STUDY ON PHYSICO-CHEMICAL PROPERTIES OF ALTERNATIVE FUELS

[1]Anghel Chiru, [1] Sorin Săcăreanu*, Ruxandra-Cristina (Dica) Stanescu

[1]"Transilvania" University of Braşov, Romania

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ABSTRACT - This paper presents aspects regarding the physico-chemical properties of some alternative fuels used for automotive applications. Fossil fuel resources are non-renewable and are mainly responsible for the increasing human related greenhouse gas emissions and consequently for global climate change. This is an incentive for the research and development of modern, efficient and sustainable technologies to produce alternative fuels. Especially in the transport sector, renewable energy resources and technologies are a feasible solution to maintain reliability, and availability for a longer period. Several engines were tested with different alternative fuels and the results regarding the pollution level and properties of the fuels are presented.

INTRODUCTION

Currently, about half of the energy consumption is accomplished by oil. The diminution of current stocks imposes us to analyze, on medium and long term, the possibilities of replacement of this form of energy with others. Some available paths are the use of nuclear and the use of renewable energy.

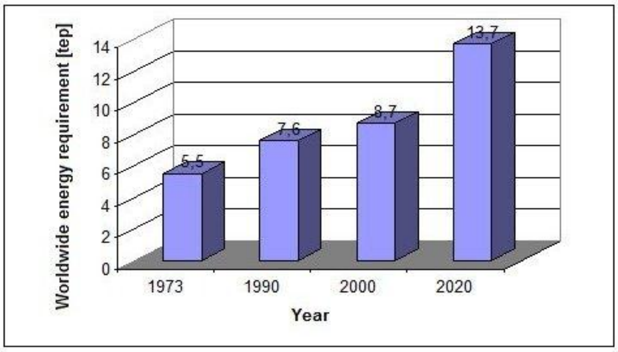


Figure 1 Mondial energy requirements.

For stopping the climate change and reliance on oil, there is a pressing need for the diversification of fuels in the transport sector in general, and for road transport, specifically. As the oil barrel price raises, the production of alternative fuels and the exploitation of the biomass reserves are starting to be a competitive and viable solution. The utilization of biomass, which is almost carbon dioxide neutral, enables the production of a multitude of biofuels that can be used with no or minor modification in actual engines, thus assuring a smooth transition to future technologies such as electric vehicles or fuel-cell.

The word biofuel is used to define all types of liquid and gaseous fuels that are mainly used in the transport sector and are produced from the renewable sources known as biomass. Some of the main advantages, in the view of the sustainable effect, consists in the fact that they are regenerable, so they will never end, they are offering a reduction of the greenhouse gas emissions, they provide regional development, social structure and agriculture, security of supply and new income ways in the agricultural domain. Humanity's primary energy requirements are exceeded many times by the continuous regenerable plants but only a small part of the available biomass can be harvested for energy use due to ecological or technical reasons. However, the amount of energy that could be obtained from biomass resources such as agriculture, forestry and waste is huge. To support the use of alternative fuels, the directive 2003/30/EC plans the target shares of alternative fuels as shown in table 1).

Table 1: EU planned target share of alternative fuels.

	2005	2010	2015	2020
Biofules	2 %	6 %	7 %	8 %
Natural Gas	0 %	2 %	5 %	10 %
Hydrogen	0 %	0 %	2 %	5 %
TOTAL	2 %	8 %	14 %	23 %

Table 2: First generation biofuel and feedstock used for production.

Biofuel type	Specific names	Biomass feed
Bioethanol	Conventional bioethanol	Sugar beet, grains
Vegetable oil	Pure plant oil (PPO)	Oil crops (e.g. rape seed)
Biodiesel	Rapseed methyl ester (RME), fatty acid metyl/ethyl ester (FAME/FAEE)	Oil crops (e.g. rape seed)
Biodiesel	Biodiesel from waste	e.g. frying and animal fat
Biogas	Upgraded biogas	(wet) biomass
Bio-ETBE		Ethanol

Until now, the biofuel production is mainly based on so called “First Generation Biofuels”. The raw material for this type of fuels is represented by food crops such as cereals, sugar beet and cane and oil seeds. The production of this type of biofuels is starting to be questioned due to the possible competition for food and fiber production. A viable alternative to these biofuels represents the biofuels produced from non-food biomass, known as “Second Generation Biofuels”. These new type fuels are using feedstock based on lignocellulosic materials such as straw, bagasse, forest residues and energy crops, including vegetative grasses and short rotation forests. In table 2 and 3 are given the main feedstock and the biofuel derivate of the first and second generation biofuels. The boundaries between first and second generation biofuels are not exactly defined; biogas is currently shifting from first to second generation biofuel.

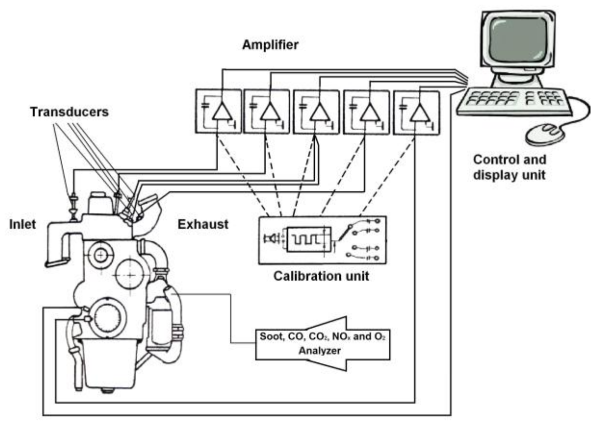
Table 3: Second generation biofuel and the feedstock used for production.

Biofuel type	Specific names	Biomass feedstock
Bioethanol	Cellulosic bioethanol	Lignocellulosic
Synthetic biofuels	Biomass-to-liquids (BtL): Fischer-Tropsch (FT) diesel Biomethylether (DME) Biomethanol SNG (Synthetic Natural Gas) Synthetic (bio)diesel Bio-Methyl-tert.-Butylether (MTBE)	Lignocellulosic
Biodiesel	Hydro-treated Biodiesel	Vegetable oils and animal fat
Biohydrogen		Lignocellulosic

In time, at Transilvania University of Brasov there were some studies and researches made on several engines for usage of natural gas, biogas, LPG, and biodiesel as energetically sources in vehicles engines. The studies had the goal to mark out the limits of the alternative fuels regarding the ecological and energetically performances.

ENGINES PREPARATION AND EQUIPMENT USED

Before starting the studies on the use of alternative fuels (LPG, natural gas, biogas, rape methyl ester) the adaptation and installation of some equipments that allowed fuelling and data acquisition in optimum conditions needed to be made.



Different engine models were use to study the energetically and ecologically performances of some alternative fuels, as well as the behaviour of the engine equipments and systems in the conditions of fuelling with these fuels.
The block scheme of the equipments used in tests is presented in figure 2. The engines were connected on stands with continuous or vortex brakes. The processed information received form the transducers and sensors allowed the interpretation of the engines limits and performances.

Figure 2 – Block scheme of the equipments used in tests.

CHARACTERISTICS OF FUELS USED IN TESTS

Table 4 – Characteristics of the fuels

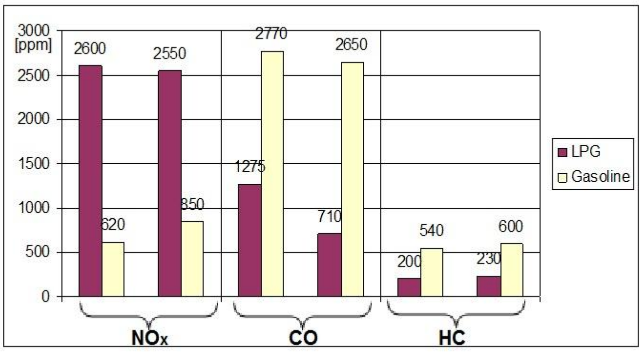
Characteristics / Fuel	Density [kg/m^3]	Lower heating value [MJ/Kg]	RON / MON	CN	Stoichiometric air-fuel ratio [Kg$_{air}$ / Kg$_{fuel}$]	Auto ignition temperature [K]	Chemical composition [kg/kg$_{fuel}$]		
							C	H	O
Gasoline C_4-C_{12}	720-780	44	91-100/ 90-90	-	14.6-14.7	530	85-88	12-15	0-4
Diesel fuel C_8-C_{25}	780-840	43.2	-	45-55	14.5-14.7	589	84-87	13-16	0
LPG Propane (C_3H_8) Butane (C_4H_{10})	510-580	45.8-50.35	95-102/ 89-100	-	12.7	730	82	18	0
Natural gas CH_4 T=273K, p=101,3 KPa	0.73-0.08	40.27-49.64	130/ 120	-	13.87 - 17.09	813	75	25	0
Biogas	0.845	18.64-22.83	115-125/ -	-	16.4	-	10-30	5-15	10-30

A short comparison of the main physical and chemical characteristics of the traditional and alternative fuels used in tests is presented in table 4 and 5.

LIQUEFIED PETROLEUM GAS (LPG)

The chemical composition of LPG depends on its origin. For instance, in Romania, LPG contains 86% propane, 10% butane and 4% pentane and cetane. LPG has a lower heating value (LHV) close to 50 MJ/kg, about 7-8% higher than gasoline or Diesel fuel but on the volumetric basis, the LHV of LPG is about 22-30% lower because it has a lower density compared to gasoline and Diesel. In Europe, the EN 589 standard defines the fuel quality and tests methods for determining the main properties. The octane number of LPG is situated between 95 – 105 RON, depending on its composition. LPG can be used to power two types of spark ignition engines; engines conceived to be fuelled with gasoline and were modified with aftermarket devices that allowed the usage of LPG and engines specially designed to use LPG only. The fuel-supply system must contain a solid tank where LPG is stocked at pressures of 0.7-1 MPa. Tests are made to ensure a resistance to 3 MPa pressure and a 50km/h frontal impact of the vehicle. The fuel is injected in liquid or gas phase in intake valve gate. An ECU controls the injector and also includes a flow regulator. The L25 engine was chosen for studying the performance of the spark ignition engines fuelled with LPG.

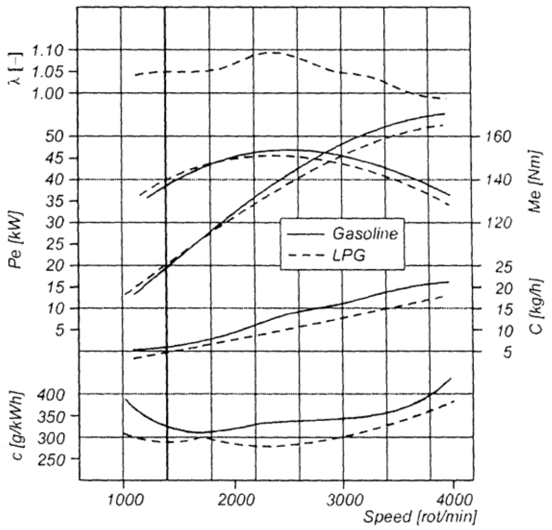
The fuel was stored at the pressure of 1.5 MPa in liquefied state in a special designed tank. The results of the tests, on stand and on the road were promising. As seen in figures 3 and 4, it was noticed that:



-The maximum torque and nominal power are achieved at the same engine speeds as for the gasoline fuelled engine;
-The maximum torque and nominal power are achieved at the same engine speeds as for the gasoline fuelled engine;
-The specific fuel consumption was lowered with 20…34 g/kWh than the case of gasoline fuelled engine;

Figure 3 – Brake and road emissions of the L25 engine.

- At the nominal power point, it was registered a nominal power drop of about 8% with a 17% reduction of the horary fuel consumption. The air/fuel ratio was kept close to the stoichiometric value ($0.99 < \lambda \leq 1.0995$);
- From the figure 3, it can be seen that the CO emissions were lowered with about 55% while the HC emissions dropped 63%; the registered NO_x emissions were much higher in the case of GPL fuelled engine.



To achieve the same torque and power performances, a raise of 0.5… 0.6 units in the compression ratio is necessary for the GPL feed engine. This raise in the compression ratio will be possible due to the fact that LPG has a higher octane number than gasoline

Figure 4 – External characteristic of tested engine.

NATURAL GAS AND BIOMETHANE

Today's road transport is based mainly on liquid fuels and introducing the gaseous fuels in the transport sector is proved to be a challenge but slowly, progress is made. There are around 5 million natural gas vehicles on the roads worldwide and the number is growing. The major automotive manufactures already offer natural gas powered vehicles or dual fueled cars (natural gas and gasoline). One of the promising future options for sustainable transport fuels and the use of gaseous fuels in the transport sector is the replacement of natural gas by biogas (or biomethane as is also known after the purification process). As a biofuel, biomethane has the advantage that it can use various feedstock sources, including wet biomass and organic waste, typically not usable for other biofuels. A typical biomethane production path (figure 5) consists in harvesting the crops, production of biogas and the cleaning step to ensure a 95 – 100 % methane composition, suitable for engine operation. Natural gas and biomethane can be stored on vehicles under two forms:

- Gas, at the environment temperature and the pressure of about 20 MPa.
- Liquefied, at atmospheric pressure and temperature of -161 ºC (112 K).

Due to the higher costs for liquefaction and tanks, the compressed form storage is preferred. The lower heating value, on the mass basis can be 10% higher than gasoline, depending on the methane proportion. Octane number values are about 130 (Research), this providing a higher resistance to autoignition.

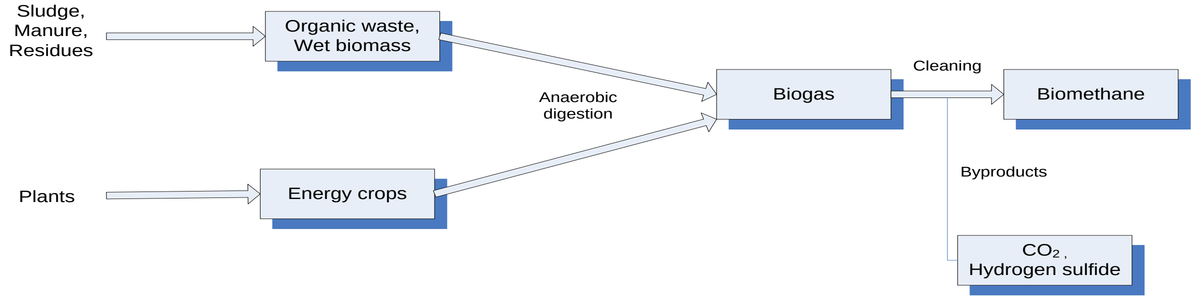


Figure 5 – Biomethane production steps.

Cleaned biogas can be used in all applications that are suitable for natural gas, so, it can be used as fuel for spark ignition engines. An increase of the spark energy is required to ensure a good ignition, around 100 – 110 MJ for the gas, compared to 30 – 40 MJ for gasoline engines. Diesel engines can also be fueled with natural gas/biomethane, but the engine has to be modified for a dual fuel combustion type, with Diesel fuel injection in a prior air-gas mixture.
Having a 50% slower laminar combustion speed than gasoline, natural gas produces a lower combustion noise but it also determines a reduction of the energetically performances. A lower NO_x level is encountered in a gas engine because of the lower cycle maximum temperature, a reduction of about 34-57% for gasoline engines and 80% for Diesel engines. The methane contains only 75 % carbon by mass, towards classical liquid fuels, which have 85 – 88 % carbon. This fact determines a reduction of the CO (44 – 63 %), CO2 (19 – 20%) and HC (52 – 63%) contents from exhaust gases. Natural gas/biomethane represents a suitable fuel for the transport sector especially for the reductions of main pollutants. In the case of biomethane, the reductions in CO_2 are even greater.

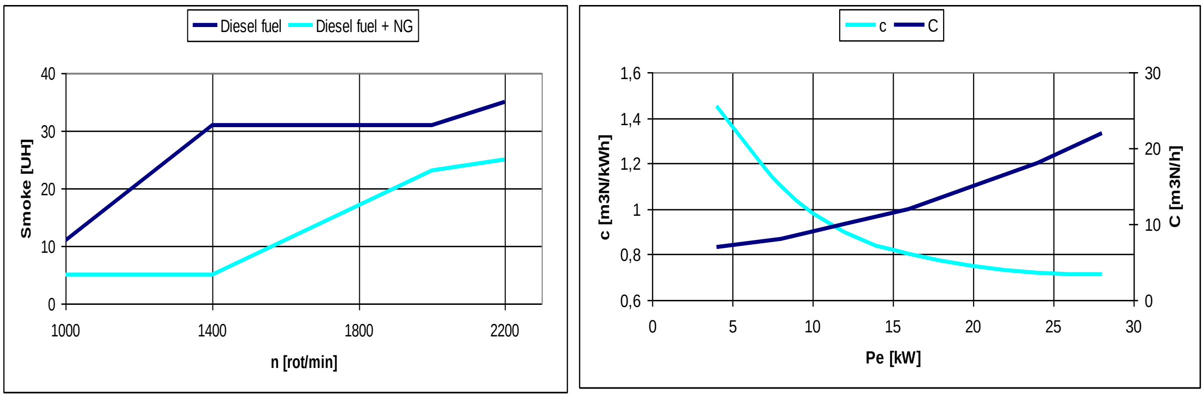


Figure 6 – Variation of smoke and fuel consuption of the natural gas fueled engine.

The fuel supply system includes: the tank, batch meter, reducer, air-fuel ratio flap, a computer for mixture control and the stirring device. In the case of spark ignition engines fueled with gas, because of the higher octane number (130 RON), the compression ratio can be increased up to 13, managing a 10 – 12% increase of the performances. Each kg of methane warms up the earth 23 times more than the same amount of CO_2 when averaged over 100 years. It is estimated that 60% of global methane emissions are coming from human-related activities. Using the methane in a combustion engine instead of wasting it into atmosphere reduces GHG emissions and represents an alternative to fossil liquid fuels. In order to modify a compression ignition engine to work with gaseous fuel and spark-plug mixture ignition, several changes have to be made. A circuit-breaker-distributor must replace the injection pump for avoiding the explosive burning, spark plugs have to replace the injectors and the compression ratio has to be reduced from 18 to 13 for 797-05 engine. Because the air-gas mixture temperature is not high enough to selfignite at the end of the compression stroke, a driving system for the optimum air-gas-Diesel fuel mixture in the combustion chamber has been developed.

According on the engine load characteristics, the gas percent from the mixture is varied between 30 and 60%, with a nominal power reduction of 5 – 10 %. In the case of gas fuelling only, the power reduction is about 20 %. This power loss is mainly because if the reduction in compression ratio with 5 units (from 18 to 13). It was also noticed a reduction in the exhaust gas temperatures with about 25 – 50K. As seen from figure 6, the smoke number drops considerably (about 25 to 70%), mainly at low and medium rpm. When natural gas was switched with biogas, the registered power loss was more severe, about 62% decrease for the same working regime than the case of Diesel fuel. The reason for this is mainly because of the reduction with 5 units in the compression ratio and also because of the poor quality of the biogas. The lower calorific value was only half of the natural gas value. With biogas, the engine works more smooth and silently.

OLEAGINOUS AND FISCHER-TROPSCH BIODIESEL

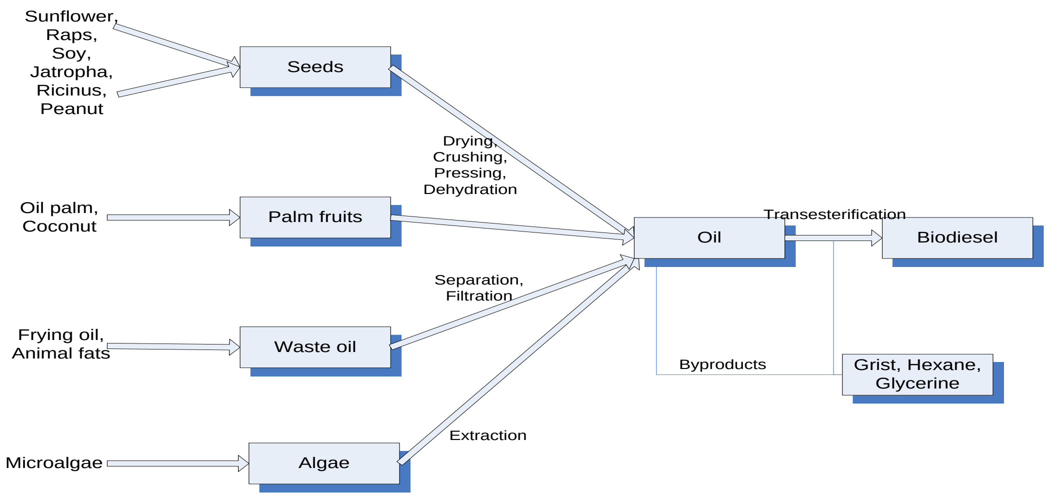


Figure 7 – Feedstock and biodiesel production.

As seen from figure 7, the feedstock for biodiesel production is represented basically by any oleaginous plant, waste oil, animal fats and algae can also be used as a viable feedstock source but the last mentioned feedstock types are not yet commercial. The most common source for biodiesel production is represented by seeds from the oleaginous plants, the choice for choosing a dedicated feedstock is made by climatic, agricultural and production reasons. Biodiesel is fully miscible with fossil diesel at any concentration. The most used blends consist in 5, 20, 30 and 100% biodiesel content and are named B5, B20, B30 and B100. From the material compatibility point of view, rubber and some type of plastic materials need to be changed because of the corrosive action of biodiesel but for blends lower than B20 should have no problems.

The low sulfur content ensures the use in engines with catalysts and the high cetane number of about 60 are influencing a good startability and low noise in operation. Biodiesel has a higher viscosity than fossil diesel and it can not be used below 0ºC without additives.

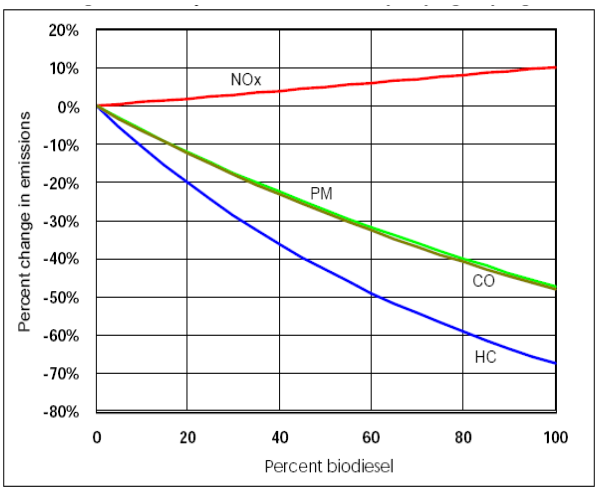


Figure 8 – Impact of biodiesel on heavy-duty engines.

Because of the oxygen content in the molecule of biodiesel, the energy content is 13% less than fossil diesel, leading in a slight power loss in the peak power output of the engine. In the case of the pollutant emissions, a lower level of HC, CO and particles is recorded with a slightly increase in the NO_x level. In 2002, the Environmental Protection Agency (EPA) has released the results of an analysis of the emissions produced by truck fleets fueled by biodiesel. The database contained no engines equipped with EGR systems or PM filters.

The results of the study are presented in figure 8. The experiments conducted in laboratories of the Automotive and Engines Department was made using different blends. The best results were recorded using the B20. The main results are presented in figure 9. The positive relative values are the better ones. The power varies in very small ranges, 1 to 2 %. The CO and HC emissions were reduced up to 60%. The NO_x and smoke emissions of were up to 30%.

In Güssing, Austria, since 2002, a Fast Internal Circulating Fluidized Bed gasification unit with 8 MW (fuel power) developed by the Institute of Chemical Engineering of the Technical University of Vienna (TUV) and AE Energietechnik, is constantly producing H_2 and CO rich syngas. An electric generator burns the gas to produce electricity and any heat recovered there is sent to the town as thermal agent. The feedstock used in the gasification unit consists in woodchips. As an appendix of the biomass-based gasification unit, TUV designed and Fischer-Tropsch (FT) installation for production synthetic diesel fuel.

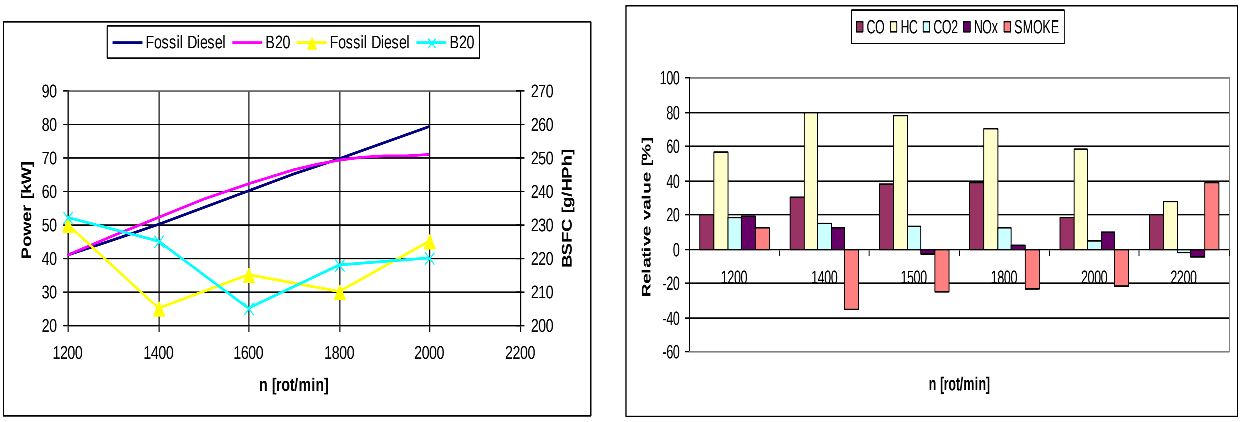


Figure 9 – Engine Power, BSFC and Emissions of B20 fueled engine.

The installation contains steam reformer, a gas cleaning step and synthesis reactor. The main fuel properties are given in table 6 in comparison with rapeseed methyl esters (RME) biodiesel and fossil diesel fuel. FT diesel fuel has a slightly lower density (10%) than fossil diesel and RME that gives it lower energy content on a mass basis. At normal temperatures the viscosity is in the interval of the fossil fuel but the cold filter plunge point is close to 0ºC, for winter time, additives are required. FT diesel has a cetanic number higher than 80 which gives the fuel good autoignition capabilities. This type of fuel can also be mixed with low quality fossil fuel to improve the cetanic number.

Table 5 – Main properties of fossil diesel, FT diesel and RME.

Parameter	Unit	Diesel	FT 1	RME
Density at 15ºC	kg/m³	820-845	775	880
Cetanic number		51	85	62
Flash point	ºC	>55	87	179
Cold filter plunging point	ºC	-26 (winter)	-3	-5
Sulph content	mg/kg	50	9,2	-
Watter content	mg/kg	200	166	85
Viscosity at 40ºC	mm²/s	2,0-4,5	2,3	3 - 6
Ash content	% (m/m)	0,01	0,0009	nc

The low sulphur and ash content helps reducing some pollutant emissions. Further research and engine tests are required to study the energetic performances and HC, CO, CO_2, NO_x and PM level compared with fossil diesel and RME.

CONCLUSIONS

In tests, alternative fuels performed well, proving that they are a viable solution to fossil fuels. In the case of the engine fueled with LPG, after the gas feeding system was mounted, the energetically performances were comparable, with differences lower than 5%.The CO and HC level were lower, however, the NO_x level was higher. For the engine feed with biogas the energetically performances were lower mainly because of the reduction in compression ratio and of the low energy content. A much cleaner biogas with high methane content is required for automotive engine applications. Rapeseed methyl esters are fully interchangeable with fossil diesel. For the same injector type, brake load and engine speed, the ignition delay, peak pressure and heat release rate are very close to the case of fossil diesel. The engines can be converted with minor or no modifications to operate with alternative fuels. The only case of a more complex fueling system was for the dual fuel feeding (diesel and gas). Using alternative fuels, the pollution level can be decreased while the performance levels are still competitive. Further ways of producing alternative fuels can provide new fuels with even better qualities.

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