EFFECT OF SODIUM CHLORIDE ON FURFURAL YIELD FROM MICROALGA

A. O. Ameh[1]*, J. E. Oguche[1], Y. Tanimu[2] and S. A. Egu[3]
[1]Chemical Engineering Department, ABU, Zaria, Nigeria
[2]Department of Botany, ABU, Zaria, Nigeria
[3]Chemistry Department, K.S.C.O.E., Ankpa, Nigeria
*Corresponding author: aoameh@abu.edu.ng

Abstract: This paper reports a study on the production of furfural from microalga biomass, specifically investigate the effect of sodium chloride (NaCl) on furfural yield from microalga by varying the amount of NaCl (0 to 60 g) at constant reaction temperature, time and acid concentration. Furfural production was carried out by hydrolysis of Pentosans to Pentoses; Pentosans in hemicelluloses is hydrolyzed with dilute mineral acids with NaCl as a promoter with heating to pentoses. Subsequent pentoses are dehydrated to furfural in a single stage process. The proximate analysis of the microalgae biomass shows high percentage content of hemicellulose (54.13%). Results obtained indicated that furfural yield increase with increase in NaCl up to an optimum after which yield dropped. The highest furfural yield of 60.3% was recorded at 30 g of NaCl. Fourier Transform Infrared Spectroscopy (FTIR) result confirm the presence of carbonyl and aldehyde functional groups at wave length of 1674.27 cm^{-1} and 2924.18 cm^{-1}, respectively while Gas Chromatogram Mass Spectrum(GC-MS) analysis of the sample confirms the presences of furfural (50.86%).

Keywords: Batch reactor, biomass, composition, hemicellulose, NaCl

Introduction

The continued combustion of fossil fuels has created serious environmental concerns over global warming due to the increased release of greenhouse gases (GHG) (Sweygers *et al*., 2016). Hence the need to replace fossil-based chemicals by renewable alternatives has led to an increased interest in the production of platform chemical originating from lignocellulosic biomass (Jones and Mayfield, 2012). It has been reported by (Tong *et al*., 2010) that in recent years, an increasing effort has been devoted to find paths to utilize biomass as feedstock for the production of organic chemical because of its abundance, renewability and worldwide distribution. This is because plant based renewable resources are a strategic option to meet the growing need for industrial building blocks as it offers economic and environmental advantages for the development of this resource base. Although, the search for an efficient process to convert lignocellulosic biomass into platform chemicals is an important challenge, it requires intensive process intensification and the effective valorization of hemicellulose, consisting primarily of C5 and C6 sugars, respectively. Microalgae are microscopic unicellular organisms capable of converting solar energy to chemical energy via photosynthesis (Ambalkar and Talib, 2012). They contain numerous bioactive compounds that can be harnessed for commercial use. The potential of microalgal photosynthesis for the production of valuable compounds or for energetic use is widely recognized due to their more efficient utilization of sunlight energy as compared with higher plants (Machado *et al*., 2016). It has a promising future in the area of chemical, food, medicine, genetic engineering and biodiesel.

Also, it has been established by Kightlinger *et al.* (2014) that, microalgae offer several advantages over terrestrial plants as a source of transportation biofuels, including high growth rates, high lipid content, the ability to grow large cultures on non-agricultural land, and the ability to rapidly improve strains and produce co-products. Machado *et al*. (2016) has opined that despite these promising characteristics, the economic viability of algae-based biofuels is still uncertain. Recent estimates place a barrel of algae-based oil at US \$450–\$2300, compared with US \$80–110 for crude oil (Alabi *et al*., 2009). Efforts to lower the cost of algae oil production are currently focused on nutrient sourcing and usage, harvesting, strain isolation, production management, fuel extraction, co-product development, and residual biomass sourcing such as proteins, furfural and glucose (Hannon *et al*., 2010). After the desired biodiesel has been extracted from harvested algae, a significant portion of residual biomass remains, with several options currently being explored for their usage. These options include anaerobic digestion of biomass to produce methane (Machado *et al*., 2016), pyrolysis of dry biomass to produce bio-oil or use as a fertilizer (Lopez *et al*., 2014).

Furfuraldehyde, commonly known as furfural, is a liquid chemical that is sourced from renewable resources. It is created from the hemicellulose components (pentosans) of matter. Microalgae contain 32% pentosans on a dry basis. Furfural its pure state is a colorless oily liquid with the odor of almonds, but upon exposure to air it quickly becomes yellow then brown and finally black. Furfural is a hazardous chemical, being both toxic and flammable. Fortunately, incidents involving furfural are very rare, which is probably due to its low volatility. The chemical formula for furfural is $C_5H_4O_2$, in structure it is a heterocyclic compound consisting of a furan ring (four carbon atoms and an oxygen atom) plus an aldehyde group (Fig. 1).
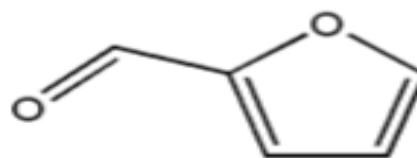

Fig. 1: Structure of furfural

The furan ring is common in nature, being a component of the sucrose molecule (Indira and Biswajit, 2012), reported that research is ongoing to make algae biofuels a more financially attractive energy option; however, it is becoming evident that the economic viability of algae-based fuels may hinge upon high-value co-products such as protein, glucose, furfural etc. Furfural is an important chemical in the synthesis of chemicals and fuels from renewable sources (Chen *et al*., 2014). Researches into furfural from biomass has been gaining interest (from corn-cobs, rice hulls, bagasse and host of agricultural plants such as pawpaw, mango etc (Ameh *et al*., 2016). It is also a versatile chemical that acts as a starting material for a large family of other chemicals and polymer products. It is important to note that the autotrophic nature of

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algae makes them a huge biotechnological value for the production of furfural. Also, its less expensive in production, does not required a large land to grow and can be harvested as many times as possible compared to agricultural sources such as beans, corn and sugar (Jeon *et al.,* 2016). Oguche *et al*. (2017) reported the effects of temperature, acid concentration and reaction time on the yield of furfural: effect of the promoter (NaCl) concentration was not covered in their investigation. Sodium chloride also known as salt or halite is an ionic compound with the chemical formula NaCl, representing a 1:1 ratio of sodium and chloride ions. With molar mass of 40 g·mol^{-1}, Sodium chloride is the salt most responsible for the salinity of seawater and of the extracellular fluid of many multicellular organisms. In the form of edible or table salt it is commonly used as a condiment and food preservative. Large quantities of sodium chloride are used in many industrial processes, and it is a major source of sodium and chlorine compounds used as feedstock for further chemical syntheses. Salt is used, directly or indirectly, in the production of many chemicals, which consume most of the world's production. It serves as a promoter during furfural production in distillation medium. Although, furfural yield has been reported to be affected by several factors such as acids concentration, temperature and reaction time; however, this study will focus specifically on using a portion of the processed microalgae biomass to synthesize furfural and investigating the effect of sodium chloride on furfural yield.

Thus, this work evaluates the feasibility of producing one of the co-products (furfural) from algae extract after biodiesel production as well as investigating the effect of sodium chloride on furfural yieldm

Materials and Methods

The microalgae were collected from waste water pond at Ahmadu Bello University (ABU), Zaria and were identified at botany department ABU, Zaria. The identified species of microalgae from the waste pond are: *Closterium species*, *Scenedesmus Opoliensis*, *Cosmarium*, *Scenedesmus Obliquus, Scenedesmus bijuga Staurastrum* SPP, *Oscillatoria* SPP, *Spirulina*, *Merismopedia* and *Ankistrodesmus falcatus (Cyanobacteria).* The microalgae were then filtered using vacuum filter and dried in oven at about 80°C and finely grounded and sieved to 1000 μm mesh size. The prepared samples were analyzed for dried moisture content, ash contents, lignin, oil content, and cellulose and hemicellulose contents after the oven drying at Institute for Agricultural Research (IAR/ABU), Zaria.

Furfural production was carried out using a batch reactor and a distillation system, while the acid hydrolysis of the microalgae samples took place in the batch reactor. Where various amounts of sodium chloride, Uniform quantity (30 g) of microalgae sample and 40 ml of 1M Concentration of aqueous Sulphuric acid, were introduced into a 500 ml 3-necked round bottom flask, fixed to a Vigreux column and a Condenser and the reaction mixture was heated. The effluent from the batch reactor experienced rapid distillation at 105°C, then the aqueous distillate mixture was collected over 40 ml chloroform in a separating funnel where two distinct layers were formed which are, the furfural-chloroform layer as well as the aqueous layer (Ameh *et al*., 2016). After 1 h of distillation (after which there was no increase in the furfural-chloroform layer), the furfural-chloroform layer was separated using a separating funnel, then poured into a conical flask. The decanted furfural-chloroform mixture was subjected to a rotary evaporation at a temperature of 65°C for 10 min where all the chloroform was observed to be evaporated leaving the furfural as the products. This procedure was repeated for varying various amount of sodium chloride (0 – 70 g) at constant reaction temperatures of 140(°C), 35 ml

concentration of Sulphuric acid, and reaction time of 60 min as well as uniform 40 ml of chloroform. The experimental set up during the research is shown in Fig. 2.
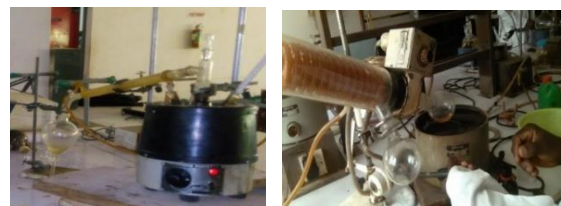

Fig. 2: Experimental set up for production of furfural from microalgae

The conversion of pentosans to furfural takes place in two steps; Hydrolysis of Pentosans to Pentoses where Pentosans in hemicelluloses is hydrolyzed with dilute mineral acids at relatively temperature to pentoses liquor. Secondly is through the Conversion of Pentoses to Furfural; the formation of furfural from pentoses is an ordinary process of dehydration with the elimination of three molecules of water (Lopez *et al*., 2012).

The stoichiometric equation for furfural formation from hemicellulose is:

$$(C_5H_8O_4)_n + nH_2O \rightarrow n(C_5H_{10}O_5) \tag{1}$$
$$n(C_5H_{10}O_5) \rightarrow n(C_5H_4O_2) + 3nH_2O \tag{2}$$
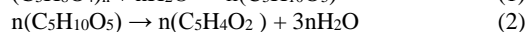
Where: n=number of moles, $C_5H_8O_4$= Pentosans, $C_5H_{10}O_5$= Pentoses, $C_5H_4O_2$= Furfural

Results and Discussion

The physicochemical properties of microalgae are presented in Table 1. Fig. 3 presents the effect of NaCl concentration on furfural yield. Figs. 4 and 5 present the FTIR of the prepared furfural and a commercial furfural sample, respectively. Figs. 5 and 6 present the gas chromatogram peaks for commercial furfural and prepared furfural, respectively. Tables 2 and 3 present the composition of prepared and commercial furfural based on area percentage.

Table 1: Composition of some physicochemical properties of microalgae feedstock used

Parameter	Value
Lignin content (%)	13.82
Cellulose content (%)	27.99
Hemicellulose content (%)	58.20
Ash content (%)	30.28
Oil content (%)	0.00
Density (g/ml)	1.17
Moisture content (%)	4.16

Fig. 3: Effect of sodium chloride on furfural yield

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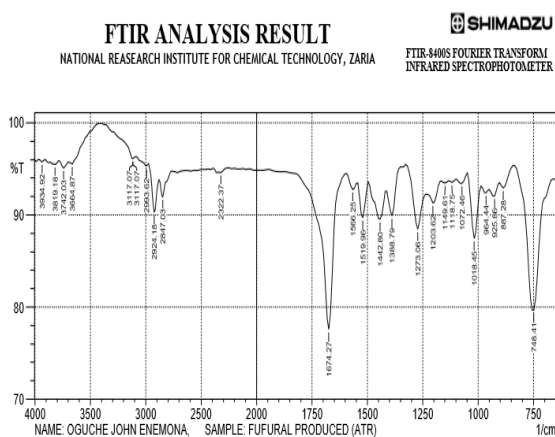e-ISSN: 24085162; p-ISSN: 20485170; October, 2018: Vol. 3 No. 2A pp. 461 – 465

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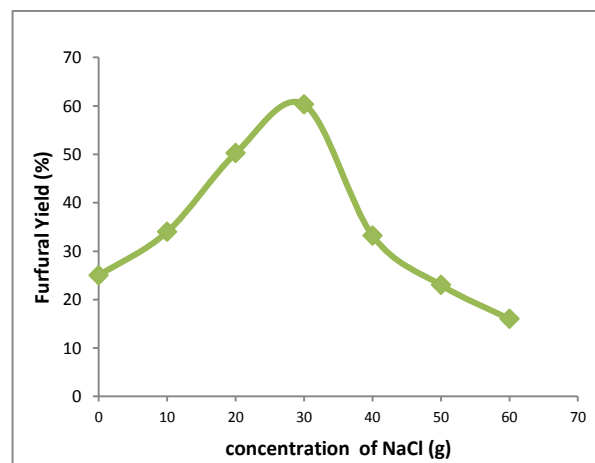
Fig. 4: Fourier transform infrared spectroscopy analysis of furfural produce
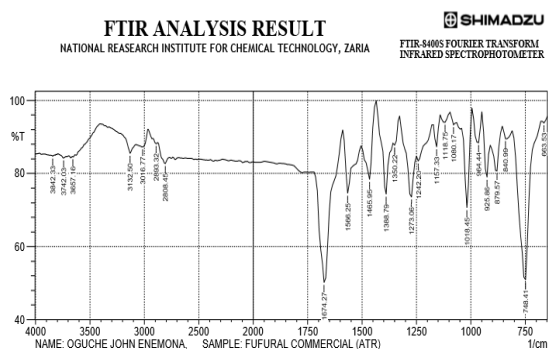

Fig. 5: Fourier transform infrared spectroscopy analysis of commercial furfural

As show in Table 1 above the microalgae had high % content of hemicellulose (54.13%) this makes it suitable as a good feedstock for furfural production. This is higher than agricultural feedstock such as sugarcane bagasse which contains 32% as reported by (Ameh *et al*., 2016); rice husk (19%) reported by (Ambalkar and Talib, 2012); maize 32 and 30 % as reported by (Chen *et al.,* 2015) and (Amir *et al*.,

2015), respectively. Thus microalgae should give higher % of furfural yield. Also the percentage oil content of the microalgae is 0.00% which indicates that it contains no biofuels (biodiesel) and hence has higher % of biomass which can be converted to furfural.

As illustrated by Fig 3, the effect of Sodium chloride concentration on the yield of furfural was studied at a constant temperature of 140ºC, reaction time of 60 min as well as 40 ml of 1M concentration of Sulfuric acids. Initially, Sodium chloride caused an increase in distillation temperature thereby leading to increase in the rate of formation of furfural thus resulting to increase in furfural yield from 25 to 60.3% but lowered the yield from 60.3 to 16% as the concentration of Sodium chloride increases from 30 to 60 g due to furfural polymerisation which leads to formation of other products such as 5-methyfurfural, furoic acids and humins. The highest yield of furfural 60.3% was observed at 30 g of Sodium chloride, and it was thought possible that Sodium chloride give an optimum temperature which accelerates the formation of furfural before decomposition could have taken place which is desirable hence the highest yield of furfural was observed at this amount of Sodium chloride. As the concentration of Sodium chloride increases (Fig. 3) from 30 to 60 g it was observed that furfural yield begins to decrease from 60.3 to 16% and no further increase in furfural yield, this is because as the concentration of Sodium chloride increases, it leads to excessive rise in temperature which results to an increase in the rate of furfural degradation, polymerization and decomposition to other by-products which is an indicatives of decrease in furfural yield observed. Also as the quantity of Sodium chloride increases, furfural distillate becomes very light pink instead of being colorless, this may be attributed to polymerization of furfural to other products as a result of rise in temperature. It was also observed that an increase in Sodium chloride leads to increase in the formation of bubbles and caused entrainment in the distillation medium as a result of rise in temperature hence an increase in Sodium chloride does not significantly increases furfural yield but prolong residence time.
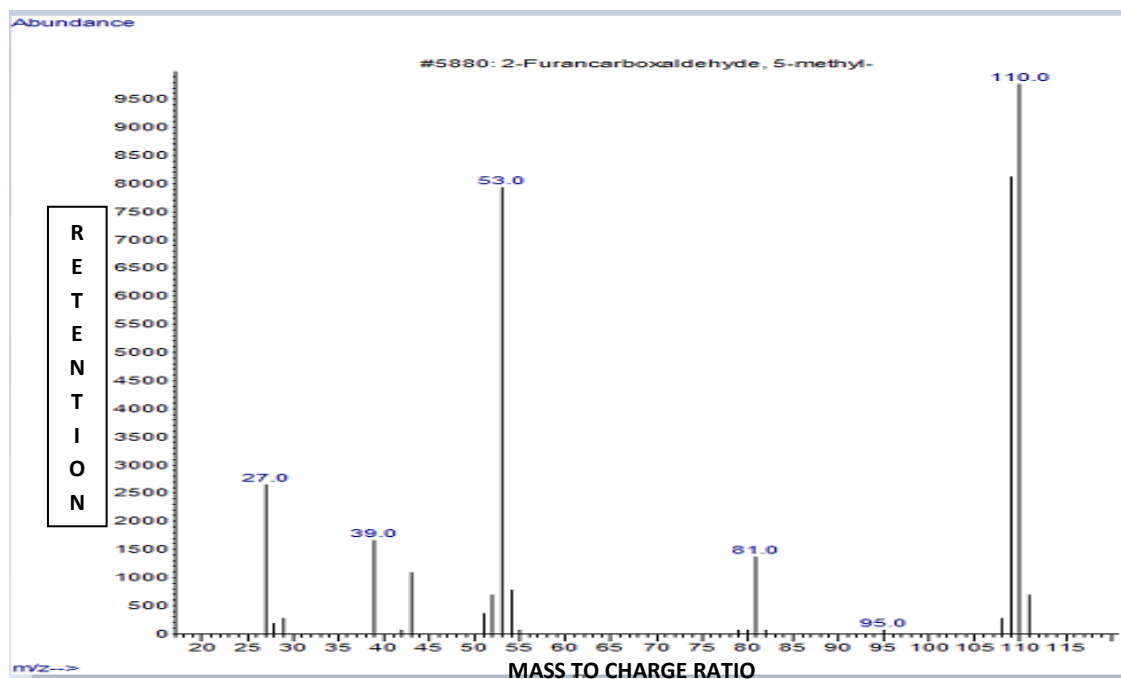

Fig. 6: Gas Chromatogram -peak of commercial furfural

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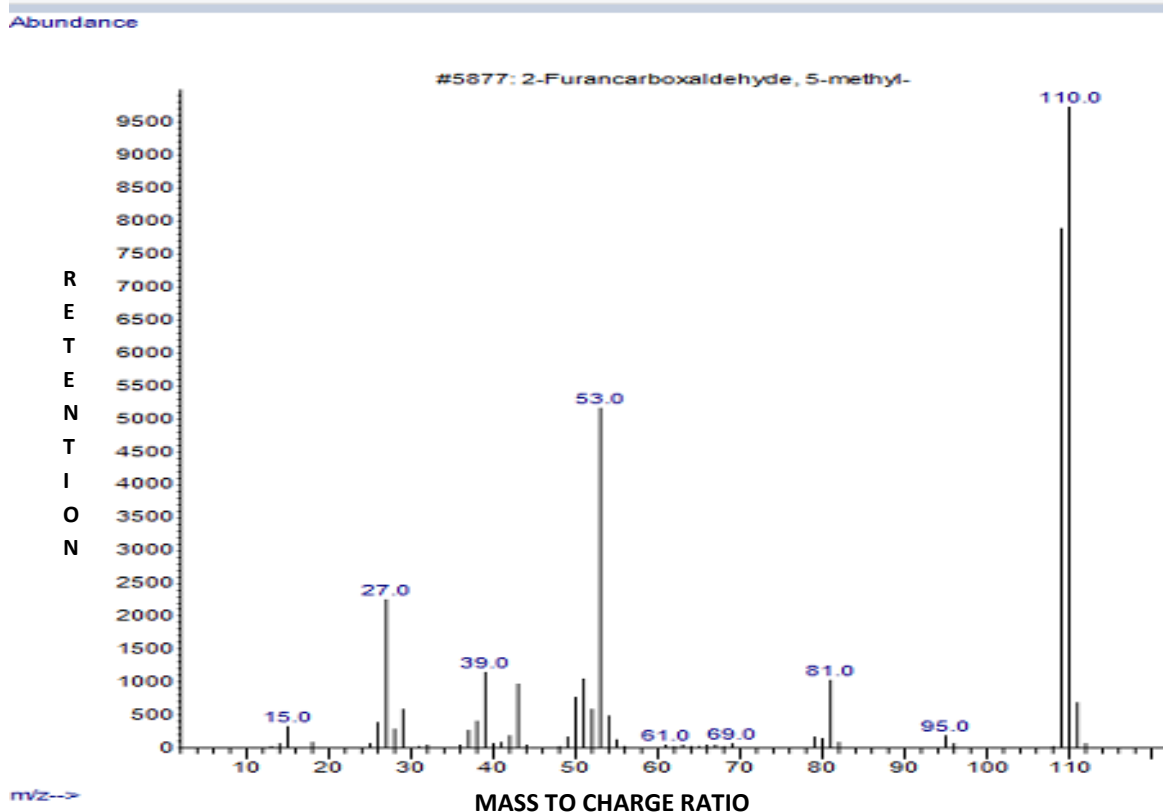
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Fig. 7: Gas chromatogram-peak furfural produce from microalgal

Furfural produce was characterized using FTIR and GC-MS, which Figs. 4 and 5 shows Fourier Transform Infrared Spectroscopy Analysis of furfural produce and Commercial Furfural and both exhibit similar trends. The Fourier Transform Infrared Spectrum exhibited a strong absorption at 1674 cm^{-1} indicating a significant functional, the presence of conjugated carbonyl C=O group. The presence of an aldehyde was further proven by two peaks attained at 3019.55 cm^{-1} and 2924.16 cm^{-1}. These absorption shows a moderate intense stretching of aldehydic C=H as shown in Fig. 5 above. Also from Fig. 5, no broad peaks were observed at the area of 3400 cm^{-1} – 2500 cm^{-1} which belong to OH group, this confirms the absence of carboxylic group. If the sample belong to ester group, when a double bond is adjacent to a strong C=C peak would have been observed in 1674.27 cm^{-1} to 1685 cm^{-1} region. The strong peaks indicated from 1566.25 cm^{-1} to 1388.79 cm^{-1} are initial stretching of C=C from aromatic ring while the aromatic bending out of plane peaks was observed from 964.44 cm^{-1} to 849.5 cm^{-1}. Two strong peaks at 1018.45 cm^{-1} and 1273.06 cm^{-1} indicates C-O stretching vibration.

The Infrared Spectrum of furfural produce was compared to that of commercial in Fig. 6 above and both followed a similar peaks trend. Results obtained from Gas Chromatogram (Figs. 6 and 7) shows that furfural has a retention time of 7.834 min with a relative abundance of 100%. The Gas Chromatogram Spectrum shows a molecular ions peaks at mass to charge (m/z) ratio of 96 which correlate to a molecular formular of furfural of $C_5H_4O_2$.

Table 2: Various constituents present in furfural produce

Constituent (S)	% Composition	Formular	Molar Mass
Thiospenecarboxylic	0.50	$C_5H_4O_2S$	128
Pentenal	0.41	$C_5H_{10}O$	86
2-Furcarboxaldehyde	50.86	$C_5H_4O_2$	96
2-Furanethanol	4.16	$C_5H_8O_2$	112
Cyclopentane	0.16	C_5H_{10}	70
Biphenyl	0.07	$C_{12}H_{10}$	154
Carbonic acids	0.32	CH_2O_3	62
P-xylene	5.38	C_8H_{10}	106
Pyridine	0.43	C_5H_5N	79.8
Benzenealdehyde	0.07	C_4H_5CHO	106.12
5-Hydroxylmethylfurfural	26.74	$C_6H_4O_2$	108
Aminopyrindine	4.16	$C_4H_5N_3$	95
Heptanonitrile	0.20	$C_7H_{13}N$	111
Benzeneacettlaldehyde	0.61	$C_9H_{10}O$	134
2-Furanone	0.50	$C_4H_4O_2$	84
2-Furanylvinylamine	0.11	C_6H_7NO	109.12
5-Methylfuranone	5.32	$C_5H_6O_2$	98.10

Table 3: Various constituents present in commercial furfural

Constituent (S)	% Composition	Formular	Molar Mass
Thiospenecarboxylic	5.32	$C_5H_4O_2S$	128
Pentenal	0.41	$C_5H_{10}O$	86
2-Furcarboxaldehyde	7.87	$C_5H_4O_2$	96
2-Furanethanol	5.32	$C_5H_8O_2$	112
Cyclopentane	0.08	C_5H_{10}	70
Azulene	0.14	$C_{10}H_8$	106
Carbonic acids	0.20	CH_2O_3	62
P-xylene	9.68	C_8H_{10}	106
Methoxylacetic	0.23	$C_3H_6O_3$	90
Tricosene	0.21	$C_{23}H_{46}$	322
5-Hydroxylmethylfurfural	17.07	$C_6H_4O_2$	108
Aziridine	0.08	C_2H_5N	43
Trifluroacetic acid	0.26	$C_2H_2F_2$	62
Formaldehyde	0.08	CH_2O	30

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However a peak at m/z of 95.0 (Fig. 7) was obtained due to loss of hydrogen to form a carbonium ion. An electron was given away by the aldehyde carbon to hydrogen to form this fragmentation since more stable cation can be formed due to formation of hydrocarbon pattern, peak at m/z of 110 becomes dominant. The Gas Chromatogram of furfural produced was compared with that of commercial furfural in Fig. 6 and both followed a similar pattern. Table 2 and 3 above shows the various constituent presents in furfural produce; furfural has higher percentage of 50.86% in furfural produce while 60.92% in the commercial furfural, thus other constituents present are due to polymerization, degredation and decomposition of furfural as a result of increase in sodium chloride and excessive rise in temperatures.

Conclusions

From the crude fibre analysis carried out on microalgae, it was observed That microalgae feedstock had higher hemicellulose contents (54.13%) compared to agricultural feedstocks such as corn cob (30%), rice husk (19%) and sugarcane bagasse (32%) as reported by (Chen *et al*., 2014) hence it is a suitable raw material for production of furfural.

The acid hydrolysis of microalgae biomass into furfural via hydrolysis and distillation was carried out while the effect of Sodium Chloride was successfully investigated by varrying various amounts of Sodium Chloride at a constant temperature, acid concentration and reaction time while the optimum condition was determined to be 30g of sodium chloride with furfural yield of 60.3%.

An increase in Sodium chloride does significantly increases furfural yield up to 60%. However, prolong residence time and it leads to excessive rise in temperature which results to an increase in the rate of furfural degredation, polymerization and decomposition to other by-products which is an indicatives of decrease in furfural yield observed. Also as the quantity of Sodium chloride increases, furfural distillate becomes very light pink instead of being colorless.

FTIR Result confirms the presence of carbonyl and aldehyde functional groups at wave length of 1674.27cm-1 and 2924.18cm -1 respectively while GC-MS results confirms the presences of furfural (50%) with the Gas Chromatogram Spectrum shows a molecular ions peak at mass to charge (m/z) ratio of 96 which correlate to a molecular formular of furfural of $C_5H_4O_2$ and a molar mass of 96g/mol.

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