

## DISCUSSION OVER CORRECTNESS OF METHODS USED FOR TEST OF RESISTANCE FUELS TO AGEING PROCESSES

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### Abstract

Research of usefulness of fuels for long-term storage is an important research of products of special use (meant for stock keeping as national or military reserves). Important fact is that fuels after storage should be used according to their initial use so their physico-chemical and exploratory properties should remain the same during the whole storage cycle. Basic condition, enabling to foresee that fuel will keep its quality at sufficient level in certain timeframe should be positive results of ageing tests. Below the doubts are presented whether methodology of evaluation is correct because of important differences in mechanisms of accelerated laboratory tests as well as real storage in typical conditions of storage tanks with large capacity. Differences in courses of chemical reactions and conditions of their initiation and course were pointed out. Scheme of equipment for marking content of existing gums, scheme of equipment for testing induction period, scheme of filtering and oxidizing equipment to test resistance of fuel to oxidation, effectiveness of collisions of molecules of reactants, scheme of chemical ageing process of fuels stored in different temperature, function for different conditions ageing process of FAME, influence of value of potential molecules energy on initializing of chemical reactions are presented in the paper.

**Keywords:** fuels, storage, fuels aging

### 1. Laboratory fast test methods of fuels ageing

Susceptibility of liquid fuels for ageing is, and in fact, it should be, a measure of usefulness of fuel for long-term storage. Fuels, which chemical composition and properties has changed because of long-term storage, can have different characteristics of combustion, connected among others, with quality of fuel-air mixture, course of combustion process and creation of deposits on hot parts of the engines [1, 2]. Parameter responsible for this phenomenon exists in each fuel specification. It can have different name and different marking techniques, but the aim is one – to establish potential ability of long term storage of hydrocarbon fuel. Each method is addressed for respective type of fuel. In case of jet fuels, content of existent gum is being marked and sometimes – non standardized property – content of potential gums. In gasolines, dedicated for engines with spark ignition, it is so-called induction period and content of existing gums (in jet fuels – content of potential gums). In fuels used in diesel engines – resistance to oxidization is being marked. Although methodology can differ and there are different evaluation criteria's, in each case, the main factor fastening process of feigned ageing is temperature. Raising temperature causes very quick degradation of fuel.

In case of jet fuels marking of content of existent gum (as products of ageing processes, which happened earlier, for instance: oxidation, polymerisation to hydrocarbons macromolecular, creation of heterorganic compounds and so on), happens when temperature is significantly higher. A sample of fuel in heating cell at 240°C undergoes jet evaporation by steam gas with the same temperature (in case of gasolines – temperature 150°C and air jet evaporation) (Fig. 1). As a result lighter fractions are evaporated. What remains are so called gum compounds, which because of their macromolecular structure have not evaporated.

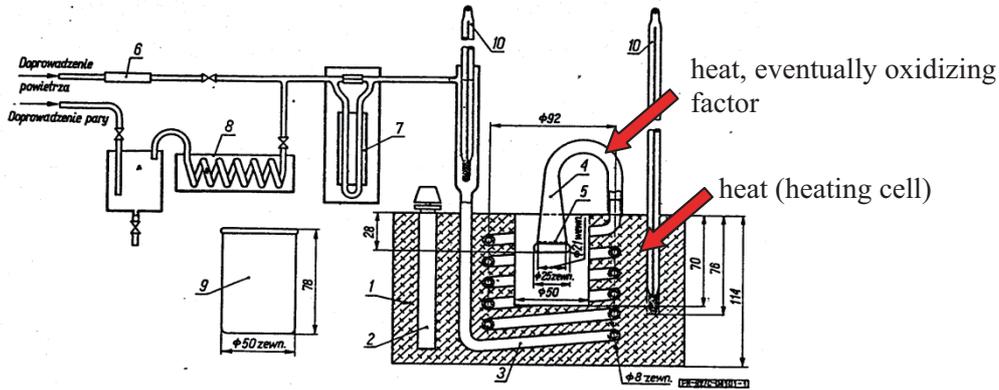


Fig. 1. Scheme of equipment for marking content of existing gums

Sometimes fuels have additional requirement – marking content of potential gums. Research is similar to the previous one, but first the fuel sample is influenced by high temperature, pressure and time. In atmosphere rich in oxygen unsaturated bonds existing in hydrocarbons molecules oxidizes or undergo polymerization to much bigger molecules (potential gums change into existing gums). Such fuel undergoes evaporation in conditions as for marking existing gums.

In gasolines apart from test described above induction period test is done which characterize resistance of hydrocarbons to oxidation. Fuel in pressure vessel is heated (temperature of test 99°C) under initial pressure 7.2 bar (Fig. 2). Time period after which oxygen pressure of changes significantly, which indicates to usage of free oxygen for chemical reactions is called induction period. Unfortunately it's value has little meaning for interpretation of real resistance of fuel to changes during long term storage.

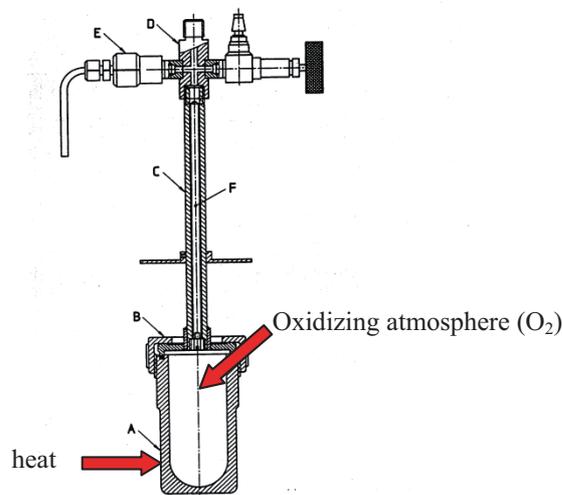


Fig. 2. Scheme of equipment for testing induction period

A bit different is test on resistance to oxidizing of fuels for diesel engines [5], but the idea is similar. Test is based on oxygenation of fuel present in water bath at temperature of 95°C (Fig. 3) for 16 hours. As a result of activity of oxygen, temperature and time, some of hydrocarbons present in fuel oxidize which is indicated by raise of macromolecular deposit. Amount of this deposit separated on the filter is a measure of fuel resistance to oxidizing.

Analysing conditions of conducting accelerated methods of fuel ageing processes – in order to determine their susceptibility to ageing processes, it must be concluded, the main factor fastening ageing process is temperature and sometimes – oxidizing factor, introduced to the process in excess.

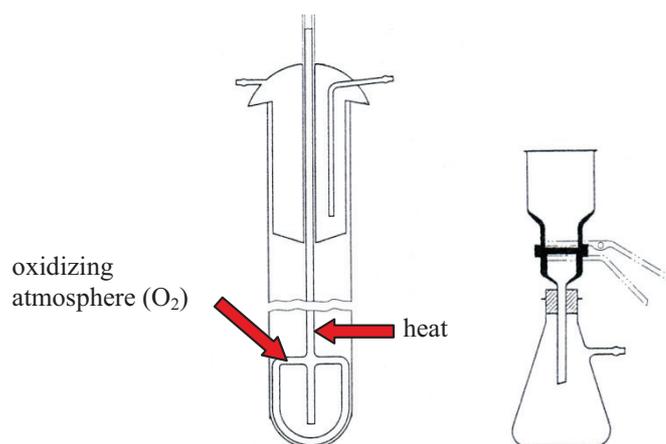


Fig. 3. Scheme of filtering and oxidizing equipment to test resistance of fuel to oxidation

## 2. Activation energy

The experience shows that fulfilling requirements described above does not guarantee usefulness of fuel for long term storage. There is no guarantee that fuel is and will be chemically stable. Therefore there is a doubt whether chosen and used methods are correct and even whether the approach is the right one. The doubt is connected with chemical kinetics theory. According to this theory the speed of reaction depends on amount of collisions of molecules of reactants per unit time. Only in case when reactive molecules will collide and electrons of atoms of one molecule enter in activity area of electric field of the other molecule, basic chemical act may happen. Not every collision leads to chemical reaction.

It depends on energy status of molecules, how long the collisions last and concentration of reactive substances (the higher concentration of reagents, the bigger amount of effective collisions). To make it happen, the energetic barrier equal to activation energy of given reaction must be overcome. In case of chemical mixtures, such as hydrocarbon fuel, many reactions can happen simultaneously. The condition is exceeding of activation energy. Therefore there is possibility that the same mixture present in different conditions (for instance thermal) will undergo different chemical reactions. In higher temperature the reactions will happen, which are not possible to initialize in lower temperature.

Active reactive complex undergoes disintegration and as a result reaction products are created or, in case of not sufficient energy in reaction timeframe it results in recombination and return to reactants (Fig. 4).

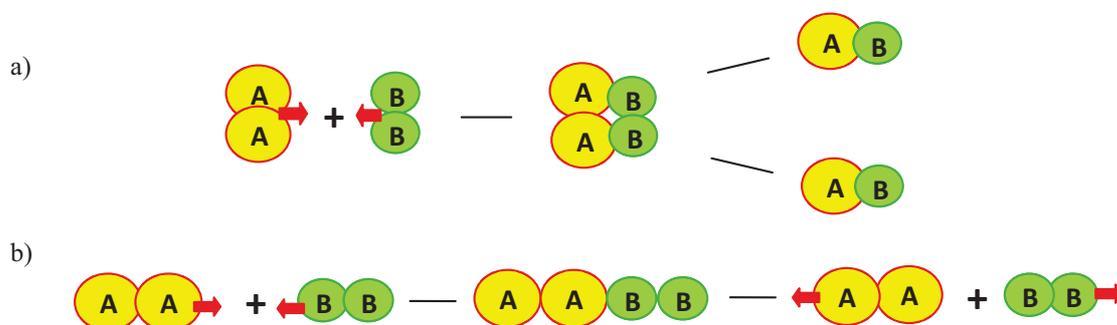


Fig. 4. Effectiveness of collisions of molecules of reactants: a) collisions leading to persistent reaction, b) non effective collisions – recombination

According to Arrhenius [ $k = A \exp(-Ea/RT)$ ], only those substrate molecules react with each other which have sufficient activation energy. Raising the temperature increases speed of reaction

because it causes rise of reagents molecules energy.

Different chemical reactions undergo with different speed. The processes, which happen among ions, are the quickest, among slow reactions, we will find many organic processes like hydrolysis, esterification, nitration. Character and structure of substances, which react with each other, influence on speed of reaction. In addition, the same substances can react with each other with different speed, depending on conditions. In case of competitive reactions, change of speed of reaction can lead to change of direction of reaction flow. It can be also influenced by more specific factors such as electromagnetic radiation (microwave, UV or visible light), ionizing radiation and ultrasonic.

### 3. Ageing precursors

Speed of reaction is directly proportionate to concentration of reactants (one or both), so as they are fewer and fewer – the speed slows down. In practice however, if we deal with fuel a mixture of hydrocarbons of very varied chemical content, during long-term storage, processes happen in a bit different way. At the beginning, the fuel is stable. It does not show changes of properties, which could indicate to change of composition as a result of any reactions. It proves that at the first stage there are no active reagents, which could react in certain conditions. With the time passing, in spite of no changes in storage conditions, some of fuel's parameters change, which is a result of chemical changes. It is observed that intensity of those changes usually grows as the time passes. Cause of this phenomenon is explained by weakening chemical bonds of potential reagents and development of ageing precursors. When their concentration is high enough, according to theory chemical kinetics (Guldberg and Waage theory), chemical reactions accelerate. Obviously only those, whose activation energy is low enough. At the same time when reaction starts, ageing doesn't slow down, so concentration of precursors doesn't decrease, which may indicate that speed of chemical reactions in which those ageing precursors are one of reagents, is slower than speed of their creation. In case of simulated ageing, high temperature causes immediate creation of many precursors. They react violently, causing significant changes of product properties, but as reagents are used up, intensity of reaction decreases. In case of real storage, concentration of precursors changes much slower and ageing process is gradual.

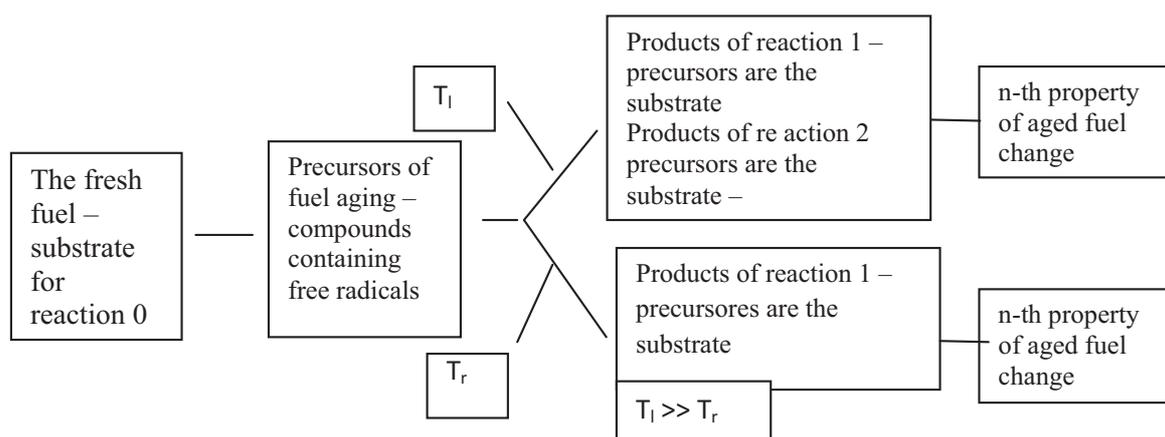


Fig. 5. Scheme of chemical ageing process of fuels stored in different temperature

The first order reaction rate is expressed as follows:

- $dc/dt = k c$ ; after integration  $\ln c_t - \ln c_0 = k t$  and consequently  $t = (\ln c_t - \ln c_0)/k$ ; because,
- $k = A \exp(-E_a/RT)$  time needed to reach concentration  $c_t$  of reaction products is,
- $t = (\ln c_t - \ln c_0)/A \exp(-E_a/RT)$ .

It is assume, that:

- quality of fuel is determined by properties listed in proper specification,
- the limit value of n-th property of fuel is reached when concentration of the product of reaction

1 reaches value  $c_{t1}$ ; activation energy for reaction 1 is  $E_{a1}$ .

Time  $t$  needed to reach concentration  $c_t$  exponentially depends on temperature of reaction mixture  $T$  [5]. When reaction 1 undergoes at high temperature  $T_1$  (fast laboratory test) the concentration of reaction 1 product  $c_t$  is reached after short time  $t_1$ . The same value of reaction 1 products concentration  $c_t$  in case the reaction undergoes at real conditions of fuels storage – mean temperature  $T_r$  (relatively low temperature), is reached after long time  $t_r$ .

$$t_1 A \exp(-E_a/RT_1) = (\ln c_t - \ln c_0); t_r A \exp(-E_a/RT_r) = (\ln c_t - \ln c_0),$$

$$t_r = t_1 A \exp(-E_a/RT_1) / A \exp(-E_a/RT_r).$$

The research carried on by Air Force Institute of Technology leader to conclusion that aging process consists of two reactions: reaction 0 – products of this reaction is substrates of reaction 1 and reaction 1 responsible for fuels aging. In this case, the above shown equations are as follows:

– for laboratory test:

$$t_1 A \exp(-E_{a1}/RT_1) = \{\ln c_t - [t_0 A \exp(-E_{a0}/RT_1)] + \ln c_{00}\},$$

where  $c_{00}$  is the initial concentration of the reaction 0 substrates,

– for real conditions of fuel storage:

$$t_r A \exp(-E_{a1}/RT_r) = \{\ln c_t - [t_0 A \exp(-E_{a0}/RT_r)] + \ln c_{00}\}.$$

Assuming, that during fast laboratory test and during real storage of the fuel both reaction 0 and reaction 1 are responsible for fuels aging, the relationship between  $t_r$  and  $t_1$  can be expressed by following dependence:

$$t_r = (\{ t_1 A \exp(-E_{a1}/RT_1) + [t_0 A \exp(-E_{a0}/RT_1)] \} - [t_0 A \exp(-E_{a0}/RT_r)]) / A \exp(-E_{a1}/RT_r).$$

In case, when  $T_1$  is too high next reaction 2 can be initiated with higher activation energy  $E_{a2}$  for which substrates are also precursors – products of reaction 0. With high probability we can say, that products of reaction 2 in different degree than products of reaction 1 will influence  $n$ -th fuel property, what is more they can influence on change of other properties. In this situation forecasting acceptable time of fuel storage based on laboratory fast test is impossible and using standardized laboratory tests will lead to wrong conclusions.

As a result of research conducted in AFIT, it was stated that mechanism of creating fuel ageing precursors is in much less depended on temperature, so fuel susceptibility to creating precursors is a good measure of susceptibility to ageing in real storage conditions.

This thesis was verified experimentally conducting process of ageing in temperature 20, 50 and 110°C. Results of kinetic tests of ageing process of tested fuel components were presented on Fig. 6.

The scheme presented above shows that in tested range of temperatures, mechanism of creating ageing precursors happens according to the same mechanism (the same value of EA) when further processes with usage of precursors as substrates happen according to different mechanisms.

#### 4. Summary

Acceleration methods described above are used for evaluation of potential usefulness of fuel for long term storage. Assumption of those methods is conducting ageing simulation in conditions enforcing much quicker chemical reactions identified with ageing than in real conditions. For this purpose, the tests are conducted in much higher temperature and in oxidizing atmosphere. In typical atmosphere of big capacity storage tank, fuel temperature depending of season hesitates between 0 and 20°C. Dynamics of changes depends on tank construction, its capacity and volume of storage fuel.

Laboratory methods, which are to simulate ageing of storage products, and more precisely, to state what is chemical resistance of fuel, foreseen conducting ageing reactions in much higher

temperature. Temperatures are even 10 times higher. Moreover, environment where reactions are conducted is highly oxidizing.

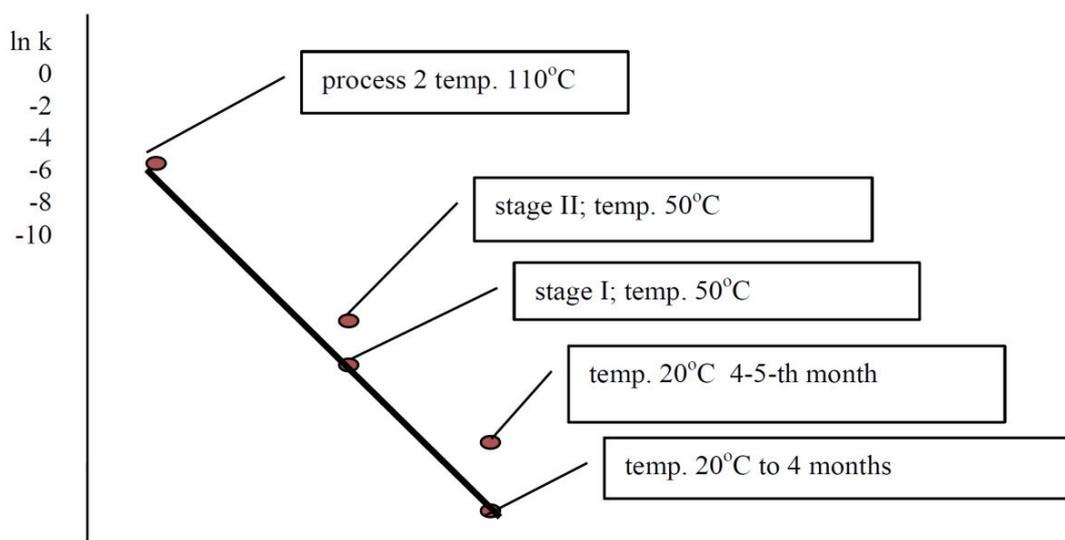


Fig. 6. Function  $\ln k = f(1/T)$  for different conditions ageing process of FAME:  $\text{tg}$  of angle of inclination  $E_a/R$ ,  $E_a$  – activation of reaction energy,  $R$  – gas constant

Therefore, conditions differ significantly. There is a doubt whether those phenomenon can be compared to each other. Because of significant difference in temperatures, in case of simulated ageing, there is a possibility of initializing such reactions, which in real conditions will never happen, because potential energy provided to the system is too small (Fig. 7).

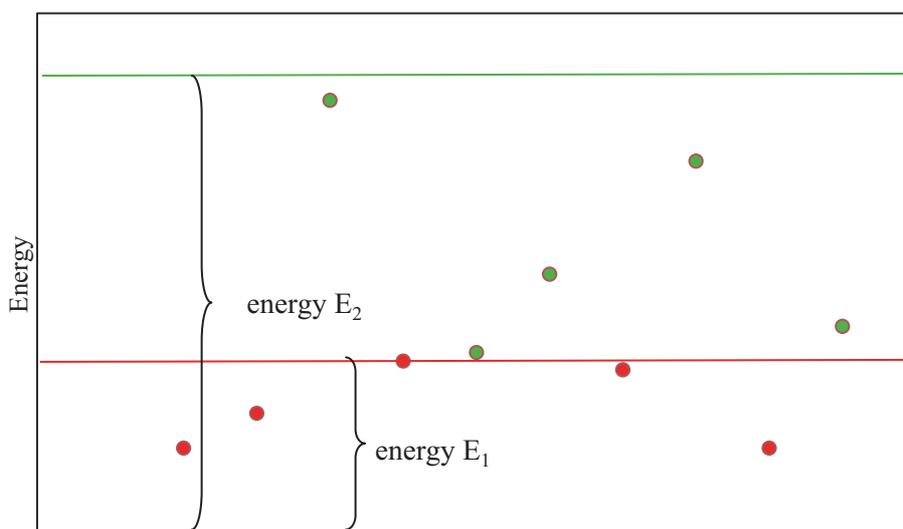


Fig. 7. Influence of value of potential molecules energy on initializing of chemical reactions

In lower temperature, presented as  $E_1$  only part of those reactions will happen (those, whose activation energy  $E_a$  is smaller than provided to chemical system energy  $E_1$ ). In case of higher temperature, presented as  $E_2$ , all chemical reactions will be initiated for which  $E_a < E_2$ , so also reactions for which energy  $E_1$  is sufficient. Therefore, we cannot discuss similarity of those two mechanisms. Moreover, higher temperature can change directions of reaction and lead to reactions, which would never happen in storage conditions. This way products of reactions which are non typical for storage are created.

What is more, in case of accelerating methods, strongly oxidizing atmosphere is important, which does not occur in reality. In this case significant amount of active reagent is provided, which can enter in reactions requiring a big amount of oxidant, and which does not occur in sufficient amount in real conditions.

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