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Extraction of Furfural ($C_5H_4O_2$) from Waste Bagasse of Agricultural Source

Lakkimsetty Nageswara Rao[*] and Lamees Al-Mukhaini

Department of Mechanical and Industrial Engineering, College of Engineering, National University of Science and Technology, Sultanate of Oman

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ABSTRACT

Furfural is an important liquid organic chemical having yellow oily nature with smell of almonds manufactured from Agro industrial wastes and residues containing carbohydrates known as pentosans and is used in refining of lubricating oils, petroleum, and diesel fuel. The raw material for the production of furfural was bagasse and chemicals such as H_2SO_4, water and NaCl. Bagasse is a waste product from sugar industry which is good source of pentosan with 25 to 27%. The main objective of the present study was to minimize the environmental impact of agriculture waste disposed from various sources having impact on environment. Based on this scenario the conversion of the agriculture waste from sugar industry to furfural to reduce the environmental effect. The experimental study has been conducted for the production of furfural from bagasse by two methods such as Soxhlet extractor and simple distillation. In this experimental analysis the various parameters such as amount of raw material, pH and temperature w.r.t time were studied. In addition to this the usage of solvents for the extraction process has been reported. The extracted furfural was analyzed by Gas chromatography and Mass spectroscopy with proper design analysis.

Keywords: Extraction; Bagasse; Furfural; Pentosans; Soxhlet extractor; Simple distillation; Gas chromatography; Mass spectroscopy

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INTRODUCTION

Wastes are any materials which are discarded after primary use, due to its worthless, and of no use. There are many types of wastes. For examples, municipal waste includes household waste, commercial waste, demolition waste, and agricultural waste, which means the waste produced on a farm through various farming activities including straw, stalks, husk, cobs, animals waste, bagasse, seeds, peels, and husk. The waste of agriculture industry constitutes a significant proportion of worldwide agricultural productivity. It has been estimated that these wastes can account for above 30% of worldwide agricultural productivity

[1-3]. Furfural is a heterocyclic aldehyde with a chemical formula ($C_5H_4O_2$).It can be produced from agricultural raw materials including corncobs, oat, wheat bran, and sawdust which containing pentosans and lingo-cellulosic feedstock. It is also obtained from xylose, via dehydration. It has others names like 2-furfural, 2-furancarboxaldehyde, and Furfural. Furfural uses as a solvent in the oil refining industry, a chemical intermediate in the production of solvents furan and tetrahydrofuran, as solvent petrochemical to extract dienes from other hydrocarbons, in plastic and nylon industry, and in Intervention produces dyes, adhesives, perfumes, fabrics, and paper production [4,5]. The residues from the processing and harvesting of some agricultural crop was listed in Table 1.

Table 1. Residues from the Processing and Harvesting of Some Agricultural crop (Agro wastes utilization: the chemists input, 2007)

Agriculture Produce	Residues Generated	Potential use of Residues
Corn, Wheat, Rice	Straw, Stalks, Husks, Cobs	Animal feedstuff, Fuel, Silica, Furfural, Compost, Chemical Feedstock
Cattle	Animals Waste e.g. Blood, Bone, Dung	Animal glue, Animal Feed Supplement, Methane Production, Activated Carbon, Manure
Sugarcane	Bagasse	Fuel, Furfural, Animal feed Particle Boards, Biopolymers
Fruits and Vegetables	Seeds, Peels, Husks	Animal and Fish Feed, Fuel Compost and Fermentation
Potatoes	Starch waste water	Sugars and Alcohols, Single Cell Protein
Oil and Oilseeds	Shells, Husk, Fibers, Sludge, Press Cake	Animal feed, Fertilizers, Fuel, Activated Carbon, Furfural

The synthesis of Furfural was carried out as per the following reactions:

- Hydrolysis of Pentosan

  Pentosan +n_x water → n_x pentose

  $(C_5H_8O_4)$ n + $nH_2O \rightarrow C_5H_{10}O_5$

- Dehydration of Pentose

  Pentose - 3x water → Furfural

  $C_5H_{10}O_5 - 3H_2O \rightarrow C_5H_4O_5$

Thus over all reaction can said to be

Pentosan-2x water → Furfural

The production of furfural requires raw materials which consist of pentosan. The pentosan content of various raw material in percent of dry mass was shown in Table 2.

Table 2. the pentosan content of various raw materials in percent of dry mass

Raw Materials	Pentosan (%)	Raw Materials	Pentosan (%)
Corn cobs	30-32	Flax shives	23
Oat hulls	29-32	Hazelnut shells	23
Almonds husks	30	Residue of olive extraction	21-23
Cottonseed hull bran	27-30	Eucaplatus wood	20
Birchwood	27	Beech wood	24
Bagasse	25-27	Sunflowers husks	25

Bagasse is a waste product from the sugar industry, and the residue of the cane after juice extraction, which is usually used as energy source in the factory at present, used as forage and raw material for the production of pulp, papermaking and particleboard. Bagasse contains pentosan with a concentration of 250-270 g/kg of the original bagasse, which mainly consists of arabinoxylan. One of the application bagasse is the production of a valuable material called furfural. This material is used in synthesis and production of various chemical compounds [6,7].

In last years of time, there is an increase of sugarcane waste in Oman that leads to increasing the agriculture waste of the sugarcane. the problem which faced is how disposed from this waste properly, because the disposal of these waste is expensive and cause large amount of pollution and the environmental impact, also it huge loss of wealth that can be used in industries, and will effect on the economics of the country, so the conversion of the agriculture waste production from sugar industry to important chemical which is furfural which help to decrease and reduce the environment impact of agriculture waste and dispose from waste properties to useful way. The main aim for present experimental study was to reduce the environmental impact of agriculture waste disposed of various sectors such as agricultural by conversion of bagasse which is a waste product from the sugar industry which is good source of pentosan to the Furfural by extraction from Bagasse by solvents such as methanol, hexane, and ethanol and compare between them which is better for extraction process that give high yield of Furfural and analyzed by gas chromatographic (GC), and mass spectroscopy (MS).This will decrease the environmental impact of agriculture waste and dispose of waste properties in a useful way.

EXPERIMENTAL SETUP AND METHODOLOGY

The experiments were carried out at Caledonian Research and Innovation laboratory of National University of Science and Technology and the analyzing of Furfural by mass spectroscopy was conducted at Sultan Qaboos University at Chemical and Petroleum laboratories.

Pretreatment

Drying of raw bagasse for two days to remove the moisture which contain in bagasse by drying operation at $100^{o}C$. After drying process it was grinded to decrease its size, after the grinding process sieve the crushed bagasse to remove the large materials. Bagasse is a waste product from the sugar industry, which contains pentosan which mainly consists of arabinoxylan. The selection of the good quality of raw materials where the quality of a bagasse tested by determine the humidity, pH and water activity because this factors of raw materials effected on the quality of furfural. After the drying, grinding, and sieving process, extract the Furfural from bagasse powder by using two methods: Simple distillation and Soxhlet extractor. Simple distillation method is a process of separate of two liquids due to different in boiling points. The liquid with lower boiling point will evaporate first, then its cools, condense and drip within the collection receiver [8-10]. As a part of experimental study H_2SO_4 used as catalyst and NaCl used to increase the rate formation of Furfural. The stages of experimental procedure were shown in Figures 1 and 2.

Figure 1. Powdered Bagasse

Figure 2. Preparation of the solution

Experimental Study for Simple Distillation

As a part of experimental study 4 g of bagasse powder, 15 ml of diluted sulfuric acid and 7 g of salt was taken in a round bottom flask, shakes until the mixture become homogeneous and is connected to the flask with tube as well as water condenser. The temperature and applied heat from oil bath was adjusted to perform the distillation process takes place until no more furfural can be seen. The similar process was repeated for three times for getting more accurate results of experimental study at different temperature, salt, amount of bagasse, contact time to study the parameters such as temperature, pH, amount of raw material and time etc.

Experimental Study for Soxhlet Extraction

The main objective of this experiment was to extract oil from bagasse powder by Soxhlet extraction process. In this experiment, n-Hexane was used as solvent and bagasse powder state in thimble to extract oil in Soxhlet extractor. The solvent had been heated to reflux and then passed through a porous thimble containing bagasse powder kept in the Soxhlet part of the setup. As only oil is soluble in Hexane the solvent and oil mixture is filtered and passed a siphon to produce continuous flow, after extraction oil more volatile component hexane was separated by simple distillation (Figures 3 and 4).

Figure 3. Preparation of the solution for Soxhlet extraction

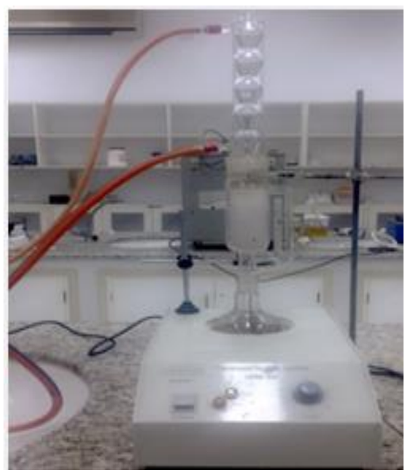


Figure 4. Soxhlet extraction setup Source

Purification of Furfural

Simple distillation was used effectively to separate liquid has at least 50^o C difference in their boiling point. As per the experimental analysis hexane has much lower boiling point 68^{o}C than furfural 161.6^{o}C. The mixture of solvent n-hexane and Furfural was kept in steam distillation, the liquid with lower boiling point (n-hexane) was evaporate and condensate then converts to liquid form implies that the separation of Furfural and n- hexane was taking place. The similar procedure was repeated by using solvents such as ethanol and methanol for study the comparison of the best solvent for extraction process which is analyzed and confirmed by using Gas Chromatography (GC).

Mass Spectroscopy

Mass Spectrometer is an equipment which used to measure the characteristics of molecules and mass of ions present in sample by converts the molecules into ions by bombarding it with electrons and then they are separated by accelerating them and placing them under an electric or magnetic field and then the ions are sorted based on their mass to charge ratio. Moreover, the ions are detected accordingly using an electron multiplier. The molecules can then be identified by comparing the known values against the derived values of charge to mass ratios [11-15].

RESULTS AND DISCUSSION

The extraction of furfural was successfully extracted from the waste of sugar cane (Bagasse), which consist of Pentosans by selecting the good quality of raw materials (Bagasse), where the quality of a bagasse tested by determine the humidity, pH and water activity, because this factors of raw materials effected on the quality of furfural. Also the well drying and grinding of bagasse, gives high quality of furfural that produced. In simple distillation method, the experiment is repeated to study the effect of various parameters with same time and different amount of raw material (Bagasse), amount of diluted Acid (H_2SO_4), temperature and amount of salt (NaCl) was shown in Table 3.

Table 3. Parameter study for the experiment

No. of Sample	1	2	3
Mass of Bagasse (g)	4	3	2
Mass of salt (NaCl) (g)	7	5	4
Amount of diluted Acid (H_2SO_4) (ml)	15	10	5
Time (min)	60	60	60
Temperature (°C)	100	70	50
Mass of Beaker (m1)	284	284	284
Mass of product (m^2)+mass of beaker (g)	384	380	378
Mass of product (m^2-m1)	100	96	94

As shown in the Figure 5, observed that the color of Furfural product was yellow which indicates one of the characteristics of the furfural. The color of furfural became darker as the temperature increase, high amount of salt and high amount of diluted acid. As shown in the figure, the sample 1 which contain the highest amount of salt, diluted acid and highest temperature, its more dark in the color, while sample 3 which contain the lowest amount of salt, diluted acid and temperature, it has lightest color. Also, the temperature, pH, amount of raw material, amount of salt and diluted acid effected on the yield of the furfural.

Figure 5. Furfural extracted in the various stages of experimental study

Effect of the Nature of Solvent on the Yield

Table 4 show the amount of furfural was extracted from the bagasse/agricultural wastes with specific volume of solvent was added. It was observed that methanol was the most efficient and higher yield of oil among the three solvents used for the study and also ethanol on the other hand was quite a poor choice of solvent for the extraction of furfural. N-hexane was only marginally better; but it can be used to extract the furfural out of remaining bagasse that had been previously treated with methanol by running the solvent extraction process for long time under a partial vacuum condition.

Table 4. Yield of furfural from different solvents

Type of solvent	Amount of solvent (ml)	Amount of oil extracted (g)
n-Hexane	250	0.5
Ethanol	250	0.06
Methanol	250	2.4

Effect of Time and Catalyst Concentration on Furfural Yield

As the data suggests, increasing the time the experimental setup was run corresponded to an increase in the amount of furfural that was obtained. The increase was almost linear in nature in the case of the concentration of the catalyst. The catalyst increased the rate at which the reaction occurred and hence improved the conversion of hemicellulose into secondary products (Table 5).

Table 5 Effect of time and catalyst concentration on the furfural yield

S.No	Catalyst	Solvent	Temperature (°C)	Time	Furfural Yield
1	1 mg/ml HCl		150	5	0.1
2	2 mg/ml HCl	Methanol	150	10	0.9
3	3 mg/ml HCl		150	24	2.4

Effect of Temperature on the Amount of Product (Furfural)

The results of the experimental analysis showed that with an increase in the temperature the amount of furfural product was also increased. The increase was contributed to the higher rate of chemical reaction which occurs with an increase in the temperature. However, continuous increase in the temperature can lead to the degradation of the product which is exactly what was observed during the experiment; hence the temperature was maintained at an optimal level to ensure that the yield was high and that there was no degradation in the quality (Figures 6 and 7).

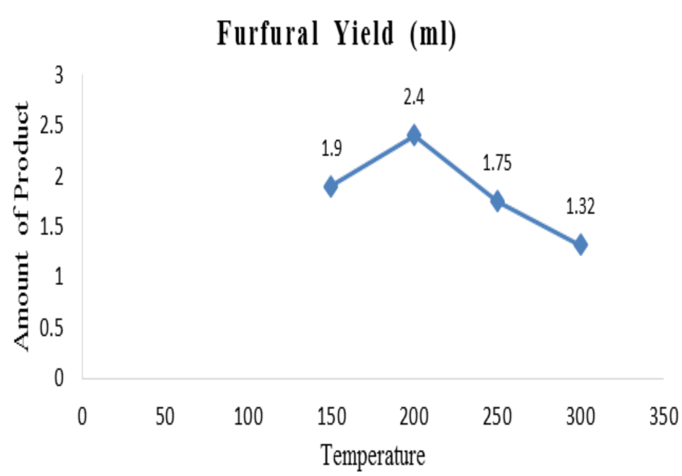


Figure 6. Variation of furfural yield with temperature

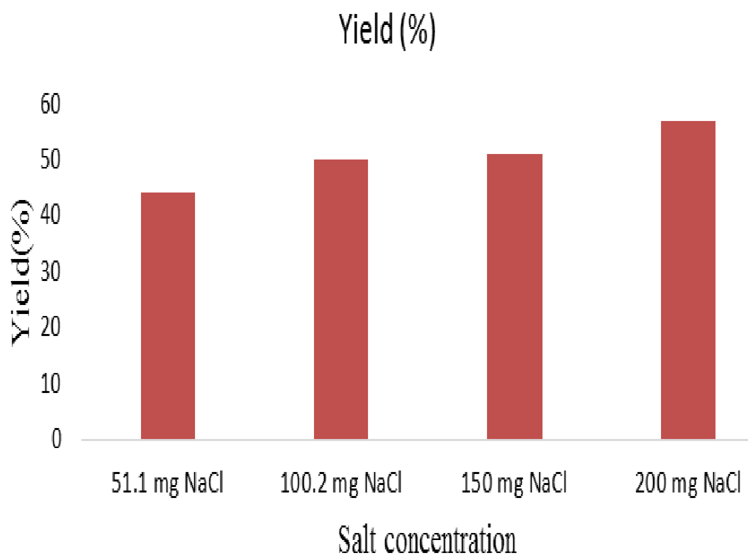
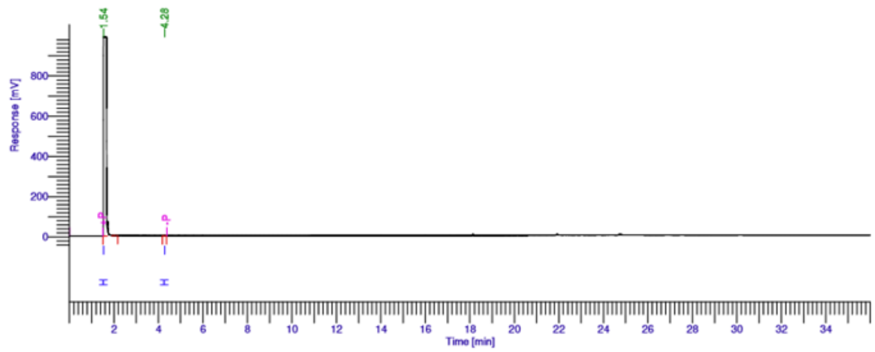


Figure 7. Effect of Salt concentration on the % yield

The concentration of sodium chloride in the bagasse fixture does contribute to the yield because the presence of sodium chloride ions shifts the solubility equilibrium of furfural to the left i.e. it reduces the solubility of furfural in water and thus allowing an easier separation between the two liquids. Additionally, the presence of chloride ions in the mixture helps in the hydrolysis of the hemicellulose process as well as the cyclodehydration reactions that convert the xylose into furfural.

Gas Chromatographic Analysis

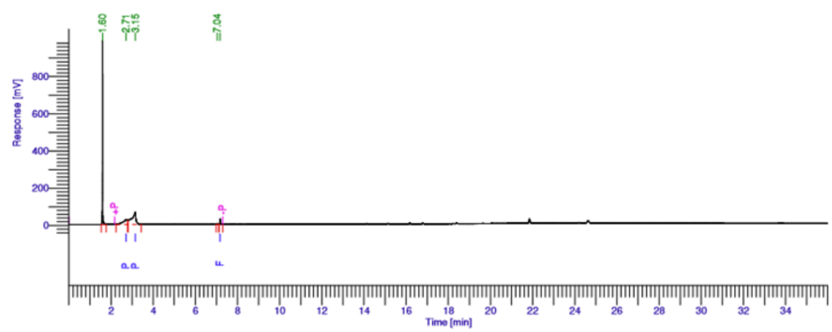
The Gas chromatographic analysis was carried out including the furfural extracted after the process of steam distillation in order to verify the purity of the sample. The Gas chromatography analysis provided information regarding the presence of the furfural compound as well as the presence of other impurities. In addition, it is also possible to know how good a particular solvent is when it is used for extracting furfural from waste agricultural products like bagasse. The Gas chromatography analysis as shown reveal that amongst the three solvents that were used, methanol seems to be more effective in the extraction of the furfural out of the bagasse. However, using ethanol seemed to have caused a certain degree of degradation of the furfural product i.e. it seemed to have been broken into several different low molecular weight compounds because furfural was not detected in the chromatogram. Additionally, using hexane in the Solvent extraction process resulted in furfural being obtained in the form of hydroxyl-methyl-furfural; a chemical compound that is closely related to furfural. The presence of hydroxyl-methyl-furfural is sign of the fact that the furfural was subjected to excess of heat treatment. Considering the yield of furfural and the results of the GC analysis, it can be safely said that the usage of methanol as the solvent during the extraction process is most efficient as the product contains higher amount of furfural and there is a greater degree of separation between the compounds; thus aiding in the separation process (Figures 8-11).



GAS CHROMATOGRAPH

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]	BL	Raw Amount	Adjusted Amount
1	Hexane	1.537	9124237.31	988778.26	99.95	99.95	BB	----------	----------
2	HydroxymethylFurfura	4.282	4841.19	1752.85	0.05	0.05	BB	0.0048	0.0048
			9129078.50	990531.10	100.00	100.00		0.0048	0.0048

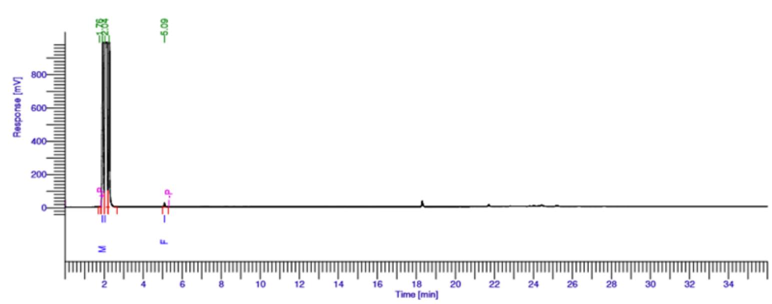
Figure 8. Gas chromatography analysis results for furfural extraction with hexane



GAS CHROMATOGRAPH

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]	BL	Raw Amount	Adjusted Amount
2	Peak1	2.707	371507.60	24830.74	27.63	27.63	BV	0.3715	0.3715
3	Peak2	3.151	912266.36	66894.10	67.84	67.84	VB	0.9123	0.9123
5	Furfural	7.178	61019.78	29462.05	4.54	4.54	*VB	0.0610	0.0610
			1344793.73	121186.90	100.00	100.00		1.3448	1.3448

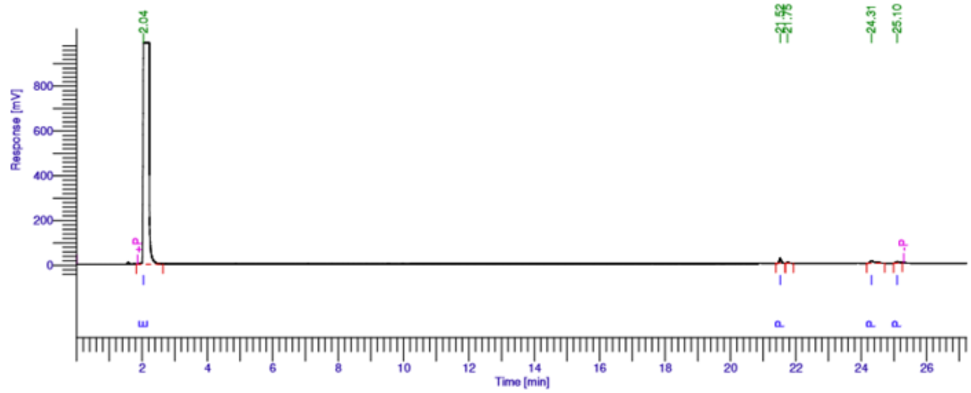
Figure 9. Gas chromatography analysis results for furfural after purification



GAS CHROMATOGRAPH

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]	BL	Raw Amount	Adjusted Amount
2	Methanol	1.911	4521917.64	988523.08	35.22	35.22	VV	----------	----------
3	Ethanol	2.037	8237787.26	988419.60	64.15	64.15	VV	----------	----------
5	Furfural	5.090	81021.08	25688.62	0.63	0.63	BB	0.0810	0.0810
			12840725.97	2.00e+06	100.00	100.00		0.0810	0.0810

Figure 10. Gas chromatography analysis for furfural extraction with methanol



GAS CHROMATOGRAPH

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]	BL	Raw Amount	Adjusted Amount
1	Ethanol	2.044	12309207.68	988614.25	97.86	97.86	BB	----------	----------
2	Peak2	21.523	105253.36	24579.37	0.84	0.84	BV	0.1053	0.1053
4	Peak 3	24.310	123920.71	11471.56	0.99	0.99	BB	0.1239	0.1239
5	Peak 4	25.101	39467.88	5461.31	0.31	0.31	BB	0.0395	0.0395
			12577849.63	1.03e+06	100.00	100.00		0.2686	0.2686

Figure 11. Gas chromatography analysis of furfural after extraction with ethanol

Gas chromatography analysis of the distilled furfural compound was done as well in order to determine the purity of the sample. Although the analysis did reveal quite a strong signal of furfural, there were smaller peaks that corresponded to the presence of secondary compounds. That meant that, the furfural which obtained by this methodology was not completely pure and perhaps needed a greater extent of refining.

Results of the Mass Spectroscopy Analysis

The peaks in the graph of Counts vs Mass-to-Charge ratio were interpreted using an online library and it was determined that the furfural sample that was collected contained some other compounds which were identified and tabulated as shown. The two identified compounds are actually complex hydrocarbon-organic compounds that are present in a wide range of plants Bagasse), well drying and grinding of bagasse. In simple distillation different parameters was studied such as amount of raw material selection, pH, operating temperature with respect to time. In the Soxhlet extractor, found out the best solvent for extraction process. The extracted furfural is analyzed by gas chromatographic (GC), and mass spectroscopy (MS) (Figure 12 and Table 6).

Table 6. Interpretation of the MS results

S.No	Mass-to-Charge Ratio (m/z)	Interpreted molecular Formula	Compound
1	495.1	C27H44O8	Pregnanediol-3-glucuronide
2	439.1	C27H38O5	Thunbergol B
3	365.8	Unkown (Mixed signal)	
5	261.2	C6H6O3	Hydroxymethyl-Furfural

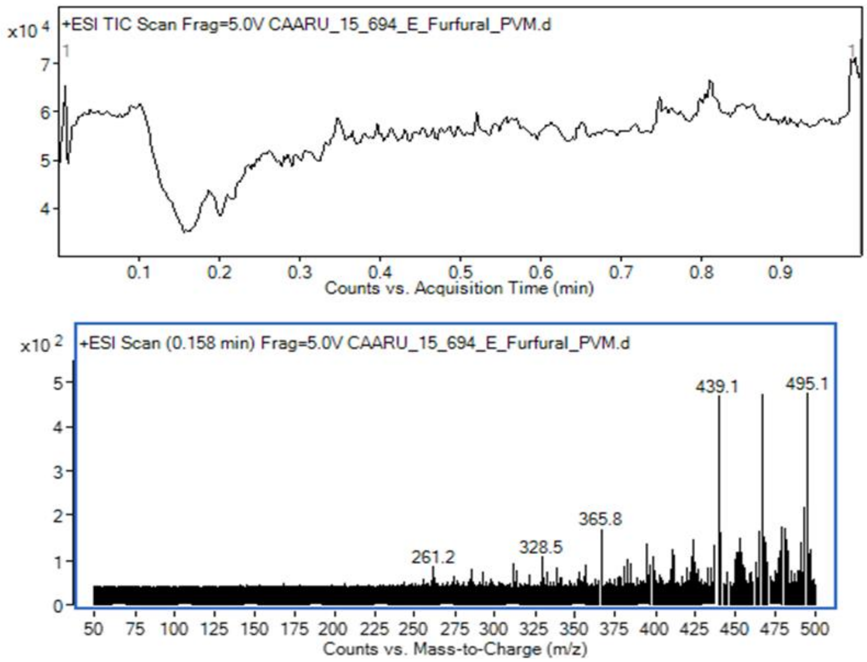


Figure 12. Mass Spectroscopy Analysis

CONCLUSION

The growing amounts of agricultural wastes that are being routinely disposed of to landfills and incinerators is of a major concern as these wastes contain significantly amounts of chemical compounds that are of a major use to us or can be used as the raw material in the synthesis of other high valued components. Although there has been a intensive strength with the usage of agricultural wastes for producing biogas in small scale applications and for making manure in farms, there still is a need to expand the possible uses for the wastes such as bagasse that are routinely disposed off from various agricultural. The experimental study has been conducted for the production of furfural from bagasse by two methods such as Soxhlet extractor and simple distillation. The parameters such as amount of raw material, pH and temperature w.r.t time were reported. The extracted furfural was analyzed by Gas chromatography and Mass spectroscopy with proper design analysis.

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