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Furfural, the Sleeping Beauty: Synthesis, Application as a Nematicide and to Improve the Viscosity Index of Raw Lubricating Oil

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Abstract Furfural was synthesized from corn cobs. The maximum yield of furfural synthesized was produced with 10% concentration of sulphuric acid, in the presence of sodium chloride as the enhancer. The functional groups and molecular weight of furfural were identified accurately, using GC- MS spectrophotometer. It has a molecular formula of $C_5H_4O_2$ and a molecular weight of 96.0. The IR spectrum indicated a very strong absorption at 1714.46 cm^{-1} which is for the conjugated carbonyl (C=O) functional group. Furfural was established to be an effective nematode control agent. A blend of furfural and phenol (1:1 ratio) at 75°C was found to be suitable for refining raw lubricating oil to obtain a viscosity index of 44.63, which is close to the minimum viscosity index recommended by SAE.

Keywords Corn cobs, Furfural, Nematode, Nematicide, Lubricating oil, Viscosity, Viscosity index

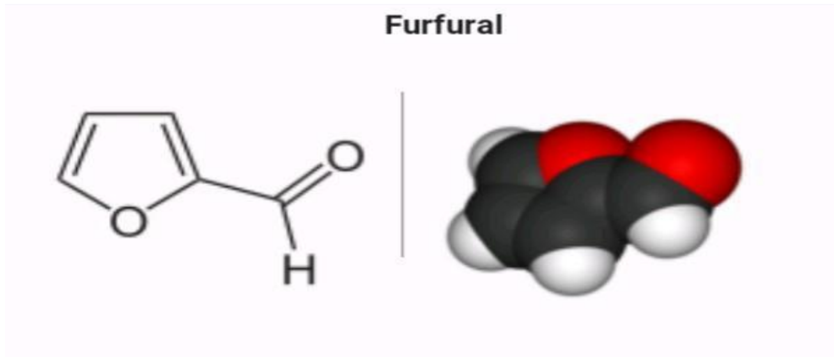
Introduction

As a result of the descending reserves and ascending prices of fossil materials and concern for environmental preservation in the last decade, the interest in the production of chemicals, based on renewable sources has increased. Among the different types of available biomass, agricultural and agro-industrial residues are of special interest, due to their abundance, renewability, and as inexpensive sources for chemicals [1].

Furfural is a natural dehydration product of xylose, a monosaccharide, often found in large quantities in the hemicellulosic fractions of lignocellulosic biomass. Furfural can become a viable renewable alternative, to manufacture many current petroleum based products at a large commercial scale [2].

In addition to attractive thermosetting properties, physical strength, and corrosion resistance, furfural is a natural precursor to a range of furan-based chemicals and solvents, including methylfuran, furfuryl alcohol, tetrahydrofurfuryl alcohol, tetrahydrofuran, methyl tetrahydrofuran, dihydropyran, and furoic acid [3].

Furfural is commercially produced by direct conversion of a whole lignocellulose material in a batch or continuous reactor [4]. Corn cobs and sugarcane bagasse are the biomass that are most frequently used in industrial furfural production because of their high xylan content; the xylan content of corn cob is 37 % wt [5] and that of sugarcane bagasse 22.2 % wt [6].



Structural formula of Furfural

Nematodes are small cylindrical worms, in most cases microscopic. They are aquatic animals that inhabit oceans and seas, freshwater courses, body fluids, and of particular importance for agriculture, the film of water, present between soil particles and in plants [7].

Fossil records show that the first parasitic relationships between nematodes and plants occurred approximately 150 million years ago. Today, the main phytopathogenic nematodes in economic terms are root-knot nematodes (*Meloidogyne* spp.), followed by cyst nematodes (*Heterodera* and *Globodera* spp.), root lesion nematodes (*Pratylenchu* spp.), the burrowing nematode (*Radopholus similis*), and the stem nematode (*Ditylenchus dipsaci*) [8].

Nematode parasitism occurs by insertion of the stylet (spear-like structure attached to the mouth of the nematode) into the plant tissue. The parasitism relationships established between these antagonistic worms, cause serious damage to the infested plant. Nematodes can trigger two kinds of symptoms; direct symptoms, such as a reduction of root mass, a distortion of root structure, and enlargement of the roots, or indirect symptoms, which include a deficiency in absorption of water and nutrients. Nematodes are considered to be important pathogens in many crops [9].

Typically, lubricating (lube) oils contain 90% base oil (most often petroleum fractions, called mineral oils) and less than 10% additives. Additives deliver reduced friction and wear, increased viscosity, improved viscosity index, resistance to corrosion and oxidation, aging or contamination [10].

Lube base oils are obtained from lube distillates of petroleum refinery, which contain a wide spectrum of hydrocarbons viz., n-paraffins, iso-paraffins, naphthenes, aromatics, asphaltenes and resinous compounds. In addition to these hydrocarbons, other compounds containing nitrogen, sulphur and oxygen are also present. In general, aromatics and polar compounds have poor lubricating characteristics such as Viscosity Index (VI) and Oxidation Stability. Nonetheless, lube fractions containing one six-membered aromatic ring, plus paraffin and naphthenes are satisfactorily used as lubricants [11].

In the manufacture of lubricating oils for automotive and industrial applications, removal of aromatic hydrocarbons from the raw lube distillates is necessary for improvement in viscosity index, oxidation stability, colour and oxidation inhibitor response [12].

This research aims at synthesizing furfural from corn cobs; determining how furfural can be applied as an effective nematode control agent and also applying same to improve the viscosity index of lubricating oil.

2. Materials and Methods

2.1. Furfural Synthesis

Corn cobs were collected locally from Anguwan Rukuba, Jos North Local Government Area of Plateau State, Nigeria. The corn cobs were washed thoroughly, using distilled water and then dried at room temperature for a period of 2 weeks. The dried corn cobs were then crushed to a mesh size of 1mm and kept in an oven at a temperature of 110°C for two hours to further dry the cobs. The dried corn cobs were then kept in an air tight container to avoid moisture absorption from the air until it was ready for use.

Using an electronic weighing balance, 30g of the corn cobs was weighed and poured into a 1000 ml beaker. Also

6.0g of sodium chloride was measured and added to the beaker containing the bagasse. 10% of acid was prepared by measuring 90ml of distilled water into a measuring cylinder then filling it up with 10ml concentrated sulphuric acid. This was then poured into the beaker, containing the corn cobs and sodium chloride and the resulting mixture was shaken vigorously to obtain a homogenous mixture.

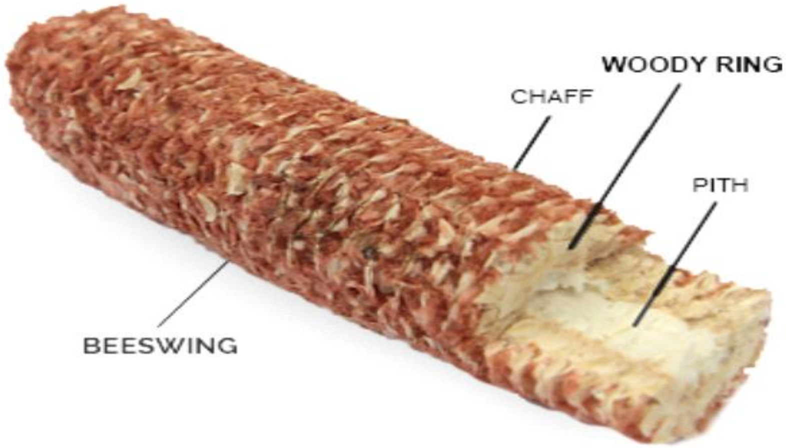


Plate 1: Corn Cob

After shaking, the mixture was taken to the autoclave where it was autoclaved for 1hr 30 min (90 min). After the 90 minute interval, the mixture was taken out of the autoclave and allowed to cool at room temperature. The now cooled mixture was then taken to a vacuum filter to filter out the bagasse residue. 50 ml of the filtrate was then placed in a separating funnel and 30 ml of chloroform was added and shaken vigorously to ensure the efficient extraction of the furfural by the organic solvent. After shaking, the mixture was allowed to separate into two layers, with the upper layer consisting of chloroform and the extracted furfural while the lower layer contained the remaining filtrate.

The same process was repeated for the remaining filtrate. The upper layer was then taken to a rotary evaporator to evaporate the chloroform so as to obtain pure furfural. The furfural was kept in an air tight container to avoid contact with air. This experiment was repeated two times, using the same volume of acid and different masses of salt.

Plate 2: The Synthesized Furfural

2.1. Nematode Extraction Technique

Root knot nematodes were extracted from the roots and rhizosphere of suspected host (tomatoes and lettuce) cultivated in Jos North LGA of Plateau state, Nigeria. The host plant roots were carefully excised and then teased with the aid of teasing pins and forceps to expose and release the nematode from the root tissue. The extraction of root knot nematode from the host plant root was done, using the modified Baermann Funnel method [13]. Baermann funnel is a regular laboratory funnel with a piece of rubber tube (about 25-30 cm long) attached to the stem of the funnel. The tube was in turn connected tightly with the aid of masking tape to a test tube which held the homogenized suspension of root knotnematodes.

The suspension of root knot nematodes collected through the Baermann funnel method was centrifuged for 15 minutes at 2000r/min and the mixture was separated into 2 equal halves and the bottom layer was kept for further analysis.

Furfural at 5 (five) different concentrations (10 mg/ml, 15 mg/ml, 20 mg/ml, 25 mg/mland 30 mg/ml) were applied to the root knot nematode suspension. Three test tubes containing untreated root knot nematode suspension were observed for comparison purposes. After 24 hours interval of treatment, 1ml of the suspension was removed from each test tube and assayed for the estimation of nematode population.

2.2. Estimation of Nematodes

Nematodes population was estimated by counting the number of active juveniles in 1ml of homogenized suspension of root knot nematodes under a binocular research light microscope at ×40magnification.

2.3. Procedure for Treating Lubricating Oil with Furfural

Furfural and phenol were added to the lubricating oil (1:1:1) ratio in a conical flask, the raffinate mixture was subjected to controlled heating, using a heating mantle. Temperatures of 75^{o}C, 95^{o}C, 115^{o}C and 135^{o}C were applied. These were left for one hour, after which separation was carried out, using a funnel, clamped to a retort stand.

Plate 3: Separation of the Mixture of Furfural, Phenol and Lube Oil

The sample was dragged and the time for flow of oil sample in seconds was recorded, using a U tube viscometer. The viscosity was then calculated by applying the formula:

$\mu = kt$ ………………………………………………………………………………… (1)

Where: “k” is a constant factor for the calibrated viscometer.

“t” is the time taken by the oil to flow through the viscometer in seconds.

“μ” is the kinematic viscosity measured in mm^2/s (cSt)

The viscosity index was calculated by using the formula

$VI = \frac{L-U}{L-H} x100$…………………………………………………………………. (2)

Where:

U is the kinematic viscosity at 40°C of the oil whose viscosity index is to be calculated (cSt). L is the kinematic viscosity at 40°C of an oil of zero viscosity index having the same kinematic viscosity at 100°C as the oil.

H is the kinematic viscosity of an oil of 100 viscosity index having the same kinematic viscosity at 100°C as the oil.

VI (cSt) is the viscosity index. The values of L and H were obtained from tables.

Plate 4: Using the U tube Viscometer to Measure Viscosity of the Lube Oil

The viscosities and viscosity indexes of the lubricating oil were determined before and after the process.

3. Results and Discussion

Table 1: Values for the Synthesis of Furfural at Different Masses of Salt and the same Volume of Acid

Mass of Sample (g)	Volume of Acid (ml)	Mass of Salt (g)	Time Taken (mins)	Autoclave Temperature ^{O}C	Quantity of Furfural Synthesized (ml)
30	150	6.0	90	170	12.7
30	150	12.0	90	170	19. 3
30	150	24.0	90	170	25.7

Table 1 shows the volumes of furfural synthesized from corn cobs, using the same mass of corn cobs and volume of dilute acid and different masses of salt. The volume of furfural produced increased with an increase in the mass of salt used. When 30 g of corn cob was used with 150 ml of dilute acid and 6.0 g of salt, 12.7 ml of furfural was obtained, while when 30 g of sample, 150 g of acid and 24.0 g salt were used, the volume of furfural produced was 25.7 ml. The furfural produced was a colourless oily liquid, with and almond smell, that turned yellowish and then brown, upon exposure to light and air.

Figure 1 is the GC-MS spectrum of the synthesized furfural. Furfural has a retention time of 5.6111minutes which shows a molecular ion peak at m/z 96.0 that correlates strongly to a molecular formula of ($C_5H_4O_2$) which is the molecular formula of Furfural.

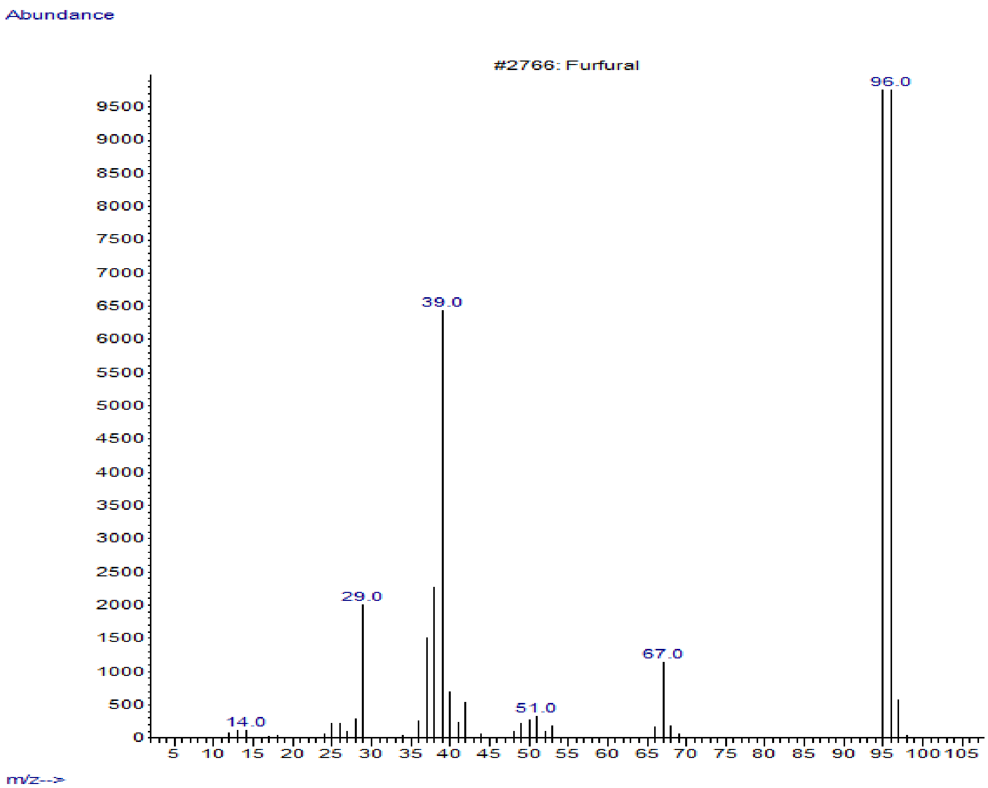


Figure 1: GC-MS spectrum of synthesized furfural

The spectrum shown on figure 1 also shows a molecular peak at m/z 95.0 $(M-1)^+$ which was obtained due to the loss of hydrogen to form a carbonium ion. An electron was given out by the aldehyde carbon to hydrogen to form this fragmentation, because it forms a more stable cation. This fragmentation peak matches that of the mass spectrum proposed by NIST (2004).

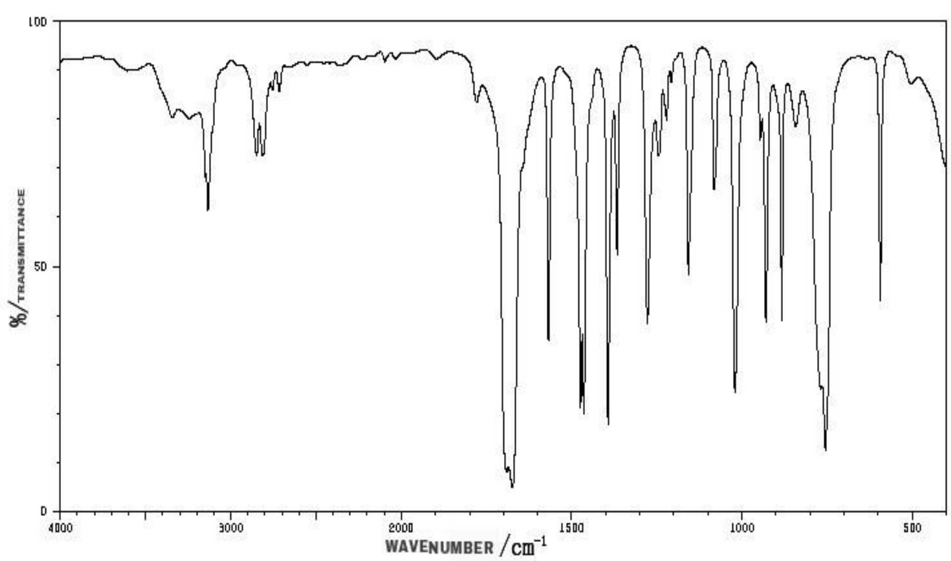


Figure 2: Infrared spectrum of synthesized furfural

The IR spectrum (Figure 2) shows a very strong absorption at 1714.46cm^{-1}. This absorption shows a very significant functional group which is the conjugated carbonyl (C=O). The absence of peak at 1763.72cm^{-1} indicates strongly the presence of aldehyde and not the ketone group [14]. Furthermore, the presence of an aldehyde was obvious, due to the existence of two peaks at 3019.55cm^{-1} and 2811.71cm-1. This IR spectrum was also compared with the furfural IR spectrum published by NIST (2004) and it suited that spectrum perfectly.

3.1 Application of Furfural as a Nematicide

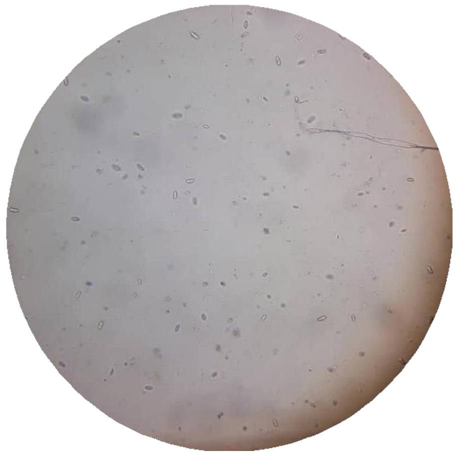


Plate 5: Untreated Nematode Suspension as Viewed under Binocular Research Light Microscope after 24 hours

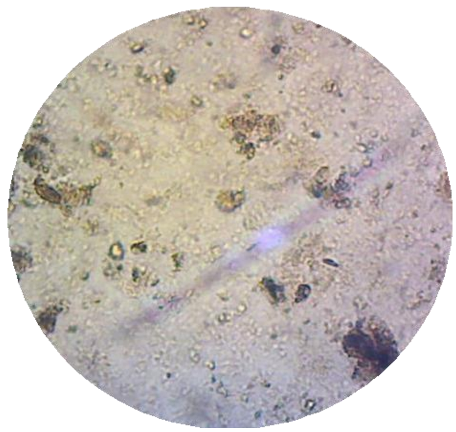


Plate 6: Effect of 10 mg/ml Furfural Concentration on Nematode Suspension, as viewed under Binocular Research Light Microscope after 24 hours

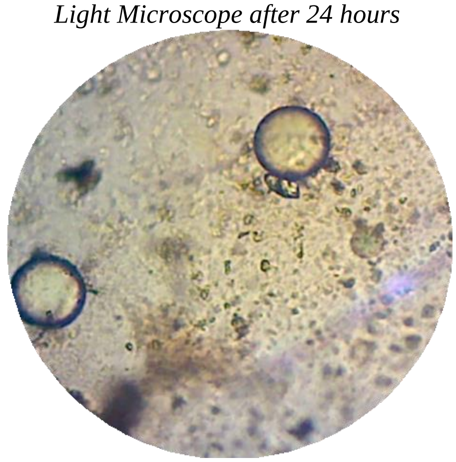


Plate 7: Effect of 15 mg/mlFurfural Concentration on Nematode Suspension, as viewed under Binocular Research Light Microscope after 24 hours

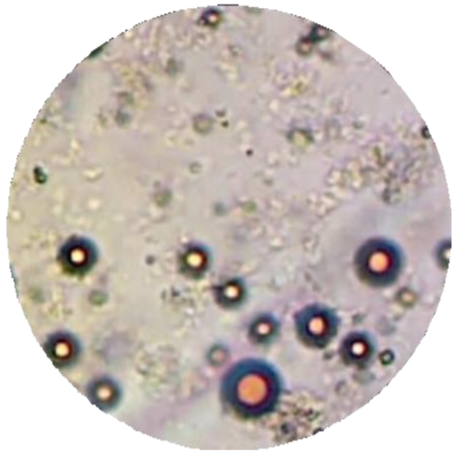


Plate 8: Effect of 20 mg/ml Furfural Concentration on Nematode Suspension, as viewed under Binocular Research Light Microscope after 24 hours

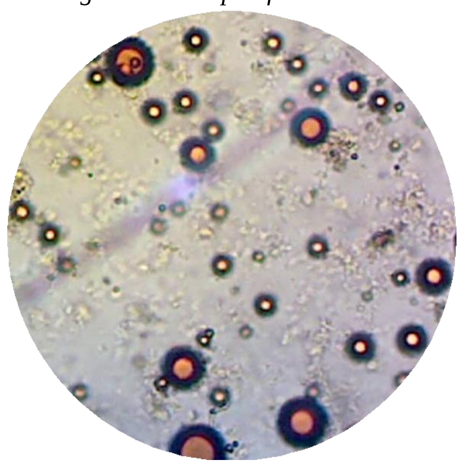


Plate 9: Effect of 25 mg/ml Furfural Concentration on Nematode Suspension, as viewed under Binocular Research Light Microscope after 24 hours

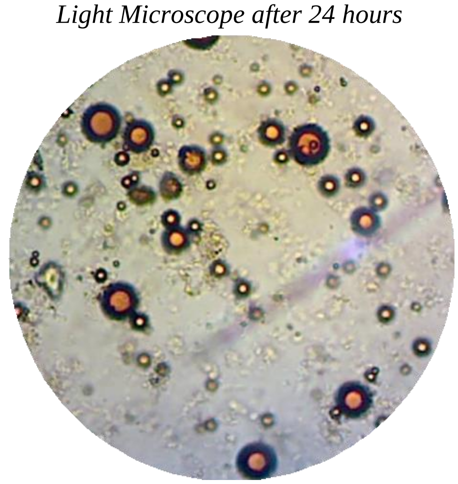


Plate 10: Effect of 30 mg/ml Furfural Concentration on Nematode Suspension, as viewed under Binocular Research Light Microscope after 24 Hours

The nematode count before the treatment and 24 hours after treatment of nematode suspension with various concentrations of furfural is presented on plates 5-10. The results obtained showed that furfural was significantly able to reduce drastically, the population of nematode in the suspension at different concentrations. Nematode

population reduction was observed through estimation by counting the number of active juveniles in 1ml of homogenized suspension of root knot nematodes under a binocular research lightmicroscope at x40 magnification.
Plate 5 shows the estimated number of active nematodes observed in 1ml of untreated homogenized nematode suspension under a research light microscope at x40 magnification. About 35 active juveniles were estimated from the control as indicated. Meanwhile, plate 10 shows the estimated nematode population of only about 3 active juveniles at 30 mg/mlfurfural concentration.
Reduction of nematode population was obtained with concentration of furfural at 15 mg/ml, 20 mg/ml, 25 mg/ml and 30 mg/ml as indicated on plate 7, 8, 9 and 10 respectively, the highest reduction was observed in plate 10 (30 mg/ml concentration of furfural). This suggests that a small concentration of furfural is highly effective in controlling nematode population.

3.2. Application of Furfural to Improve the Viscosity Index of Lubricating Oil

Table 2: Viscosity and Viscosity Index values of Raw and Blended Lubricating Oil at Different Temperatures

Temperature (^{O}C)	Viscosity (Ns/m^2)		Viscosity Index	
	RLO	**TLO**	**RLO**	**TLO**
75	0.026	0.015	18.22	44.63
95	0.024	0.020	16.74	25.67
115	0.023	0.020	13.25	24.78
135	0.022	0.020	10.23	21.24

RLO = Raw lube oil; TLO = Treated lube oil

Furfural was blended with phenol at ratio1:1 to increase its solvent power. After treating the lubricating oil which had a viscosity of 0.026, and a viscosity index of 18.22 with the furfural/phenol blend at different temperatures, it was observed that 75^{O}C produced the best viscosity of 0.015, and a viscosity index of 44.63, which is a good viscosity index as compared to the standard (4.0) given by SAE (Society of Automotive Engineers).

4. Conclusion

Furfural was successfully synthesized from corn cobs. From the results obtained, it was noted that some parameters influenced the yield of furfural obtained and were identified as acid concentration and the mass of salt used. The maximum yield of furfural synthesized was at 10% concentration of sulphuric acid with the presence of sodium chloride as the enhancer in the synthesis. The functional groups and molecular weight of furfural were identified accurately using GC- MS equipment. It has a molecular formula of $C_5H_4O_2$ and a molecular weightof 96.0. Furfural is a liquid, with a smell similar to that of almond. It was colourless but turned yellowish and then brown upon exposure to light and air.
It was established that furfural can be used as an effective nematode control agent. Its physical and chemical properties suggest that it has a potential for application in chemical formulations and applications.
Refining of raw lubricating oil using, a blend of furfural and phenol was feasible; the results showed that at higher temperatures the viscosity of the lubricating oil increased. However, at lower temperatures, the viscosity index increased.
It was established that a temperature of 75^{o}C is suitable for the refining of lubricating oil to obtain a good viscosity index of 44.63, which is close to the minimum viscosity index (40) recommended by the Society of Automotive Engineers (SAE).

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