

A comparative study on selected physical properties of diesel–ethanol–dodecanol blends

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The article presents findings of the comparative analyses of the selected physicochemical parameters of diesel fuel and diesel-ethanol blends with the addition of dodecanol, used to stabilise the blend Diesel fuel and the blends were tested for density, flash point, and cold filter plugging point. The physicochemical properties were assessed in seven samples with different proportional volumes of ethanol contained in diesel fuel. Homogeneous blends were produced by adding 5% dodecanol to blends containing between 5% and 30% ethanol. The study was conducted to assess the selected physicochemical properties of diesel-ethanol blends with the addition of dodecanol and to compare the obtained results with the requirement of EN590:2022-08.

Key words: diesel fuel, ethanol, dodecanol, alternative fuels, physicochemical properties

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1. Introduction

The emission of toxic compounds produced during the combustion of fuel by internal combustion engines is a major source of environmental pollution. In order to reduce the negative impact of vehicles powered by internal combustion engines, increasingly stringent standards are being introduced for the emission of harmful compounds contained in exhaust gases [24]. This leads to further advancements in internal combustion engines, which consequently results in increased complexity of their design and the widespread use of electronics to enable precise control and diagnostics [25]. Toxic emissions can be reduced for instance by optimizing the shape of combustion chamber and the fuel injection parameters [6, 27, 28].

Another way to reduce emissions of carbon dioxide (CO₂) and toxic compounds such as particulates and nitrogen oxides (NO_x), generated by diesel engines, is to use alternative fuels [29, 30]. These fuels, associated with low environmental risks, should originate from renewable resources and they should be readily available. Within this group of fuels, those of plant origin, mainly alcohols, are becoming increasingly popular because of their high oxygen content (about 35%), low viscosity and good atomization. Furthermore, alcohols such as ethanol, methanol, propanol, butanol and pentanol can be produced during the process of biomass fermentation.

Ethanol is the most widely used alcohol because it is obtained from renewable resources in the course of a simple and cost-effective production process, and it has high oxygen content [2, 8].

There are three main ways of using ethanol to power a diesel engine. These are: direct injection of ethanol into the intake manifold, direct injection of ethanol into the cylinder by a separate injector, and the use of diesel–ethanol or ethanol–biodiesel blends [4, 9]. Compared to the first two, the latter method has considerable advantages owing to its simplicity. The use of this type of blend makes it possible to avoid costly changes to the engine design, and may only require certain adjustments to be made [2, 23].

However, the miscibility of ethanol in diesel fuel is limited and depends on temperature changes and water content in the fuel; even a small amount of water can lead to stratification of the blend. To improve miscibility and avoid stratification of the blend, it is possible to apply dodecanol (C₁₂H₂₆). It is obtained by reducing methyl esters [32]. It is a colorless water-insoluble solid with a melting point of 24°C. It exhibits good solubility in both of the aforementioned fuels and has been used as a stabilizer in diesel-ethanol blends [7]. Homogeneous blends were produced by adding 5% dodecanol to blends containing between 5% and 30% ethanol. This proportional content of dodecanol was used to ensure miscibility [19, 22].

Experimental studies show that a higher concentration of ethanol in a diesel blend results in a reduction of nitrogen oxides and particulates, but can lead to an increase in exhaust gas temperature, carbon monoxide (CO) emissions at low and medium engine load and an increase in the amount of unburned hydrocarbons (HC) [2, 3, 10].

Alternative fuels differ in terms of physicochemical parameters from conventional fuels. It is important to identify the differences in the basic physicochemical parameters of alternative fuels because they determine behavior of a given medium in different conditions. To this end, the experimental tests were carried out to:

- measure the density at 15°C
- fraction composition
- calorific value
- measure the flash point (FP)
- measure the cold filter plugging point (CFPP).

The density of fuel is an important parameter, as it influences the amount of fuel injected into the combustion chamber. Consequently, a decrease in fuel density can lead to reduced engine power, increased fuel consumption, and alterations in the emission of toxic compounds in exhaust gases. Additionally, density can affect the rate of pressure build-up in the cylinders, gas-dynamic processes, the range of the sprayed fuel stream, the fuel pressure in the injection lines, and the fuel spray digestion time.

Substitute fuels differ in calorific value compared to diesel fuel. An appropriate correction of the injection time should be selected to guarantee an equivalent amount of fuel injected into the combustion chamber. The distillation characteristics are determined by normal distillation, during which the fuel is separated into fractions with different boiling points. The fractional composition determines the volatility of diesel fuel, which affects its ignition properties and determines the course and completeness of the combustion process. Another parameter that determines the usability of the fuel is the cold filter plugging point temperature, which defines the lowest temperature at which the fuel can be used.

The flash point does not directly affect the combustion process in diesel engines. It classifies the fuel into the appropriate fire hazard class.

Since that the aforementioned parameters affect the operational properties and safety of handling this type of fuel, and considering the lack of research on this fuel type, this issue is discussed in this article.

2. Description of research methods

The physicochemical properties were assessed in seven samples with different proportional volumes of ethanol contained in diesel fuel. The fuels subjected to the analyses are shown in Table 1. Homogeneous blends were produced by adding 5% dodecanol to blends containing between 5% and 30% ethanol. This proportional content of dodecanol was used to ensure the miscibility of the blends [20, 22]. The samples were made from diesel fuel, the selected parameters of which are presented in Table 2 as well as dehydrated ethanol with the main properties shown in Table 3. The selected parameters of dodecanol are presented in Table 4.

The fuels prepared for testing were stored in closed containers due to the hygroscopic nature of ethanol.

Table 1. List of fuels subjected to tests

Sample description	Percentage [% v/v]		
	Dodecanol	ON	Ethanol
ON	0	100	0
ON-ET5	5	90	5
ON-ET10	5	85	10
ON-ET15	5	80	15
ON-ET20	5	75	20
ON-ET25	5	70	25
ON-ET30	5	65	30

Table 2. Properties of diesel fuel [32]

Parameter	Unit	Value
Cetane number	–	51.7
Viscosity (40 °C)	mm ² /s	2.516
Polycyclic aromatic hydrocarbons content	%(m/m)	2
Sulfur content	mg/kg	5.9
Water content	%(m/m)	0.008
Density	g/cm ³	0.833

Table 3. Basic properties of ethanol [17]

Parameter	Unit	Value
Alcohol content (20°C)	%	99.9
Autoignition temperature	°C	425
Water content	%(m/m)	≤ 0.1
Methanol content	mg/100 cm ³	< 0.6
Ester content	mg/100 cm ³	< 0.2
Density	g/cm ³	0.789

Table 4. Basic properties of dodecanol [18]

Parameter	Value	Unit
Melting/freezing point at a pressure of 101.3 kPa	24	°C
Autoignition temperature	275	°C
Flash point	134.8	°C
Solubility in water (25°C)	0.037	g/l
Density (25°C)	0.843	g/cm ³

Density was measured using DMA 4500 M apparatus (Fig. 1), with the following technical parameters [14]:

- measuring range: density 0–3 g/cm³, temperature from 0 to 90°C
- accuracy: 5·10⁻⁵ g/cm³, 0.03°C
- sample volume: minimum 1 ml.

Density of the blends was determined by the standard PN-EN ISO12185:2002. Figure 1 shows the screen of DMA 4500 M apparatus, which can be used to measure density following the standard, during the measurement of the parameter in ON-ET20 blend at 15°C.



Fig. 1. Density meter DMA 4500 M

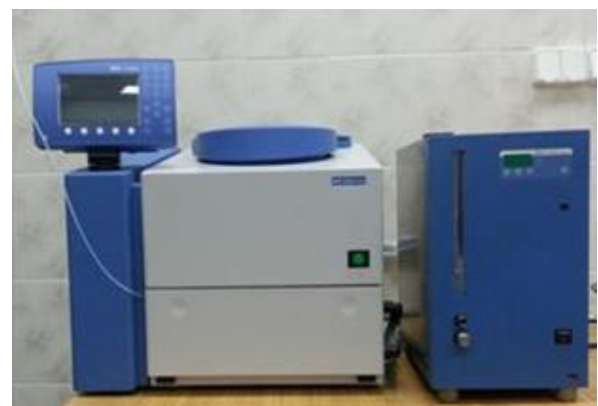


Fig. 2. Calorimetr IKA C5000

The study of the higher heating value (HHV), based on which the Lower Heating Value (LHV) of the fuel was determined, was carried out using the isobaric method using a measuring system with the IKA C5000 calorimeter (Fig.

2). The device is characterized by the following selected parameters [11]:

- oxygen filling station integrated with the calorimeter and automatic emptying of the bomb after the measurement
- measurement range: max. 40 000 J (corresponds to the temperature increase of the calorimetric vessel to approx. 40 K)
- measurement accuracy: ± 0.0001 K
- measurement time: adiabatic method 14–18 min, isoperibolic method 20–22 min, dynamic method 8 min.

- sample temperature measuring range: -69 – $+35^{\circ}\text{C}$
- sample volume: 45 ml
- programming of the negative pressure of the drawn sample.



Fig. 3. Distillation analyzer OptiDist

The fractional composition of the tested blends was determined using the OptiDist apparatus (Fig. 3). The apparatus is characterized by the following parameters [15]:

- volume of the tested sample: initial volume range 0–103%, resolution 0.03 ml, accuracy ± 0.1 ml, automatic calculation of distillation residue
- vapor temperature: range 0– 450°C , Pt 100 sensor IEC 751
- receiver chamber: temperature range 0– 40°C .

The test apparatus was configured for the 4th group, which corresponds to a typical diesel oil, thanks to which the main parameters of the apparatus configuration were the same for each of the tested blends. Such a setup of the apparatus made it possible to carry out comparative tests of the tested fuels with diesel oil.

Another physicochemical parameter impacting the possibility of using fuel at low temperatures is the factor known as CFPP. Another physicochemical parameter affecting the possibility of using the fuel at low temperatures is the CFPP coefficient, which was determined based on the standard PN-EN 116:2015-09. The value of the cold filter plugging point corresponds to the temperature at which the final completed filtration process starts. The measurement of the cold filter plugging point was performed using the automatic apparatus FPP 5Ds (Fig. 4) with the following parameters [12]:

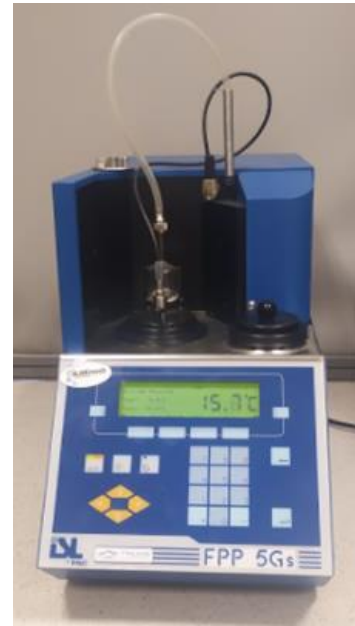


Fig. 4. CFPP tester FPP 5Gs

Measurement of flash point was performed following PN-EN ISO2719:2016-08.

Measurement of the flash point was performed using HFP 339 tester (Fig. 5) with the following parameters [14]:

- sample temperature measuring range: 0– 400°C , resolution 0.1°C
- the rate of heating: 0.5 – $14^{\circ}\text{C}/\text{min}$ – depending on the test method
- ignition source: electrical coil igniter; frequency of ignition depends on the selected method 0.5 – 5°C .



Fig. 5. Flash point tester HFP 339

3. Results and Analysis

Fuel density impacts engine performance characteristics [16]. A change in fuel density affects engine power output because of the different weight of the fuel injected [1]. Density was measured at a temperature of 15°C, in line with PN-EN ISO12185:2002.

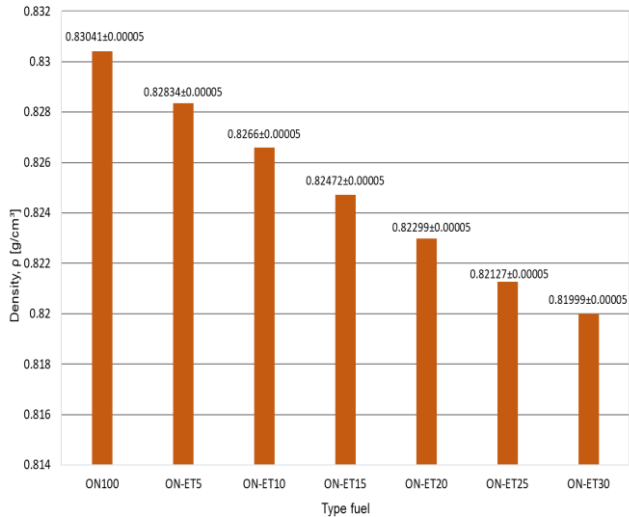


Fig. 6. Density of the fuel samples tested (at 15°C)

Based on the results presented in Fig. 6, it can be observed that an increase in the proportional content of ethanol results in an approximately 0.2% decrease in density. The lowest density was identified in the ON-ET30 blend, containing 30% ethanol and 5% dodecanol; in this case, there was approximately a 1.2% decrease in density relative to the reference diesel fuel sample. All the fuels, with the exception of ON-ET30, met the density requirements defined by the regulations [26]. The uncertainty of (± 0.00005 g/cm³) was established by the test device supplier.

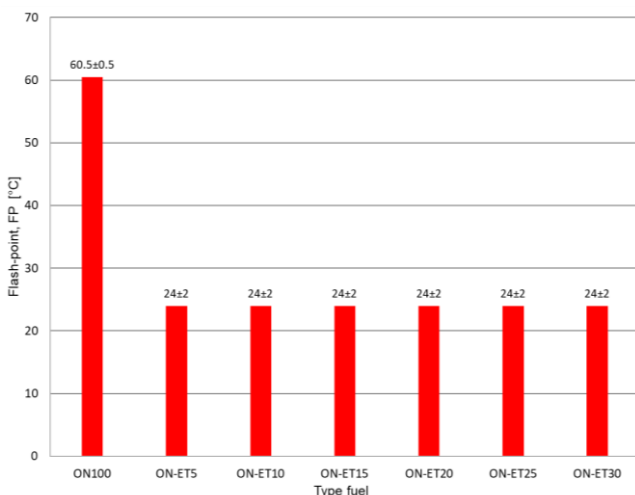


Fig. 7. Flash point of the fuel samples tested

FP is a decisive factor in establishing the necessary precautions for fuel handling.

The FP was taken as the lowest temperature at which the ignition of the flammable blend with air occurred.

The highest value of flash point, identified in diesel fuel sample, was 60.5°C ± 0.5 (Fig. 7). In contrast, all the blends formed vapours that ignited at an ambient temperature of 24 ± 2 °C. All samples with the addition of ethanol ignited at ambient temperature during the test immersion of the igniter (without heating the sample).

CFPP determines the lowest temperature at which a fuel can be used. Based on the value of CFPP, diesel fuels are designated to be used in specific seasons, depending on weather conditions. The CFPP value quantitatively indicates the solidification of paraffinic hydrocarbons, where excessive paraffinic hydrocarbon crystals can obstruct the flow of fuel through the fuel system. The present study applied winter diesel fuel ON100 as the reference sample. The tests performed in line with PN-EN116:2015-09 produced results presented in Fig. 8, which show that in the case of diesel fuel ON100 the value of CFPP was -25 °C. Compared to all the samples investigated, the fuel ON-ET10, with 10% ethanol content, was found with the lowest value of cold filter plugging point amounting to -30 °C. The improvement of low-temperature properties may result from the addition of dodecanol, which improves low-temperature properties for low concentrations of ethanol in diesel fuel [21]. This blend meets Grade F requirements for temperate climates and Grade 1 requirements for Arctic climates, as does the fuel sample ON-ET5. On the other hand, the highest cold filter plugging point values of -17 °C, and -18 °C were measured in the case of ON-ET30 and ON-ET25 samples, respectively. These blends meet Grade E requirements defined for temperate climates. The remaining fuels also satisfy Grade F requirements for temperate climate.

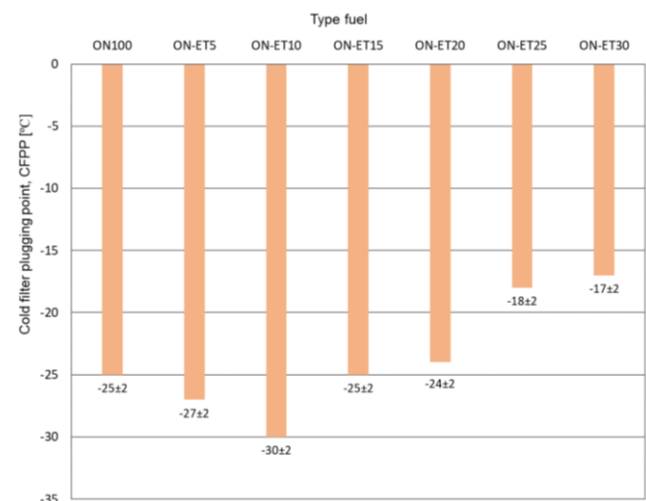


Fig. 8. Cold filter plugging point of the fuel samples tested

Figure 9 displays the higher heating value results for the tested blends. Among them, ON100 fuel exhibits the highest heat of combustion value at 44.25 MJ/kg, while the lowest value of 38.62 MJ/kg is observed for the ON-ET30 fuels.

In Fig. 10, the results of the lower heating value for all tested blends are shown. Diesel fuel demonstrates the highest calorific value of 41.74 MJ/kg. As the ethanol concentration increases, the calorific values decrease. The mixture

of ON-ET30 has the lowest calorific value at 37.58 MJ/kg compared to the other fuels.

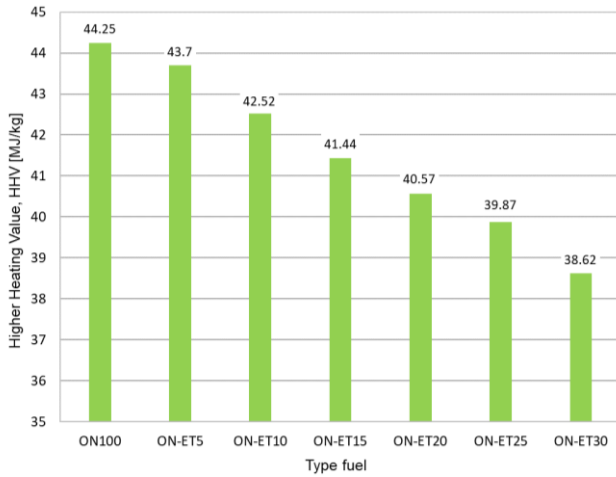


Fig. 9. Higher heating value for the tested blends

An important indicator determining the operational value is the fractional composition of fuels. On its basis, it is possible to determine not only the volatility affecting the speed of starting the engine but also its tendency to form vapor locks that cause interruptions in its operation.

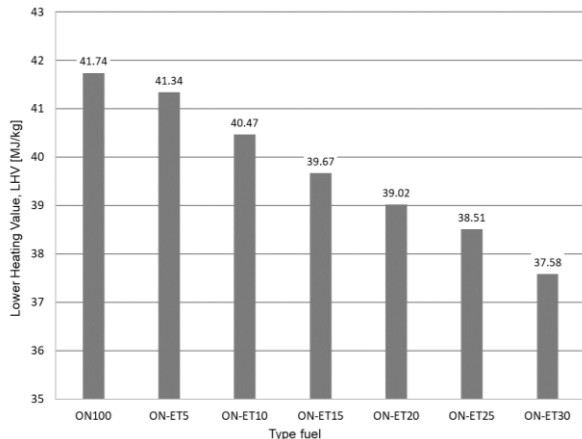


Fig. 10. Lower heating value for the tested blends

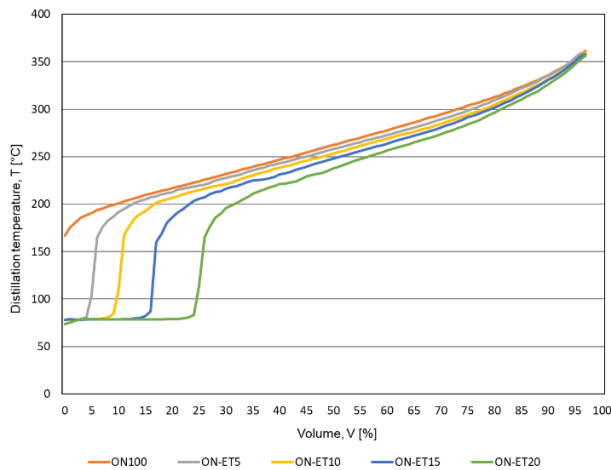


Fig. 11. Distillation curves for the tested fuels

In Table 5 presents the values temperatures corresponding to the subsequent stages of their evaporation, while Fig. 11 presents them graphically using distillation curves.

Table 5. Degree of fuel evaporation as a function of temperature

Parameter	T _S	T _{10%}	T _{50%}	T _{90%}	T _F
	°C	°C	°C	°C	°C
ON	167.19	200.87	262.30	335.96	361.87
ON-ET5	77.77	191.87	258.03	335.35	358.74
ON-ET10	77.78	109.09	253.21	331.62	359.99
ON-ET15	78.09	78.72	248.07	331.16	355.75
ON-ET20	73.63	78.43	237.69	326.32	352.60
ON-ET25	–	–	–	–	–
ON-ET30	–	–	–	–	–

The obtained distillation curves (Fig. 11) show that up to the temperature of 180°C the following were distilled: 1% of ON100 fuel, 7% ON-ET5, 12% ON-ET10, 18% ON-ET15, 27% ON-ET20. Up to the temperature of 250 °C, 42% ON100, 44% ON-ET5, 47% ON-ET10, 51% ON-ET15, 56% ON-ET20 were distilled. The highest distillation start temperature was recorded for ON100, amounting to 167.11°C, and the lowest, amounting to 75.46°C, for the ON-ET20 mixture. The requirements of the norm for the result of distillation of 95% of the fuel fraction to the temperature of 360°C were met by all blends for which distillation was possible. Only for fuels marked ON-ET25 and ON-ET30 the distillation curves could not be determined. In order to obtain distillation curves for these fuels, it would be necessary to perform the measurement under reduced pressure distillation conditions, which would require the use of other apparatus.

4. Conclusions

Based on the experimental tests and analysis of the results, the following conclusions have been formulated:

- based on the obtained results, it can be concluded that fuel blends in which the ethanol content does not exceed 25% meet the requirements of the EN 590:2022-08 standard regarding density and cold filter plugging point;
- increase in ethanol content resulted in approximately 0.2% decrease in the density, and the lowest density was identified in the fuel blend with 30% ethanol and 5% dodecanol; in this case, density was approximately 1.2% lower than in diesel fuel;
- the fuel sample ON-ET30 did not meet the fuel density-related requirements specified in the regulation of EN 590:2022-08;
- the flash point, which is an indicator for precautions to be taken when handling the product, has decreased from 60.5°C in diesel fuel to 24°C in the case of all the diesel-ethanol blends, changing the classification of these fuels from Class III to Class II fire hazard. None of the mixtures of diesel fuel with ethanol and dodecanol meet the requirements of the standard EN 590:2022-08;
- cold filter plugging point tests have shown that fuels with ethanol content up to 25% can be used in winter; on the other hand the blends with 25% content of ethanol or higher can be used during transitional periods;

- increase in the share of ethanol in fuel sources of reduced heating value and calorific value. The lowest calorific value was reduced by approx. 10% compared to diesel oil was obtained for the ON-ET30 blend. The ON-ET5 blend obtained the highest calorific value of the tested blends of diesel oil and ethanol and was lower by 1% in relation to the base diesel oil;
- fuels containing ethanol additives exhibit the lowest initial distillation temperature of 10% of the mixture, which proves the high presence of the light fraction in the fuel. This can lead to a significant increase in pressure within the cylinders, ultimately impacting the engine's durability and noise levels in a negative manner. It may intensify the combustion process and result in significant increases in cylinder pressure, which in turn adversely affects the durability and noise level of the engine operation. It can also lead to the formation of vapor locks in the fuel system, which can disrupt the injection process and consequently impact the deterioration of engine performance parameters;
- fuels containing 5% to 20% volume of ethanol are characterized by lower distillation temperatures ($T_{50\%}$) compared to diesel fuel. This can influence the reduction in the time needed to form the fuel-air mixture, consequently enhancing the combustion process.

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Nomenclature

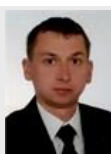
$C_{12}H_{26}$	dodecanol	HHV	higher heating value
CFPP	cold filter plugging point	LHV	lower heating value
FP	flash point	ρ	density

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