Testing of Biodiesel Products: Key Titration Applications

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The U.S. Biodiesel industry currently represents less than 0.5% of the total diesel fuel market (approximately 239 billion liters) annually. Obviously there is quite a way to go before Biodiesel becomes a mainstream energy source. Various factors including the amount of available feedstock (including high feedstock costs), controlling fuel quality, building an infrastructure, and the food or fuel dilemma are some obvious obstacles along the way.

In terms of costs versus benefits, there are a number of mitigating factors to consider when assessing the sustainability of using Biodiesel produced by conventional means, at least at this early point in our Biodiesel initiative.

1. Increased demand for crop-based feedstocks shorten supply and drive commodity prices up. Many third-world countries really feel the effect of diverting food crops to fuel, giving this issue considerable worldwide attention lately.

2. The United States transport infrastructure still cannot cost-effectively serve the Biodiesel supply chain. This limits the amount and increases the cost of product reaching the market.

3. During transportation and storage, the inherent tendency of Biodiesel to form equipment-damaging oxidation products and poor cold-flow properties, making stability monitoring an important job. This paper describes how utilizing a multi-function titration system can help provide a cost-effective solution for this purpose. It is important to note that its usefulness also extends back to helping control product quality during the production phase.

Another challenge revolves around maintaining and monitoring Biodiesel fuel quality. The ASTM Biodiesel fuel specification D6751 has been modified several times since its conception over 5 years ago. The industry is hard at work to keep the fuel standard appended and updated to meet upcoming challenges. This paper deals with how a common laboratory instrument, namely an automatic titrator, can be utilized to understand and measure various properties of Biodiesel. Most laboratories have access to titration equipment and hence a bird in the hand is worth two in the bush – start with tools already in the lab to measure the basic properties of newly designed Biodiesel Blends.

There are several important properties of Biodiesel fuels that can be determined using a variety of titration methods. These methods include Karl Fischer titrations (Coulometric/Volumetric) for water content, Potentiometric titrations to determine acidic or basic properties, and Redox (oxidation-reduction) titrations to indicate relative amounts of unsaturated hydrocarbons in a given sample. The aforementioned Titration procedures have been adopted as standard test methods by standardization organizations such as the American Society for Testing and Materials (ASTM), the International Organization for Standardization (ISO), the Japanese Industrial Standards (JIS) and various other international standards.

The water content of a BioDiesel sample is a critical parameter in predicting the stability of the bulk product for storage & transportation purposes. BioDiesel is very susceptible to the effects of Oxygen, which quickly degrades the product to the point it is unfit for service, and high water contents (>0.1%) contribute significantly to this process. The Karl Fischer titration method has long been used to measure the full spectrum of water content in a multitude of sample types - be them solid, liquid, or gas. BioDiesel samples can be analysed using either Coulometric KF or Volumetric KF techniques - the preferred being Coulometric due to its high accuracy & precision at low moisture levels (<100 ppm), and overall ease-of-use. Standard test methods include ASTM D6304, E1064, ISO 760, and JIS K2275. Volumetric KF is better suited to high-water (>30%) or non-homogenous samples. Standard test methods employing the Volumetric techniques include ASTM E203 and ISO 760. Each technique utilizes the same basic chemistry, differing only in the manner in which the water-reactive Iodine complex is introduced into the test solution. In Coulometry it is generated in situ by application of an electrical current – in Volumetry it is dosed in by an automatic Buret. (Please refer to the following illustrations).

Another important parameter indicative of the quality of BioDiesel is Total Acid Number (aka TAN or Neutralization Number), expressed as the number of milligrams Potassium Hydroxide required to neutralize one gram of sample. This test is carried out as a Potentiometric Titration described in standard test methods ASTM D664, ISO 6619, and JIS K2501. The TAN of a sample can also be used to calculate its Free Fatty Acid content – a key process parameter to monitor in BioDiesel production, where FFAs are converted to Fatty Acid Methyl Esters (FAMEs). When performing Potentiometric Titration to determine Acid number it is recommended to use an Automatic Potentiometric Titrator in order to simplify running the test while minimizing human error. The Titrant used in this test is 0.1 mol/L of KOH 2-propanol solution. And the Mixed Solvent to be titrated is a 500:5:495 ratio of Toluene, Pure Water, and 2-Propanol respectively.

The Soap content of BioDiesel is another test that can be run using a Colorimetric Titration technique where the sample is titrated with a standard Hydrochloric Acid solution (in Acetone) to the Bromophenol Blue endpoint.

Redox Titrations are based on oxidation-reduction reactions between the analyte & the titrant, indicated by changes in the electrical potential of the test solution. A BioDiesel application of the Redox Titration is determination of the Iodine Value, which is related to the degree of unsaturation (number of Carbon double & triple bonds) of the sample, which, in turn, is another indicator of the fuel's stability. A higher Iodine Value number indicates a higher quantity of double bonds in the sample, with corresponding lower oxidation stability. The Iodine value of Biodiesel can vary significantly based on the feedstock used. For example, Rapeseed Methyl Ester has a Iodine Value number of 97, compared to an Iodine Value number of 133 for Soy Methyl Ester. Many Biodiesel fuel standards specify an upper limit for the Iodine Value of fuel in order to meet the specification. The downside to Iodine Value is the fact that the value does not take into account the positions of the double bonds. Therefore, Iodine Value is not necessarily the best indicator of a fuel's oxidation stability.

Titration is a very useful and practical analytical technique for determining a number of important properties of BioDiesel fuels. There are several general types of titrations, each capable of determining a different applicable property. Whether you are determining water content by Coulometric Titration, neutralization number or soap content by Potentiometric Titration, or Iodine number by Redox Titration, an automatic titrator is a valuable instrument already available in most testing laboratories and can prove to be quite useful in solving many of your Biodiesel testing requirements.

A commercially-available titration system configured for the determination of Water Content, Total Acid Number, & Iodine Value.