
# RECENT ADVANCEMENTS IN TEST METHODS FOR EVALUATION OF BIOETHANOL

The increased effort for renewable sources of energy has promoted a variety of alternate energy sources introduced into industry. One of these renewable sources of energy is biomass and biofuel. Biomass is organic renewable material that comes from animals and plants which has provided roughly 5% of the United States' total energy usage in 2020. There are many sources of biomass such as wood, agriculture and different types of biological wastes [1]. Within these sources is ethanol which is a renewable fuel that is made from different plant materials, mainly starch in corn grain [2], and is used as a blending agent with gasoline to decrease the amount of carbon monoxide and other smog causing emissions [3]. The main method of obtaining ethanol from biomass is through a process known as fermentation. During this process, bacteria and yeast metabolize plant sugars and produce ethanol. This process is also a positive energy balance meaning it takes less energy to produce the ethanol than the energy contained within the fuel itself [2]. On top of this it acts as a replacement for gasoline and diesel in machines that use them. It has a higher octane content and has significantly lower carbon dioxide and hydrocarbon emissions than gasoline and diesel fuels [4].

The demonstrated usefulness of bioethanol as a clean renewable energy source has led to various test methods being implemented to test the different properties of the fuel. These properties can be separated into both physical and chemical properties of the fuel. Depending on the vegetation used for the extraction of bioethanol, the physical and chemical properties may vary substantially. Thus, a variety of test methods must be utilized in order to test these physical and chemical properties in order and gauge the effectiveness of the bioethanol to be used as fuel source.

There have been many recent developments when it comes to the production of bioethanol. Some of these advancements have come from analyzing the best raw materials to draw bioethanol from. As previously mentioned, bioethanol comes from a variety of different plant materials. However, researchers have found that the best source of bioethanol production would come from areas with tropical climates due to the nutrient-rich soils they provide [5]. The performance that bioethanol has on engines was also analyzed with comparison to gasoline. A study conducted by Yoon et al. [6] measured the performance of bioethanol in spark-ignition (SI) engines in terms of combustion and emissions reductions at various charge air conditions. Some of the properties that were measured of the bioethanol and gasoline used within the study can be found in Table 1 [6].

*Table 1. Properties of Gasoline and Ethanol used in SI Engine Study [6]*

| Properties | Gasoline | Ethanol |
|---|---|---|
| Chemical formula | $C_nH_{1.87n}$ | $C_2H_5OH$ |
| Molecular weight (kg/kmol) | 114.15 | 46.07 |
| Density (kg/m$^3$ at 20 °C) | 732 | 792 |
| Oxygen (wt%) | 0 | 35 |
| Octane number (RON) | 86–94 | 105–108 |
| Boiling point (°C) | 25–230 | 78.5 |
| Latent heat of vaporization (kJ/kg) | 289 | 854 |
| Auto-ignition temperature (°C) | 257 | 423 |
| A/F ratio (by volume) | 14.7 | 9.0 |
| Lower heating value (MJ/kg) | 43.8 | 26.7 |

Ethanol contains about 35% oxygen, and for the same amount of induced-air, more ethanol is needed to satisfy the stoichiometric air–fuel ratio, which is about 9 to 1 for ethanol. The oxygen content in ethanol plays an important role at higher engine speeds where the available time is insufficient to form a stabilized mixture. These effects produce a superior combustion performance [6]. This is shown through the data in Figure 1a and 1b, where both the volumetric efficiency and brake specific fuel consumption (BSFC) was measured against the engine speed in rpm for both bioethanol and gasoline. The bioethanol showed a better performance in both the volumetric efficiency and brake specific fuel consumption (BSFC) as the air intake temperature decreased within the study. This shows that bioethanol can be a great alternative to conventional fuels in terms of energy efficiency in addition to the previously mentioned benefits.

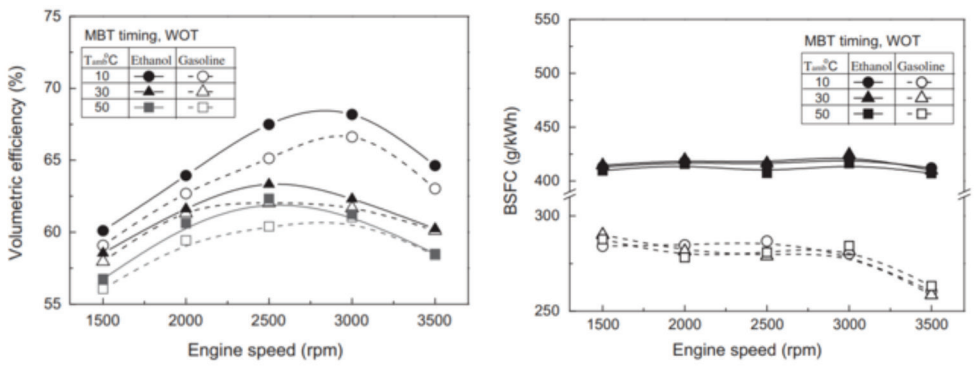


*Figure 1a (left) and 1b (right). The volumetric efficiency and BSFC (g/kWh) of both bioethanol and gasoline when measured against the engine speed (rpm) [5].*

According to the study done by Meenal et al. [7], there are 4 generations of biofuels. The first and least viable option are biofuels derived from food crops since the energy industry would have to directly compete with the food consumption industry. Second generation biofuels include biomass

*Table 2. Compositions of different Lignocellulosic Biomasses [7]*

| Biomass | Cellulose (%) | Hemicellulose (%) | Lignin (%) | Ash (%) |
|---|---|---|---|---|
| Sugarcane bagasse | 32–48 | 19–24 | 23–32 | 1.5–5 |
| Corn stalk | 39–47 | 26–31 | 3–5 | 12–16 |
| Rice husk | 31.3 | 24.3 | 14.3 | 23.5 |
| Rice straw | 28–36 | 23–28 | 12–14 | 14–20 |
| Wheat Straw | 33–38 | 26–32 | 17–19 | 6–8 |
| Groundnut shell | 35.7 | 18.7 | 30.2 | 5.9 |
| Coconut shell | 29.7 | NA | 44.0 | 0.5 |
| Corn stover | 38–40 | 28 | 7–21 | 3.6–7.0 |
| Cotton waste | 80–95 | 5–20 | – | – |
| Softwoods | 45–50 | 25–35 | 25–35 | NA |
| Hardwoods | 40–55 | 24–40 | 18–25 | NA |
| Newspaper | 40–55 | 25–40 | 18–30 | 8.8–1.8 |
| Algae (green) | 20–40 | 20–50 | NA | NA |

and biowaste, which as of right now are the most feasible option and the option that is trying to be optimized. Third generation biofuels are algae, and fourth generation biofuels are photobiological solar cells, both of which are not yet possible as more research is needed to verify the validity and actual process for implementing these options. So far there have only been recent advancements in second generation bioethanol production. It is first vital to understand the general stages of bioethanol production: pretreatment, saccharification and fermentation processes. This 3-step process is how lignocellulosic biomass, which is the byproduct from agricultural and many related industries, gets converted to bioethanol. Lignocelluloses are composed of 40-60% cellulose which is the actual ingredient that is used to produce energy, 20-40% hemicellulose, and 10-25% lignin [7]. The 3-step process separates the rigid and unimportant components such as hemicellulose and lignin away from the cellulose and converts it to bioethanol.

Pretreatment is the process in which the lignocellulosic biomass is "treated" to make it easier to work with and continue with the other steps in the process. While different substances require different types of pretreatment processes because of their different physical characteristics, five main objectives remain the same: reducing the crystallinity, avoiding the degradation of the sugars, minimizing the formation of unnecessary products, recovering the lignin for future use, and minimizing the energy usage to minimize the costs [7]. There are multiple different types of pretreatment methods and they have progressed from solely physical methods to now physio-chemical methods. At first, processes such as grinding or pyrolysis would be used, which either require too much energy or would create unnecessary byproducts, both of which could not be applied on the industrial scale because it is inefficient. The most common method of treating biomass involves using dilute acid to separate the lignin and hemicellulose from the cellulose and then heavily cleaning the resulting product before moving onto the next step [7]. These methods are expensive and are not completely feasible or ideal on an industrial scale which prompts the need for either different chemicals that are easier to use than acids such as ionic liquids, or coming up with hybrid methods that involve both physical and chemical processes. Two such methods are steam explosions and wet oxidation. Steam explosions involve exposing harder and more rigid biomasses to steam which soften them up and allow chemicals to release the lignin and hemicelluloses. Wet oxidation uses water and hydrogen peroxide at high enough temperatures to the point where water acts as an acid and separates the unwanted products from the cellulose, these reactants are cheap and are easy to obtain and on top of that you wouldn't have to worry about cleaning the product which makes it less costly when used on an industrial scale.

Pretreatment of the biomass is just the first step that leads to the next step of saccharification, which converts the resulting cellulose into simpler sugars such as glucose and xylose. These sugars then undergo fermentation which converts them into the final product, bioethanol. There are multiple different methods for achieving this end result as well, the first involving the separation of the saccharification and fermentation processes, but this results in the buildup of sugar which in the end affects the overall bioethanol yield [7]. The second process is doing these processes simultaneously in one reactor, which reduces the buildup of sugar but also makes it hard to optimize either process since they are both occurring at the same time, making this one not as ideal either. The final process uses a single microbial community to do both processes in one step, which means it forms the glucose and xylose and instantly converts it to bioethanol. This method is called consolidated bioprocessing since it takes both processes and consolidates them into one step. This method is heavily popular among researchers as it can be optimized by using genetically modified organisms. Using genetically modified organisms would mean that one specific type of bacteria wouldn't have to be used but a community or combination of bacteria could be engineered to work together to accomplish these processes in one step ultimately improving the yield and efficiency. This process is at the forefront and is currently being studied so that it can be used on a much larger scale.

*Table 3. Table listing the Chemical Properties of Bioethanol and their Associated Test Method [8]*

| Parameter | Test method |
|---|---|
| Boiling Point, °F | ASTM D2892 |
| Density, lb/gal | ASTM D1298 |
| RVP, psi | ASTM D 323-99a |
| Flashpoint, °C | ATM D93-13 |
| Heat of vaporization, Btu/lb | ASTM E2071 |
| Autoignition point, °F | ASTM E659, ASTM D1929 |
| Flammability Limit, % | ASTM E918 |
| Air: Fuel Ratio, Weight % | |
| Flame Temperature, °F | |
| Heat of Combustion, Btu/gal | ASTM D240 |
| Octane number | ASTM D 2700 |
| Lower Heating Value, Btu/lb | ASTM E711, ASTM D5865 |
| Higher Heating value, Btu/lb | ASTM E711, ASTM D5865 |
| Melting point, °F | ASTM D 87 |
| Specific Gravity | ASTM D 1298-99 |

There are a variety of properties that need to be examined with different test methods within bioethanol. These properties can be divided within two categories, physical and chemical properties. An example of some of these properties can be found in Table 1a with their corresponding test methods associated with them. These properties are crucial to understanding the effectiveness and efficiency of bioethanol as a fuel. A few properties that will be focused on are the gum content, viscosity and the flash point of the bioethanol fuel.


*Figure 2. K33780 Koehler Existent Gum Evaporation Bath [11]*

The gum content within a fuel is a crucial component for determining the quality of a bioethanol fuel. The gum content is the residue that is left over from the evaporation of fuel done under controlled conditions [9]. The gum content dictates the amount of precipitation that forms on the surface of the fuel induction system and the stickiness of the inlet valve. The precipitation formation is caused by the evaporation process in the fuel. The insoluble gum may also clog the fuel filters as well which may lead to a decrease in the efficiency and performance of the fuel [10]. The gum content within bioethanol can therefore indicate the quality of the fuel.

The gum content within a fuel can be examined with the test method known as ASTM D-381. This test method can be examined using the Existent Gum Evaporation Bath produced by Koehler Instrument Company. This apparatus allows for a 50 mL sample to be evaporated in an aluminum block bath under controlled conditions of temperature and the flow of air or steam [11]. Using controlled flow of air or steam depends on whether an aviation turbine or motor fuel is being utilized. The residue from the evaporation is collected, weighed, and then reported as mg/100 mL. If testing for motor fuel, the residue is collected, weighed before and after being extracted with heptane, and then reported as mg/100 mL [12].

An important chemical property measured in fuels is the viscosity of the fuel. The viscosity is the measure of the internal friction of a fuel [13]. The viscosity of a fuel depends on the temperature as it decreases as temperature increases. The instrument used to measure viscosity is known as a viscometer. The viscosity of a fuel has many important properties pertaining to storage and use of the fuel. If the viscosity of the fuel is too thick, it will make the engine difficult in pumping, igniting the burner, and flowing. In addition, the high-level viscosity in the fuel worsens the atomization, which will initiate the formation of carbon deposition on the cylinder wall of the engine [10]. Thus, it is important to measure the viscosity of a fuel in order to prevent such wear on the engine.

The viscosity is tested in accordance with the ASTM test method D-445. This test method can be used with the KV5000 Kinematic Viscosity Bath with Optical Flow Detection System produced by Koehler Instrument Company. This instrument contains high accuracy temperature control with dual digital displays that show the set point and actual bath temperature which is displayed in either or [14]. This is important as a closely controlled and known temperature is needed to measure the time for the fixed volume of fuel to flow under gravity through the capillary of the calibrated viscometer. The kinematic viscosity produced is the product of the measured flow time and the calibration constant of the viscometer. Two determinations are needed to calculate the kinematic viscosity result which is determined by averaging the two acceptable determined values [15].

*Figure 3. KV5000 Koehler Kinematic Viscosity Bath with Optical Flow Detection System [14]*

Just like the viscosity, the flash point of a fuel is an important chemical property that must be measured. The flash point is the lowest temperature where the fuel can evaporate and form a combustible gas [16]. The flash point is used to determine the safety regulations of a fuel for exportation of the fuel [17]. The higher the flash point, the safer the fuel is to handle. The flash point of a fuel can be measured using the test method ASTM D-93. This test method can be used with the K71000 Automatic Pensky-Martens Closed Cup Flash Point Tester developed by Koehler Instrument Company. This instrument comes with two flash detector systems including a thermocouple and ionization ring detection [18]. These are important as precise detection is needed in order to conclude the test. The brass test cup is filled to the inside mark with test fuel and fitted with a cover, is heated and the specimen stirred at specified rates, using one of three specified procedures within the ASTM D-93 Documentation. An ignition source is directed into the test cup at regular intervals with simultaneous interruption of the stirring. The test concludes when a flash is detected and the flash point is recorded [17].


*Figure 4. K71000 Koehler Automatic Pensky-Martens Closed Cup Flash Point Tester [18]*

While optimizing the process for producing bioethanol is very important, different vegetables and organic plant matter actually produce different types of bioethanol with varying properties that have to be considered. As shown in Table 2 different types of plant matter have varying amounts of cellulose which would affect the quality of the bioethanol produced.

| No. | Material | Bioethanol content (%vol) | Methanol content (mg/l) | Water content (%vol) | Cu content (mg/kg) | Cl content (mg/l) | Gum content (mg/100ml) |
|---|---|---|---|---|---|---|---|
| 1 | *Amorphopallus variabiliti* | 94 | 0.0049 | 0.202 | 0.072 | 17.758 | 5.2 |
| 2 | *Mucasea* | 93 | 0.0088 | 0.653 | 0.052 | 39.547 | 1.4 |
| 3 | *Solanum lyycopersicum* | 94 | 0.0013 | 0.684 | < 0.01 | 35.354 | 6.5 |
| 4 | *Alocasia macrorrizha* | 93 | 0.0052 | 0.353 | 0.095 | 19.651 | 11.5 |
| 5 | *Maranta arundinacealinn* | 94 | 0.0029 | 0.435 | 0.056 | 15.732 | 9.8 |
| 6 | *Saccharum officinarum linn* | 95 | 0.0024 | 1.035 | < 001 | 30.654 | 1.3 |
| 7 | *Amorphophallus campanulatus* | 93 | 0.0037 | 0.253 | 0.083 | 21.543 | 4.6 |
| 8 | Bioethanol Standard [21] | 99.5 min | 300 max | 1.0 max | 0.1 max | 40.0 max | 5.0 max |

*Table 4. Physical properties of Bioethanol produced from seven different vegetables [19]*

| No | Material | pH value (mg/l) | Heating value (kcal/kg) | Density (g/cm$^3$) | Viscosity (cSt) | Flash point (°C) |
|---|---|---|---|---|---|---|
| 1 | *Amorphopallus Variabiliti* | 2.5 | 6786 | 0.858 | 2.762 | 15 |
| 2 | *Mucasea* | 5.8 | 5524 | 0.824 | 2.149 | 12 |
| 3 | *Solanum Lyycopersicum* | 5.3 | 5696 | 0.817 | 2.843 | 13 |
| 4 | *Alocasia Macrorrizha* | 3.8 | 6445 | 0.836 | 1.961 | 16 |
| 5 | *Maranta Arundinacealinn* | 4.6 | 5969 | 0.796 | 3.054 | 14 |
| 6 | *Saccharum officinarum linn* | 8.5 | 8756 | 0.801 | 1.637 | 13 |
| 7 | *Amorphophallus campanulatus* | 4.7 | 5892 | 0.823 | 2.376 | 19 |
| 8 | Bioethanol Standard [21] | 6.5-9.0 | 6380 | 0.789 | 1.525 | 12 |

*Table 5. Chemical properties of Bioethanol produced from seven different vegetables [19]*

As seen above in tables 3 and 4 the bioethanol produced can have varying effects on properties such as the bioethanol content, water content, viscosity, and flash point which all have drastic effects on how they will operate in different machinery. Properties such as bioethanol content are clearly important because you'd want to produce a product that is as close to bioethanol as possible being shown as 99.5% bioethanol in table 3. The water content is also important as a lower amount of water means that the fuel is of a higher quality and according to table 3 the maximum amount of water allowed is 1% and 6 of the 7 vegetables produce a product that falls well below that value [19].

This data clearly shows to us that it is very important what types of plant matter or biomass are used as the base or starting material for bioethanol. Each has its own strengths and weaknesses but this in and of itself is something that needs to be researched more, while the process for producing bioethanol is a challenge engineers and researchers must work to optimize. The actual materials used can also be enhanced in some way to make quality bioethanol.The excess plant matter from different industries could also be used, they could be genetically modified to enhance their existing properties and make them more useful in the industries they are already used in [19]. The plant matter could be modified so that the excess matter would have properties that have a higher cellulose content, lignin, higher or lower pH, etc. to give the bioethanol produced using the excess plant matter better qualities that more closely resemble or may even be better than the current industry standard [19].

Currently bioethanol is the next logical step for making industries more renewable and more efficient. It provides a clean energy source that can replace gasoline and diesel in most scenarios with little to no changes in existing machinery. That is why it is important to be able to test bioethanol's properties and improve current methods for producing it. Improvements to the recent test methods for bioethanol prove to be significant as well since the better the actual test methods are the more accurate the results and properties of new types of bioethanol will be. Of course, this is only the first step towards more renewable energy, but it is pivotal in making the switch from fossil fuels and other nonrenewable energy sources to renewable ones.

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