

Diesel Fuel Oxidation Study: A Comparative Study, Part II

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ABSTRACT

For decades, ENISO12205 test has been used to evaluate the long term storage stability of diesel fuels. Nowadays, new biocomponents especially FAME has increased the need to create faster and more appropriate test method to measure the long term storage stability. Developments in engine technology have also raised the need to create a new method to evaluate the thermal stability of diesel fuels. These new methods should have correlation to field experience. As an example it has been shown that Rancimat (EN15751) and PetroOXY EN16091 have a correlation when fuel contains more than 2% FAME. Rancimat is not applicable for FAME free fuels, so correlation based PetroOXY limit should be limited to fuels containing more than 2 vol% FAME.

Study on oxidation stability test methods and their correlation to real life were continued and deepened (part 1: SAE 2013-01-2678). ENISO12205 and PetroOXY EN16091 test methods did not have a correlation according to the earlier studies. Also the tested fuels did not show any signs of oxidation or deterioration during the engine tests, where they were exposed to high temperature and pressure. For further studies, a range of different type of fuels was prepared to see how they differentiate in the stability test conditions. PetroOXY method was applied after the ENISO12205 test in order to evaluate if there is any stability reserve left in the fuels after being exposed to test temperature. Additionally, filterability characteristics of the fuels were studied after ENISO12205 test by using filter blocking tendency test (FBT, IP387). Fuel aging in PSA DW10 engine was studied by taking a sample from the fuel return flow before it entered back to the fuel tank. The fuel had been exposed to high pressure and temperature shortly without passing through a fuel filter after the exposure.

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INTRODUCTION

Fuel properties have been changing during the recent decades. For example, in Europe sulphur level in diesel fuel has reduced from 1000 to 10 mg/kg. It has been shown earlier that severe hydrotreating and catalytic cracking did not worsen the storage stability. [1]. No outburst of storage stability issues in the field have risen since the introduction of low sulphur fuels.

Tightening emission and fuel consumption regulations have led to developments in the engine and fuel injection system designs, which can be seen as increased injection pressures and fuel temperatures.

In EN590 specification, ENISO12205 test is used for evaluating the long term storage stability. When biodiesel (FAME=fatty acid methyl ester) was introduced to the markets, another stability test was needed to investigate the long term storage stability. Rancimat EN14112 was introduced to study the stability with fuels containing more than 2 vol% FAME. Rancimat EN14112 method has been further developed and

the method is nowadays EN15751. Today, both tests (ENISO12205 and EN15751) are required in EN590 if the fuel contains more than 2 vol% FAME. Karavalakis G. et al [2] found that increasing the FAME content in diesel fuel oxidation stability measured with Rancimat test will be impaired. Also, the fossil base fuel had an effect on Rancimat result.

ENISO12205 test does not in fact measure the oxidation stability reserve, but rather measures the amount of insoluble oxidized material formed under the test conditions. The Rancimat evaluates the oxidation stability reserve better, but it is not applicable for fuels without FAME. [3]

Both of the above mentioned methods are very time consuming; ENISO12205 takes for 16h and minimum duration for EN15751 is 20h (B2-B7 fuels). There is a need to develop a new method, which should be rapid and valid for all kind of fuels. PetroOXY EN16091 method has been proposed for this purpose. Detailed descriptions of various methods can be found in part 1: SAE 2013-01-2678. [4]. From the same paper can be found that for example cetane improver 2-EHN decomposes at the temperature 110°C and due to this

worsens the PetroOXY result. The same phenomenon can also be seen if ENISO12205 is performed at 115°C temperature. Using 2-EHN in production of winter grade diesel is necessary for fulfilling the cetane number limit in EN590.

Earlier studies have shown a correlation between PetroOXY and Rancimat [4], [5]. These methods have similarities in the test procedures.

FBT method (IP387) was used to test filter blocking tendency. This test is able to indicate the presence of insoluble oxidized material with particulate size higher than 1.6 microns. The most critical issue in the vehicle is if poor fuel stability causes formation of solid material in the fuel tank. This material will most probably be collected by the fuel filter and it will cause blockage.

Petiteaux et al. [6] have found out that the pore size of the fuel filter material has a big role to the results. They have also tested a fuel aged by ENISO12205 method with two different filter pore sizes. Pressure drop from filter was observed when using 5µm filter but not with 8 µm filter. Impurities picked by the filter have been studied also earlier and it has been found out that some of them are fuel originated, but there are also other impurities like water, inorganic material etc. collecting to the filter [7]. Barker [8] et.al. have isolated black material from the blocked fuel filter. Analyses showed that this material has some similarity to coke formed at refining industry, even though the H/C ratio from coke differs. Some metals were found, mainly calcium and iron, but the conclusion was that deposits found from filters are mainly carbon.

Test Fuels

Four different fuels (Table 1.) were tested in this study and detailed analyses can be found from appendix 1. All fuels meet EN590:2013 specification, except HVO which fulfills TS15940:2012 specification. All tested fuels were without any additives and also without FAME. For the fuels used in the engine tests lubricity additive was added.

Table 1. Test fuels

Fuel code	Applicable standard	Fuel explanation
EN590 B0 (S)	EN590 (2013)	Summer grade fossil diesel batch 1
EN590 B0 (S1)	EN590 (2013)	Summer grade fossil diesel batch 2
EN590 B0 (W)	EN590 (2013)	Winter grade fossil diesel
HVO	TS15940 (2012)	100% renewable diesel NEXBTL

Following test were performed for these fuels seen in the table 2.

Table 2. Fuel tests

	EN590 B0 (S)	EN590 B0 (S1)	EN590 B0 (W)	HVO
PetroOXY EN16091	x	x	x	x
PetroOXY EN16091 (two consecutively)	x	x	x	x
ENISO12205	x	x	x	x
FBT after ENISO12205 (without filtering)		x	x	X
PetroOXY EN16091 after ENISO12205 (filtered)	x	x	x	x
ENISO12205 at 115°C	x		x	x
ISO6619 after ENISO12205 at 115°C(TAN) (filtered)	x		x	x
PetroOXY EN16091 after ENISO12205 at 115°C (filtered)				
PetroOXY EN16091 after engine test	x		x	x

Experimental

The aim of this test series was to obtain more understanding on what is happening to the fuels during stability testing and in an engine. Earlier it was found that PetroOXY results were improved after an engine test. It was proposed that oxidized compounds were possibly collected by the fuel filter and this caused the improved oxidation stability results. This phenomenon was studied in the PSA DW10 engine.

After ENISO12205 at 95 °C test FBT and PetroOXY were used to evaluate if there is filter blocking tendency and secondly any stability reserve left after exposing the fuels to test conditions. After the corresponding test at 115 °C, acid number and PetroOXY tests were made. Additionally, two PetroOXY tests were performed consecutively for each fuel to evaluate if any oxidation reserve is left.

ENGINE TESTS (PSA DW10)

In the paper "oxidation stability: a comparative study part1" it was shown that the oxidation stability properties of different fuels were improved, when the fuel had been exposed to high temperature and pressure in the engine's injection system. In the paper it was proposed that, possibly the compounds very reactive to oxygen are already oxidized during the engine test and are collected by the fuel filter. To study this phenomenon further, the following test was performed with the same engine as in the previous study (table 3).

Three fuels were used for the engine tests: EN590 B0 (S), EN590 B0 (W) and HVO. The aim was to feed the fuel into the fuel injection system and then capture the fuel from the return flow line before it passes through a fuel filter. By this, it was possible to study the changes in the fuel stability immediately after exposing it to high temperature and pressure. The test was performed on idle and on 2000 r/min full load.