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PROXIMATE ANALYSIS, CONCENTRATION OF HEAVY METALS AND THERMODYNAMIC OF OIL EXTRACTION FROM *COCO NUCIFERA*

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ABSTRACT: The proximate analysis, concentration of heavy metal and thermodynamic of oil extraction from *coco nucifera* using ethanol and n-hexane has been studied. The proximate, heavy metals and thermodynamic properties determined were ash, moisture, crude lipid, crude protein, crude fibre, carbohydrate, sodium, magnesium, potassium, calcium, iron, zinc, enthalpy, entropy and gibbs free energy. The nutritional value obtained were 0.76, 8.43, 47.18, 11. 63, 5.94 and 26.06% for ash, moisture content, crude lipid, crude protein, crude fibre and carbohydrate respectively. Sodium and Magnesium demonstrated the least concentration whereas, Potassium showed the highest concentration in the coconut oil. The thermodynamic parameters obtained at 363K for ethanol and n-hexane are Enthalpy (2.206 and 1.44KJ), Entropy (33.538 and 23.209J/K) and Gibbs free energy (-9.967 and -6.984KJ) respectively. The positive value of the system entropy indicates that the system is disordered and the reaction is irreversible. The negative values of the Gibb's free energy confirm the spontaneity of the reaction, while the positive value of enthalpy implies that the reaction is endothermic.

Keywords: *Coconut oil, Solvent. Coco nucifera, Proximate Analysis ,Heavy metals Thermodynamics.*

INTRODUCTION

The major source of triglyceride is usually vegetable fat and oil, whose provenance is usually plants. At ambient temperature, fats are solids whereas oils are liquids. Fats and oils may have similar compositions, but chemically, their constituents differ because fat is always triglyceride of a saturated fatty acid while oil is often the triglyceride of unsaturated fatty acid (Belsare and Badne, 2017). Oils and fats are imperative constituents of human diet. They basically serve as food or ingredient in human food products. They contain some fat soluble vitamins (FSV) and are rich in caloric value and dietary energy (FSSAI, 2015).

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Coconut fruit (*coco nucifera*) which is generally grown extensively and being utilized as nut and food in the world, is an important source of oils and fats (Obasi *et al.,* 2012). The calorific value and nutritive value of coco nut seeds makes it a good source of oils and fats, hence they are regarded as one of the most paramount fruit of all palms (Onifade and Jeff-Agboola 2003; Odoemelam, 2005; Akubugwo *et al*., 2008).

Several products can be obtained from coconut fruits and this makes it commercially viable (Kyari, 2008). Coconut oils are quite stable and rarely becomes rancid. They do not require high temperature treatment during processing and extraction process. The consumption of coconut oils decreases the Low Density Lipoprotein (LDL) level in the human body, hence reducing the risk of heart disease in humans (Padmini *et al.,* 2014). Most vegetable oil are capable of undergoing rancidity . Rancidity entails oxidation of oil, whether incomplete or complete oxidation. It denotes oil hydrolysis upon exposure to air. It is primarily classified into three, which are microbial rancidity (involving microbial actions and activities in break down of fat), oxidative rancidity and hydrolytic rancidity. Hydrolytic rancidity occurs when triglycerides hydrolyzes causing the release of free fatty acid, hence resulting to foul odour (Sergey, 2014). In other to minimize these effects, there is need for effective and proper extraction of oils from coconut. Coconut oil are quite stable and rarely become rancid. Furthermore, coconut oil does not require high temperature treatment and its branches and leaves are not destroyed during the harvest. Generally, thermodynamic consideration of an oil extraction process are necessary to ascertain whether the process is spontaneous or not This study will help to provide a more eco-friendly vegetable oil which is less toxic to human. Coconut oil has been tested for use as an industrial feedstock for biodiesel used in diesel engine as fuel. This paper aims at determining the thermodynamic effects and the proximate analysis (nutritional value) and thermodynamic of coconut oils extracted from coconut fruits using ethanol and n-hexane.

MATERIALS AND METHODS

Sample Collection and Preparation

All the reagents used were of BDH analaR grade and all the glassware and sample bottles were cleaned

Matured coconut fruits were duly harvested from the trees. The fruits were preserved for 3 weeks and thereafter, their husks were adequately detached from their shells. The shells were carefully removed from their endocarps (edible and fleshy part). These coconut fleshy and edible parts were cut, sliced into pieces and were oven dried at 57 to 67^oC for period of 96 hours. The dried coconuts were subsequently ground and wrapped in a Whatman filter paper. They were then subjected to oil extraction process using n-hexane and ethanol by a means of soxhlet extraction.

Oil Extraction Process from the Coconut Fruits

The analysis was carried out by measuring a known amount of the ground coconut fruit, which was wrapped in a filter paper and was carefully dropped in a soxhlet extractor joined with a round bottom flask (1000ml capacity). Ethanol (500ml) was gradually poured into the flask prior to soxhlet extractor attachment. The flask was placed on top of a heating mantle with a thermostat for temperature regulation. The extraction was carried out at 60mins and at different temperatures (60, 70, 80 and 90^oC). The coconut oil was separated from the solvent by a means of rotary evaporator. The process was repeated using n-hexane as solvent for coconut oil extraction.

Ash content determination

GSJ: Volume 7, Issue 12, December 2019
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A measured amount (5g) of coconut oil sample was poured in a crucible of known weight. Thereafter the crucible was placed in a furnace at 730^oC for a period of 65mins. The initial weight of the crucible was subtracted from the new weight, which gave rise to the ash content of the coconut oil.

Moisture content determination

In the moisture content determination, 10g of coconut oil was poured in a dish of known weight. The dish was placed in an oven at temperature of 104^oC for 55mins. The dish was removed from the oven and placed in desiccators for cooling. Thereafter the new weight of the dish and the coconut oil were calculated and the values were used for moisture content determination.

Crude Protein Determination

A measured volume (3 ml) of the coconut oil sample was into a flask which was subjected to heating for 33 min after the addition of paraffin wax to reduce foaming of the sample. The mixture was cooled and 90 ml of distilled water was added to it. 25 ml of sodium sulphate was further added and adequately stirred. 40 percent sodium hydroxide solution (80 ml) was added to the mixture and the flask was subsequently subjected to distillation unit for heating. Thereafter some distillate (50ml) was collected and ammonia solution (50ml) was added to it. The solution was further titrated using solution of hydrochloric acid. The values were then used for calculation of percentage crude protein.

Crude Lipid Determination

A measured amount (4g) of coconut oil was weighed into an extraction flask of known weight. Petroleum ether (3ml) was added to it and the mixture was heated adequately with constant refluxing. The petroleum ether was evaporated by distillation and the flask was weighed.

Heavy Metal Determination

The sample was digested with H_2S0_4 and then transferred into cleaned plastic container for AAS analyses. The digested samples were analysed using Perkin Elmer Atomic Absorption Spectrophotometer model number Buck Scientific 210 The heavy metal contents of the extracted coconut oils were determined.

RESULTS AND DISCUSSION

Table 1: Proximate analysis of the coconut oil

S/N	Nutritional Value	Amount (%)
1	Ash	0.76
2	Moisture content	8.43
3	Crude Lipid	47.18
4	Crude Protein	11.63
5	Crude Fibre	5.94

GSJ: Volume 7, Issue 12, December 2019
ISSN 2320-9186

6	Carbohydrate (CHO)	26.06

Table 2: Metal concentrations of the extracted coconut oil

S/N	Metals	Coconut oil extracted with ethanol	Coconut oil extracted with n-hexane
1	Sodium (mg/Kg)	2.5308	1.70151
2	Magnesium (mg/Kg)	1.02485	1.75216
3	Potassium (mg/Kg)	8.48952	6.25510
4	Calcium (mg/Kg)	4.38192	4.02102
5	Iron (mg/Kg)	5.86052	5.38219
6	Zinc (mg/Kg)	3.51725	1.83252

The result of the ash content analysis is presented in table 1. The result revealed that the coconut oil ash content is given as 0.76 %. The ash content of the oil entails the inorganic residues present in the coconut oil, often determined after complete oxidation of organic matters in the oil. Ash content determination is one of the proximate analyses usually carried out on oil when evaluating its nutritional value. It is a measure of all mineral present in the coconut oil (Baraem, 2017). The low amount of the ash content in the coconut oil implies that a small amount of mineral matter is present in the coconut oil. Similar observation was also reported by Probir *et al*., 2014).

The result of the moisture content analysis showed that the coconut oil moisture content is given as 8.43 %. The mount of moisture in coconut oil often vary depending on the moisture content present in the source, hence affecting the coconut oil quality, colour, taste and percentage yield. An increased moisture content of coconut oil, practically increase its colour from light brown colour to dark brown colour. Increased amount of moisture also reduces the percentage yield of the coconut oil. High moisture content further reduces the quality and the shelf life of coconut oil. During the extraction process, oil recovery is always low if the moisture content of the coconut oil is high (Mahmoud *et al.,* 2014; Juliet *et al.*, 2017). The low moisture content obtained from this analysis clearly indicates that the coconut oils have a higher percentage yield, light brown colour, good quality, increased shelf life and quick oil recovery during extraction process. This result corresponds to the report of Akinoso *et al*., 2006; Mahmoud *et al*., 2014.

The results of the crude lipid, crude protein, crude fibre and carbohydrate content are presented in table 1. The result demonstrated that the crude lipid, protein and fibre content are given as 47.18 %, 11.63 % and 5.94 % respectively. This obviously revealed that the coconut oils have moderate lipid content with low protein and low fibre content. Similar observations were reported by Probir

GSJ: Volume 7, Issue 12, December 2019
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et al., 2014. The carbohydrate content of the coconut oil is given as 26.06 %. The increased carbohydrate content resulted to decrease in crude lipid content.
The metals concentrations of the oils extracted from coconut are presented in table 2. The concentrations of the metals that are present in the coconut oils include, Sodium (1.70151 and 2.5308 mg/Kg), Magnesium (1.02485 and 1.75216 mg/Kg), Potassium (8.48952 and 6.25510 mg/Kg), Calcium (4.38192 and 4.02102 mg/Kg), Iron (5.86052 and 5.38219 mg/Kg) and Zinc (3.51725 and 1.83252 mg/Kg) for coconut oils extracted with ethanol and n-hexane respectively. Sodium and magnesium demonstrated the least concentration whereas potassium showed the highest concentration in the coconut oil.

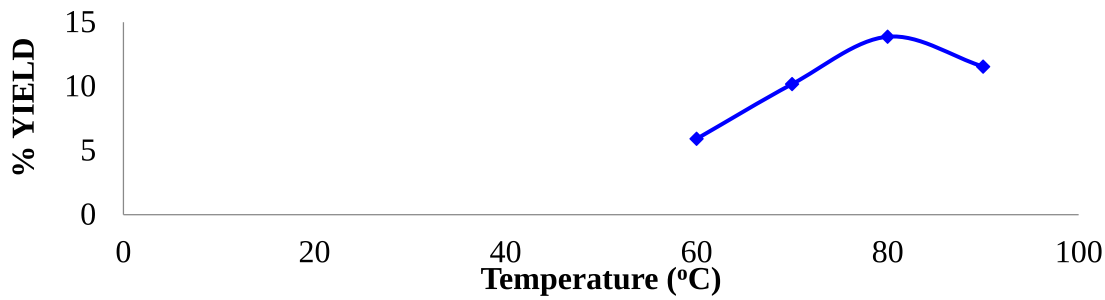

Figure 1: Effect of extraction temperature on percentage yield using ethanol

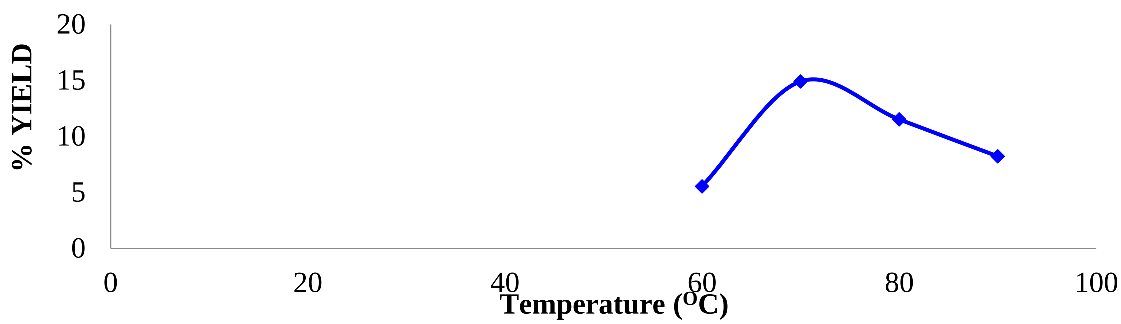

Figure 2: Effect of extraction temperature on percentage yield using n-hexane

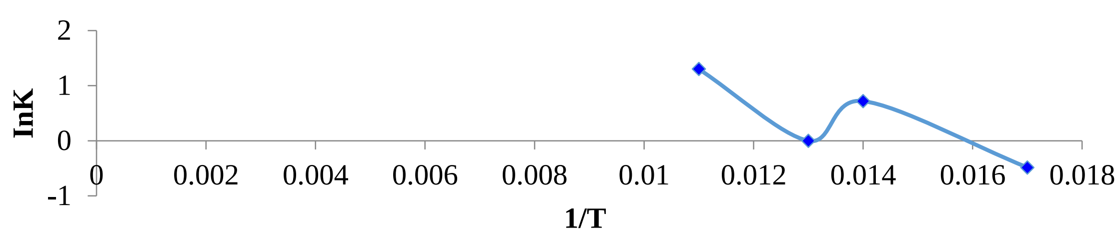

Figure 3: Thermodynamic of coconut oil extraction using ethanol

GSJ: Volume 7, Issue 12, December 2019
ISSN 2320-9186

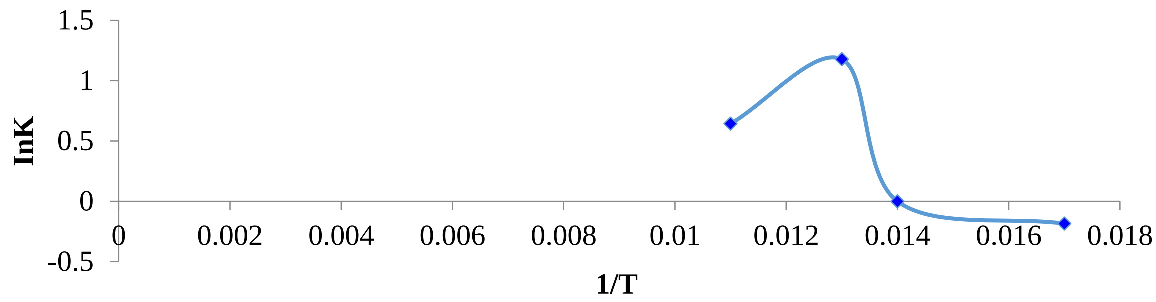

Figure 4: Thermodynamic of coconut oil extraction using n-hexane

Table 3: Result of coconut oil extraction using ethanol at varying temperature

Vol. of Ethanol used (ml)	Wt. of Coconut (g)	Temperature used Per Extraction (^{0}C)	Vol. of Oil Produced (ml)	Wt of Oil Produced (g)
500	100	60	7.31	5.90
500	100	70	12.9	10.17
500	100	80	19.18	13.86
500	100	90	15.08	11.53

Table 4: Result of coconut oil extraction using n-hexane at varying temperature

Vol. of n-Hexane used (ml)	Wt. of Coconut (g)	Temperature used Per Extraction (^{0}C)	Vol. of Oil Produced (ml)	Wt of Oil Produced (g)
500	100	60	9.68	5.54
500	100	70	21.31	14.91
500	100	80	16.29	11.52
500	100	90	13.97	8.22

Table 5: Thermodynamic properties of extracted coconut oil using ethanol

S/N	Temperature (^{o}C)	Temperature (K)	Enthalpy (H) KJ	Entropy (S) J/K	Gibbs Free Energy (G) KJ
1	60	333	2.206	33.538	-8.961
2	70	343	2.206	33.538	-9.296
3	80	353	2.206	33.538	-11.838
4	90	363	2.206	33.538	-9.967

GSJ: Volume 7, Issue 12, December 2019
ISSN 2320-9186

Table 6: Thermodynamic properties of extracted coconut oil using n-hexane

S/N	Temperature (°C)	Temperature (K)	Enthalpy (H) KJ	Entropy (S) J/K	Gibbs Free Energy (G) KJ
1	60	333	1.440	23.209	-6.287
2	70	343	1.440	23.209	-6.520
3	80	353	1.440	23.209	-6.752
4	90	363	1.440	23.209	-6.984

The result demonstrated that increasing the extraction temperature from 60°C to 80°C increased the weight and volume of the extracted coconut oils from 5.9g to 13.86g and 7.31 ml to 19.18 ml respectively. The optimum percentage yield presented in figure 1 was obtained at 80°C. Further increase in temperature to 90°C decreased the weight and volume of the extracted coconut oil to 11.53 gram and 15.08 ml respectively. This observation could be attributed to the boiling point of the solvent (ethanol) used during extraction. Ethanol has a boiling point of 78.8°C, hence below and beyond its boiling point, a minimized quantity of the oil was obtained, whereas the highest amount of coconut oil was obtained near the boiling point (80°C) of ethanol. The result confirmed that temperature is a paramount extraction property, which affect the quantity and the percentage yield of coconut oil extraction from coconut fruits, using ethanol as a suitable solvent.
The results also demonstrated that increasing the extraction temperature from 60°C to 70°C increased the weight and volume of the extracted coconut oil from 5.54 gram to 14.91g and 9.68 ml to 21.31 ml respectively. Figure 4 revealed that the optimum percentage yield was obtained at 70°C. At 80°C, the weight and volume of the extracted coconut oil are 11.52m and 16.29 ml. Further increase in temperature to 90°C gradually decreased the weight and volume of the extracted coconut oil to 8.22 gram and 13.97 ml respectively. This observation could be attributed to the boiling point of the solvent (n-hexane) used during oil extraction. N-hexane has a boiling point of 68.3°C, hence below and beyond its boiling point, a minimized quantity of the oil was obtained, whereas the highest amount of coconut oil was obtained near the boiling point (68.3°C) of n-hexane. The results also confirmed temperature as an important extraction property, which affect the quantity and the percentage yield of coconut oil extraction from coconut fruits, using n-hexane as a suitable solvent.
Generally, oil extraction using ethanol as a solvent gave a higher percentage yield than oil extraction using n-hexane. With respect to the extraction time, oil extraction using ethanol as solvent produced 31.73 ml (26.38g) of coconut oil while oil extraction using n-hexane produced 28.15 ml (23.88g) of coconut oil. This denotes that ethanol has a better extraction efficiency than n-hexane.
The thermodynamics properties of the coconut oil obtained from figures 3 and 4 are presented in tables 5 and 6. The results obtained from the oil extraction using ethanol as solvent are 2.206 k and 33.538 J/K for enthalpy and entropy respectively. The Gibb's free energies are -8.961, -9.296, -11.838 and -9.967 K for the various temperatures 333 K, 343 K, 353 K and 363 K respectively. The reaction enthalpy and the system entropy are both positive, while the Gibb's free energies (G) are negative. The positive value of enthalpy denotes that the reaction is endothermic (no heat was evolved). This implies that energy (inform of heat) is needed to initiate and drive the reaction. The positive value of the system entropy connote that the system is highly disordered and the reaction

GSJ: Volume 7, Issue 12, December 2019
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is irreversible. The negative values of the Gibb's free energy confirm the feasibility and spontaneity of the reaction. A reaction is always spontaneous when entropy is positive, resulting to negative value of Gibb's free energy. Similar observations were also reported by Sarina *et al*., 2013; Nwabanne, 2012.
The results obtained from the coconut oil extraction using n-hexane as a solvent are 23.209 J/K and 1440 KJ for the system entropy and reaction enthalpy respectively. The Gibb's free energies are -6.287, -6.520, -6.752 and -6.984 KJ for 333 K, 343 K, 353 K and 363 K respectively. The positive values of the entropy and the enthalpy connotes the irreversibility of the reaction and also affirms that the reaction is endothermic. The negative values of the Gibb's free energy clearly indicate that coconut oil extraction from coconut fruits is a spontaneous and feasible reaction. The results agreed with the report of Sarina *et al*., 2013; Nwabanne, 2012.

CONCLUSION

Coconut oils are edible oil which are usually extracted from matured coconut fruits using soxhlet or batch extraction processes. Soxhlet extractor was utilized in this study for coconut oil extraction from matured coconut fruits using ethanol and n-hexane as solvents. The result confirmed that temperature is a paramount extraction property, which affect the quantity and the percentage yield of coconut oil extraction from coconut fruits, using ethanol and n-hexane because the volume and weight of coconut oil produced using both ethanol and n-hexane increased with increasing extraction time. The result demonstrated that increasing the extraction temperature from 60^{o}C to 80^{o}C increased the weight and volume of the ethanol-extracted coconut oil from 5.9g to 13.86g and 7.31ml to 19.18ml respectively.
The results also demonstrated that increasing the extraction temperature from 60^{o}C to 70^{o}C increased the weight and volume of the n-hexane extracted coconut oil from 5.54g to 14.91g and 9.6ml to 21.31ml respectively.
It was also observed that ethanol gave a higher percentage yield of coconut oil extracted from the coconut fruits than n-hexane. The positive value of the system entropy indicates that the system is disordered and the reaction is irreversible. The negative values of the Gibb's free energy confirm the spontaneity of the reaction, while the positive value of enthalpy implies that the reaction is endothermic.

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