Production of clean energy from agri-food residues

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Received: 21/11/2021 Accepted: 24/06/2022 Published online: 17/07/2022

Abstract

Transportation is one of the sectors that contribute the most to energy consumption and one that depends on the use of fossil fuels. The continuous combustion of fossil fuels generates a significant emission of greenhouse gases into the atmosphere. In recent years, the level of greenhouse gases has increased in the atmosphere; causing global warming. These gases remain harmful to both the environment and human health. This study consists of producing and purifying hydrated bioethanol from agri-food by-products. For that case, after alcoholic fermentation, hydrated bioethanol has been purified according to two methods: fractional distillation and A4 type molecular sieves. Moreover, the characterization of biofuels was carried out using gasolines with addition of 5 and 10% bioethanol. The most relevant parameters studied are: ASTM distillation, density, Reid vapor pressure (RVP), octane number, calorific value, flash point and sulfur content. It has been found that the addition of 10% of ethanol produced from agri-food by products to gasoline leads to the increase of the RON from 98 up to 100. The Sulphur content of gasoline fuels with oxygenates additives blends falls in the range of 0.0023 and 0.0026 wt%.

Keywords: *Agri-food by-products, bioethanol, purification, octane number, sulphur content*

I. Introduction

In recent years, research has increasingly focused on the development of alternative biofuels transportation. The use of byproducts-derived biomass as renewable energy sources remains very promising option compared to fossil fuels which are the main producers of greenhouse gas emissions [1]. Faced with the unavoidable disappearance of petroleum reserves as well as the adverse effect on the ecology related to the increase of a fossil fuel supply, there is a growing interest for advanced renewable energies. Biofuels are a reliable option for the future and can be considered as the base of the sustainable supply in clean and reliable energy and environment friendly.

Currently, the two most prevalent and viable biofuels are bioethanol and biodiesel, both are suitable for use an internal combustion engines, either neat or in blends in any proportion with conventional fuels.

Biodiesel is derived from different sources, and can be produced by the transesterification of vegetable oils, animal fats and even soap stock.

Bioethanol can be produced by the fermentation of a wide variety of feed stocks if they contain sugars, starch or cellulose. The latter includes solid waste of agricultural residues, agro-industrial wastes, liquid waste of food and related industrial wastewater or dedicated energy crops [2, 3]. These raw materials must be available in bulk quantities and their use does not compete with food crops. The agricultural by-products, particularly, lignocellulosic biomass seems more promising feedstock to reach this goal and for producing biofuels. Besides, two feed stocks can be used at the least costly way and in a large-scale: maize in the United States and sugarcane in Brazil.

The choice of raw material depends on its high availability and its chemical and physical properties and the processes that lead to a high percentage of bioethanol in the long term.

Bioethanol production consist of three main steps: hydrolysis of complex sugars into glucose, yeast cells convert glucose into ethanol and carbon dioxide and distillation, biofuels are used in various applications such as: transportation, heating, cooling, manufacturing and electricity sector [4].

This study consists of producing and purifying hydrated bioethanol from expired orange juice provided from New Algerian Cannery of Rouïba (NCA-Rouiba). For that case, after alcoholic fermentation, hydrated bioethanol has been purified according to two methods: fractional distillation and A4 type molecular sieves. The comparison between bioethanol-gasoline blend and the common fuel has been carried out in term of the ASTM distillation, density, RVP, Octane number, sulfur content, flash point.

II. Material and methods

A. Raw materials

The raw material selected in this study is the expired orange juice provided from the New Algerian Cannery of Rouïba (NCA). The plant is located at Rouiba, near of Algiers (Algeria).

This plant is ranked amongst the top ten in term of producing and selling of fruit juices in Algeria and covers up to 90% of national market [5].

The composition of the substrate regarding total sugars, proteins, is depicted in Table 1. It can be seen that the carbohydrates in substrate can reach 110.7 g/L, this substrate seems suitable for bioethanol production. The hydrolysate is stored at 4°C until subsequent use throughout the experimentation period.

Table 1: Composition of expired orange juice.

	Orange juice	
Energy	kcal	46
Total solids	° Brix	14
Carbohydrates	g/L	110.7
Proteins	g/L	1.5
Fats	g/L	0.5

B. Experimental setup and bioethanol fermentations

The bioreactor used for bioethanol fermentations is given in Fig. 1. Experiments have been performed in a cylindrical bioreactor of 0.355 m height and a diameter of 0.15 m, equipped with a double-bladed paddle. Its total volume is 5 litres with an effective volume of 3 L. The mixing was promoted by the double-bladed paddle of 0.13 m of diameter, the impellers separation was about 5 cm and the low impeller was located at a distance about 1/3 above the bottom. The double-bladed paddle rotates at 150 rpm, inducing an axial flow inside the fermenter. The ratio of bioreactor diameter to impeller one was about 1.15. The reactor has been fitted with a jacket of height of 0.165 m. The bioreactor was sealed with the stainless hopper lid including several pipes in order to record different parameters such as the pH, the temperature, the conductivity and the ethanol degree. Fermentations of expired orange juice have been carried out by using the *Saccharomyces cerevisiae* strain VdH2. The experiments have been performed at initial pH adjusted to the value of 4.5 under temperature of 33°C.

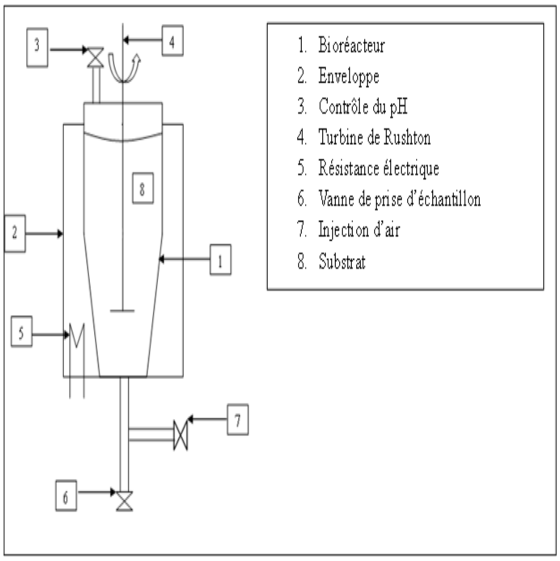

Figure. 1: Experimental setup

C. Molecular sieve bioethanol dehydration

Molecular sieves selected in this study are Alumino-Silicates A4 zeolites crystallized in a way that they form a porous molecular structure with perfectly defined pore diameters (Table 2).

The zeolites are passed through several steps before their use, the first step consist of their drying at 105 °C for 24h, to check that they do not contain moisture, then they were put in a desiccator for 2 hours. The experiments have been carried out during 72h using in a closed tube testing containing 50g molecular sieves with 50ml of bioethanol, the degree of alcohol has been measured using a portable density meter brand DMA35.

Table 2: Zeolites characteristics

.Property	Granules
Nominal pore diameter (Å)	4
Density "non compacted" (kg/m^3)	640
Density (packed) (kg/m^3)	690
Diameter (mm)	1,6
Resistance to fouling (kg)	5
Heat of adsorption (kcal/kg H_2O))	1000
Water capacity at equilibrium (-)	22%
Water content (at packaging) (-)	1.5%

D. Determination of the octane number

Octane number is a parameter that indicates the anti-knock for the fuels to be used in spark ignition vehicles. It provides the ability of fuel to resist knocking during compression and prior to ignition inside the combustion chamber.

The octane number has been measured using the co-operative fuel research (CFR) engine in which the reference fuel is a mixture of iso-octane and n-heptane which will give the same engine performance as could be achieved by the actual fuel sample. Note that iso-octane does not detonate (ON = 100) and n-heptane is very explosive (ON = 0). Thus, if an engine runs with 100% pure iso-octane, the power rating is 100% (knock free) and is defined as an octane number of 100. If the engine is run with n-heptane, a straight chain hydrocarbon, there will be tremendous knocking in the engine and the octane number is taken as zero. If the engine is run with a mixture of isooctane and n-heptane with different proportions, the engine power rating will fall with the decrease in the proportion iso-octane in the fuel [6]. It can be measured as follows:

Gasoline has an ON = X if in this engine it behaves from a detonation point of view like a standard mixture composed of X% by volume of isooctane and (100-X%) of n-heptane.

• Research octane number (RON): represents the anti-knock properties of fuel at low speed (low speed 600 rpm, at a temperature of 25°C);

•Motor Octane Number (MON): represents the anti-knock properties of fuel at high speed (high speed: 900 rpm and high load, at a temperature of 150 °C).

In this study, pure gasoline was blended with 5% and 10% bioethanol and tested on a CFR engine to determine the octane number of the resulting blends (Figure 2).

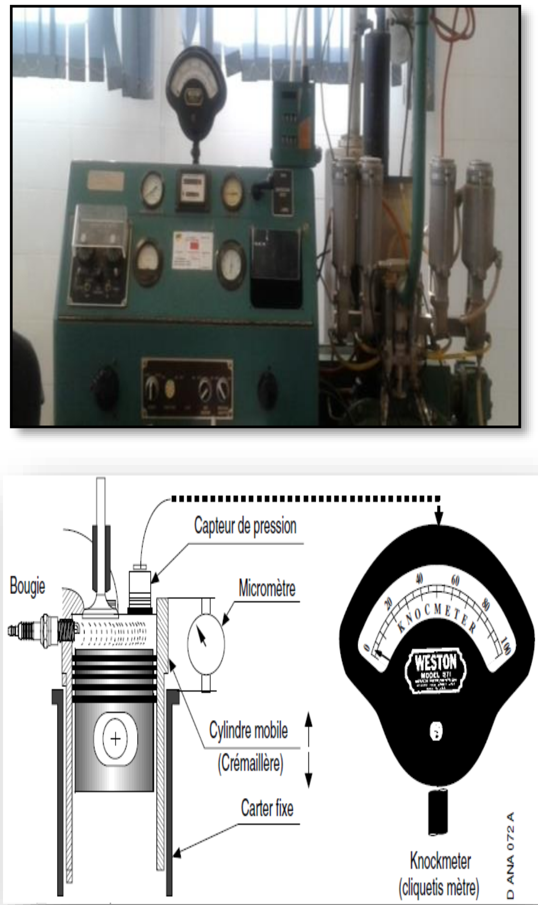

Figure 2: CFR Engine

III. Results and discussion

A. Fermentation of expired orange juice hydrolysate

The profile of total sugars and ethanol production of expired orange juice is given in Fig. 3. It can be seen a fast-total sugars consumption of orange juice substrate during the first hours of fermentation process, leading to a value of 50.88 g/L after 4h, corresponding to the ethanol production of about 13.49 g/L. The ethanol yield per consumption sugar is 0.476 g/g. This bioethanol production can be attributed to the initial amount and uptake of sugars by the yeast growth even though. These findings are lower than that reached by [7] which used the date fruits in the larger fermenter, the value obtained is close to 31 g/L, as well as when using coconut milk, pineapple juice and tuna juice [8]. The agri-food by products, substrate seems as a promising for the *Saccharomyces cerevisiae* strain

VdH2 to convert accumulated sugars into ethanol. To improve the bioethanol production, it is important to use the expired orange juice as co-substrate with lignocellulosic biomass.

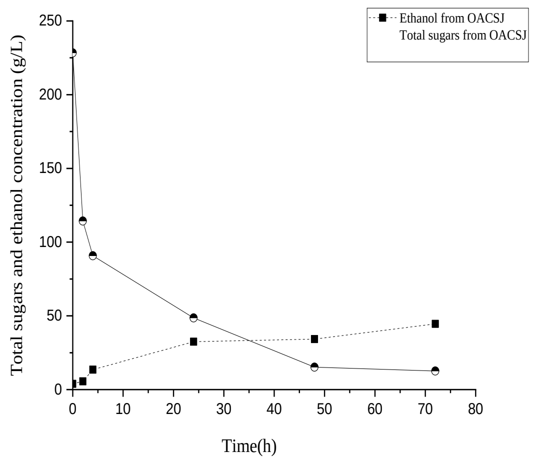

Figure 3: Bioethanol production and total sugars from fermentation of expired orange juice

B. Fractional distillation and bioethanol dehydration

The degree of fermentation of the wort did not exceed 81%, in such case, bioethanol needed to be distilled to concentrate the ethanol to a value greater than 95%, and this allowed blending of bioethanol with conventional fuels. The bioethanol was separated out from the wort in a series of six distillations (including reboiler and condenser) by using a distillation column, this yielded to alcohol level about 95.5. To break the azeotrope and to get in anhydrous ethanol with a better alcohol degree, extraction using cyclohexane solvent (20%) was performed. This solvent was chosen based on previous studies (Viele *et al*., 2013). In such case the alcohol level reached about 96.7

C. Characteristics of biofuel

- *ASTM Distillation curves*

The fuel distillation range can significantly affect the engine performance. It can be separated into different fractions by means of heating, vaporizing, collecting and condensing of the fuel. The test was performed under atmospheric pressure according to the standard ASTM D86 with 100 mL of ethanol-super gasoline.

The rising fuel vapors were collected into a measuring cylinder after their condensate through a coolant. The experimental data are depicted in Figure 4. It can be found that the temperatures increased with the increase of fraction of vaporized mixture with respect to their composition and their boiling points. It can also be found that the addition of ethanol to gasoline up to 10% did not affect the temperature of the vapor.

As the heating of fuels proceeded, more mixtures of hydrocarbon vapors with increasing boiling points were collected whatever the gasoline blends. The boiling temperatures were 49.85 and 47.68 °C, at 10 and 5% bioethanol-gasoline, respectively. The light fractions were easy to spray, which was an important needing for combustion in internal combustion engines.

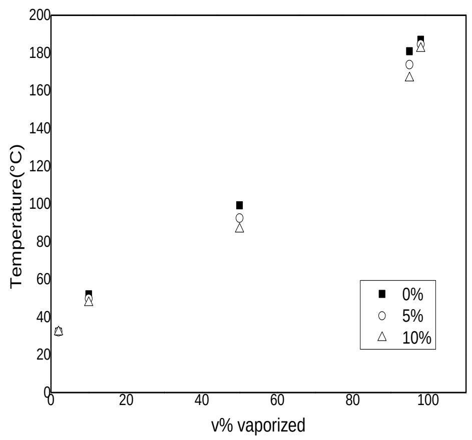

Figure 4: ASTM distillation curves of blends of super gasoline with bioethanol

- *Octane number*

A fuel mixture needs to meet specification for volatility and octane. In fact, both proprieties are most important for gasoline. Octane rating is a unit of measurement established by the automotive industry to determine the antiknock quality of fuels. It is considered as the performance indicator of a gasoline's resistance to auto-ignition and knock during compression in the cylinder of the spark-ignition gasoline engine. Comparison of research octane number of blends with bioethanol and blends without bioethanol is shown in Table 3. It can be seen that gasoline may appeared to have distinct octane ratings when it is mixed with bioethanol from agri food residues. When 5% and 10% of ethanol are added to super gasoline, the RON increased from 95 up to 97.8 and to 100, respectively. In such case, the sulphur content of gasoline fuels with bioethanol blends falls in the range of 0.0023 and 0.0026 wt%.The ethanol from agri food residues with gasoline blends provided higher octane rating. The presence of isoparaffins and alcohol in gasoline fuels enhance the octane level (anti-knock).

Table 3. Biofuel bends characteristics.

Biofuels		Octane number	Density at 15°C	Lower calorific value	Reid vapor pressure	Sulphur content	Copper strip corrosion (3 h at 50 °C)
% v/v		-	(kg/m^3)	(kcal/kg)	(kPa)	Wt %	Rating
ASTM		D 2699	D 1298	-	D 323	D 5453	D 130
	Min	85	725	-	65	-	-
	Max	-	780	-	80	0,05	1b
Super gasoline		95	749.5	8228.6	33	0.0026	1a
Super gasoline +5% ethanol		97.8	750.9	8335.8	37	0.0025	1a
Super gasoline +10% ethanol		100	753.1	8443.6	40	0.0023	1a

IV. Conclusions

This work is based on the production of biofuels from agri-food waste by alcoholic fermentation, and the determination of biofuel blends physicochemical properties. It has been found that expired orange juice is a good raw material for the production of bioethanol due to his high carbohydrates content, it contains about 110.7 g /L.
The light fractions were easy to spray, which was an important needing for combustion in internal combustion engines. At 10% boiling temperature, the temperatures achieved were 49.85 °C (5% bioethanol-gasoline); 47.68 °C (10% bioethanol-gasoline).
Adding 10% ethanol to gasoline increased the octane number of the mixture by around 5; this is an agreement with the standard which requires an octane number greater than 85 for gasolines; and it also reduced the sulphur content from 0.0026% to 0.0023%Our biofuels are low in sulphur content, are not corrosive and can contribute to reduce air pollution.
The incorporation of bioethanol from agri-food by-products into conventional fuels has improved certain physicochemical and combustion properties of the fuel blends.

Abbreviations

ASTM : American Society for testing and materials
RVP : Reid Vapor Pressure
RON : Research Octane Number
NCA-Rouiba : New Algerian Cannery of Rouïba
ON : Octane number
MON : Motor Octane Number

Acknowledgments:

This study was carried out in the laboratory of Transfer Phenomena, USTHB. Our great gratitude to the laboratory of NAFTAL in Dar el Beida where the experiments concerning the incorporation of biofuels into conventional fuels were carried out.

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