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NEW ALTERNATIVE FUELS FOR I.C. ENGINES - A REVIEW

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Abstract

Increased environmental protection concern, growing energy demand and need to reduce the dependency on crude oil cause that the world is looking for new and renewable energy resources. Many alternative fuels are applied currently but their share in the global energy market is, as for now, quite small. The most promising new alternatives for fossil fuels seem to be: dimethyl ether, hydrogen, Fischer-Tropsch fuels. Growing interest is currently observed also in the field of fuel oxygenates, such as: alcohols, dimethyl carbonate and ethers. Their addition to conventional or reformulated fuels has positive influence on engine performance and emissions.

In the paper a review of new alternative fuels and fuel components for I.C. engines has been performed, including physico-chemical properties of these fuels, their sources and technological aspects of production, as well as recent data on R&D work and application.

1. Introduction

Trends to set restrictions on toxic components and greenhouse gases emissions, observed currently, cause that standards referring exhaust emission from vehicles are more and more rigorous. In such a situation the fuel, lubricant and additive industries are forced to looking for new products to meet new specifications. This can be achieved by reformulation of existing fuels or by introducing alternative fuels. Interest in alternative fuels is also a result of concerns over consumption of the primary energy sources that are limited.

The term "alternative fuels" refers to such energy carriers that are not of crude oil origin, have respectively high heating value and their combustion causes lower (in comparison with conventional fuels) pollution of the natural environment. Many alternative fuels have been applied to combustion engines for many years, e.g. liquefied petroleum gas, compressed and liquefied natural gas, biodiesel, alcohols. However, researchers are still carrying on investigations on new energy carriers. The obtained results in many cases appear to be promising. Some of new alternative fuels can be directly applied, as neat fuels; other can be used as fuel components. One of important advantages of these fuels is diversification of its sources. More widespread use of new alternative fuels needs resolving many problems relating to production, distribution and application (e.g. cost effectiveness, on-board storage, distribution infrastructure, safety of use). Acceptance of users plays also an important role.

The aim of this paper is to characterise new alternative fuels from the point of their sources, properties, methods of production and application to I.C. engines.

2. Fuels

2. 1. Dimethyl ether

Dimethyl ether (DME) [1,2] is one of the simplest ether compounds and is widely used as propellant for aerosols. DME is a gas at ambient temperature and pressure but it can be liquefied under low pressures (0.5 MPa at 25°C). It can be produced from natural gas (dehydrogenation of methanol) or from biomass (gasification). It is non-toxic, non-corrosive and non-carcinogenic and in the case of leakage it decomposes very rapidly in the atmosphere. From an ecological point of view, DME can also be a good fuel for C.I. engines because it burns easily and produces low emissions. It has a high cetane number of about 60. DME lubricity properties are poor because of its very low viscosity (about 1/30 of that of diesel fuel) and to avoid the premature injection equipment wear, introduction of lubricity additives is needed. The main physical and chemical properties of DME compared with diesel fuel are shown in Table 1.

Table 1. Physical and chemical properties of DME and diesel fuel [3]

Properties	DME	Diesel fuel
General formula	CH_3-O-CH_3	C_xH_y
Molecular weight, g/cm^3	46.07	190-220
Carbon content, % mass	52.2	86
Hydrogen content, % mass	13	14
Oxygen content, % mass	34.8	0
Density in the liquid state, g/cm^3	0.668	0.84
Kinematic viscosity at 40^{0}C, mm^2/s	0.15	2.0 – 4.5
Boiling point, ^{0}C	-24.9	189-360
Autoignition point, ^{0}C	235	250
Heating value, MJ/kg	28.43	42.5
Heat of vaporization, kJ/kg	410	250
Stoichiometric ratio, kg/kg	9.0	14.6
Cetane number	55-60	40-55

Neat DME is a good fuel for C.I. engines because engine fuelled with it shows excellent combustion characteristics resulting in low emissions [4]. Due to that it was considered to be promising fuel for C.I. engines for 21st century [1, 2]. Moreover, engine after some modifications, exhibits higher thermal efficiency than C.I. engine fuelled with diesel fuel – Fig. 1. DME engine has also reduced simultaneously NO_x and smoke, though normal C.I. engine exhibits trade-off between NO_x and smoke [5]. Especially good results were obtained with application DME and EGR to C.I. engine [6]. In a normal C.I. engine application of EGR (in order to reduce NO_x) results in decrease of thermal efficiency and increase of CO, HC and smoke emissions. In DME fuelled engine NO_x decreases linearly with EGR ratio – Fig. 2 while thermal efficiency and smoke level rather do not depend on EGR ratio – Fig. 3 and Fig. 4. Emissions of CO and HC increase a little with increase of EGR ratio, but remain still very low compared with that of C.I. engine [6].

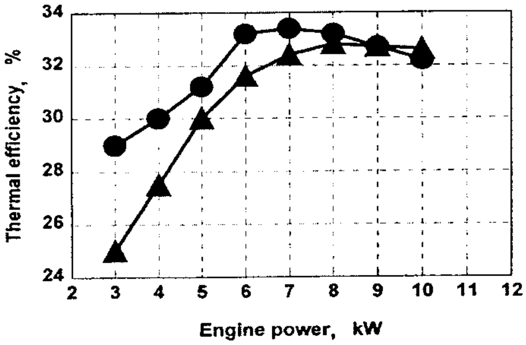


Fig. 1. Comparison of thermal efficiency of DME engine and diesel fuel engine for engine speed n= 1800 rpm [6]

● - DME fuel
▲ - diesel fuel

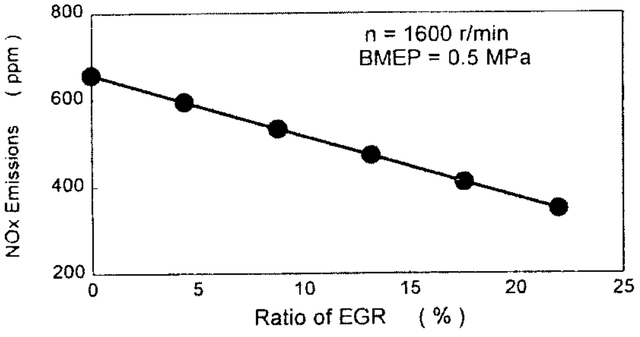


Fig. 2. NO_x emissions from C.I. engine with EGR vs. EGR ratio [7]

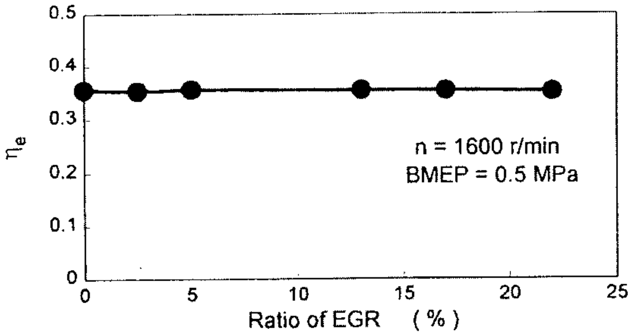


Fig. 3. Thermal efficiency of C.I. engine with EGR vs. EGR ratio [7]

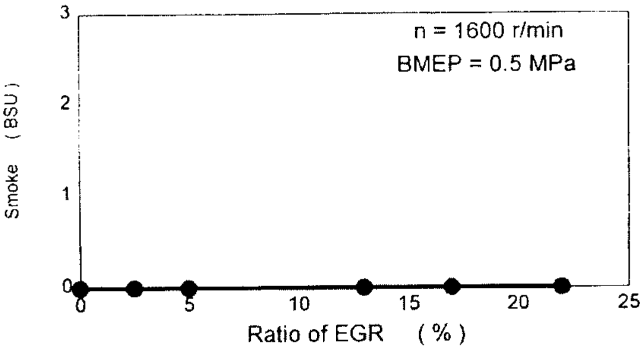


Fig. 4. Smoke emissions from C.I. engine with EGR vs. EGR ratio [7]

DME may be obtained on-board vehicle with the use of methanol conversion [7]. Disadvantage of methanol is its poor ignition behaviour. This disadvantage may be overcome by conversion methanol to DME according to the reaction:

$$2\ CH_3OH \rightarrow CH_3OCH_3 + H_2O$$

and fumigation of it to C.I. engine. The most promising due to the effectiveness and cost was catalyst γ-Al_2O_3 [7].

At ambient temperature and pressure DME is a gas, and therefore it must be introduced into the engine cylinder by fumigation in the air on the vehicle. Fumigation of DME (by 5-30%) improves ignition behaviour of methanol, which is still a main fuel to C.I. engine. Methanol burner on the vehicle was a heat source for start up [7]. In DME fuelled engine vapour lock may appear. In order to eliminate this, the fuel system supply pump, regulator and a buffler can be added [5].

Summing up, fuelling C.I. engine with DME results in:

- simultaneous reduction of NO_x and smoke,
- linear reduction of NO_x with increase of EGR ratio,
- slightly increase of CO and HC emissions but remain still at a low level,
- improvement of ignition behaviour of methanol fuelled C.I. engine (fumigation of DME),
- total deficiency of sulphur in exhaust gases.

At present DME is a fuel for experimental Volvo city bus [8]. DME is carried at 5 bar pressure in five tanks, what enables the same range as 267 dm3 of diesel fuel. The DME engine fulfils Euro 4 emission test (Table 2).

Table 2. DME – Volvo engine emission [8]

Pollutant	DME engine	Euro 4 limit
NO_x	3.0	3.5
PM	0.002	0.002
THC	0.12	0.46
CO	0.25	1.5

2. 2. Fischer-Tropsch fuels (GTL fuels)

The Fischer-Tropsch process, developed in 1920's, is used to obtain hydrocarbons from synthetic gas (a mixture of CO and H_2) in the presence of catalyst, at high pressure and temperature. The basic mechanism of this process is as follows:

$$2nH_2 + nCO = n(-CH_2-) + nH_2O$$

where $-CH_2-$ represents basic building block of the paraffin molecule.

The product spectrum can be controlled by the choice of the catalyst, process configuration and operating conditions. Generally, higher temperatures (> 320°C) and iron based catalyst favour the production of lighter hydrocarbons suitable for gasoline production, while cobalt based catalyst and lower process temperatures (< 250°C) tend to produce paraffins in the diesel range. Obtained hydrocarbons are subsequently refined into fuels. Germans used this method during the Second World War to supply their army with fuels and as well as in South Africa during the apartheid era. Synthetic gas can be produced from coal and biomass but natural gas is expected to be the primary feedstock. Converting natural gas to a liquid through a Fischer-Tropsch technology provides an opportunity to expand the use of natural gas and lower the transportation cost (natural gas is four times more expensive to transport than oil) from remote sources of low-cost gas.

Fuels obtained in this way are called F-T fuels or GTL fuels because of the gas-to-liquid nature of the process. For diesel fuel the term FTD (Fischer-Tropsch Diesel) is commonly used. FTD has very good properties as a fuel for C.I. engines: exclusive paraffinic composition with predominating linear or lightly-branched chains, high cetane number, cloud point below −10°C, extremely low sulphur, aromatics and toxics content. Limited experimental data suggest higher rates of biodegradation for F-T fuels relative to conventional [9]. Typical properties of Fischer-Tropsch diesel are given in Table 3.

Table 3. Typical properties of Fischer-Tropsch diesel in comparison to conventional fuel [10]

Property	Typical No. 2* diesel	Low T FTD	High T FTD (PetroSA COD)
High heating value, MJ/kg	43-48	45-48	45-48
Density at 15°C, g/cm^3	0.8464	0.7695-0.7905	0.8007-0.8042
Distillation, °C			
IBP	174	159-210	230
50%	253	244-300	254
90%	312	327-334	323
FBP	344	338-358	361
Cetane number	44.9	>74	~50
Sulfur content, ppm	300	<1	<1
Aromatics content, %vol	~30	0.1-2	~10
Hydrogen content, % wt	13-13.5	~15	~14.4

* the most common grade of diesel fuel, designed for use in all diesel application. No. 2 diesel meets all ASTM D 975 specifications.

FTD, like other zero or low aromatic fuels, has very poor lubricity properties. Lubricity enhancing additives must be used to protect the fuel injection equipment from wear. Fischer-Tropsch fuels are not widely used today but extensive research is under way to commercialise them for vehicle use. Concern Sasol is the world leader in Fischer-Tropsch technologies.

2. 3. Hydrogen

Hydrogen is not a primary fuel found in nature but it can be produced from various materials such as: natural gas, methanol, coal, biomass and water. Currently hydrogen is produced most commonly through steam reforming of hydrocarbon feedstock. Another ways to produce this gas are: steam methane reforming, coal gasification, biomass gasification, and electrolysis. It may be stored compressed, liquid as well as chemically or physically bounded with the storage material (e.g. as metal hydrides). The most desirable property of hydrogen as an automotive fuel is its clean-burning. If pure hydrogen is used as a fuel, only water is a product. Physico-chemical properties of hydrogen as a fuel are given in Table 4.

Table 4. Physico chemical properties of hydrogen as a fuel [11]

Properties	Hydrogen
General formula	H_2
Molecular weight, g/cm^3	2.02
Density of the liquid, kg/dm^3	0.070
Density of the gas, kg/m^3	0.090
Minimum autoignition temperature, °C	570
Heating value, kJ/kg	120 971
Energy content of the carburetted mixture at an equivalence ratio of 1, kJ/ dm^3	2.92
Stoichiometric ratio	34.5
Octane rating (RON)	60

Today, the use of hydrogen as an automobile fuel is primarily limited to experimental and prototype vehicles. One group of such vehicles burns hydrogen directly in modified I.C. engines. The second group are electric powered vehicles that use hydrogen in fuel cell.

According to the European transport and energy policy, the use of alternative fuels shall be 20% by the year 2020. Currently, the European Community supports some project aimed to develop new concepts, strategies and tools for clean and safe transportation. Great part of such projects concerns hydrogen. For example, the project CUTE (Clean Urban Transportation for Europe), that has an aim to develop a role of hydrogen and fuel cell in urban transport. CUTE is the largest projects of this type throughout the world.

3. Additives

3. 1. Oxygenates: ethers and alcohols

Oxygenates – oxygenated organic compounds, are added in small amounts to fuels in order to promote combustion of reach mixtures. They are locally available oxygen sources. Oxygenates have significantly different physical properties than hydrocarbons so their level in fuels is limited. Oxygenated organic compounds have a high octane (or cetane, respectively) number. Reformulated gasoline requires oxygenates to provide octane. Oxygenate fuels show lower emission of some pollutants, particularly carbon monoxide.

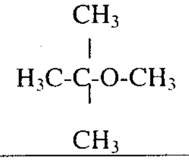
The most popular oxygenated constituents for gasoline are: alcohols (methanol, ethanol, tert-butyl alcohol – TBA) and ethers (methyl tertiary butyl ether – MTBE, ethyl tertiary butyl ether – ETBE, tertiary amyl methyl ether – TAME). They contain 1 to 6 carbon atoms per molecule. Because they show good anti-knock properties, they are good substitutes for aromatics. Alcohols have been used in gasoline since the 1930s, and MTBE was first used in commercial gasoline in Italy in 1973. Some properties of the most commonly used oxygenates and of gasoline are shown in Table 5.

Table 5. Selected properties of the most commonly used oxygenates and of gasoline [12]

	Motor Octane Number (MON)	Research Octane Number (RON)	Boiling point, (°C)
Ethers			
MTBE	101	118	55
ETBE	102	118	72
TAME	99	109	86
Alcohols			
Methanol	92	107	65
Ethanol	96	130	78
TBA	95	105	71
Gasoline	82-88	92-98	26-230

Oxygenates can be produced from fossil fuels (e.g. methanol, MTBE, TAME) or from biomass (e.g. ethanol, ETBE). MTBE is produced by reacting methanol (from natural gas) with isobutene in the liquid phase using a sulfonic resin catalyst at the temperature between 50 and 80°C. Isobutylene was initially from refinery catalytic crackers or petrochemical olefin plants, but nowadays it is produced from butane. Physical and chemical properties of MTBE are presented in Table 6.

Table 6. Physical and chemical properties of MTBE [12]

Chemical formula	$C_5H_{12}O$
Molecular structure	 $H_3C-\overset{CH_3}{\underset{CH_3}{C}}-O-CH_3$
Carbon content, % mass	68.1
Oxygen content, % mass	18.2
Hydrogen content, % mass	13.7
Physical state (at normal temperature and pressure)	Colourless liquid
Boiling point, °C	55.2
Melting point, °C	-108.6
Flash point, °C	-30
Autoignition temperature, °C	425
Flammability limits in air, % vol	1.5-8.5
Relative density, g/cm^3 at 20°C	0.7405
Vapour pressure, mm of Hg at 25°C/ Pa at 25°C	245/3.34E+4
Refractive index at 20°C	1.3690

The major concern with oxygenates for gasoline is connected with their very good water solubility and very slow biodegradability. Their toxicological effects are being investigated now. Some results suggest that they can be carcinogenic. MTBE is believed to cause groundwater contamination. Some gasoline producers switch from blending MTBE to ethanol. Ethanol as a replacement of MTBE is the best for reasons relating to costs and availability.

Oxygenated constituents for diesel oil, such as: dimethyl ether, dimethyl carbonate, diethyl carbonate, rapeseed methyl ester, dimethyldiglycol and dihexylether function in the same way as alcohols and ethers when added to gasoline.

3. 2. Dimethyl carbonate

Dimethyl carbonate (DMC) is a liquid at ambient temperature and pressure. It is colourless, non-toxic and non-corrosive. It can be blended with diesel fuel in any proportion [13]. DMC offers high promise as an additive for diesel fuel because it contains 53% (by weight) of oxygen. Their main physical and chemical properties compared with diesel fuel are shown in Table 7.

Table 7. Physical and chemical properties of DMC and diesel fuel [13]

Properties	DMC	Diesel fuel
General formula	$C_3H_6O_3$	C_xH_y
Molecular weight, g/cm^3	90.1	190-220
Carbon content, % mass	40	86
Oxygen content, % mass	53.3	0
Hydrogen content, % mass	6.7	14
Density in the liquid state, g/cm^3	1.079	0.84
Kinematic viscosity at 40°C, mm^2/s	0.625	2.0 – 4.5
Boiling point, °C	80	189-360
Autoignition point, °C	220	250
Heating value, MJ/kg	15.78	42.5
Heat of vaporization, kJ/kg	369	250-290
Stoichiometric ratio, kg/kg	3.5	14.6
Cetane number	35-36	40-55

Currently, DMC is produced from phosgene and methanol, with HCl produced as by-product. Because phosgene is an extremely toxic and dangerous chemical, many companies are looking at developing environmentally friendly alternatives to eliminate phosgene and minimize by-product formation. One of such alternatives can be DMC production from methanol, carbon monoxide and oxygen in the presence of copper chloride catalyst with 5% KCl additive:

$$2CH_3OH + CO + \tfrac{1}{2} O_2 \rightarrow CH_3\text{–}OCOO\text{–}CH_3 + H_2O$$

Dimethyl carbonate has similar properties as diesel fuel and is added to it [6] or fumigated with inlet air [14] in order to improve diesel engine combustion characteristics resulting in decrease of smoke and CO emissions. There is linear dependence of smoke level and DMC addition: smoke will be reduced by 20% for every 10% of DMC added. The influence of the content of DMC in DF and DMC blend on smoke and CO emission is shown in Fig. 5 and Fig. 6. Also slight improvement of thermal efficiency and simultaneous increase of NO_x emission was observed. – Fig. 7.

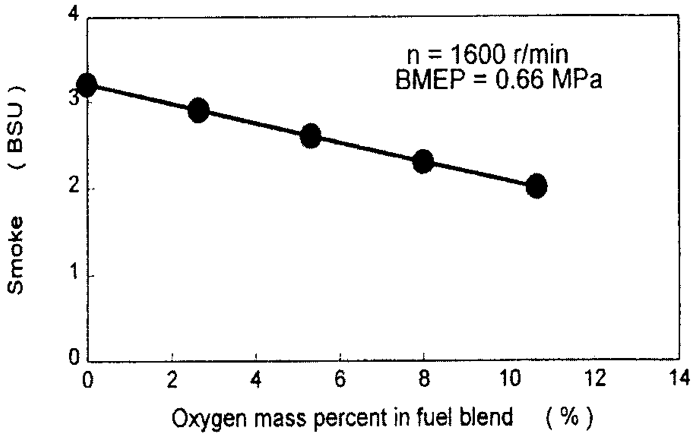


Fig. 5. Smoke as a function of the oxygen content in DMC and DF blend [7]

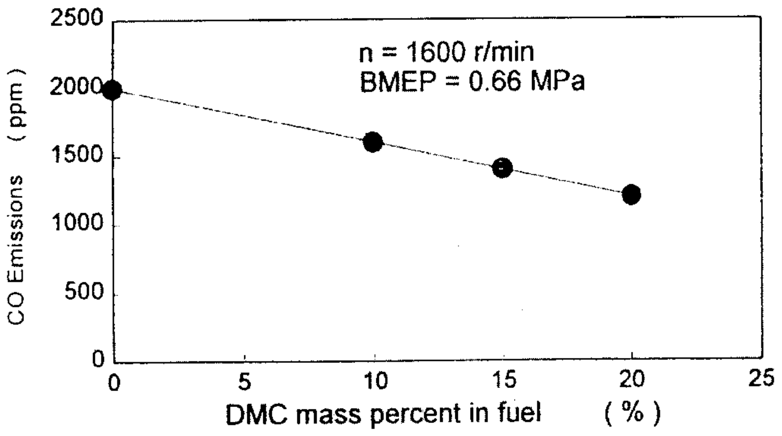


Fig. 6. CO emissions from C.I. engine vs. DMC mass fraction in DMC and DF blend [7]

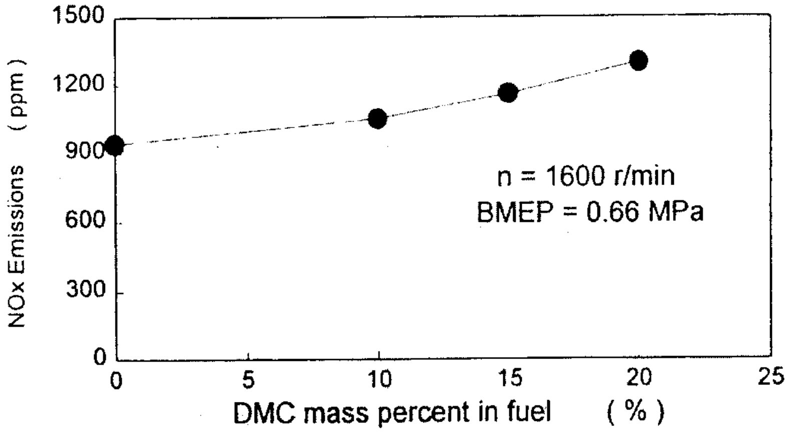


Fig. 7. NO_x emissions from C.I. engine vs. DMC mass fraction in DMC and DF blend [7]

Emission characteristics result from combustion characteristics of DMC and DF blends:

- With addition of DMC premixed (kinetic) combustion phase is prolonged, while mixing controlled diffusive combustion phase is shortened.
- The maximum cylinder gas pressure, rate of pressure rise, rate of heat release and the fraction of fuel burned increase with addition of DMC in the fuel, especially at high load. At low load the influence of DMC addition is less visible.

Summing up, DMC addition to diesel fuel:

- reduces smoke and CO emissions,
- improves slightly thermal efficiency,
- increases NO_x emissions.

7. Summing up and conclusions

Using alternative fuels is inevitable from two main reasons: economical (limited crude oil resources) and ecological (necessity to limit exhaust gas emission). The whole world has to increase a share of alternative fuels in the fuel-energetic balance sheet. First of all, very important for 21st century will be to secure sustainable urban transportation based on alternative fuels. During the last years a number of organisations have been actively engaged in the development of new alternatives for vehicle application

The review shows that very promising for 21st century are such fuels as: dimethyl ether, Fischer-Tropsch fuels, hydrogen as well as fuel additives, e.g. dimethyl carbonate or ethers. Most of new alternative fuels can be produced from natural gas or biomass. From this group hydrogen (called also "a fuel of the future") is the most promising alternative but a lot of research has to be done to solve technical and technological problems connected with its application. Fischer-Tropsch fuels, in turn, seem to have the greatest chance to be applied soon because of very advanced development in their technology.

Progress in the field of alternative fuels is very often limited by high costs of their production and distribution. At present, they cannot be produced at competitive prices relative to conventional fuels. Of course, widespread use of them has to be preceded by profound ecological, economical and technical analysis of the entire life cycle and comparison with conventional fuels.

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