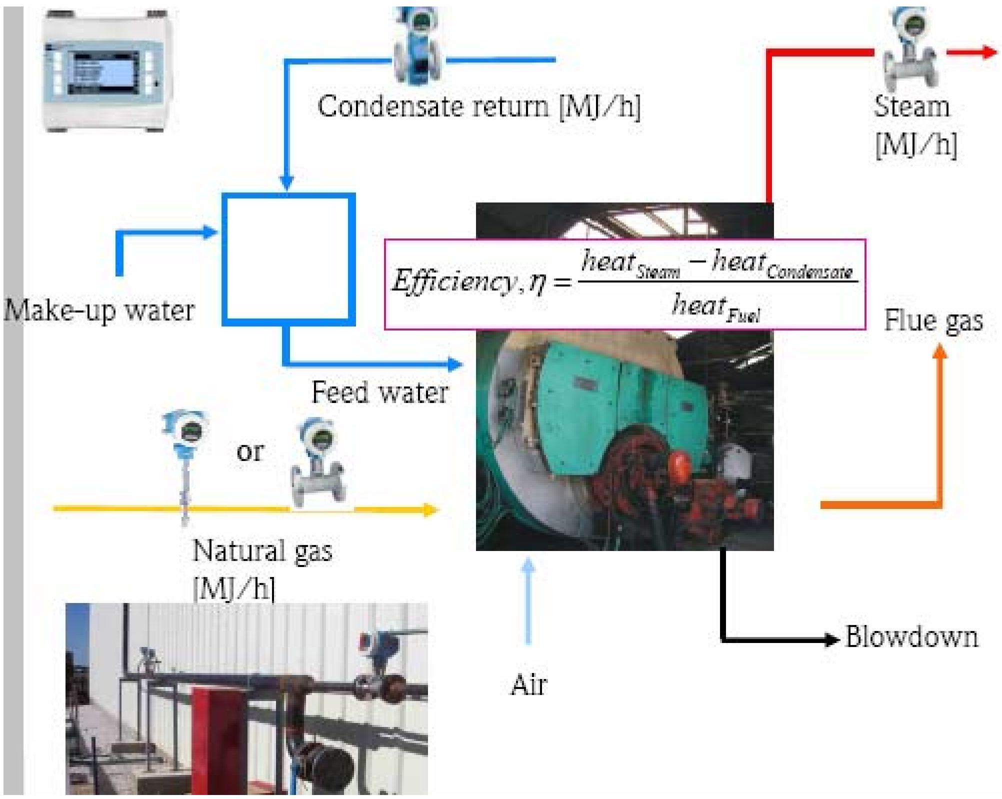
Inventory: (Chemicals and Biodiesel/Glycerin) with Tuning Fork level-switch and Radar level

- Production products: Biodiesel, Glycerin and Fatty Acid storage
- Incoming chemicals: Caustic, Acid, Methanol, Recovered Methanol
- Millimeter accuracy radar (Micropilot) provides accurate inventory information without the need for periodic maintenance/calibration
- High alarm tuning fork level switches (Liquiphant) are tied into shut down systems to prevent overspill events

Utilities – fuel, boiler (water, steam generation)

- Feed water measurement via Prowirl vortex flowmeter.
- Steam energy measurement via Prowirl vortex flowmeter with integral temperature correction
- Drum level measurement via TDR level eliminates inaccuracies and corrections of DP level approaches
- Temperature measurement with Omnigrad transmitter

Utilities – fuel, boiler (water, steam generation)



Sources

The Case for Biodiesel Submitted for: ENVIRON 550 Professors: Gretchen Hund; Kevin Laverty
June 2003

Biodiesel Production Technology: National Renewable Energy Laboratory
January 2004

A Review of the Engineering Aspects of the Biodiesel Industry
for the Mississippi Biomass Council Jackson, MS
MSU E-TECH Laboratory Report ET-03-003
August 2003

Worldwide Review on Biodiesel Production: Prepared for
IEA Bioenergy Task 39, Subtask "Biodiesel" Prepared by
Austrian Biofuels Institute

A World Wide Review of the Commercial Production of Biodiesel –
A technological, economic and ecological investigation based on case studies:
Institute für Technologie und nachhaltiges Productmanagement
Umweltschuty und Ressourcenökonomie

Biodiesel Feasibility Study: An Evaluation of Biodiesel Feasibility in Wisconsin University Wisconsin
Madison March 2005

Liquid biofuels for transportation in Brazil report: Prepared by Fundacoa Brasileira para o
Desenvolvimento Sustentavel – FBDS on behalf of Cooperacao Tecnica Alema -GTZ

The National Biofuel Policy: Ministry of Plantation Industries and Commodities Malaysia
March 21 2006

Internal Endress+Hauser sources

07.05/SCUSA

USA	Canada	Mexico	International
Endress+Hauser, Inc. 2350 Endress Place Greenwood, IN 46143 Tel: 317-535-7138 Sales: 888-ENDRESS Service: 800-642-8737 Fax: 317-535-8498 inquiry@us.endress.com www.us.endress.com	Endress+Hauser Canada 1075 Sutton Drive Burlington, ON L7L 5Z8 Tel: 905-681-9292 800-668-3199 Fax: 905-681-9444 www.ca.endress.com	Endress + Hauser México, S.A. de C.V. Av. Gustavo Baz No. 43 Fracc. Bosques de Echegaray Naucalpan de Juárez, C.P. 53310, Estado de México México Phone: (52) 55-5371-1110 Fax: (52) 55-5371-1128 E-mail: eh.mexico@mx.endress.com	For international locations visit: www.endress.com/worldwide