

II. BIOFUELS AND BIOTECHNOLOGIES

ON THE WAY TO IMPROVE BIO-ETHANOL PRODUCTION FROM WOODEN BIOMASS AS APPROPRIATE ALTERNATIVE FUEL FOR SPARK IGNITION ENGINES

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ПОДОБРЯВАНЕ НА ПРОИЗВОДСТВОТО НА БИОЕТАНОЛ ОТ ДЪРВЕСНА БИОМАСА КАТО ПОДХОДЯЩО АЛТЕРНАТИВНО ГОРИВО ЗА ДВИГАТЕЛИ С ВЪТРЕШНО ГОРЕНЕ

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Abstract: Bio-ethanol has been proved to be a better alternative fuel to SI Engines for reasons concerning classic fuel economy, lower emissions' levels and promising industrial obtaining methods by using chemical and biological means. Bio-ethanol is the main product to be achieved through the fermentation of the sugar-compounds that are themselves obtained from wooden biomass. The primary biomass source comes from a special poplar clones harvested from three different zones of Romania in order to offer a comparison basis in terms of biomass production efficiency. Among all the known industrial fermentation methods of the sweet compounds extracted from biomass, this paper reveals a new and more efficient process given by the enzymatic fermentation.

Keywords: Bio-ethanol, wooden biomass, enzymatic fermentation, efficiency, low emissions.

INTRODUCTION

Bio-fuels have an increasing utilization in the internal combustion engines applications in order to improve the engines economical performances and to limit the levels of the exhaust emissions. Among these new types of fuels, alcohols, especially ethanol and methanol have received recognition of their capacities to replace the use of the classic fossil fuels.

Ethanol has been proved to be an efficient substituting fuel in the spark ignition (SI) engines due to its good miscibility with gasoline and to provide better results concerning the hydrocarbons and CO₂ concentrations from the exhaust gas emissions. Therefore EU market policies encourage the further development of the automotive industry using ethanol-gasoline dual fuelling technologies [1]. Ethanol produced from the biomass extracted from the rapid cycle poplar-clones presents certain benefits in terms of production, environmental protection and fuel properties (high heating value, good miscibility with gasoline, good viscosity and lubrication, high boiling and low freezing temperatures etc).

This paper presents original results based on bio-ethanol obtained through enzymatic fermentation of the sugar compounds extracted from wooden biomass (obtained by bio-hydrolysis using Metha Plus L100 that contains β- glucanases, cellulases and xylanases) which is a new method for bio-ethanol

preparation. This one has been harvested from special poplar clones with rapid growing cycle (coded as Sacrau 79, AF-8 and Turcoaia) coming from three different regions of Romania. The alcoholic fermentation process was achieved by using *Saccharomyces Cerevisiae*. The resulting product is submitted to breakage, azeotropic distillation and physic-chemical characterization for its further mixing with gasoline.

Nowadays, ethanol is the main fuel that should partially replace gasoline in Spark Ignition (SI) engines. Ethanol is a synthetic chemical product but it could be also obtained through biochemical methods from mono-saccharides, oligosaccharides or polysaccharides [2].

Ethanol or ethylic alcohol (CH₃-CH₂-OH) is a transparent, uncoloured, biodegradable liquid with low toxicity and minimal environmental impact. Theoretical combustion of ethanol leads to carbon dioxide and water. As a fuel it has a high octane number and it is used to increase the octane number of the petroleum-based fuels. The mixture ethanol-gasoline proves to increase the engines combustion efficiency and to drop the gas emissions levels (especially hydrocarbons and CO₂).

A well known and used mixture is made out of 10% ethanol and 90% gasoline (E10) to replace as an alternative fuel the classic one [3]. Although SI engines could operate at 100% ethanol, modified

engines use mixtures with maximum 85% ethanol due to the lack of lubricating capacity of the injection system. This problem found its solution by using special fuel additives but with a significant increase of the fuel costs. The limitation of the maximum amount of ethanol in the fuel mixtures is imposed by the lower heating value of ethanol which is 1.6 times lower than the lower heating value of gasoline.

EXPERIMENTAL WORK AND RESULTS

Three sorts of poplar wood flour were used in order to obtain bio-ethanol from lignocellulose raw material:

A-F8, 3-years old Turcoaia and Sacrau-79.

Cellulose degradation was achieved in sulphuric acid medium. The use of a 75% limit of sulphuric acid concentration was imposed because of the carbonization of the raw material. Therefore, two methods were initially proposed and tested for the hydrolysis of wooden raw material.

Chemical method I:

Into a three-necked flask (2 Litter volume) equipped with impeller-type stirrer and descending condenser 250 gm of A-F8 poplar wood flour and 1250 mL solution of H_2SO_4 with 4.5% concentration were introduced (with a 1.03 gm/mL density). The flask was immersed in a thermostatic bath at 50 °C for 24 hours. Then, the final suspension was filtered on G3 sintered glass crucible. The solid residue was reintroduced in the flask and subjected to hydrolysis with 30% concentration H_2SO_4 . 1200 mL of sulphuric acid solution were added in the flask and then immersed in silicone oil bath at 100 °C for 6 hours [3]. Following its cooling, the suspension was filtered and the two obtained solutions were mixed and subjected to neutralization with $Ca(OH)_2$.

Neutralization should be carefully done due to the intensive blooming of the reaction mass. This operation was performed using weak acid pH (6.5) and the solution (1782 mL) was fermented with *Saccharomices cerevisiae* (5 gm) in anaerobic medium. A hydraulic resistance was used in order to remove CO_2 resulted from the fermentation process and to prevent air penetration in the flask. After fermentation, the mixture was subjected to simple distillation and the distillate was collected between 75 and 80 °C (140 mL). This distillate suffered further rectification to obtain 95% purity ethanol.

Due to the small volume of the distillate a Vigreux-type column was used. After the rectification process, a quantity of 70.7 mL (56.5

gm) ethanol was obtained, with a boiling point of 78.15 °C corresponding to a purity of 95%.

Chemical method II:

The lignocellulose raw material suffered a two-step hydrolysis. The first step was achieved with 10% concentration sulphuric acid (with a density of 1.034 gm/mL) at 100 °C for 4 hours. After filtration, the solid product was hydrolyzed with 30% concentrated sulphuric acid at 100 °C for 6 hours [3].

The testing conditions and the test bed components were similar to the first method. The solutions obtained after the two steps were mixed, neutralized with $Ca(OH)_2$ up to a pH value of 6.5 and 2028 mL of fermentation solutions were finally obtained. After fermentation, distillation and rectification there were obtained 65.2 mL of ethanol with 95% concentration.

The other sorts of poplar wood flour were also processed by applying these two methods. The results are presented in Table 1, in which the fourth column, for each of the tested species the percentage is given by the ratio between the ethanol obtained mass (in grams) and 100 grams of used raw wooden material. As following, a third different method in order to proceed to the hydrolysis of the biomass has been applied. This consists in the enzymatic hydrolysis of the lignocellulose.

Enzymatic method:

The poplar clones were pre-treated with weak acid: 10 gm. of biomass were introduced in 100 mL 1% concentration sulphuric acid solution and autoclaved at 121 °C for 30 minutes. Pre-treated biomass was separated by filtration under vacuum and washed with three volumes of water to remove the chemical inhibitors resulted from the pre-treatment process (furfural, hydroxymethyl furfural, acids, salts). The resulted cellulose was also removed as it has an inhibitory effect upon cellulose. There were obtained approximately 7.5-8.5 gm. of substrate after drying at 50 °C for 4 hours. Wood residues that contain approximately 70-80% carbohydrates could be raw materials for glucose and alcohol obtaining.

Enzymatic hydrolysis strongly depends on the pH value. As the pH domain is limited, the pH control is compulsory. The pH value has a tendency to decrease during hydrolysis process.

Direct physical contact between cellulose enzymes and substrate molecules is indispensable for hydrolysis, which is dependent on the chemical nature of the physical structure of cellulose enzymes [4].

Enzymatic hydrolysis is performed with MethaPlus L 100 (β -glucanase, cellulose, xylanase) provided by BIOPRACT GmbH, Germany [5].

Table 1. Bio-ethanol production by applying chemical methods

Method	Produced Bio-Ethanol		
	A-F8		
	mL	gm	%
Chemical I	70.7	56.5	22.6
Chemical II	65.2	52.2	21.28
	3-years Turcoaia		
	mL	gm	%
Chemical I	64.7	51.8	20.72
Chemical II	67.6	54.1	21.64
	Sacrau-79		
	mL	gm	%
Chemical I	65.5	52.4	20.96
Chemical II	73.2	58.6	23.44

The hydrolysis medium contains 1% yeast extract, 2% peptone and 7.5% pre-treated substrate. The nutrients introduced within the hydrolysis environment are used by the yeast extract in the fermentation step. Enzymatic hydrolysis was done in the following conditions: pH of 4.8-5. 55 °C temperature, 220 rpm stirring rate, reaction time of 20 hours. Finally, samples are collected to determine the concentration of the reducing sugars.

Miller method was used to evaluate the concentration of reducing glucides based on 3,5-dinitrosalicilic acid. Reducing sugars reduce 3,5-dinitrosalicilic acid to 3-amino-5-nitrosalicilic acid, which is orange by colorimetric measurements at a wave-length $\lambda=640$ nm.

Fermentation process is performed at 28 °C for 3 days by the inoculation of the hydrolyzed environment with *Saccharomyces cerevisiae* EC1118 yeast.

Table 2. Comparison between bio-ethanol production levels applying all the methods

Method	Bio-ethanol [gm/100 gm of raw mass]		
	A-F8	3-years Turcoaia	Sacrau-79
Enzymatic Method	21	22.3	21.9
Chemical Method I	22.6	20.72	20.96
Chemical Method II	21.28	21.64	23.44

Alcohol was purified by azeotropic distillation and finally it was obtained a product with the following characteristics: uncoloured liquid, 0.789 gm/cm³ density at 20°C, boiling point at 78 °C, miscible with water, refractive index of 1.361, 1.2 mPs viscosity (at 20 °C) [6].

Table 2 shows the comparison between the values of bio-ethanol quantities in grams, obtained when all the three methods are applied starting from 100 grams of raw wooden material.

PRELIMINARY CONCLUSIONS

Enzymatic hydrolysis process of the lignocellulose materials is very complex.

The use of enzymes eliminates the use of polluting chemical products used in chemical hydrolysis. The ethanol amounts obtained by enzymatic method are similar to those obtained by the chemical process.

Although the enzymatic process is more expensive, this method is non-polluting and could become economically viable by further researches.

The products from the enzymatic hydrolysis are not toxic therefore they could be used as animal food or fertilizers.

The produces bio-ethanol proves to have all the requested technical characteristics in order to get used as an alternative fuel in the Spark Ignition engines. All thermodynamic characteristics of the produced bio-ethanol samples could be compared to those listed in Table 3.

FURTHER INTENDED INVESTIGATION

Bio-ethanol proves to be an appropriate mixing compound to form fuel mixtures together with gasoline. Table 3 presents a comparative list of the main physical and thermodynamic properties of bio-ethanol and E85 bio-ethanol-gasoline blend, which gives the maximum mass participation of ethanol in such typical dual mixtures.

In order to perform the combustion of these mixtures inside the cylinder of the SI engine it has been verified their stability given by ethanol miscibility in gasoline, without using any kind of chemical stabilisers.

Low heating values of the mixtures are good enough to preserve engine brake power when switching the engine operation from 100% gasoline to E10 and E15 bio-ethanol-gasoline mixtures especially at part-loads and low speeds operating regimes [7][8].

Table 3. List of main physical properties of bio-ethanol and E85

Characteristic	Bio-ethanol	E85
Equivalent molar weight (kg/kmole)	46,1	–
Carbone (% mass)	52.2	56 – 58
Hydrogen (% mass)	13.1	13 – 14
Oxygen (% mass)	34.8	29 – 30
Water (% mass)	< 6.2	2.9 – 6.6
Phosphorus (ppm)	–	< 0.5
Sulf (ppm)	–	< 30
Density (at 15°C and 1 bar) (g/cm ³)	0.8 – 0.82	0.78 – 0.80
Boliling temperature (°C at 1 bar)	78	49 – 80
Melting temperature (°C)	- 114	–
Autoignition temperature (°C)	423	> 257
Low heating value (MJ/kg)	25 – 27	27 – 29
Octane number	108.6	107
Vaporization specific heat (kJ/kg)	923	836
Specific heat (kJ/kg*K)	2.4	2.3

First, a computer modelling program of describing the air-fuel formation, combustion and heat release from the inside of engine cylinder will be improved. The projected data will help to estimate the real impact of the engine operation when bio-ethanol and gasoline mixtures are used [9].

The laboratory test bed consists in a fully-equipped Dacia-Renault commercial four-cylinder SI engine coupled to an hydraulic dynamometer (see Fig.1). The engine has the following features: 45 kW -maximum power, 4 in line cylinders, 9:1 compression ratio, 5000 rpm maximum speed, 0.95 relative air-fuel ratio at maximum power [10, 11].

The experimental program will consider a relative wide range of engine loads and speeds (0 to 50% load and 850 to 3000 rpm speed), especially those characterising the urban operating regimes. Ethanol substituting rates will be chosen inside the range 0 to maximum 20% [12].

The main objectives will consist in gaining the engine performance by saving classic fuel amounts and overall by measuring a decrease of the CO₂ and hydrocarbons emissions levels.

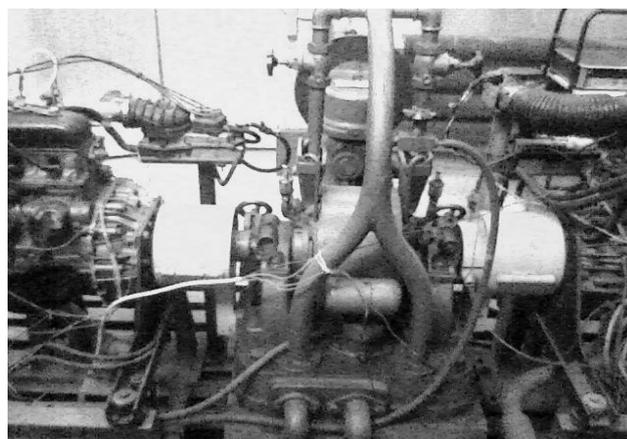


Fig.1. SI Engine equipped test-bed

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