

## Use of blends of gasoline with biomass pyrolysis-oil derived fractions as fuels in an Otto engine

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### ABSTRACT

The objective of this paper is to report our results on the behavior of an Otto engine working with gasoline blended with a fraction rich in esters of carboxylic acids derived from biomass pyrolysis bio-oil, hereby called as "Bioflex". Sugarcane trash undergoes a fast pyrolysis process at the PPR-200 pilot plant to produce the bio-oil at Unicamp (Brazil). The process of separating carboxylic acids from bio-oil, the production of esters from these acids, the process of blending these esters with gasoline as well as the results of the use of this blend in an Otto engine of 4 kW capacity – component of a 2 kW<sub>e</sub> generator – are described. Trial tests determined that it is possible to blend up to 14 vol.% of Bioflex with gasoline type C used in Brazil. The engine performance with this blend compared to the performance of the engine working with pure gasoline resulted in identical power output and fuel consumption. The results showed that it is technically feasible to use blends of carboxylic acid esters derived from the biomass pyrolysis bio-oil with gasoline in conventional Otto engines.

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### Introduction

The transportation sector, the petrochemical industry, and fossil fuel-based power generation are increasing their demand for fuels steadily worldwide. In 2006 oil consumption was 84.6 million barrels per day, and this consumption is expected to rise to 116.6 million barrels per day by 2030 (EIA, 2009). The need for alternative sources of energy to offset the increase in the oil demand and the environmental impact – especially due to CO<sub>2</sub> emissions – caused in part by the growing use of fossil fuels, have triggered intensive research on options for the production and use of alternative fuels, and preferably derived from renewable sources. Biomass residues are an important source of renewable energy to produce liquid fuels.

Many countries worldwide have some important sources of biomass residues. In the case of Brazil, weather and geographical conditions, as well as land availability, have allowed the cultivation of various agricultural crops, such as sugarcane, which generate two important "by-products" in the sugar and alcohol manufacturing process: sugarcane bagasse and sugarcane trash.

The sugarcane bagasse has traditionally been used as fuel, when fed into boilers, to generate steam and power within the sugar and/or

ethanol production facility. However, nowadays sugarcane bagasse is recognized as a material with potential to produce ethanol (by hydrolysis) and other by-products with higher commercial value. Regarding sugarcane trash (tops and leaves), this material shows the potential to substitute sugarcane bagasse in boilers or as feedstock for gasification or pyrolysis. In Brazil, one contributing factor in the search of other uses for sugarcane trash is related to the existence of environmental laws in the State of São Paulo (Brasil, 2002). These laws have incorporated a gradual process to limit flaring as method of cleaning the sugarcane before the harvesting process. Therefore, the search for technologies that could allow the use of sugarcane trash and other by-products of agro-industry to produce energy is generating much attention in Brazil.

Within the thermo-chemical processes applicable to the production of liquid fuels from biomass, fast pyrolysis and gasification, complemented by gas synthesis (Fisher–Tropsch process), are considered technically feasible options (Lineiro and Lamonica, 2005). Through these technologies it is possible to use different types of biomass, including waste generated by some sectors of the agro-industry, to produce liquid fuels. This paper reports the production and use of a fraction of bio-oil obtained from sugarcane trash through fast pyrolysis.

The use of pyrolysis bio-oil as a fuel in gas turbines, diesel engines or boilers to generate steam, has been reported (Czernick and Bridgwater, 2004). However, there are few systems, mostly boilers,

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## Nomenclature

G100 C	Brazilian Gasoline which consists of until 25 vol.% of ethanol, called Gasoline Type C.
G100 A	Pure Gasoline (without ethanol), called Gasoline Type A.
G90–B10	Mixture of 90 vol.% of Gasoline Type C with 10 vol.% of Bioflex.
Bioflex	In this work, we refer to as Bioflex the so called esters of carboxylic acids derived from fast pyrolysis bio-oil, produced at <i>Bioware</i> (Brazil).

which operate at a commercial level using bio-oil as fuel. The possibility of using bio-oil in diesel engines has also been explored (Czernick and Bridgwater, 2004). Nevertheless, the utilization of bio-oil in this type of engines has not reached a commercial scale due to technical problems associated with their use. Some of these problems are described elsewhere (Aubin and Roy, 1990; Ba et al., 2004; Chiamonti, et al., 2003; Chiamonti, et al., 2004; Garcia-Perez et al., 2004; Oasmaa, et al., 2003; Oasmaa and Kuoppala, 2004; Pelaez-Samaniego, et al., 2008; Shiahadeh and Hochgreb, 2000).

Most types of biomass studied show important quantities of carboxylic acids within the pyrolysis bio-oil (Garcia-Perez, 2005). The use of these acids as a fuel additive to petroleum based fuels is reported in this paper, showing the feasibility of running an Otto engine with mixtures of carboxylic acid esters from sugarcane trash pyrolysis bio-oil with gasoline.

Although other bio-oil compounds could be used as fuel additives, we have focused on carboxylic acids. One element contributing to carboxylic acids use is associated with the feasibility of transforming them into esters via the transesterification processes. If the abundance of these compounds within the bio-oil (up to 15% mass of bio-oil) (Bridgwater et al., 2002) is added to this fact, it is noted that the carboxylic acids are the most interesting compounds within pyrolysis bio-oil for use as commercial fuels extenders.

## Experimental

### Raw material used

The sugarcane trash used in this study was obtained from the Equipav Plant, located in Promissão (State of São Paulo). This trash was sun dried and later ground, to reduce the particle size. A 5 mm particle size was the best option for the fast pyrolysis process at PPR-200 pilot plant (See [The PPR-200 Pyrolysis facility at Unicamp](#)). Physical and chemical analyses were conducted on the trash, at the laboratories of the Brazilian Association of Portland Cement (ABCP) in São Paulo (SP), and in the Brazilian Institute of Environment and Renewable Natural Resources (IBAMA) in Brasília (DF). The methods and standards used in the sugarcane trash composition are shown in [Table 1](#).

**Table 1**  
Methods and standards for physical and chemical sugarcane trash analysis.

Property	Method/standard
C, H, N, S	ASTM E777, E778 and E775
Proximate composition	Fixed carbon and volatiles Ash Moisture Content
Particle size distribution	ASTM E872 and E897
Bulk density	ASTM E830 and E1102
High heating value	ASTM E871
Cellulose, hemi-cellulose and lignin content	ASTM D293–93 ASTM E873–82 ASTM E711–87 LPF/IBAMA; TAPPI Standard T203 Om–93 (1996)

### The PPR-200 Pyrolysis facility at Unicamp

The experimental process started with the production of bio-oil using the sugarcane trash as feedstock at the PPR-200 pilot facility built, owned, and operated using technology developed by UNICAMP. The experimental facility at pilot scale is based on the fluidized-bed technology and works with air as a fluidizing agent.

Biomass is fed by a conveyor (1) to the silo (2); the biomass is brought down with help of a biomass dispenser (3) that supplies the material to the screw feeder (4) ([Fig. 1](#)). The screw feeder transports and unloads the biomass inside the fluidized cylindrical reactor's bed (5), where the fluidization of biomass particles occurs, thanks to the oncoming air from the perforated plate (6); thus, the pyrolysis of sugarcane trash occurs.

The byproducts of the pyrolysis process leave the reactor by the top of the pyrolysis reactor and are directed to two mechanical cyclone type separators (7), allowing the retention of the solid part of the pyrolysis products (fine charcoal particles). The fine charcoal particles separated descend to the valves (8) where samples are collected, and then to the charcoal storage drums (9). The non-solid fractions and fine charcoal particles not retained in the mechanical separators move onto a wet separator (10), where a secondary separation occurs. Products not retained in the wet separator reach the bio-oil separator (11).

The cylindrical reactor (200 kg/h capacity) has an internal diameter of 417 mm and internally has an inner coating made of refractory insulation. It uses an inert material bed during its operation. The data acquisition system records and stores the temperature within the reactor by means of 14 thermocouples located along the height of the reactor and at the output of the recovery system. Data tracking includes the removal of charcoal samples in the lower section of the cyclone through the valves as well as samples of bio-oil and acid water in the reservoir of the liquids recovery system.

### Characterization of bio-oil and charcoal

[Table 2](#) shows the standards used in the determination of the bio-oil and the charcoal samples resulting from the sugarcane trash pyrolysis process.

### Biofuel production route

A determined mass of bio-oil is reacted in a sodium bicarbonate solution in a ratio 1:1 by means of constant agitation, with a mechanical shaker. As the reaction occurs, the release of gasses takes place, causing an increase in the total volume of the mixture. The criteria for the total dissolution of bio-oil soluble stage is the disappearance of the gas bubbles in the liquid phase and the change of its pH to a value higher than 7. The low acidity liquid phase is separated by decantation and then it is neutralized by the addition of sulfuric acid, until pH = 2. The process is shown in [Fig. 2](#).

During the neutralization process, a release of gasses and a change in the color of the solution from yellow to black are observed. This acid phase goes through a filtration process and is later mixed with the same amount of ethanol; the mixture is then refluxed and distilled, resulting in a mixture of bioflex-water and distillation waste. The water is removed by further distillation, using ethylene-glycol.

### Preparing gasoline-bioflex blends

Gasoline Type C, which contains up to 25 vol.% of ethanol, is sold in the Brazilian market. Pure gasoline (without ethanol) receives the name of gasoline Type A, which is not available at gas stations. In this study, the possibilities of mixing Bioflex with the two types of gasoline were assessed. An experimental procedure was developed to mix 10 to 50 vol.% of bioflex gasoline blends.

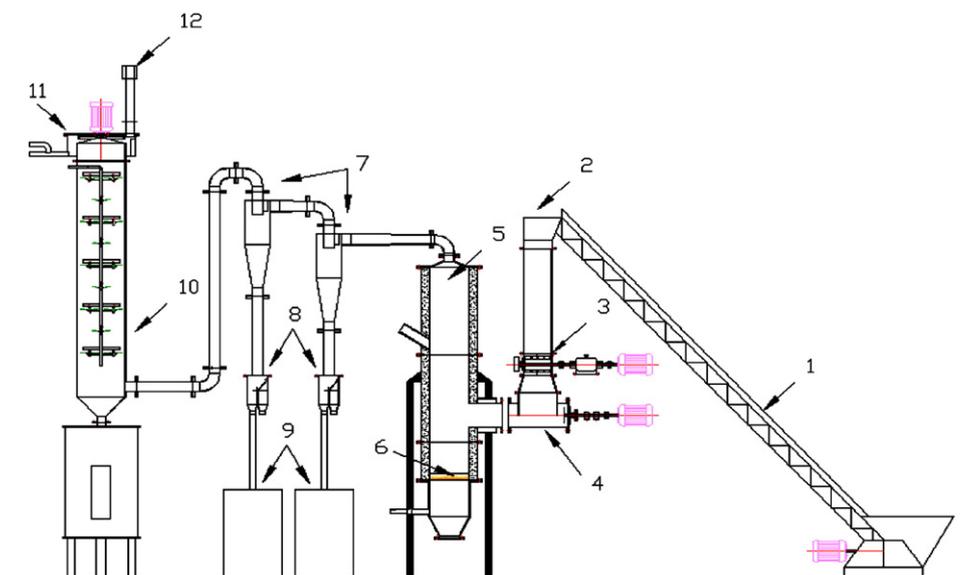


Fig. 1. PPR-200 pyrolysis utility at Unicamp.

During the blending process, special attention was paid in the agitation process, due to the possibility of gas release. The parameter used to halt the agitation was the absence of released gasses itself. This gas release is attributed to chemical reactions occurring during the mixing process.

The composition of the blends was determined by analyzing the properties of the resulting blends. In cases where blends were not complete, the separation of the stages was visible due to the presence of a different color. This allowed to measure the volumes of each fraction and to calculate the percentages of mixed and non-mixed phases.

Finally, the stability of the mixtures in the time was evaluated; this consisted on leaving the flask containing the mixture at rest for up to 45 days. During this period, a separation of the phases was not observed.

#### Installation used to evaluate blends as fuel during power generation

The analysis of the behavior of blends as fuel in an engine was performed in a system that consisted of a generator (supported by an Otto engine) and an electric circuit to use the electricity generated (Fig. 3). Instruments to measure current intensity (A) and tension (V) with a data logger system were installed. Load (energy consumption) was determined by means of a multiple electrical resistance (R), able to vary its capacity from 1000 to 2000 W, in ranges of 200 W.

The evaluation consisted of the determination of the generated power behavior and engine fuel consumption as different loads were

applied to the electricity generator. The fuels used by the Otto engine were: a) gasoline Type A, b) gasoline Type C and c) a G90–B10 blend. A Branco® motor-generator, which characteristics are shown in Table 3, was employed for the test. Minor modifications to the motor-generator fuel supply system were conducted to facilitate measurements of fuel consumption.

## Results and discussion

### Sugarcane trash properties

Some of the properties of the sugarcane trash used in this study are presented in Table 4. The cellulose content is similar to that of sugarcane bagasse; however, the hemicellulose content in the trash is 10% higher than in the sugarcane bagasse. Lignin in trash is also slightly higher than in the sugarcane bagasse (18.26%). The higher content of hemicellulose makes this feedstock ideal for production of acetic acid.

The chemical composition and the higher and lower heating values of the sugarcane trash are indicated on Table 5. The Higher Heating Value (HHV) of sugarcane trash is lower than the HHV of almost all types of wood, as shown elsewhere (Jenkins et al., 1998). The carbon content is similar to that of sugarcane bagasse (Lineiro and Lamónica, 2005), but slightly lower than the C content in the wood (Jenkins et al., 1998). The content of H, N and S is similar to those in sugarcane bagasse (Lineiro and Lamónica, 2005) and wood (Jenkins et al., 1998). However, the sugarcane trash presents high ash content (11.57%). The presence of ash has an impact on the charcoal composition (see Table 8).

The results of the analysis to determine the composition of the sugarcane trash ash are shown in Table 6. The presence of high potassium in ash influences the pyrolysis process because the possibility of mixing ashes with refractory bed. If it occurs, the fusion temperature of bed material becomes lower, with a consequent sinterization problem.

### By-products of sugarcane trash fast pyrolysis

#### Bio-oil

The yield of bio-oil from sugarcane trash was not very high. The highest yield obtained was 25–30 dry mass% of bio-oil. The charcoal

Table 2  
Standards used in the characterization of bio-oil and/or charcoal.

Property	Standard
Density	ASTM E873–82
Water content in bio-oil	Karl Fischer ASTM D1744
Viscosity	ASTM D445–88
Chemical composition	C, H and N S ASTM D5291–92 ASTM D4239
Proximate composition	Fixed carbon Volatility Ash ASTM E870, D5142–90 ASTM D1762–84 ASTM D1762–84, D5142–90

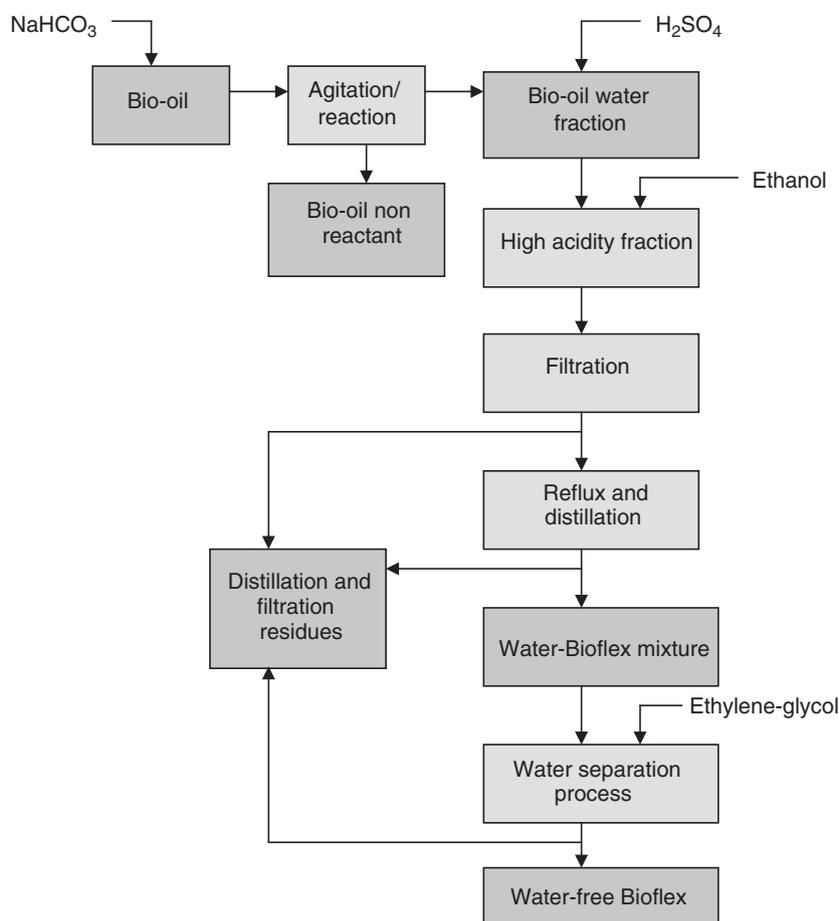


Fig. 2. Path for Bioflex production by means of esterification of high acidity bio-oil fractions with ethanol.

yield was 20 dry mass% and the aqueous phase was around 10 dry mass%. The bio-oil properties are presented in Table 7. It can be seen that the carbon content is slightly lower than in the bio-oil obtained from wood (55 to 58%), the hydrogen content was slightly higher than in the bio-oil from wood (of 5.5 to 7%) (Bridgwater et al., 2002), and there are small amounts of sulfur in the sugarcane trash bio-oil. However, the water content is very low (16.24%), favoring its heating value.

#### Charcoal

The physical and chemical properties of charcoal resulting from the sugarcane trash pyrolysis are shown in Table 8. High ash content and high fixed carbon could influence the direct use of this charcoal as fuel.

#### Properties of fuel blends

The operation of blending bioflex with gasoline type C was possible up to 14 vol.% of bioflex within Gasoline Type C; however, in

the case of Gasoline Type A, only 5 vol.% of bioflex was blended with this type of gasoline. Because the ease of handling constant values, it was decided to assess 10 vol.% bioflex in gasoline Type C (blending G90–B10).

Table 9 shows the fuel properties of gasoline, bioflex and G90–B10 blends used during the tests in the generator. The LHV of bioflex is around 13% higher than LHV of pure ethanol. It is also observed that MON and RON are not affected after blending gasoline type C with bioflex.

#### Results on the operation of the Otto engine

The results of the behavior of the power output of the electric generator in different working conditions, such as different loads and with the three different fuels: gasoline type A (G100 A), gasoline type C (G100 C), and blends G90–B10, are shown in Fig. 4.

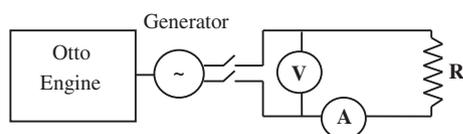


Fig. 3. Scheme of the experimental installation used for measuring the performance of the generator.

Table 3  
BRANCO Motor-generator characteristics.  
Source: Branco (2006).

Type of motor	4 Times, 4 kW
Volume/capacity	163 cm <sup>3</sup>
Compression ratio	8.5/1
Nominal power	4 kW at 3600 rpm
Nominal torque	10.8 N m at 2500 rpm
Theoretical fuel consumption	302 g/(kW h)
Generator	2.0 kVA
Voltage	115 V/230 V, one phase
Frequency	60 Hz

**Table 4**  
Properties of sugarcane trash.

Bulk density	306 kg/m <sup>3</sup>
Particles diameter average	0.62 mm
Cellulose content	41.42 ± 1.08%
Hemicellulose content	32.65 ± 0.24%
Lignin content	22.82 ± 1.63%
Moisture content	50 mass%

**Table 5**  
Chemical composition of sugarcane trash.

Sulfur (S)	Mass%	0.08
Carbon (C)	Mass%	44.7
Hydrogen (H)	Mass%	5.8
Nitrogen (N)	Mass%	0.45
Ash	Mass%	11.57
Volatile matter	Mass%	81.55
Moisture content	Mass%	9.92
Fixed carbon	Mass%	6.90
High Heating Value (HHV)	MJ/kg	17.74
Low Heating Value (LHV)	MJ/kg	16.50

**Table 6**  
Chemical composition of sugarcane trash ash.

Chemical composition	Mass% content
Loss at fire	0.57
Silicon dioxide (SiO <sub>2</sub> )	52.62
Alluminium oxide (Al <sub>2</sub> O <sub>3</sub> )	15.80
Ferric oxide (Fe <sub>2</sub> O <sub>3</sub> )	3.93
Calcium oxide (CaO)	5.76
Magnesium oxide (MgO)	5.27
Sulfur trioxide (SO <sub>3</sub> )	2.73
Sodium oxide (Na <sub>2</sub> O)	0.12
Potassium oxide (K <sub>2</sub> O)	7.80

Statistical analysis showed that the results of Power vs. Load (electrical resistance) are similar for the three fuels. This leads us to believe that there are no significant differences in the values of power generated when commercial fuel used in Brazil (G100 C) is replaced by blends of 90 vol.% of gasoline type C and 10 vol.% of Bioflex.

The results of the evaluation of fuel consumption, in conditions of maximum load (164 Ω) are shown in Fig. 5.

Through statistical analysis it was concluded that the values of fuel consumption in the three cases (three fuels) are similar. This means that there is no significant effect of the type of fuel on a specific consumption of the engine.

**Table 7**  
Chemical composition and Higher and Lower Heating Values of pyrolysis bio-oil obtained from sugarcane trash.

Chemical composition	(S)	Mass%	0.06
	(C)	Mass%	53.95
	(H)	Mass%	7.42
	(N)	Mass%	0.84
Proximate composition	Ash	Mass%	0.48
	Volatiles	Mass%	91.16
	Fixed carbon	Mass%	7.01
Higher Heating Value	(HHV)	MJ/kg	23.12
Lower Heating Value	(LHV)	MJ/kg	21.46
pH	–	–	3.20
Water content	–	Mass%	16.24

**Table 8**  
Chemical composition and Higher and Lower Heating Values of charcoal.

Chemical composition	(S)	Mass%	0.12
	(C)	Mass%	50.90
	(H)	Mass%	2.69
	(N)	Mass%	0.69
	(O) by difference	Mass%	46.29
Proximate composition	Moisture content	Mass%	1.20
	Ash	Mass%	42.86
	Volatiles	Mass%	21.92
	Fixed carbon	Mass%	35.10
Higher Heating Value	(HHV)	MJ/kg	16.42
Lower Heating Value	(LHV)	MJ/kg	15.85

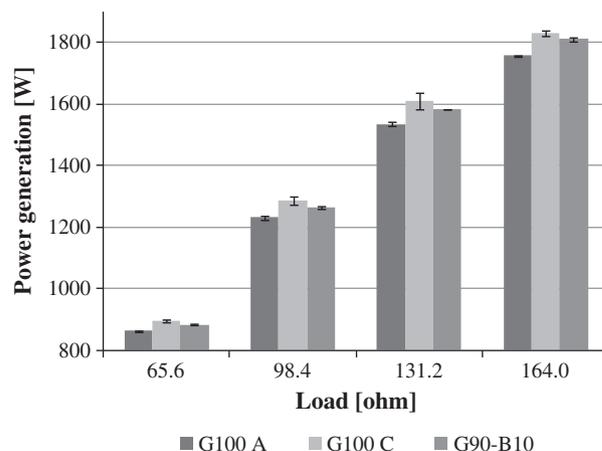
**Table 9**  
Properties of gasoline and gasoline-bioflex mixtures as fuels.

Type of fuel	Lower Heating Value (MJ/kg)	MON (ASTM 2700–01)	RON (ASTM 2699–01)
Gasoline Type A (G100 A)	43.6	–	–
Gasoline Type C (G100 C)	40.1	82.1	95.3
Pure bioflex	30.3	–	–
Blend G90–B10	39.1	83.2	97.6
Ethanol	26.8	–	–

## Conclusion

The results of the tests conducted in the generator indicate that the use of Bioflex – a fraction rich in esters of carboxylic acids derived from biomass pyrolysis bio-oil – as an additive to Brazilian gasoline Type C, in volumes of up to 10%, does not affect the operation of the Otto engine. Power and specific fuel consumption in the generator are statistically similar for gasoline Type A, gasoline Type C, and blends of 10 vol.% of bioflex with gasoline Type C. This result is of interest because carboxylic acids are present in pyrolysis bio-oils regardless of the type of biomass used for bio-oil production.

The great advantage of using bio-oil fractions as gasoline additive lies in the possibility of using different agro-industrial wastes to produce bio-oil through pyrolysis. The geographical and weather conditions of each country can define the type of agro-industry residual biomass for the production of bio-oil. In the case of Brazil, the energy potential of sugarcane trash is huge. This material offers the possibility to produce fuels via fast pyrolysis.



**Fig. 4.** Behavior of the power generated for different load conditions for the three fuels (G100 A, G100 C, and G90–B10).

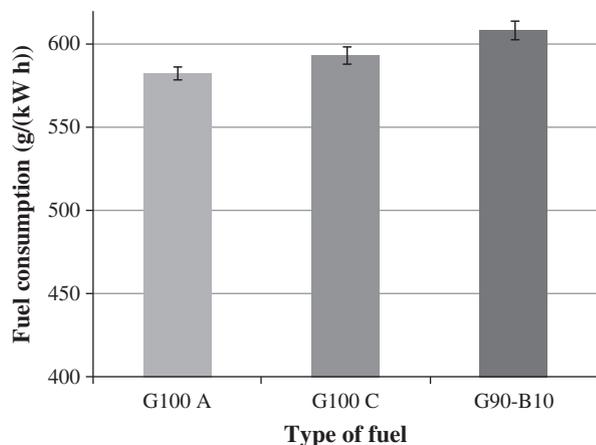


Fig. 5. Engine fuel consumption when the engine operates with the three fuels (G100 A, G100 C and G90-B10) at maximum load.

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