SLOVENSKI STANDARD
kSIST-TP FprCEN/TR 17225:2018

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Goriva in biogoriva - Ocenjevanje metod določevanja oksidacijske stabilnosti za destilatna goriva in njihove mešanice z metilestri maščobnih kislin (FAME)

Fuels and biofuels - Assessment on oxidation stability determination methods for distillate fuels and blends thereof with fatty acid methyl esters (FAME)

Mitteldestillatkraft- und -brennstoffe und Biokraftstoffe - Bewertung der Verfahren zur Oxidationsstabilitätsbestimmung für Mittteldestillatkraft- und -brennstoffe und deren Mischungen mit Fettsäure-Methylestern (FAME)

Carburants et biocarburant - Assessment des méthodes determinations de la stabilité à l'oxydation pour distillats et mélanges avec esters méthyliques d'acides gras (EMAG)

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Fuels and biofuels - Assessment on oxidation stability determination methods for distillate fuels and blends thereof with fatty acid methyl esters (FAME)

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This draft Technical Report is submitted to CEN members for Vote. It has been drawn up by the Technical Committee CEN/TC 19.

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EUROPEAN COMMITTEE FOR STANDARDIZATION
COMITÉ EUROPÉEN DE NORMALISATION
EUROPÄISCHES KOMITEE FÜR NORMUNG

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European foreword

This document (FprCEN/TR 17225:2018) has been prepared by Technical Committee CEN/TC 19 "Gaseous and liquid fuels, lubricants and related products of petroleum, synthetic and biological origin", the secretariat of which is held by NEN.

This document is currently submitted to the Vote on TR.

During revisions of standards EN 14112, EN 15751, EN 16568 (Rancimat, [17]) and EN 16091 (PetroOxy), CEN/TC 19/JWG 1 "Vegetable fats and oils and their by-products for use in automotive fuels (Joint working group with CEN/TC 307)" felt the need to create a document that provides extended background information on oxidation stability test methods complementing the abstracts given in Annex A of EN 14112, EN 15751 and EN 16568 as well as in Annex C of EN 16091.

This report also gives an overview about the work done by CEN/TC 19/JWG 1 on the correlation between the Induction Period of the Rancimat and PetroOxy test methods.

Introduction

All fuels, whether of fossil source or biogenic origin, constantly degrade. Although the bulk composition remains largely unchanged, the presence of oxygen, higher temperature and catalytically active metals accelerate oxidation of less stable compounds present, thereby generating ageing acids and oligomerization and polymerization products. The complex and varying composition of fossil diesel fuels and the interactions of FAME and its inherent side-products with base diesel fuel components make it difficult to understand fuel ageing mechanisms at a molecular level. The determination of oxidation stability of fuels is therefore addressed by phenomenological techniques. Most test methods to characterize fuel oxidation stability are based on the determination of specific parameters, e.g. polymer formation, acidity increase, or oxygen consumption.

It has been established that the phenomenon of fuel ageing consists of two consecutive phases, starting with the depletion of the ageing reserve with few chemical changes to the bulk material, followed by the fuel ageing process itself during which the fuel is badly decomposed forming ageing polymers and acids (Figure 1, Table 1). Fuel oxidation takes place via a free radical chain process, initiated by the abstraction of a hydrogen atom from the fuel molecule and the addition of molecular oxygen to form hydroperoxides.

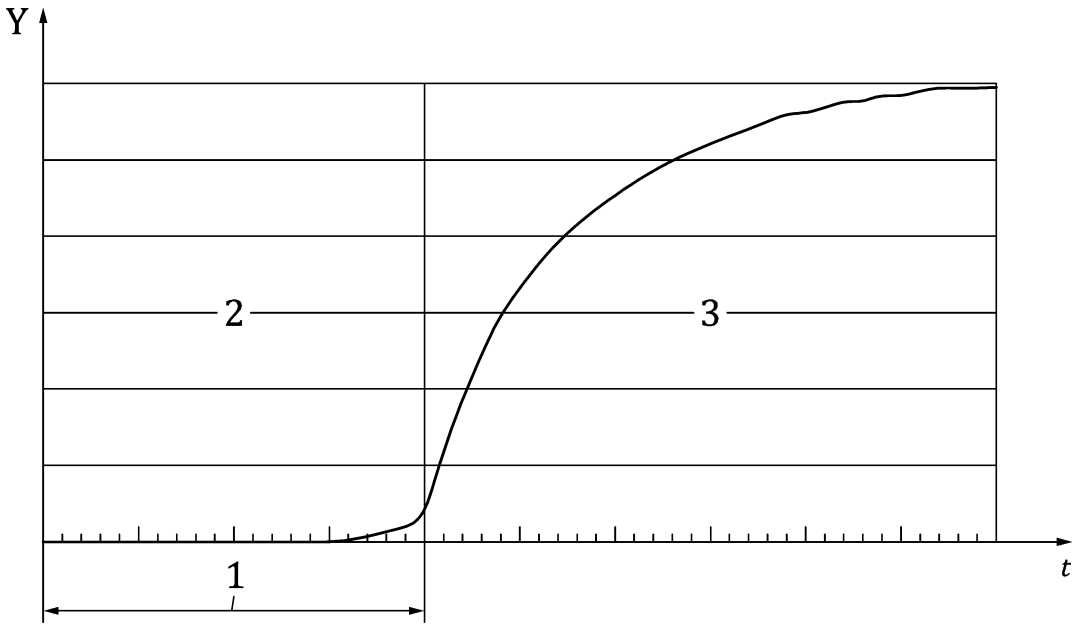
Following chemical reactions proceed into two directions: a) Fragmentation of the molecule generates aldehydes, ketones and short-chain carboxylic acids; b) interlinking of the molecules yielding oxygen bridged dimers and polymers.

Diesel fuel oxidation is influenced by the chemical constituents of diesel fuel (e.g. specific sulphur- and nitrogen-containing compounds) and contaminants (e.g. metal impurities). There are many different chemical reactions, which can occur simultaneously and sequentially, fuel molecules are either fragmented or increased in their size, e.g. by di-, oligo- and polymerization. These reactions rapidly increase after a period when little or no chemical oxidation took place. This time interval before fuel oxidation gets started significantly is called Induction Period.

Stress imposed on the fuel by heat in the presence of oxygen does not necessarily result in immediate fragmentation or dimer/polymer formation. The reserve capacity of the fuel to resist oxidation is called ageing reserve, which is related to the Induction Period [1, 2].

Test methods in Figure 1 marked with an asterisk are mentioned in this report for additional information, but are not the focus of this work.

Rancimat EN 14112 EN 15751 EN 16568	EN ISO 12205 [18], ASTM D2274 [19] IP 306 mod.* [20]
PetroOxy EN 16091 ASTM D7545 [21]	Δ-acid no. method, JIS draft* [8], CEN/TR 16885 [10], ASTM D6468* [22]



Key

1 period for the depletion of the ageing reserve (Induction Period)
2 ageing reserve
3 fuel ageing process, strong formation of acids and polymers
t time, h
Y property (such as acid number, conductivity, acidity, polymer formation, etc.)

Figure 1 — Two consecutive phases of fuel ageing and test methods relevant for each phase

Table 1 — Overview about parameters and conditions of oxidation stability test methods

	Rancimat **EN 14112** **EN 15751** **EN 16568**	**PetroOxy** **EN 16091** **ASTM D 7545**	**EN ISO 12205** **ASTM D 2274**	**IP 306**	**IP 306 mod.**	**ASTM D 4625**	**Δ-Acid method JIS draft**	**ASTM D 6468**
Title	Determination of oxidation stability by accelerated or rapidly accelerated oxidation method	Determination of oxidation stability by rapid small scale oxidation test (RSSOT)	Determination of the oxidation stability of middle distillate fuels	Determination of oxidation stability of straight mineral oil	Modifications proposed in [3] to adapt IP 306 to diesel fuels, FAME blends and neat FAME	Standard test method for sistillate fuel storage stability at 43 °C	Determination of oxidation stability of FAME-blended diesel fuels	Standard test method for high temperature stability of distillate fuels
Scope/Determination	Oxidation stability by means of measuring the Induction Period	Stability under accelerated oxidation conditions by measuring the Induction Period	Inherent stability of middle distillate petroleum fuels under accelerated oxidation conditions	Tendency of straight (i.e. plain) mineral oil to oxidize, expressed as total oxidation products (TOP)	Inherent stability under accelerated oxidation conditions	Inherent storage stability of distillate fuels under mild aging conditions with limited air exposure	Acid value increase after accelerated oxidation conditions	Relative stability of middle distillate fuels under high temperature aging conditions with limited air exposure (venting)
FAME content[a]	B100 (EN 14112) B2 to B100 (EN 15751) B2 to B50 (EN 16568)	B0 to B100	B0 (EN ISO 12205 ASTM D 2274) B0 to B7	B0	B0 to B100 [3]	B0	B0 to B5	B0

	Rancimat **EN 14112** **EN 15751** **EN 16568**	**PetroOxy** **EN 16091** **ASTM D 7545**	**EN ISO 12205** **ASTM D 2274**	**IP 306**	**IP 306 mod.**	**ASTM D 4625**	**Δ-Acid method JIS draft**	**ASTM D 6468**
Oxidation stability parameter	Ageing reserve	Ageing reserve + partial fuel ageing	Fuel ageing behavior by fuel oxidation products	Fuel ageing behavior by fuel oxidation products	Fuel ageing behavior by fuel oxidation products	Fuel ageing behavior by fuel oxidation products	Fuel ageing behavior by fuel oxidation products	Fuel ageing behavior by fuel oxidation products
Parameter	Induction Period by conductivity increase in water cell	Induction Period by oxygen pressure drop	Amount of total insoluble sludge	Amount of total insoluble sludge + volatile acidity + soluble acidity	Amount of total insoluble sludge + sludge from soluble polymers + volatile acidity + soluble acidity	Amount of total insoluble sludge	Acid increase by soluble acidity	light reflectance by filterable insoluble sludge
Sample amount	3,0 g (EN 14112) 7,5 g (EN 15751) 7,5 g (EN 16568)	5 ml	350 ml	25 g	25 g	400 ml	350 ml	50 ml
Temperature	110 °C (EN 14112) 110 °C (EN 15751) 120 °C (EN 16568)	140 °C	95 °C	120 °C	120 °C	43 °C	115 °C	150 °C
Time	—	—	16 h	48 h	16 h	up to 24 weeks	16 h	1.5 or 3 h

	Rancimat EN 14112 EN 15751 EN 16568	PetroOxy EN 16091 ASTM D 7545	EN ISO 12205 ASTM D 2274	IP 306	IP 306 mod.	ASTM D 4625	Δ-Acid method JIS draft	ASTM D 6468
Oxidant	10 l/h Air	700 kPa Oxygen	3 l/h Oxygen	1 l/h Oxygen	1 l/h Air	ambient air pressure, no blow-through	3 l/h Oxygen	ambient air
Catalyst	no	no	no	no	no	no	no	no
Dilution of aged fuel	—	—	no	no	10 to 20-fold excess of heptane for Bx	no	—	—
Precision (reproducibility)[b]	0,26 X + 0,23 (EN 14112) 0,1903 8 X + 0,3726 9 (EN 15751) 0,139 5 X + 0,288 8 (EN 16568)	0,086 3 X + 1,377 2 (EN 16091)	10,6 (0,1 X)^{0,25} EN ISO 12205	precision for insoluble sludge not reported	no full validation performed	2,20$\sqrt{X}$	no precision available	-0,428 1 X + 44,08 (1,5 h) -0,303 4 X + 34,11 (3,0 h)

Total insoluble sludge is defined as solid sediment (sum of filterable sludge and sludge adherent to the inner walls of the glass tube).

Sludge from soluble polymers is defined as the amount of polymers dissolved in the aged fuel but precipitated as sludge after dilution of the aged fuel with heptane.

Soluble acidity is defined as the acidity in the aged fuel sample.

Volatile acidity is defined as the acidity in the collecting vessel with the water phase.

[a] FAME content which is validated with precision statement. Method can be applicable for blends containing higher FAME contents.

[b] The precision of the test methods is given as complimentary information. Parameters and conditions of oxidation stability test methods are different limiting the significance of a direct comparison of precision statements. x is the mean of two results.

1 Scope

This document provides an overview of existing oxidation stability methods, with an emphasis on differences between the Rancimat (EN 14112/EN 15751) and PetroOxy (EN 16091) tests.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

EN 14112, *Fat and oil derivatives - Fatty Acid Methyl Esters (FAME) - Determination of oxidation stability (accelerated oxidation test)*

EN 15751, *Automotive fuels - Fatty acid methyl ester (FAME) fuel and blends with diesel fuel - Determination of oxidation stability by accelerated oxidation method*

EN 16091, *Liquid petroleum products - Middle distillates and fatty acid methyl ester (FAME) fuels and blends - Determination of oxidation stability by rapid small scale oxidation method*

3 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

- IEC Electropedia: available at http://www.electropedia.org/
- ISO Online browsing platform: available at http://www.iso.org/obp

3.1
ageing reserve
reserve capacity of the fuel to resist oxidation

3.2
break point
in the Rancimat test, the break point reflects the moment of beginning oxidation when the formation of volatile acids increases rapidly; and in the PetroOxy test, the break point is the pressure which is 10 % below the maximum pressure observed in the test apparatus

Note 1 to entry: The break point is differently defined depending on the testing procedure.

3.3
fuel ageing
oxidation of the fuel, forming ageing acids and polymers

3.4
Induction Period
IP
time elapsed until significant oxidation of fuel begins

3.5
inter-laboratory study
ILS
ring tests in which independent laboratories gather precision data for test methods using the same set of subsamples

3.6
sludge
insoluble, solid sediment formed during fuel oxidation

3.7
soluble acidity
amount of acidic hydrogen representing acids in the aged fuel sample

3.8
total acid number
quantity of potassium hydroxide used as a base to neutralize acids in fuels

3.9
total acidity
sum of soluble and volatile acidity

3.10
total insoluble sludge
sum of filterable sludge and sludge adherent to the inner walls of the test tube

3.11
volatile acidity
amount of acidic hydrogen representing acids in the collecting vessel with the water phase

4 Test methods quantifying fuel ageing products

4.1 History

Historically, the focus of laboratory tests for oxidation stability was on the second phase: quantifying the products post ageing. In these tests, the fuel is treated with heat and air or pure oxygen for several hours under well defined oxidation conditions. The polymeric and acidic fuel ageing products formed are quantified. Ageing polymers, also commonly referred to as sludge, can be analysed following the gravimetric procedures in EN ISO 12205 or ASTM D2274.

4.2 Generic oxidation stability test

In this type of test the amount of insolubles or sludge after ageing is determined. The test was developed to estimate the storage stability of middle distillate fuels. Test conditions in EN ISO 12205 and ASTM D2274 are identical. The fuel is treated at 95 °C for 16 h while oxygen is bubbled through the sample. Since specific field storage conditions differ from test conditions and also vary to some extent, an accurate prediction of the amount of sludge that will form is not possible. Most diesel fuels and diesel blends with FAME show only little sludge formation in this test because they are generally sufficiently stable at 95 °C that their ageing reserve will not be completely depleted within 16 h [4]. Only extremely unstable, e.g. thermally pre-stressed fuels, give significant sludge formation in the EN ISO 12205 test. The lack of fuel differentiation by this method led to the development of tests under more severe oxidation conditions, e.g. based on the IP 306 test that is performed at 120 °C. An additional reason to not consider EN ISO 12205/ASTM D2274 as oxidation stability parameter of diesel/FAME blends was the observation that only a part of the polymerized ageing products formed precipitates. A significant amount of the polymerized ageing products remains in solution depending on the aromatic content of diesel fuel, in particular if the aromatic content exceeds thirty volume percent [3].