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ORIGINAL PAPER

Effects of NanoTag Markers in Palm Methyl Esters and Their Blends with Petroleum Diesel

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Abstract Given the critical need to address smuggling and unauthorised usage of subsidised diesel, the Malaysia Government introduced fuel marking for subsidised diesel under the NanoTag Program in April 2006. NanoTag markers mixture consists of VisioTag (dye) and NanoTag (immunoassay marker) were spiked into palm methyl esters (PME) and its diesel blends. The blending ratio tested was 5, 10 and 20% (by volume) of fatty acid methyl esters (FAME) in diesel fuel. Both NanoTag and VisioTag markers were found to be stable in PME and blended fuel after 9 months of storage. The concentration of the NanoTag marker (MTK-021) remains consistent as determined by HPLC–UV detector. No colour change or discolouration was observed for the VisioTag marker. Other important fuel quality parameters such as acid value, oxidative stability, and moisture content of the samples were studied. The results showed that NanoTag markers pose no significant measurable effects on blended PME and diesel fuel quality upon storage up to B20.

Keywords Biodiesel · Palm methyl esters · Oxidative stability · Acid value · NanoTag markers

Introduction

Blending of biodiesel or FAME in petroleum diesel has been long regulated in certain countries especially in the European Union, United States and South East Asia region. The main factors that have driven the biodiesel program worldwide are environment protection, energy security and support of the agricultural sector.

There are two technical components that need to be considered in order to implement the biodiesel program successfully, namely competent biodiesel specifications and engine warranty. The most recognised FAME specifications are EN 14214 and ASTM D6751. Recently ASTM has introduced a new test parameter for FAME blending stock to measure minor contaminants by a cold soak filtration test [1]. Many cases of fuel filter blocking have been reported in the United States and Europe since the use of FAME in diesel blends due to formation of insoluble components in the fuel [2–4]. Countries that mandate the use of biodiesel normally create their own biodiesel standards based on these two international specifications with some adaptation to the local condition e.g. for the first time, the Philippines standard of coconut oil biodiesel has specified content of lauric methyl esters at minimum of 45 wt% in the biodiesel [5]. The members of Worldwide Fuel Charter (WWFC) have recommended that FAME should have oxidative stability at minimum of 10 h induction period instead of 6 and 3 h as stipulated in EN 14214 and ASTM D6751, respectively [6]. Harmonisation of the existing FAME specifications on regional basis is the current focus activities which gears towards resolving the biodiesel fuel quality issues.

In terms of engine warranty, the maximum blending ratio of biodiesel in diesel is restricted by the warranty statement from the original equipment manufacturers

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(OEM) such as fuel injectors and automotive producers which at current status given the extended warranty to diesel engine up to B5 (5% of biodiesel (by volume) that meets EN 14214 or ASTM D6751 specifications in 95% fossil diesel (by volume) across the board. However, some injector manufacturers have given their warranty up to B20 (e.g. Ford 6.7L diesel) and the upward trend will potentially increase the usage of biodiesel globally.

Fuel policies are different from country to country. The Malaysian Government provides subsidies for diesel, petrol and selected key commodities given its widespread consumption by the Malaysian public, as well as its importance in facilitating economic growth. Diesel in particular has a high multiplier effect as a key source of energy for key sectors that drive the economy, i.e. transportation, fisheries, industrial sectors, and etc. As a matter of policy, the Malaysian government provides diesel subsidies for fishermen, public transport vehicles, designated land transport vehicles and river boats. The industrial sector is not eligible for diesel subsidies, wherein commercial prices that fluctuate according to the prevailing market price are applicable to them.

Due to the lower price of subsidised diesel compared to industrial diesel, there is a tendency for unauthorised consumption of subsidised diesel by non-eligible users. As world oil prices began to escalate whilst subsidised prices remained low, it gave rise to increased subsidised diesel abuse. Given the critical need to address subsidised diesel abuse, the Ministry of Domestic Trade, Cooperatives and Consumerism (“MDTCC”) introduced fuel marking for subsidised diesel under the NanoTag Program in April 2006 with the following objectives to deter and reduce smuggling and unauthorised use of subsidised diesel; and to reduce the government’s diesel subsidy expenditure whilst ensuring that the eligible sectors/target groups continue to receive subsidies [7].

Fuel marking is practiced in developed and developing nations around the world to reduce leakages of subsidies and/or tax exempted products. For example, fuel markers are used for diesel in the USA, the United Kingdom, the European Union and Thailand.

Under the NanoTag Program [operated by Teras Kimia Sdn Bhd (TKSB)], subsidised diesel is marked with visual and covert markers. Subsidised diesel marking is conducted at supply points across Malaysia (oil terminals). The visual marker, known as VisioTag is to enable users of diesel to distinguish between subsidised and non-subsidised diesel. The covert marker known as NanoTag, functions as another layer security which can only be identified by a proprietary field testing method. The proprietary field testing method enables MDTCC to conduct field enforcement and facilitate on-site identification of those who are illegally in possession of subsidised diesel. These on-site tests are also forensically verified by Kimia Malaysia. MDTCC uses the results of field tests and forensic reports from Kimia Malaysia to institute action against the non-eligible users.

In view of the stringent biodiesel specifications and engine warranty issues, the study has been formulated to determine the stability of NanoTag and VisioTag markers in palm biodiesel (PME) and diesel blends. Other related fuel properties over 9 months of storage were also be discussed.

Materials and Methods

Commercial petroleum diesel and PME used in this study were obtained from PETRONAS and Sime Darby Biodiesel Sdn. Bhd., respectively. The mixture of VisioTag (dye) and NanoTag markers, Immunoassay (IAS) column, extraction solution containing alcohol and phosphate salt were obtained from TKSB. All chemicals and solvents used were of analytical grade. NanoTag marker is a marker composed of a hapten or a hapten covalently bound to another chemical compound such as polymeric and other chemical compound proprietary to TKSB [8]. VisioTag is a synthetic red diazo dye (CAS Number 92257-31-3) with the chemical name 1-[(4-(phenylazo)-phenyl)azo]-2-naphthol, mainly used as a fuel dye in fiscal marking.

Sample Preparation

Samples for PME and diesel blends (B5, B10 and B20) were prepared by adding a specific amount of biodiesel into diesel (by volume). The spike level for B5 was in accordance to the actual concentration of markers used for current diesel marking. The blended sample was homogenised by hand-shaking for 5 min before introduction of markers into the samples.

Multilayer marking technology was applied in this study where all samples were spiked with several markers (in a mixture) to provide multi-layer security and verification capabilities. The mixture contains a coloured dye (VisioTag) and two covert NanoTag markers namely MTK-02.1 and MTK-02.3. The stock solution contained 1.7% of MTK-02.1, 1.1% of MTK-02.3 and 16.5% of VisioTag in a heavy naphtha solvent. The amount of spiked levels for these markers is more than double the actual practice of current addition of markers in the subsidised diesel mixture was spiked into 13 L of B5, B10 and B20 samples, then 3 and 6 mL of markers mixture were spiked into 13 L of B100 samples. All samples were homogenised and stored in the dark at a temperature between 28 °C and 30 °C inside a clear glass bottle. Samples for analyses were withdrawn from a single bottle allowing oxygen replenishment at sampling. Each sample was then subjected to visual observation for colour intensity, qualitative determination of MTK-02.1 and MTK-02.3 markers using IAS column, quantitative HPLC analysis of MTK-02.1 marker and other fuel properties e.g. acid value, moisture content and oxidative stability for a predefined storage interval i.e. daily, weekly, monthly. The abovementioned parameters were observed for a storage period of 8 months, which is based on the consumption rate of diesel used as back-up fuel in power plant in Malaysia.

Qualitative Determination of MTK-02.1 and MTK-02.3 Markers

A small amount of sample (50–100 mL) was withdrawn from the storage bottle and placed inside an extraction bottle. The alcohol phosphate solution (20–30 mL) was added to the bottle, which was capped tightly and shaken vigorously for 1 min. The bottle was allowed to settle until two clear layers had separated completely. While keeping the extraction bottle upside down, the spout of the extraction bottle was opened over the open end of the syringe body and the bottle squeezed firmly until the lower layer was dispensed into the syringe that was attached to an IAS column. The sample was gently pushed through the IAS column containing an antibody gel. The appearance of pink and purple colour bands on the column indicated the presence of MTK-02.1 and MTK-02.3, respectively (please refer to Fig. 2 under "Results and Discussion").

Quantitative Determination of MTK-02.1 Marker by Using HPLC–UV Detector

A basic HPLC–UV system equipped with dual gradient pumps and a reverse phase C18 column (id 4 μm and 10 cm length) was used for the analysis of MTK-02.1 marker. The IAS column (prepared as above) containing marker was eluted with 2 mL methanol and diluted with 6 mL water. The sample (50 μL) was subjected to HPLC analysis at 550 nm wavelength with the mobile phase system consisting of methanol: water at 40:60 ratio from 0 to 9 min; 9 to 13.5 min with methanol: a water ratio of 15:85 and 13.5 to 15 min with methanol: water ratio of 40:60. The flow rate of the mobile phase was 1.0 mL/min. Quantification of the components was performed using a five-point external standard calibration assay, with R^2 values of >0.9900.

Determination of Fuel Properties

All samples were analysed for their fuel properties related to storage. The moisture content of sample was analysed by the Coulometric Karl Fischer titration method according to ISO 12937; the total acid value was determined by automatic Metrohm titrator according to EN 14104:2003 and oxidative stability using Rancimat method according to EN 14112:20003.

Results and Discussion

The initial concentrations of markers (by calculation) in different types of blended samples are tabulated in Table 1 below. A higher level of VisioTag marker (in ppm) was introduced into the sample as compared to covert NanoTag markers (in ppb). The VisioTag marker consists of a red-coloured dye which is sensitive to UV light and its colour intensity will reduce over time if subjected to extensive exposure to sunlight. In commercial terms, the presence of the red-coloured dye in diesel basically indicates that the particular batch of diesel is a government-subsidised diesel fuel. In order to study the effect of VisioTag marker in PME and PME/Diesel blends for a long period of storage, all test samples were purposely stored in the dark at 28–30 °C to

Table 1 Sample blending formula and markers concentration (by calculation)

Sample	Blending formula (vol/vol)	Spiked of markers mixture (mL)	NanoTag		VisioTag (ppm)
			MTK-02.3 (ppb)	MTK-02.1 (ppb)	
B5	5% PME + 95% diesel	0.3	328	522	4.95
B10	10% PME + 90% diesel	0.3	328	522	4.95
B20	20% PME + 80% diesel	0.3	328	522	4.95
B100 (1)	100% PME	3	3,287	5,220	49.5
B100 (2)	100% PME	6	6,574	10,440	99.0
B5 (control)	5% PME + 95% diesel	0	0	0	0
B10 (control)	10% PME + 90% diesel	0	0	0	0
B20 (control)	20% PME + 80% diesel	0	0	0	0
B100 (control 1 and 2)	100% PME	0	0	0	0

mimic the actual storage condition of diesel fuel. At the end of 41 weeks of storage, no colour change or discolouration of the samples were observed for all the samples spiked with the VisioTag marker. This indicates the stability of VisioTag markers in B5, B10, B20 and B100 upon 8 months storage without deterioration of VisioTag. The effect of metals on storage stability was not evaluated in this study.

A quick technique using an IAS column for qualitative detection of Nanotag markers, MTK-02.1 and MTK-02.3 was applied in this study to verify the stability of Nanotag markers in the presence of PME in diesel [8]. The binding of MTK-02.1 and MTK-02.3 with the antibody gel give distinctive pink and purple colour bands on the IAS columns. No changes of band colour intensity tested on the IAS column were observed for all PME/diesel blends and neat B100 samples stored during experimental period.

To further evaluate the stability of NanoTag markers in PME/diesel blends and B100, qualitative analysis of MTK-02.1 using HPLC was carried out. The concentration changes of MTK02.1 were considered not significant with the percentage of coefficient variation between 5 and 9%. Figure 1 shows the concentration of MTK-02.1 marker in B5, B10, B20 and B100 monitoring over a period of 41 weeks. No degradation of the MTK-02.1 marker in blended PME/Diesel samples with spiking level of 600 ppb was detected at the end of week 41. The marker was found to be non-reactive towards neat PME sample at an exaggerated testing concentration up to 10,000 ppb.

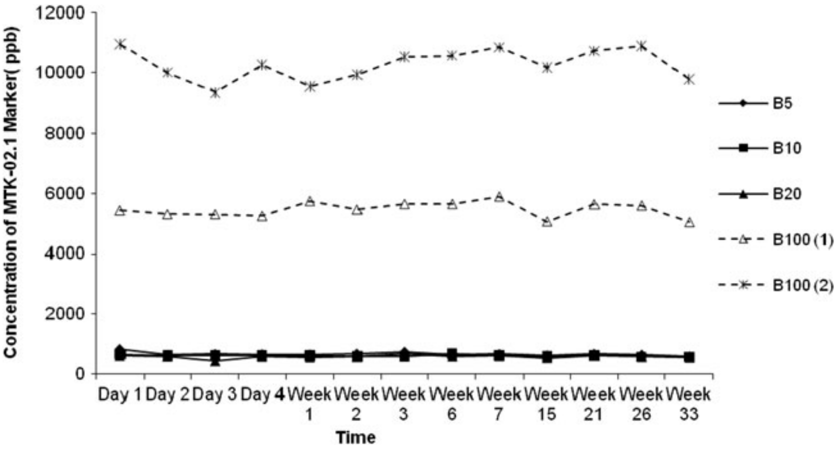
Moisture Content, Acid Value and Oxidative Stability

The effects of NanoTag and VisioTag Markers in PME were studied by spiking of NanoTag Markers in neat PME at different various concentrations (referred to Table 1). Moisture or water content is an important fuel quality parameter that indicates the potential of microbe growth in the fuel which ultimately may cause blockage of fuel filters. A high moisture content is associated with hydrolysis of fuel that converts FAME into free fatty acids. Free water also tends to promote the corrosion of engines and injection systems as it reacts with chromium and zinc [9]. The moisture content in FAME is capped at less than 500 ppm or 0.05 wt% as compared to 0.025 wt% in diesel [10, 11]. Water is introduced into FAME during biodiesel manufacturing process for the purpose of neutralising the excess catalysts (typically methoxide or hydroxide). Water is adequately removed during the drying stage of FAME in the plant. The moisture content in PME with and without spiking of NanoTag and VisioTag markers is shown in Fig. 2. The initial content of moisture in the control PME sample was 0.047 wt%. However, spiking of NanoTag markers reduced the moisture content in PME to 0.036 wt% during day 1. Moisture uptake by PME is expected as PME is hygroscopic in nature. The moisture content doubled in all samples after 4 months of storage. However, the PME samples spiked with NanoTag markers have been able to maintain the moisture content at less than 0.05 wt% for 52 days without nitrogen blanketing.

The moisture contents in PME and diesel blends with and without spiking of NanoTag Markers are shown in Fig. 3. The initial moisture content in diesel was 150 ppm or 0.015 wt%. Blending of PME into diesel has insignificant effects on overall moisture content in blended samples due to a low level of the PME blending ratio. The non-hygroscopic nature of diesel has helped to maintain the moisture content of all blended samples for 2 months storage up to a blending ratio of 20 wt% PME (B20). Moisture content was observed to increase gradually in all samples for the period of study. Nitrogen blanketing of the storage tank for PME and diesel blends is recommended to curb the increase in moisture content if there is a long period of storage of the fuel before use is anticipated.

The European and the United States have specified their individual limit of stability of FAME under the prescribed

Fig. 1 Concentration of MTK-02.1 marker in B5, B10, B20 and B100 samples against storage time



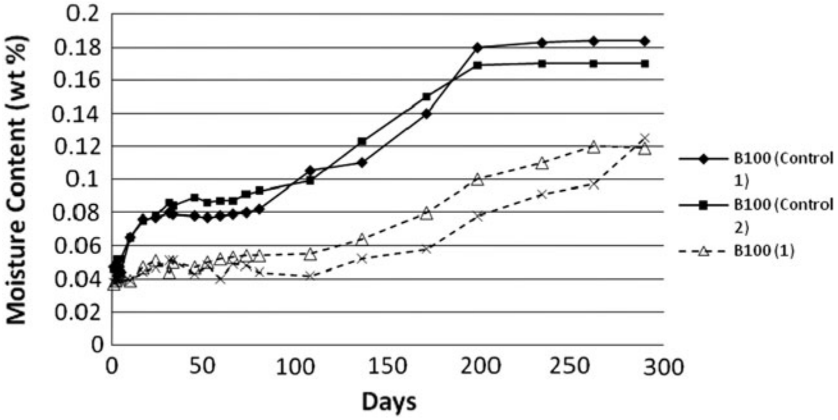


Fig. 2 Moisture content of PME with and without spiking of NanoTag markers

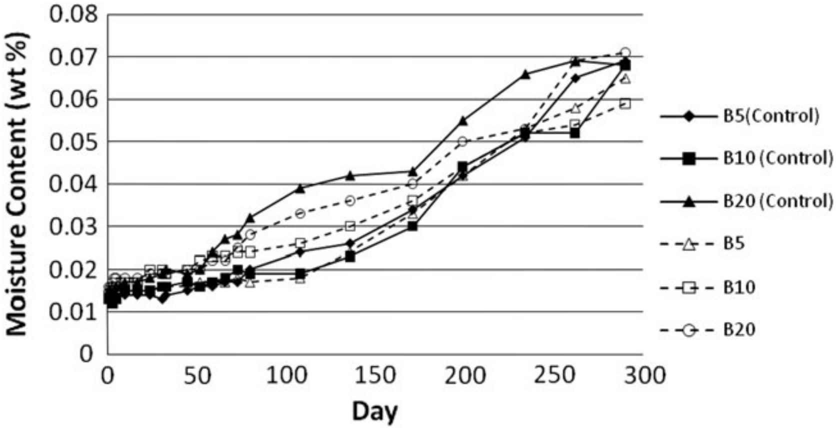


Fig. 3 Moisture content of PME and its diesel blends with and without spiking of Nanotag markers

specifications of EN 14214 and ASTM D6751 for a 6- and 3-h induction period, respectively. The test method allows FAME to be heated at 110 °C under a constant stream of air bubbling through the sample to accelerate the thermal oxidation process by detecting the volatile acids formed. Common raw materials such as rapeseed, soybean and used cooking oils, having a relatively lower oxidative stability compared to PME simply because of the high level of saturation in palm oil and the presence of a large amount of antioxidants e.g. tocopherols and tocotrienols. The different in chemical compositions in FAME and diesel have made FAME more sensitive to oxidative degradation than fossil diesel. An intermediate product called hydroperoxides are produced during the initial oxidation of FAME, which can be very devastating to elastomers or if polymerised, may produce sediments and gums that clog fuel filters and cause deposits in fuel injectors.

Figure 4 shows the induction period of PME with and without spiking of NanoTag markers. As expected, the PME was very stable towards fuel oxidation with an induction period of 27 h. Generally, a reduced induction period of 2–3 h was observed for PME spiked with Nanotag markers as compared to the control. This is probably due to the release of hydrogen peroxide by the antibody reaction with water molecules which acts as strong reducing agent in the fuel. The metals present in the heavy naphtha solvent will possibly act as an oxidising agent which may effect the oxidative stability of fuels and in this case has not been evaluated. However, in general, all PME samples remained oxidatively stable for the first 5 months of storage without nitrogen blanketing followed by a drastic reduction in the induction period ranging from 6 to 12 h until the end of the study. The oxidative stability of PME stays well above the minimum limit of 6 h as specified in EN14214 after 9 months of storage. The induction period of more than 48 h were recorded for B5, B10 and B20 samples throughout the study.

The acid value (AV) measures the total mineral acids and free fatty acids contained in a fuel. It is an important parameter that is related to corrosion and formation of deposits in engine. The AV limit set under EN14214 and ASTM D6751 was set at less than 0.5 mg KOH per gram of FAME. The presence of moisture will promote hydrolytic cleavage of ester bonds with prolonged storage which will gradually increase the AV of FAME. The AV of neat PME and its diesel blended fuels was found to comply within the limit of 0.5 mg KOH/g at the end of 9 months storage (Figs. 5 and 6). Equal magnitudes of the increase in

Fig. 4 Oxidative stability of PME with and without spiking of Nanotag markers

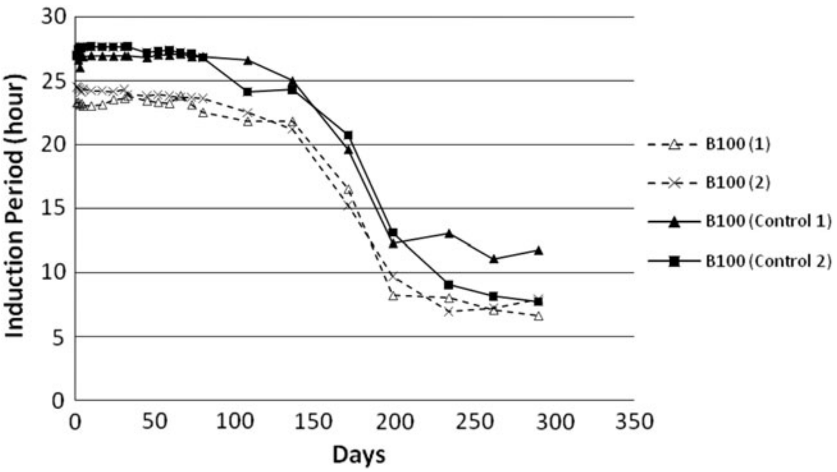


Fig. 5 The acid value of PME with and without spiking of NanoTag markers

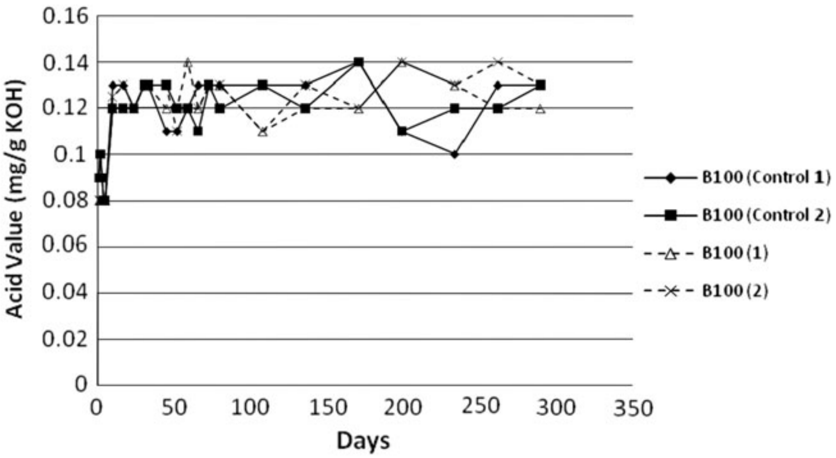
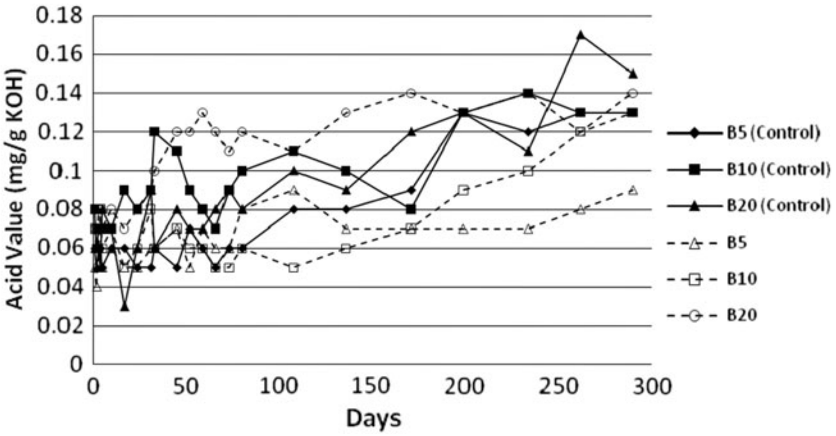


Fig. 6 The acid value of PME and its diesel blends with and without spiking of NanoTag markers



AV were observed for both control samples and samples spiked with NanoTag markers which indicates that there is no significant effect on Nanotag markers in the fuels in terms of AV.

Conclusion

NanoTag and VisioTag markers used in differentiating the type of subsidised and non-subsidised diesel have no measurable effects on PME and its diesel blends up to B20. Those fuels spiked with NanoTag and VisioTag markers exhibits similar fuel characteristics compared to control samples during 9 months of storage. The concentrations of NanoTag and VisioTag markers remain similar as compared to the initial concentration strongly suggesting that NanoTag and VisioTag markers are inert to PME and their diesel blends at the blending ratios tested.

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