

Inorganic fuels mixtures for automotives propulsion engines

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Abstract The objective of this study is the evaluation of the opportunity to use an inorganic oxygenated compound as ammonium nitrate or urea, to reduce fossil fuels pollution. Our research takes into account the ammonium nitrate water solution, mixed with diesel fuel, in various proportions, as fuel for a diesel engine. The results are very promising, the reduction of the consumption is near 20% and the reduction of particulate matter emission is near 75%, without particulate filter on the exhaust pipeline. The paper intends to explain the ammonium nitrate influence in this process. It is to consider the role of the oxygen which is released in the process of ammonite decomposition in the engine cylinder and the role of the atomic nitrogen, which results in the same process, as fuel with a great energetic value. The energy released at the formation of a nitrogen molecule, N₂, with his triple chemical bond N≡N, is almost the same as the carbon burning but without CO₂ as reaction product.

Keywords: combustion and mechanical efficiencies, binary fuel, chemical supercharging.

1. Introduction

The automotive propulsion, means today for 95% of the vehicles, internal combustion engine. Statistics show that half the CO₂ quantity released in the air by burning fossil fuels has its origin in the automotive engine [1]. The reduction of the CO₂ emission in this case can be done by modifying the fuel composition. The threshold of 140g CO₂/km emission for vehicles is the equivalent of a fuel consumption less than 5 liter / 100 km.

The main ways to reduce fuel consumption for the propulsion system of the automotive are:

a) Increasing the performance of the propulsion system, regarding the fuel efficiency in the engine and the reduction of fuel consumption through the optimization of the management of integrated propulsion system, engine – gearbox – transmission – wheel. Each component of this system is able to contribute to the reduction of mechanical losses which are covered by the mechanical work done by the engine.

b) Reduction of the carbon content of the engine fuel, the carbon being the source of CO₂, by burning). Theoretically the reduction of the carbon content of a fuel is done by using fuels with less carbon in the molecule, like the alcohols, which

have a smaller calorific power compared to gasoline or diesel fuel, by 40% for the ethylic alcohol and by 57 % for the methanol.

In the frame of the same theory, it will be very efficient to add to the oxygenated fuel (alcohols) molecular hydrogen (H₂ gas). This solution is apparently very elegant but inefficient as a result of the poor solubility of the H₂ in liquid alcohols, less than 1% in normal conditions, while the minimum economically attractive concentration is around 5% in volume, additional H₂.

c) The use of a new type of fuels with a very low concentration of carbon and more hydrogen atoms in the molecule. We do not discuss here the use of pure hydrogen as fuel for piston engine because of his poor heat efficiency of the engine due to its poor resistance to compression and also due to the economic issue regarding its price of production, transportation and storage.

2. Actual situation of the fuel inventory used for the automotive propulsion

The conventional fuels for thermal engine are gasoline, diesel fuel, kerosene, diesel marine and the heavy fuel all originated from crude oil. It is a fact the slow but inevitable reduction of crude oil reserve and known deposits [1]. The advantage of these

types of fuels is that they are easy to use, they have a big energetic density, 41500 kJ/kg, and they are dedicated to thermal engines, Otto engine, Diesel engine, naval engine, or turbo engine. Also the transportation of crude oil, the processing plants, and the distribution network are already in place and very dense.

From this perspective the nearest unconventional fuel are the vegetable oil for Diesel engine and the alcohols for Otto engine. The advantage of these "fuels" is that they use "regenerative" primary sources like sugar cane, or potatoes. If the decision will be to use intensively this alternative, the problem is what to do, eat or drive a car?

Another energy source wide- spread and easy to extract and burn is the methane gas. This one is used in big power plants and for domestic use. The use of CH₄ as fuel for piston engine, especially in road transportation is very punctual for very different reasons, like the gas explosion psychosis, to economic reasons. The use of CH₄ on a large scale for transportation means new engines adapted to this fuel and a new distribution network (tank station). Actually the CH₄ dedicated engines are used in co-generative or regenerative plants where the piston engine run an electric generator, and the heat of the exhaust gases and cooling system are used to heat water for domestic purposes.

An example of a hydrogenated compound without any carbon in the molecule is the ammonia, NH₃. This chemical compound can be used as fuel for piston engine as shown in **table 1**. In the same category we can put the ammonium nitrate NH₄NO₃ (AN), the hydrate of hydrazine N₂H₄H₂O - known as a rocket fuel and urea (NH₂)₂CO. As you can see all

these compounds are very rich in nitrogen and hydrogen.

Regarding the latest fuel category, with a powerful inorganic character, this one can be considered like **energetic accumulator**.

3. Researches regarding the use of energetic accumulators to the vehicles propulsion

The ammonia, the ammonium nitrate and urea are compounds with very special properties characterized by high synthesis energy. This synthesis energy is coming from classical energy sources like fossil fuels, atomic power or water energy. The synthesis energy is accumulated in the chemical bonds of the compound. Notice that all the compounds contain nitrogen and hydrogen. These two elements have the most energetic bond in the class of diatomic molecules. The energy values of the chemical bonds from these compounds are presented in Table 2. The ammonia and the ammonium nitrate can be synthesized from the H₂ obtained from water hydrolysis or thermolyses process and the N₂ from the distillation of liquid air at -197°C.

Those compounds accumulate energy in the synthesis process and later this energy is released in the burning chamber of the engine to be transformed into mechanical work. This is why these compounds can be considered as energetic accumulators. They transfer the primary energy in the burning chamber of the engine through the chemical bonds energy [2].

The use of these substances as fuels raises very delicate problems compared to classical fuels.

Table 1. Properties of chemical compounds used as fuel for piston engine

	Hydrogen	Diesel Fuel	Gasoline	Ammonia	Methanol
Calorific Power [kJ/kg]	117.040	42.636	43.054	18.684	21.318
Max. burning temperature [°C]	2750	2400	2600	2500	2700
Boiling temperature [°C]	-252	250-350	110-120	-33	65
Auto ignition temp. [°C]	570-650	260	440	660	500
Vaporization heat [kJ/kg]	451	292	438	1358	1086
Minimum ignition energy [mJ]	0.18	0.30	0.30	9	0.27
Flame speed [cm/s]	300	100	37-100	10-33	50
Octane number (Research)	130	-	91-100	10-35	50
Cetane number	-	35-60	-	7	3-10
Density at 15°C [kg/m ³]	0.0889	0.84	0.73	0.61	0.8
Air /Fuel Ratio (stoichiometric)	0.029	0.068	0.068	0.165	0.160

Table 2. Energy values corresponding to different chemical bounds [2]

Biatomic Molecules	Bond energy [kJ/mol]	Double Covalent Bond	Bond energy [kJ/mol]
H - H	435	C = C	610
O = O	497	C = N	615
N ≡ N	944	C = O	748
Covalent Bond	Bond energy [kJ/mol]	N = N	418
H - C	413	N = O	606
H - N	388	Triple Covalent Bond	Bond energy [kJ/mol]
H - O	463	C ≡ C	836
N - N	163	C ≡ N	890

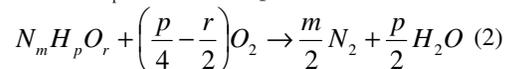
The ammonia is a very common chemical compound for chemical industry in developed economies, but its use in the engine is only in experimental step as a result of its toxicity and transportation problems. The NH_3 is in liquid phase at 170 kPa and normal temperature [3].

The ammonium nitrate is classified along with other compounds, as cellulose nitrate, fulmicoton, trinitro glycerin, as explosives. If the intention is to reduce the reaction speed from "explosive", supersonic speed, to normal burning process, meter per second, it must be done an addition of disperser or neutral compound to reduce the concentration of the active substance resulting the reduction of the reaction speed. The kinetic equation of first degree chemical reaction shows that the reaction rate is proportional with the concentration, C:

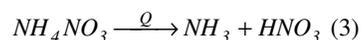
$$-\frac{dC_a}{dt} = k_1 C_a \quad (1)$$

where k_1 is proportionality constant, C_a is the reactant concentration.

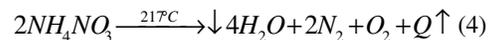
From a thermodynamically point of view, for chemical accumulator it's preferable to use as compounds, hydrogen, nitrogen and carbon dioxide. If we consider the general formula of this virtual fuel been $N_m H_p O_r$, the decomposition reaction will be:



In our specific case, the ammonium nitrate decomposition reaction has two stages. If heated at moderate rate, first the ammonium nitrate is melting. The melting point is at 169°C. After this temperature, if heated, the liquid AN de-composes non-violently following the reaction [3]:



At 217°C or more, the AN de-composes violently with heat and oxygen release:



Because of the release of a big quantity of molecular oxygen, the decomposition process in a burning chamber of an engine is like a chemical supercharging of the engine. The chemical supercharging with nitrogen compound it's known as "NO_x buster" for racecars. In this case the chemical supercharging is done with dinitrogen pentoxide N_2O_5 injected in the burning chamber or in admission.

In our facilities we mixed by volume pure ammonium nitrate water saturated solution, to the normal temperature, with diesel fuel in the following proportion [4]:

Diesel fuel	-----	55%
Pure ammonium nitrate	-----	32.2%
Water	-----	10.8%
Emulsifier	-----	2%

This binary fuel (BF) is injected in the burning chamber of a diesel engine. The physico-chemical process is the following:

- the fuel jet spread in the cylinder is heated, the water from the BF evaporates releasing the ammonium nitrate from the solution;
- the ammonium nitrate as very small particles reaches 217°C and decomposes with heat release, oxygen and atomic nitrogen;

Table 3. Effect of the burning of binary fuel, on engine performance

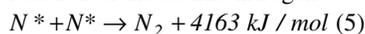
	Engine speed (rev/min)	Power (kW)	Specific diesel fuel cons. (g/kWh)	Specific binary fuel cons. (g/kWh)	Smog emission %	Diesel fuel reduction (kg/h)
DIESEL FUEL	1200	43	272	-	75	-
	1800	48	307	-	87	-
	2300	65	299	-	95	-
BINARY FUEL	1200	43	239	435	14	1.30
	1800	48	217	397	26	4.25
	2300	65	207	370	38	6.10

- the oxygen is oxidizing the diesel fuel particles from the interior of the fuel jet, producing the supercharging effect;

- the heat release perform the general thermal efficiency of the burning process;

- the atomic nitrogen N^* produced by the decomposition of the AN reacts with another N^* following the chemical law stipulating that, always the most probable reaction will be the one consuming or releasing the greater chemical energy. Table 2 shows the energy content of, the triple bond of the nitrogen molecule N_2 being the greatest among the energy bounds evaluated. The energy released in this process of nitrogen atom "fusion", into a nitrogen molecule, increases the total amount of energy released in the oxidation process of binary fuel. **Table 3** shows a summary of the effect of the burning of binary fuel, on engine performance.

Previously, a thermodynamic calculation for the engine fueled with binary fuel has been done [4]. Comparing this data with the experimental data obtained on the research facilities, the results show that the calculus underestimates experimental data. A second round of calculation has been done considering also the thermal energy released by the "fusion" reaction of the atomic nitrogen:



In this case, the calculated data fit almost perfectly to the experimental data, less than 3% difference. This experiment proves the energetic contribution of the atomic nitrogen during the thermodynamic cycle of an engine fueled with binary fuel. The binary fuel is considered as an energetic accumulator and it is the one providing a chemical supercharging of the engine.

4. Conclusion

The use of binary fuel to perform the chemical supercharging has salutary influences on the engine performances. The fuel consumption is reduced by 25-30% without a reduction of engine power. The use of binary fuel drastically reduces the smog and the particulate emission, especially at high speed and load of the engine. This phenomenon is due to a better atomization of the fuel jet in the burning chamber, a complete burning process due to the extra oxygen resulted from the decomposition of the ammonium nitrate.

The real power of the engine is increased with a factor between 15 – 25% and contributes to increase of the maximum speed of the engine possibly due to a better burning process.

This research will be continued in the future in order to better understand the contribution of the nitrogen to the increase of the engine performance.

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