Water detection in alcohol blended fuels

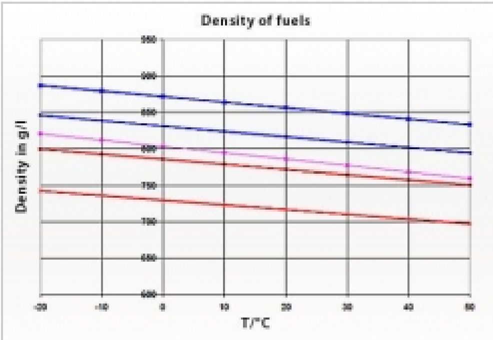
The global necessity of the reduction of CO2 emissions has led to ordinances in many countries for the use of so called biofuels. The most propagated ones are ethanol and biodiesel (RME) that are produced from plants having absorbed an equivalent amount of CO2 from the atmosphere during growth that is emitted again after the combustion. These biofuels are mainly used as an admixture to conventional gasoline and diesel for two reasons. One reason is its limited availability. The second reason is that most vehicles to date are not capable to use higher percentage of admixture of the biofuel. On the vehicle side there are problems with the resistance of elastomers to this fuels as well as the difference in the combustion properties /DGMK Report 645/. In the last years more and more flexible fuel vehicles (FFV) were put on the road equipped with automatic fuel quality sensor being capable to use gasoline from 0 % to 100 % ethanol content. New cars are equipped with sealings that can withstand moderate percentages of biofuel admixture. In order to gather experiences many countries have started with an admixture of 5 % ethanol to the gasoline (E5) and in the meantime several countries have increased the limit by ordinance to 10 % ethanol (E10). But there are also higher percentages in the market like E25, E50, E85 up to E100. Partially similar problems are encountered by the admixture of methanol to gasoline. The stimulus to use methanol is not the CO2 reduction goal but the limited availability of crude oil and foreign exchange in some countries. A substantial amount of methanol is produced from coal and admixed up to 25 % (M25). One further serious problem on the vehicle side due to the alcohol admixture is the increased wear in the engine by corrosion. Formic acid is formed by the combustion of blends and attacks cylinder and piston but also the engine oil content and therefore the bearings. Special coatings help to protect these components in modern vehicles. The acid formation is even stronger for the methanol admixtures.

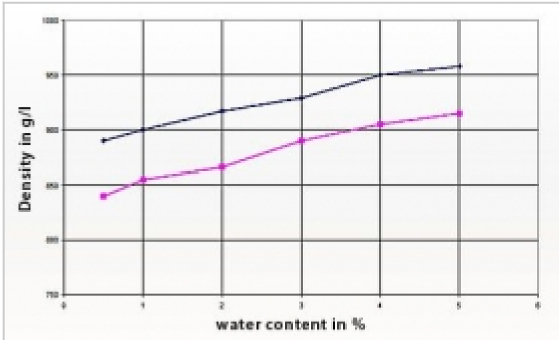
There are problems not only on the vehicle side but also significant challenges on the side of the fuel production and in the distribution logistic. The problems in the distribution will be the main topic of the following discussion. The fuel changes vapour pressure and octane number if ethanol is added. Therefore the basic gasoline must be changed in its composition in order to compensate for these effects. The next problem is the much higher solubility of the ethanol blends to sludge and water that might be present in a storage tank. This causes many problems after a product change in the tank from a conventional gasoline to a gasoline blended with alcohol. The main problem is the frequent clogging of the fuel filters in the dispenser. Therefore many oil companies decided to clean the tanks before storing a blend. But also the attack to elastomers and increased corrosion of metals that have been used for the pipe work has been observed.

Automatic Tank Gauges

For the operation of storage tanks automatic tank gauges (ATG) are used since about 25 years. They eliminate the need of the use of the dip stick and are much more accurate and allow for many new features in the application as for example the optimisation of the logistics by using the level data from a remote computer system. The performance requirements for such ATG’s are given in the European standard /EN 13352/. It states the necessary accuracy for the product level determination, the temperature measurement and the water level detection capability. The latter feature is mandatory because without the detection of a water contamination there is a risk that the vehicles refuelled will stop running.

The water detection process is dependent of the type of ATG. For capacitive probes the water is detected by the difference in dielectric constant, for ultrasonic probes in the difference in acoustic impedance and in floater systems by the density. The floater systems on the basis of the magnetostrictive principle have by far the biggest market share and the corresponding challenges are therefore considered in more detail.



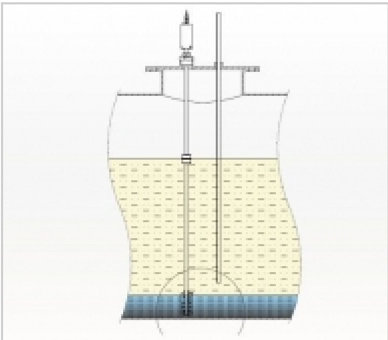


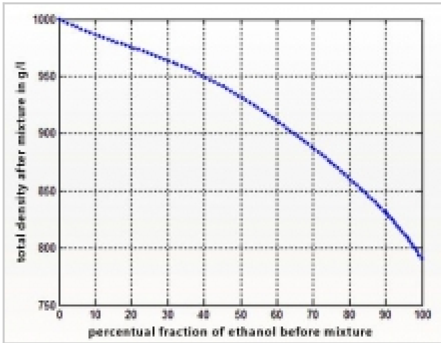
Water detection in standard fuels

The tolerance bands for the densities of fuels and its temperature dependencies are exhibited in ***figure 1***. The density data for gasoline is displayed according to the standard EN 228 and for the diesel fuel according to the standard EN 590. Without alcohol admixture to the fuel intruded water will collect at the bottom at the tank and will have a density close to 1000 g/l. So the easy solution is to choose one water detection float with a density of about 900 g/l for all types of fuel and it will float if a water layer is present and the ATG will display the water level and give an alarm signal. The other possibility is to use two different water detection floats with different densities for gasoline and diesel for example with a densities of 840 g/l and 950 g/l respectively. The disadvantage of latter solution is that the water detection float has to be exchanged if the stored product is changed.

Properties of the separation phase in alcohol blends

Now with the introduction of alcohol blends the situation changes significantly. When water trickles in a tank with an alcohol blend stored it will **not** form a water layer at the bottom with a density close to 1000 g/l. There will be a certain wash out effect of the alcohol from the fuel into the water layer reducing the density of the separated phase. The degree of the wash out is dependent on several parameters (see below). Alcohols are completely mixable with water so the alcohol will be dissolved in the separated phase. In figure 1 it can be seen that the ethanol's density is close to but somewhat higher than the density of standard gasoline (this is also true for methanol). So it is expected, that dependent upon amount of alcohol extracted from the fuel there will be a decrease in the density of the separation layer at the bottom. In order to determine these effects more quantitatively mixing experiments have been performed on the laboratory scale. As a basis a definite alcohol free gasoline was used kindly supplied by the research lab of an oil company. From this basic fuel blends with different mixtures of ethanol and methanol were prepared for the experiments. To these blend samples step by step water was added with a pipette. If the water solubility limit was exceeded a separation occured and its volume was determined in the measuring jug. The volume of the separation phase exceeds at some point the volume of the water added. This additional volume is due to the alcohol wash out. Now it is well known that there is shrinking effect in the water/ethanol system due to the change in the intermolecular interaction in the mixture. This has taken into account in order to determine the alcohol volume **before** the admixture to the water and to determine the actual density of the separated phase. The degree of the wash out is dependent on the original alcohol content, the temperature and the duration, if no stirring was applied. By stirring this process could be considerably accelerated. In the experiments a reproducible stirring procedure was applied. Typical results of mixing water to E5 and E10 blended fuels on the density in the separation layer are shown in ***figure 2***. Because the mixing effect in real tanks will not be so thoroughly as in the laboratory container, it can be assumed that generally the density of the separation layer will be somewhat above the values as exhibited in the figure 2.





Water detection in ethanol blends

In order to detect separation phase in E5 a water detection float of about 880 g/l should be used. Such a water float can be still universal for diesel fuel and gasoline up to E5.

What happens at even higher alcohol contents with the densities of the separated phase? The first effect is that an increasing amount of water remains solved in the fuel (see DGMK Report 645). For E10 the dissolved water content is around 0.3 % whereas for E25 it can be already 1 %! For the separated phase the measurements show that the density approaches more and more the value of the ethanol itself. So there is no chance to discriminate a phase separation with only one float for gasoline and diesel. So a float with a density close to the gasoline value with 820 g/l should be chosen for the blends exceeding E5. Such a solution secures the separation layer detectability up to E20. For even higher concentrations the separation layer cannot be detected by a float. This is due to the fact that the density of such a separation phase can be even lower than 820 g/l at higher temperature (compare figure 1 for the temperature decrease). The only chance is to measure the density and the temperature by a density sensor in the tank bottom. If the measured density leaves the tolerance corridor given by the fuel standard such a system can issue an alarm signal. An example of an installation is exhibited in the ***figure 3***.

For ethanol mixtures from 50 % up to 100 % concentration there will not be a phase separation for a water content under 5%. The water content remains dissolved but increases the density of fuel. So the only chance is also to use the fuel density as a measure of a possible water contamination. In countries like Brazil there is an E100 traded containing about 3.6 % of water (azeotropic mixture). Because water is admixable at arbitrary amounts the quality must be assured by controlling the density. The water-ethanol system is accurately known and the density characteristic is given in ***figure 4***.

From the initial slope (-4,3 g/l per percent) at the side of high ethanol concentration it can be concluded that for a density sensor with an accuracy of ±2 g/l a concentration change of 0.5 % of water content can be detected. So a fraud by adding water can be diagnosed within this limit.

Taking E85 as an further example it can be shown, that indeed the water concentration can be determined in the range of about 2% water. The increase in uncertainty with respect to E100 is due to the fact that the 15% of gasoline admixed to the fuel has a similar variance as standard gasoline without alcohol. Furthermore the admixed concentration is not fixed but varies in the range of ± 5 %. In a PTB investigation /PTB 2008/ Wolf and Rinker have determined the temperature dependence of the density of different ethanol mixtures including E85. The deviation from these values can be used to estimate the percentage of a possible water contamination from density and temperature data.

Bibliography:

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