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Assessment of Bioethanol Production from Christ Thorn (*Ziziphus Spina Christii*) Fruit's Pulp and Seed

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Abstract

Bioethanol is one of the bioenergy sources with high efficiency and low environmental impacts. In this work, bioethanol was synthesized from Christ thorn fruit's pulp and seed. The proximate compositions of the fruit's pulp and seed were conducted using standard procedure described by the Association of official analytical chemist (AOAC) to estimate the carbohydrate content of both the pulp and the seed. The results indicate that the carbohydrate composition of the pulp and seed were 49.7% and 25.74% respectively. Bioethanol was produced using various substrate levels (2g, 4g, 6g, 8g and 10g) for both the pulp and the seed for a continuous fermentation time of 96 hours. Comparative analysis of the bioethanol yield indicates that the pulp gave higher yield than the seed throughout the fermentation times.

Keywords: *Ziziphus Spina Christii, Bioethanol, Christ Thorn, Fermentation.*

1. Introduction

Increase in world's energy demand and the progressive depletion of oil reserves motivate the search for alternative energy sources, especially those derived from renewable materials such as biomass. The quest for alternative energy necessitated a number of ways from which electricity is produced; including wind farms, hydropower and solar [1]. However, about 40% of the total energy consumption is dedicated to transport which largely require liquid fuel such as gasoline, diesel or kerosene which are all sourced from crude oil. Dependency on crude oil has two major drawbacks: burning fossil fuel contributes to global warming and importing oil creates a dependency on oil producing countries. Also it was estimated that the decline in worldwide crude oil production began before 2010. In addition, it was predicted that annual global oil production would decline from the current 25 billion barrels to approximately 5 billion barrels by 2050 [2]. These concerns generally, pose a serious challenge to both the developed and the developing nations whose economic growths heavily depend on oil, and the consequences of inadequate oil availability could be very severe.

Biofuels are being investigated as potential complement and substitutes for current high pollutant fuel obtained from conventional sources. Biofuels have been used to provide energy since ancient times [3]. Increasing the use of biofuels as means of energy generation purpose is of particular interest nowadays, partly because biofuels provide means of energy security and offer environmentally friendly alternative to convention fossil fuels [4]. One of the candidate of these renewable energy resources is bioethanol. Research has shown that bioethanol is one of the bioenergy resources with high efficiency and low environmental impact [5]. It has been reported that "As an additive ethanol, serves as a fuel volume extender, an oxygenate, net zero carbon emission, biodegradable, an octane rating enhancer and renewable [6].

Bioethanol is manufactured from the fermentation of sugars obtained from biomass. Bioethanol feedstock can contain either sucrose (e.g. sugarcane, sugar beet) or starch (e.g. corn, wheat) or be a lignocellulosic material (e.g.

sugarcane bagasse, wood and straw) [7]. Corn and sugarcane are the feedstock used in the US and in Brazil, respectively, which are the largest ethanol producers in the world [8]. Sugarcane is so far the most efficient raw material for bioethanol production [6].

However, despite the advantages of using bioethanol on environment and as an alternative and complement to petroleum base gasoline, it is also accompanied with challenges. This challenge is the food security. Corn, wheat and other cereals that supposed to be consumed by man is converted to bioethanol. The need to search for other raw materials that is not used as traditional food crop is imperative. Based on the literature available, no previous record on use of *ziziphus spina-christi* in bioethanol synthesis.

In this work we produced bioethanol from Christ thorn (*ziziphus spina-christi*) fruit's pulp and seed; and the proximate analysis of the bioethanol was also conducted.

2. Bioethanol Production from Christ Thorn

2.1 Christ Thorn Fruit

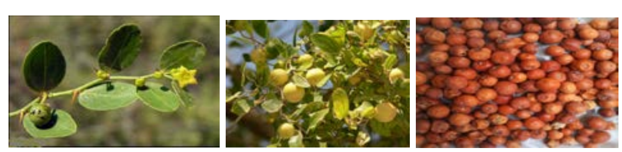
Christ-thorn (*Ziziphus spina-christi*) known as 'magarya' in Hausa language; kuslu in Kanuri language; and 'Sidr' in Arabic language is a member of the Rhamnaceae family.

The plant *Ziziphus spina-christi* is readily distributed in the Sahara and Sahel, from Senegal to the Sudan and Arabia where the annual rainfall is about 50 – 300mm or on periodically inundated sites. It grows in dry conditions and are conspicuously thorny, often the thorns in pairs one being straight and other curved. It has numerous small, sometimes minute teeth like leaves [9].

The genus *Ziziphus* has medicinal importance as all parts of the plant are used by the local Hausa people in north eastern part of Nigeria to help maintain a healthy life style. Christ thorn has been reported to have activity against bacterial and fungal pathogens that are normally quite resistant to modern medications [8]. It is used extensively for the treatment of ulcers, wounds, eye diseases, bronchitis febrifuge, and diuretic and as anti-inflammatory agent for healing skin diseases such as atopic dermatitis. Similarly, different parts of the plant are used for various medicinal purposes among the local populace of northern Nigeria. It is widely reported that majority of the rural population in northern Nigeria use Christ thorn extensively for its medicinal and economic importance [6].

The plant bears edible fruits which is usually consumed when dried. The fruit is brown in colour when dried. In most cases, the large fraction of the fruits are not used but perished. It is expected that if the fruit is assessed as feedstock for biofuel production, it might be economical, since the plant grows in the desert, this may help check desert encroachment and also serve as feedstock for bioethanol synthesis.

Fig. 1 *Ziziphus spina-christi* tree modified from [10]



(a) (b) (c)

Fig. 2 *Ziziphus spina-christi* modified from [10]
(a) Leaves (b) Raw fruit (c) Seeds

2.2 Bioethanol

Ethanol is a member of a group of organic chemicals called alcohols. Ethanol has the chemical formula of CH_3CH_2OH, with the -OH (hydroxyl group) being the functional group. Because of the presence of the --OH hydrogen bonding is quite common. Ethanol is a primary alcohol since the hydroxyl group is attached to a carbon atom which is itself attached to only one other carbon atom. Ethanol is a clear, colourless liquid with a characteristic sweet smell; melts at –114.1°C, boils at 78.5°C, and has a density of 0.789 g/ml at 20°C [11]. The low freezing point has made it useful as the fluid in thermometers for temperatures below –40°C, the freezing point of mercury, and for other low-temperature purposes, such as for antifreeze in automobile radiators.

Ethanol burns with a clear, soot free flame and is often used as a fuel for portable stoves. Complete combustion yields carbon dioxide and water. When reacted with sodium, ethanol produces hydrogen gas and sodium ethoxide (CH_3CH_2ONa). Ethanol can be chemically oxidized using a mixture of concentrated sulphuric acid and sodium dichromate to produce the aldehyde, ethanol (also called acetaldehyde). Further oxidation yields ethanoic acid (also called acetic acid) and carboxylic acid. Ethanol is completely miscible with water existing as a constant boiling mixture of 95.6% ethanol and 4.4% water [12].

3. Methodology

3.1 Determination of the proximate composition of *ziziphus spina Christi* fruit.

Proximate analysis was conducted to determine dry matter, crude protein, crude fibre, ether extract or fat, ash, carbohydrates and nitrogen free extract (NFE) according to the method described by Association of official analytical chemist (AOAC) [13] for both the pulp and the seed of the fruit.

3.2 Sample preparation.

Post-harvest Christ thorn fruit and seed were taken and sun dried to remove the moisture present. The dried pulp and seed were milled to fine grained particles. The powdered sample was autoclaved to eliminate any unwanted micro-organisms present before undergoing acid hydrolysis. For both pulp and seed, 2g, 4g, 6g, 8g and 10g samples were weighed and placed in different conical flasks which were labelled accordingly. Each of the prepared samples was hydrolyzed in 50ml of 0.1M dilute sulphuric acid and allowed to soak in the acid solution for 1 h, there after washed in distilled water and filtered for fermentation.

3.3 Culture media preparation.

A100ml of culture media was prepared, the following formulation was adopted; 3g of peptone (bacteria peptone), 0.2g of potassium chloride, 0.1g of magnesium sulphate, 0.25g of sodium chloride, 0.25g of sodium trioxonitrate (Na_2NO_3) and 20g of glucose were added to 50ml of distilled water and the mixture was agitated thoroughly. More distilled water was added to bring the media solution to 100ml. To the 100ml media solution, 0.5g of yeast (*Saccharomyces cerevisiae*) was added, covered and then placed in a shaking incubator.

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3.4 Fermentation procedure.

The pH of the five (5) autoclaved and hydrolyzed samples were adjusted between 5.0-5.5. To each sample 10 ml of the cultured media was pipetted and added. Thereafter the samples were properly covered with cotton plugs and placed in a shaking incubator for the fermentation process. The concentration and the pH of bioethanol produced in the course of fermentation were measured at 24 hours interval for 96 hours using a UV spectrophotometer and pH meter respectively. After 96 hours when there is no appreciable increase in bioethanol production, the samples were removed and filtered for distillation. The final product was distilled at temperature range of 60-80^{o}C. The distillate was analyzed to determine the physical and chemical properties of the ethanol.

4. Results and Discussion

4.1 Determination of the proximate composition of *ziziphus spina Christi* fruit.

Results obtained for the proximate analysis of the Christ thorn pulp and seed are presented in Tables 1 and 2 respectively.

It could be seen that the Christ thorn's pulp nearly doubles its seed in carbohydrate and ash contents. However, the seed is about 30% higher in the crude protein, crude fibre and fat contents compared to the pulp.

Table 1: Christ Thorn Pulp Composition

CRUDE PROTEIN (WT %)	FAT (WT %)	CRUDE FIBRE (WT %)	ASH (WT %)	CARBO-HYDRATE (WT %)
21.0	10.	17.0	2.0	49.7

Table 2: Christ Thorn Seed Composition

CRUDE PROTEIN (WT %)	FAT (WT %)	CRUDE FIBRE (WT %)	ASH (WT %)	CARBO-HYDRATE (WT %)
29.7	15.0	25.0	1.0	25.7

4.2 Analysis of the bioethanol concentration for various substrate levels.

Table 3 through Table 9 present the concentration of the synthesized bioethanol for various samples of the Christ thorn seed and pulp at different fermentation times.

Table 3: Bioethanol concentration for Christ thorn pulp after 24 hours

Mass of sample (g)	pH	Absorbance	Concentration (10^{-3}mmol/l)
2	5.2	1.672	1.300
4	5.3	1.303	1.280
6	5.0	1.694	1.233
8	5.2	1.593	1.248
10	5.0	1.328	1.325

Table 3: Bioethanol concentration for Christ thorn pulp after 48 hours

Mass of sample (g)	pH	Absorbance	Concentration (10^{-3}mmol/l)
2	4.2	1.798	1.588
4	4.6	1.443	1.603
6	4.7	1.136	1.553
8	4.5	1.065	1.444
10	4.8	1.726	1.466

Table 4: Bioethanol concentration for Christ thorn pulp after 72 hours

Mass of sample (g)	pH	Absorbance	Concentration (10^{-3}mmol/l)
2	3.8	1.950	1.790
4	3.6	1.037	1.800
6	3.5	1.435	1.775
8	3.5	1.198	1.705
10	3.6	1.198	1.677

Table 5: Bioethanol concentration for Christ thorn pulp after 96 hours

Mass of	pH	Absorbance	Concentration

sample (g)			(10^{-3}mmol/l)
A2	3.0	1.966	1.999
4	3.1	1.983	1.999
6	3.2	1.995	1.980
8	3.3	1.978	1.930
10	3.0	1.945	1.890

Table 6: Bioethanol concentration for Christ thorn seed after 24 hours

Mass of sample (g)	pH	Absorbance	Concentration (10^{-3}mmol/l)
2	5.0	1.448	1.200
4	5.0	1.600	1.280
6	5.2	1.310	1.106
8	4.9	1.316	1.042
10	5.1	1.525	1.525

Table 7: Bioethanol concentration for Christ thorn seed after 48 hours

Mass of sample (g)	pH	Absorbance	Concentration (10^{-3}mmol/l)
2	5.0	1.521	1.445
4	5.0	1.316	1.443
6	5.2	1.745	1.436
8	4.9	1.542	1.305
10	5.1	1.872	1.355

Table 8: Bioethanol concentration for Christ thorn seed after 72 hours

Mass of sample (g)	pH	Absorbance	Concentration (10^{-3}mmol/l)
2	4.4	1.651	1.688
4	4.0	1.746	1.643
6	4.2	1.726	1.700
8	4.0	1.528	1.605
10	3.9	1.733	1.580

Table 9: Bioethanol concentration for Christ thorn seed after 96 hours

Mass of sample (g)	pH	Absorbance	Concentration (10^{-3}mmol/l)
2	3.2	1.198	1.888
4	3.4	1.600	1.860
6	3.2	1.310	1.890
8	3.1	1.316	1.988
10	3.1	1.525	1.794

4.3 Bioethanol Concentration as function of fermentation times

The concentration of bioethanol derived from the fermentation of the acid hydrolyzed Christ thorn seed and pulp starch was found to increase steadily with fermentation times. This implies that that the sugar is being fermented by the activity of the selected enzyme (yeast; *saccharomyces cerevisae*). The trends show that the bioethanol concentration for all the substrates levels considered was lowest in the first 24 hours and highest after 96 hours of fermentation. Figures 3 through 7 illustrate the variation of bioethanol concentration with fermentation times for the selected masses of substrate for both seed and pulp.

In all the fermentation runs, it could be observed that the Christ thorn's pulp consistently gave higher bioethanol yield compared to the seed ranging from about 2% to nearly 20% higher across all the considered substrate levels considered in this work. This trend is consistent with the compositional analysis that shows higher carbohydrate content observed in the pulp relative to the seed discussed earlier.

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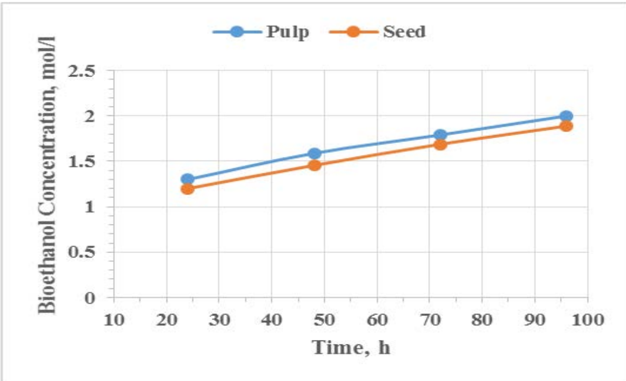

Fig. 3 Concentration of bioethanol with time for 2g substrate samples of pulp and seed

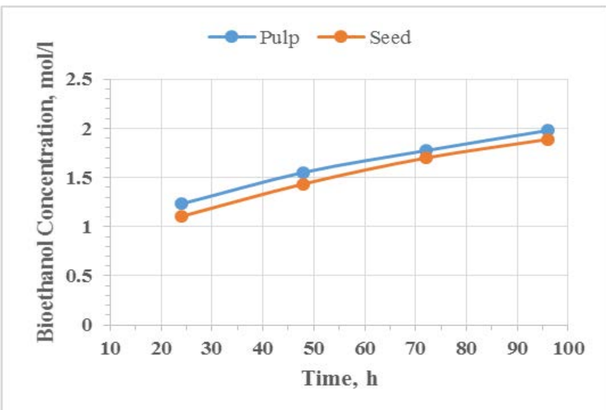

Fig. 4 Concentration of bioethanol with time for 4g substrate samples of pulp and seed

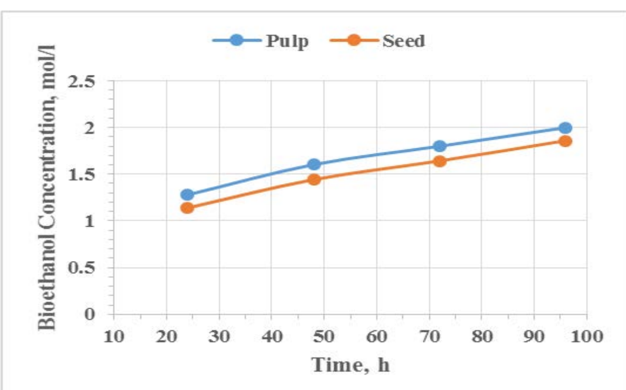

Fig. 5 Concentration of bioethanol with time for 6g substrate samples of pulp and seed

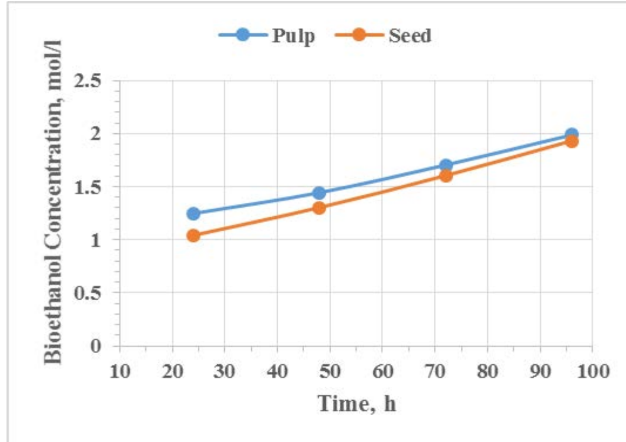

Fig. 6 Concentration of bioethanol with time for 8g substrate samples of pulp and seed

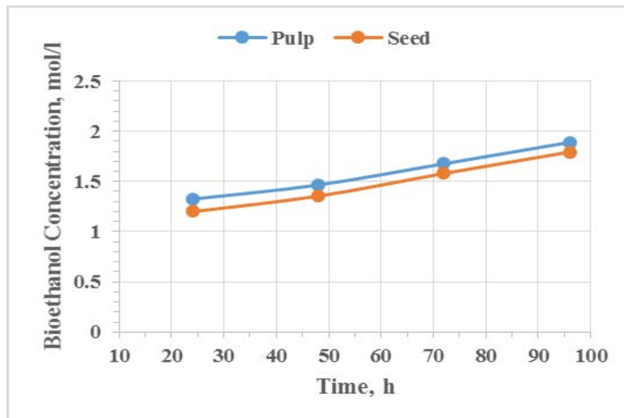

Fig. 7 Concentration of bioethanol with time for 10g substrate samples of pulp and seed

4.4 Volumetric Measure of Bioethanol of Christ Thorn Pulp and Seed

Here we have compared the volumetric quantities of bioethanol produced for various substrates levels investigated in this work as shown in Figure 8.
Again, as expected, the Christ thorn's pulp gave about 25% higher volumes of bioethanol compared to the seed for all substrate levels.

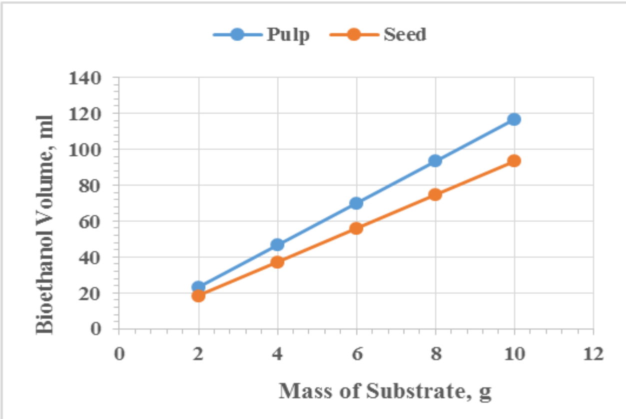

Fig. 8 Volume of bioethanol collected with time for various masses of substrate for both pulp and seed

4.5 Some Determined Properties of the Bioethanol Synthesized from Christ Thorn's Pulp and Seed

We have compared some selected pysico-chemical properties of the bioethanol produced in this work to the previous work as presented in Table 10. We have observed that both the flash point and the specific gravity are higher than respective values that were reported in previous works. This differences could be attributed to the fact that the bioethanol produced contains some higher amount of water (about 30%) compared to that reported in previous work (about 20%).

Table 10: Properties of bioethanol produced Christ thorn's pulp and seed

Property	This work	Literature
Boiling point (^oC)	70	78.4 [12]
Flash point (^oC)	20	19.2 [13]
Specific gravity	0.821	0.7890 [14]

5. Conclusions

The result presented in this work showed that both the pulp and seed of Christ thorn have reasonable amount of carbohydrate 49.7% and 25.7% respectively which can be hydrolysed for fermentation to produce bioethanol.

After bioethanol synthesis it was demonstrated that the pulp maintained consistently about higher bioethanol yield relative to the seed for all fermentation times. The volume of bioethanol distilled from all the fermented substrate samples showed that the pulp gave about 25% more volume of bioethanol compared to the .

The determined properties of the bioethanol synthesized; specific gravity, flash point and boiling point agree well with those reported in the previous works.

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