Biofuel Development and Standardisation

Dr. Raj Shah and **Vincent Colantuoni, Sales Application Engineer, Koehler Instrument Co. Inc.**
1595 Sycamore Avenue, Bohemia, New York 11716, USA. Tel: (631) 589-3800 Email: vcolantuoni@koehlerinstrument.com

Currently, Biodiesel and Bioethanol are the two major forms of Biofuels being sold and distributed around the world. These fuels however, only represent a fraction of renewable fuel necessary to make an impact on the global energy crisis. There are multiple obstacles that still need to be overcome in order for these Biofuels to become a mainstream energy source. A major challenge originates from issues dealing with international trade and transportation of Biofuels. These issues range from feedstock costs and availability of feedstock to fuel quality and the International Compatibility of Biofuel Testing Standards. These fuels both face similar problems and steps are being taken toward resolving these issues. ASTM International has recently published new specifications for a broader range of Biodiesel Blends. Advancements in other bio- or alternative energy technology have widened the scope of what we see as feasible solutions to our energy problems. These developments and advances are a positive sign for the alternative fuels industry, and could result in a more timely solution to this global problem.

We can begin discussing the challenges of the Biodiesel Industry from the beginning, the Feedstock. Issues begin to arise even before Biodiesel becomes Biodiesel. The usability of vegetable oil feedstock is of utmost importance. Currently, the cost of the feedstock used to make Biodiesel is very high. This is due to the availability of this feedstock in that they will always have other uses other than as an energy source. It's primary use being food for human nutritional needs. Only a fraction of vegetable oil production is available for non-food use. This dilemma is better known as "Food vs. Fuel". To simply grow and produce more vegetable oil and use it for fuel would simply not work. There is a finite amount of land and other natural limitations that make this notion unfeasible. We must develop "New Agriculture" such as Algae that does not compete with food crop for land use. A public policy initiative would act as a catalyst and push the thinking in this direction. This policy should be a performance based policy that pays according to performance not production. Ultimately, a system of Development and Sustainability must be in effect in order for the growth of Biodiesel to be successful.

Quality Control is another challenge facing the Biodiesel industry. One major difference that separates Biodiesel from Petro-diesel is how Biodiesel behaves under extreme temperature conditions. Cold flow properties in the winter and oxidation stability in both the summer and winter are major issues in the Quality control of Biodiesel. These properties do differ slightly based on the feedstock in which the fuel is produced. For example, Biodiesel derived from palm oil, tallow, or used cooking oils generally have worse cold-flow properties than Biodiesel derived from soybean or canola oil. (Building Biodiesel, pg 7). The Oxidation Stability of Biodiesel greatly differs from that of Petro-Diesel. The rate at which this oxidation occurs increases with higher temperatures. Therefore, storage during the summer months will cause Biodiesel to deteriorate rapidly. The chemical composition of Biodiesel also contributes to its oxidation. Again, the composition depends on the feedstock in which the Biodiesel is produced. Biodiesel composed of unsaturated fatty acid alkyl ester-like linoleic and linolenic acid esters are more susceptible to oxidation than saturated fatty acid esters. (Biodiesel Magazine, Peng Ye).

The diversity among existing Biodiesel Testing Standards is a result of a number of factors. The first factor being that some existing specifications have been formulated mainly around the locally available feedstock. This diversity of feedstock is then translated into significant divergences in specification properties of the derived fuels. Another factor contributing to the discrepancies in the specification properties is the fact that some specifications, such as those in the U.S. and Brazil, are based on use as a blend stock or extender for fossil based diesel fuel, while others, such as the European specification, is based on use as a 100% fuel for engines and as a blending component in hydrocarbon based fuel. (ASTM, white paper, pg 20). Furthermore, Biodiesel standards in Brazil and the U.S. are applicable for both fatty acid methyl esters (FAME) and fatty acid ethyl esters (FAEE), whereas the current European Biodiesel standard is only applicable for fatty acid methyl esters (FAME). Another source for the differences in the Biodiesel specifications from region to region is the predominance of the types of diesel engines most common in that region. For example, the most prominent diesel engine in Europe is found in passenger cars. This diesel engine is fairly different than the heavy duty diesel engines found in the U.S. and Brazil. The different engines amount to differences in the emissions regulations that govern these engines. These diverse emissions regulations then contribute to differences in the Diesel Specifications amongst the regions. Because the Biodiesel specifications of the region were based upon their corresponding diesel specifications, the regional differences were therefore carried over to the Biodiesel specifications.

ASTM international has recently published new and revised biodiesel standards. These standards include revisions for the Diesel Fuel Oil (D975) and Fuel Oil (D396) specifications to include an allowance for up to 5 percent biodiesel. ASTM D6751, the specification for Biodiesel Fuel Blend Stock (B100) for middle Distillate fuels, has also been revised to include a requirement that controls minor compounds using a new cold soak filterability test. The entirely new specification is for Diesel Fuel Oil, Biodiesel Blend (B6-B20) and is designated D7467. This specification covers finished fuel blends of between 6 (B6) and 20 (B20) percent biodiesel for on- and off-road diesel engine use. (ASTM Standardization News). The participation from various institutions such as petroleum corporations, biodiesel manufacturers, engine companies, military representatives, government representatives, researchers and academics all assisted in the standards' development. The Chair of the ASTM Biodiesel Task Force, Steve Howell stated, "We have engine interests, petroleum, interests, biodiesel interests and third parties. It took cooperation and a lot of data and information sharing between all those parties to reach consensus on these specifications." (ASTM Standardization News). These new biodiesel blend specifications ultimately represent the next step taken to make biodiesel a mainstream energy source.

The challenges facing the Bioethanol industry are similar to those of the Biodiesel industry. Bioethanol also creates the "Food vs. Fuel" dilemma. This ethical obstacle has already raised the price of food significantly. Cellulosic Ethanol, a biofuel produced from non-edible parts of plants, can be the solution to this dilemma. The transportation of Bioethanol yields yet another challenge. Bioethanol cannot be shipped through an existing gasoline pipeline system because it is easily contaminated by water and will corrode the pipeline. Therefore, Bioethanol needs to be shipped by means of truck or rail. These modes of transportation are both more expensive and slower than pipeline transport and in turn add to the cost of Bioethanol. In order for Bioethanol to become a mainstream energy source, transport vehicles will have to be retrofitted for Bioethanol, or governments will have to build or fund pipelines explicitly for Bioethanol.

The Bioethanol specifications are more closely aligned amongst the three regions than the Biodiesel specifications. Please see *Table 1* below for a detailed comparison of Bioethanol Specificaation among the three regions. This is based on a number of factors. Starting at the molecular level, Bioethanol is a single chemical compound. Biodiesel is not a single chemical entity. It is derived from several types of feedstock that can translate to variations in the performance characteristics of the finished fuel (ASTM, white paper, pg 14). Similarities in the three Bioethanol specifications are also largely due to the fact that they all originate from a single (Brazilian) specification. However, differences have arisen due to market developments, climatic conditions in each country and region and feedstock variances. The Bioethanol specifications are so similar in that the Tripartite Task Force concluded that there is no technical specification that constitutes an

Property	US		Brazil		EU prEN 15376
	D 4806	D 4806 Undenatured	Anhydrous	Hydrous	
Colour	Dye Allowed, but not mandated	Dye Allowed, but not mandated	Dye mandated for in country, but not for export	Dye prohibited for in country	Dye Allowed, but not mandated
Ethanol Content, vol %, min	92.1	93.9	99.6[3]	-	[96.8]
Ethanol + C3-C5 sat. alcohols, vol %, min	-	[98.4][2]	-	-	98.8
Total Alcohol, vol %. min	-	[98.95]	99.6	95.1	[99.76]
C3-C5 sat. alcohols, vol %, max	-[1]	[4.5]	-	-	2.0
Water content, vol %, max	1.0	1.05	[0.4]	[4.9]	0.24
Density at 20C, kg/m³, max	-	-	791.5	807.6	-
Methanol, vol %, max	0.5	0.53	-	-	1.0
Denaturant, vol %, min/max	1.96 / 5.0	No Denaturant	No Denaturant	No Denaturant	Set By Country 0/1.3
Hydrocarbons, vol %, max	-	-	3[4]	3[4]	-
Solvent-washed gum, mg/100mL, max	5.0	5.3	-	-	-
Gum or Resid by Evap, mg/100ml, max	5 (washed gum)	5.3 (washed gum)	-	5 (washed gum)[5]	10 (unwashed)[5]
Electrical Conductivity, uS/m, max	-	-	500	500	-
Sulfate, mg/kg, max*	4	4.2	-	4	Working
Inorganic Chloride, mg/kg, max	40.	42.1	-	1	25
Copper, mg/kg, max	0.1	0.105	0.07	-	0.1
Sodium, mg/kg, max	-	-	-	2	-
Iron, mg/kg, max	-	-	-	5	-
Acidity, mass % (mg/L), max	0.007 (56)	0.0074 (58.9)	0.0038 (30)	0.0038 (30)	0.007
pHe	6.5-9.0	6.5-9.0	-	6.0-8.0	Dropped
Phosphorus, mg/L, max	-	-	-	-	0.5
Sulfur, mg/kg, max	30.	5	-	-	10
Appearance	Clear & Bright	Clear & Bright	Clear & No Impurities	Clear & No Impurities	Clear & Bright

Table 1. Detailed Comparison of Ethanol Specification (ASTM, White Paper, pg 89)

(1) Not specified by can be calculated for US. (Heavy alcohol content = 100 - ethanol content - methanol - water content)
(2) Numbers in [ ] are calculated estimates and not specified limits
(3) Limit only applies to ethanol not produced by fermentation from sugarcane or ethanol contaminated by other types of alcohol
(4) Applies only to imported ethanol
(5) Procedures are likely different.

	n-Butanol	Ethanol	Gasoline
Specific Gravity @ 60°F	0.814	0.794	0.720 - 0.775
Heating Value, MJ/L	26.9 – 27.0	21.1 – 21.7	32.2 – 32.9
Research Octane Number (RON)	94*	106 – 130*	95
Motor Octane Number (MON)	80 – 81*	89 – 103*	85
RVP of 5% and 10% Alcohol/Gasoline Blends, psi	6.4* / 6.4*	31* / 20*	_†
Oxygen, wt%	21.6	34.7	< 2.7
Water Solubility at 25°C, %	9.1	100.0	< 0.01

Table 2. Properties of n-butanol, ethanol and gasoline (Cascone, S5)

** Gasoline blend values of the alcohol octane numbers and vapor pressures.*
† For comparison, the summer / winter specifications for gasoline are < 7.8 / 15 psi.

impediment to trade given the current situation (ASTM, white paper, pg 10). Water content however, is a specification that yields a problem. The water content level is set at significantly different levels amongst the three specifications. The European Union specification has the lowest limit, thus requiring additional drying and testing by Brazil and U.S. exporters wishing to supply the EU market (ASTM, white paper, pg 10).

Recently, the U.S. denatured ethanol standard was converted to an undenatured basis in order to make the U.S. specification more comparable to both the Brazil and EU specifications. The unit of measure in the three specifications has also been converted to a common basis. Some key standards that the Task Force is looking into universalising are the inorganic chloride content, electrolytic conductivity and of course, water content. Water content is the most difficult parameter to agree upon because it is based upon the ethanol content of the gasoline-ethanol blend that the individual countries use and the amount of ethanol used in gasoline is tied to each country's regulatory framework, making negotiated changes to this parameter difficult (ASTM, white paper, pg 67). The phosphorous content parameter is only found in the European Union specification. In an attempt to universalise this parameter, the US and Brazil have agreed to collect data in order to determine the phosphorous levels in their products and from this data determine whether a phosphorous level specification should be adopted (ASTM, white paper, pg 67). For inorganic chloride content, the US and EU have agreed to review the specification in an attempt to lower the limit closer to the Brazil limit. In addition, the US has recently updated their specification with the inclusion of two new ion chromatography test methods for determination of inorganic chlorides and sulfates (ASTM, white paper, pg 70).

Advancement in second generation Biofuel production technology has attracted significant attention. It is becoming more feasible that fuels such as Biobutanol, Cellulosic Ethanol, and synthesized higher-chain alcohols will aid in solving our energy problems. These technologies are becoming increasingly more efficient and will ultimately compliment or replace Bioethanol altogether. The technology for cellulosic ethanol is getting closer to commercialisation and deems to be a direct replacement for corn ethanol. This is because Cellulosic Ethanol does not compete much with food production and it has a better carbon emissions profile.

Biobutanol also has great potential to replace bioethanol. Butanol's properties make it a much more attractive biofuel than ethanol with respect to gasoline blending, distribution and refueling, and use in existing vehicles (Cascone, S5). Please see *Table 2* for a detailed property comparison of n-butanol, ethanol and gasoline. Biobutanol can also be produced commercially today unlike other advanced biofuels such as cellulosic ethanol, fermentation hydrocarbons and algal biodiesel. The challenge being to improve the commercial process enough to produce large volumes while remaining economically competitive. Biobutanol has also been found to be more toxic to humans and animals in the short term than ethanol or gasoline, and it is not clear to whether butanol will degrade the materials commonly used in automobiles that come into contact with motor fuels. (Cascone, S5).

Higher-chain alcohols have also been given serious consideration as an ethanol replacement. This is due to recent advances in Metabolic Engineering Techniques. Metabolic Engineering is a field that merges genetic engineering, physiology and systems engineering. Metabolic engineers have made significant progress in the production of fuel-grade compounds due to rapidly expanding genomic information, molecular biology techniques and high-throughput tools. These compounds have higher energy densities, lower vapor pressures, and are not corrosive. Resulting in a fuel that can circumvent or alleviate many of the problems associated with ethanol. (Higashide, Liao, S20).

To cover all the areas discussed, a variety of agencies must be involved. This makes finding a universal solution to make Biofuels a mainstream energy source much more complicated. The Food vs. Fuel dilemma involves organisations such as the Department of Agriculture and the Department of Energy, in the United States alone. Alignment of the International Biofuels Standards will require a large investment of time and effort in testing and research by specialists in laboratories, test facilities, and private companies around the world. But, the emerging of new technologies, the refining of existing techniques and the ongoing development and alignment of testing standards will make for a quick and balanced solution to the global energy crisis.

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