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Aspects of storage and corrosion characteristics of biodiesel

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ABSTRACT

Process and corrosion engineers have critically addressed compatibility of biodiesel components in petroleum refinery infrastructure because of different processing, storage and dispatching histories of shipments. Concerns were related to aging and corrosion and to accumulation of a bottom layer in the dedicated storage tank. Corrosion tests were executed in a microcosm test environment modified to the recommended practice of ASTM G4-01 procedure. Colloid chemical properties and technology of biodiesel refining operations can plausibly explain different material responses at different temperatures. The sampled bottom layer consisted mainly of glycerides, resembling characteristics of extract byproducts that are separated in trans-esterification in biodiesel synthesis. This bottom layer exerts both beneficial and detrimental effects. The positive side is that it extracts polar components and by this improves quality. The negative side is that it reduces resistance of the oil against aging. There was no risk of detrimental effects in terms of corrosion of storage tank materials. Overall progress of corrosion is controlled by the slightly alkaline bottom layer via neutralizing the oxidation products and exerting protection to metallic surfaces. Microbial degradation can only pose risks if normal and prudent conditions are not observed. Upon extended incubation microorganisms that are present in the bottom layer below the level detection limit, can develop countable colonies, if nutrients are available and conditions are favorable. It can be concluded that there is no risk of significant corrosion in storage and downstream infrastructure if the stored biodiesel meets standard quality specifications and storage conditions are normal.

1. Introduction, corrosion and storage stability of biodiesel

Biodiesel, by definition is a mixture of methyl esters of C_{14}–C_{24}, fatty acids. Production has matured to become an essential component to formulated automotive diesel fuels [1]. Petroleum refineries, produce and purchase biodiesel consignments to formulate commercial fuel products to the most economic combination of available components. Constrains and economic circumstances influence decisions for storage or use. Containments in dedicated biodiesel storage tanks come form different shipments from different suppliers. Biodiesel must resist aging and/or oxidation along the extent of storage and must not risk deterioration of the storage tank as well as construction elements of transfer and blending. Commercial automotive fuels contain carefully compounded additives to meet relevant product standards. Because of the biological origin of the feedstock, differences in technologies and operational scales and routines, some of the properties of shipments can be different. It is possible that some degree of contradiction in the cited articles is related to this difference in origin and processing oils and greases of biological origin.

Storage stability has not been directly included into the specifications of standards for biodiesel fuel. Oxidation stability has usually been accepted as a proxy to this property. Resistance to degradation is tested in Rancimat test under accelerated conditions, by bubbling 20 l/h air into 3 g of oil at 110 °C [2,3]. In an autocatalytic oxidation chain reaction the reactive carrier stream of air transfers corrosive intermediates of peroxides and light fatty acids into distilled water in which a sharp increase in conductivity indicates that the oil in test lost capacity to resist oxidative degradations. Standard specifications require a resistance oxidation of at least 6 h under these drastically severe conditions. Dunn [4] concluded that accelerated tests give reliable characterization of oxidation stability of biodiesel component methyl soyate, but further studies are needed to validate conclusions under “real world” conditions.

The standard “Copper strip corrosion test” method employs submersion of polished copper strip coupons into the bulk of biodiesel at 50 °C for 3 h [5]. Rating is done by comparing changes in appearance against a scale of reference. This test is relevant only if copper, brass or bronze constituents are present in the construction element [6]. The test does not provide a reliable indication for possible corrosion in large tanks, usually made of carbon or mild steel in petroleum refineries. Holding times are longer by orders of magnitude, while temperatures are significantly cooler in storage tanks.

It has been known for long in petroleum product development practice that corrosion and oxidation symbiotically coexist. Antioxidants effectively control oxidation and provide protection against corrosion,

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while corrosion inhibitors protect against oxidation by persistent absorption on reactive sites of potentially catalytic metal surfaces. This passivation through formation of a monomolecular layer of the functional group, by physical or chemical sorption onto the metallic surface, prevents direct contact of the active metal and the liquid fuel substrate. Jung et al. concluded that amine based antioxidants influenced storage and oxidation stability, and also did improve antiwear properties too [7]. Antiwear protection provided by methyl esters of C_{14}–C_{24}, fatty acids is similar, the polar functional ester group adhered onto the metal and the apolar hydrocarbon chain provided lubrication. The finding of Lee et al. [8] supports this too. Biodiesel components did exert protection against microbiological contamination and corrosion under storage conditions. Cohesive forces are weaker at warmer temperatures, corrosion and oxidation are significantly higher under significantly warmer conditions. Fazal et al. [9] immersed corrosion coupons in fossil and biodiesel samples at room, 50 °C and 80 °C temperatures. Significant increase in the rate of corrosion and in iron content of the oil was reported for a period of 50 days in storage. The final conclusion was that corrosion mechanisms contributed to oxidation instability of the fuel. The presence of biodiesel components was identified to influence the increase rate of corrosion. Similar conclusions were drawn by evaluation of product characteristic degradation at higher storage temperature [10]. Temperature dependence of rate of oxidation can be described by Arrhenius type correlation [11]. It has been accepted that storage stability of middle distillate diesel fuel for a week in standard test method ASTM D4625-04, performed at 43 °C is equivalent to 1 month of storage at 17 °C [12].

In contrary to the findings of protective influence of biodiesel Hu et al. [13] carried out immersion tests at 43 °C and concluded that the mechanism of corrosion is mainly controlled by chemical reactions. Corrosion rates of carbon steel immersed in diesel containing biodiesel components were almost tenfold higher than the corrosion rates in plain fossil diesel. Copper was most susceptible to corrosion, stainless steel showed good resistance. Observations and findings of Maru et al. [14] are related to 30 times higher tendency for water absorption of biodiesel than petroleum diesel fuels. The water content accepted by product standard in commercial biodiesel is up to 500 ppm. Water content may be present in dissolved or in dispersed form in biodiesel. Colloid chemical properties of fatty acid methyl esters control and improve efficiency of refining biodiesel [15]. Phase separation is rarely perfect in biodiesel technologies and water can remain in the final biodiesel product in a finely dispersed form. Water is necessary for hydrolysis of fatty acid methyl esters either by chemical or microbial process. Aktas et al. [16] argued that the accelerated corrosion was a consequence of acidic intermediates formed in the hydrolysis of biodiesel. Anaerobic microbial corrosion of construction elements in settled bottom layers of automotive diesel fuel storage tanks was reported by Sorensen et al. [17]. It has been concluded that different microorganisms are present at a time and interact differently in fuel degradation. Presence of biodiesel in the fuel mix affected the type and activity of microorganisms. Pullen and Saeed [18] did also conclude that microbial growth was the main cause of oxidative degradation under storage conditions. Wang et al. [19] showed that electrochemical corrosion of carbon steel occurs when biodiesel is exposed to seawater. In observing diligent storage instructions it is unlikely to prevail favorable conditions for corrosion controlled by electrochemical phenomena related to biodiesel in fuel terminal.

Studying the interaction between different types of biodiesel and metal parts of a diesel engine Kaul et al. [20] found that non-ferrous metal elements are susceptible to corrosion only if they are in contact with high-sulfur fuel. Fernandes et al. [21] reported that galvanized and carbon steels proved compatibility with biodiesel. There was no specific biodiesel property that was significantly affected by storage for 56 days. It has been concluded that presence of air and increase in temperature exerted more influence than the consequences initiated by hydrolysis. Conclusions of du Plessis et al. [22], in harmony with the recommendations of Dunn [4] were similar. It was concluded, that exclusion of air retards oxidation of sunflower biodiesel, indifferent of temperature, if storage stability is tested at or above 30 °C. Peroxide values, UV absorption, free fatty acid contents, viscosity and anisidine values indicated the progress of oxidation.

Table 1
Selected properties of samples.

Property	Dimension	Value	EN14214
Biodiesel			
Ester content, %	EN14103	97.1	Min. 96.5
Specific gravity @ 15 °C, g/cm^3	ISO 3675	0.886	0.860–0.900
Viscosity @ 40 °C, mm^2/s	ISO 3104	4.62	3.5–5.0
Flash point, PM, °C	ISO 3679	above 200	Min. 120
Conradson, 10% residue, %	ISO 10370	0.18	Max. 0.3
Ash, sulfated, %	ISO 3987	0.01	Max. 0.02
Contaminants, mg/kg	EN12662	21	Max. 24
Oxidation stability @ 110 °C, h	EN14112	Above 6	Min. 6
Water, mg/kg (ppm)	ISO 12937	430	Max. 500
Acid number, mg KOH/g	EN14104	0.15	Max. 0.5
Methanol, %	EN14110	0.15	Max. 0.2
Mono-glycerides, %	EN14105	0.58	Max. 0.8
Di-glycerides, %	EN14105	0.18	Max. 0.2
Tri-glycerides, %	EN14105	0.17	Max. 0.2
Total glycerol, %	EN14105	0.20	Max. 0.25
Iodine number, g/100 g	EN14111	117	Max. 120
Microorganism, CFU/ml	Envirocheck	Nil	Not specified
Bottom layer (there is no standard specification in place)			
Ash, sulfated, %	ISO 3987	0.03	
Water, %	ISO 12937	0.8	
Glycerol, %	See [24]	96.7	
Microorganism, CFU/ml	Envirocheck	Nil[#]	
Neutralization no., mg KOH/g	EN14104	1.4	
pH		9.5	

[#] Note: below the limit of detection (10^3 CFU/ml) within 5 days. Testing the presence of microorganism colonies after 5 days was out of scope.

The market survey analysis of a fail rate of more than 45% of samples of commercial diesel fuel having biodiesel in composition in terms of inadequate oxidative stability was a warning [23]. Corrosion engineers of the refinery associated this loss of resistance to oxidation to a complex process of aging in storage and fuel supply chain infrastructure. They have expressed serious concerns about the extended holding times. Both process and corrosion engineers have critically addressed compatibility of biodiesel components with different processing, storage and dispatching histories. The present article reports about a study that was requested on this ground. The prime interest was to learn about corrosion characteristics and risks associated to storing different batches of biodiesel in dedicated operational storage facilities of an operational petroleum refinery under real world conditions. Test routines and conditions have been developed and streamlined to reproduce possible degradation phenomena in real storage tanks under possible operational conditions.

2. Experimental

Biodiesel and settled bottom layer were sampled from an operational storage tank dedicated to store automotive fuel blending biodiesel component in an operational refinery in Hungary. The storage tank operates by a routine of fill and discharge. In filling fresh shipments of biodiesel are mixed into the existing content. The withdrawn streams have different production histories, but meet standard quality specifications. Due to periods of cleaning cycles the settled layer could have been accumulated along 5 years in the operation. Standard sampling procedure was employed. Properties of the fuel and settled layers were tested according to EN14214. The fuel fully met the standard specifications, the relevant data are presented in Table 1. Glyceride content of the bottom layer was tested by an HPLC routine developed by Fekete et al. [24].

Corrosion tests were executed according to the recommended practice of procedure of ASTM G4-01 "Corrosion tests in plant