**International Journal of Academic and Applied Research (IJAAR)**
**ISSN: 2643-9603**
**Vol. 4, Issue 8, August – 2020, Pages: 27-32**

# Comparative Synthesis of Furfural with Inorganic and Organic Acidic Hydrolysis of Discarded Corncobs as a Precursor for Catalytic Hydrogenation into Tetrahydrofuran.

**Olabimtan Olabode.H[1], Opeyemi Adegboyo[2], Okibe Ora. P[3], Samuel Florence.A[4], Asmita Basu[5],**

[1, 3] National Research Institute for Chemical Technology, Department of Industrial and Environmental Pollution, Zaria Kaduna State, Nigeria.
[2]Federal Polytechnic, Department of Science Laboratory Technology, Ilaro, Ogun State, Nigeria.
[4]National Research Institute for Chemical Technology, Department of Scientific and Industrial Research, Kaduna State, Nigeria.
[5]KIIT University Patia Bhubaneswar, India.

**Corresponding author email**:*Olabode4angel@gmail.com*

***Abstract:*** *Maize corn is agro-waste biomass with the component of pentosan, a five-carbon polymer that applies for the production of furfural, a precursor to the synthesis of tetrahydrofuran as a synthetic polymer subunit. Inorganic($H_2SO_4$) and organic($CH_3COOH$) acidic hydrolysis at 1M concentration, $100^oC$ refluxing temperature with 50gram of the cobs powder in the presence of NaCl catalyst under distillation at $162^oC$ were developed. The entire process activated the conversion of the pentosan from the maize cob into furfural which economically can be hydrogenated with a palladium catalyst at $220^oC$ in achieving tetrahydrofuran. Classical aniline-acetic anhydride test confirmed the presence of furfural with the two distillates ($H_2SO_4$ and $CH_3COOH$) at the yields of 42 and 35% respectively. Selected physicochemical properties such as densities, refractive indices, water solubilities, viscosities, boiling points, dielectric constants, and surface tensions were conducted according to standard methods. GCMS and FTIR of the distillates were also analyzed under the same analytical conditions.*

**Keywords:** Corn cobs, furfural, acidic hydrolysis, catalyst, tetrahydrofuran.

## 1.0 INTRODUCTION

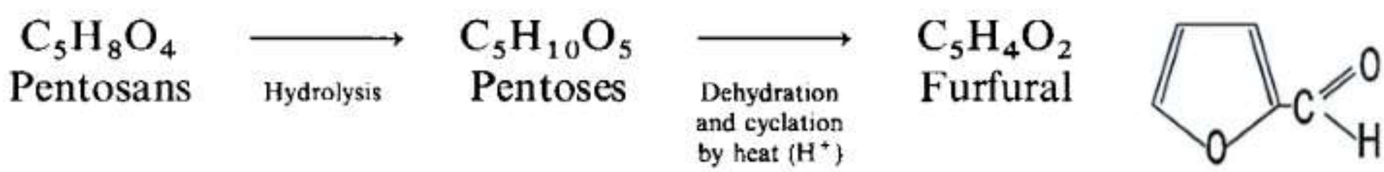
Corn cobs are wastes with the exclusion of the grains around the husks. The production and processing of corn in the early twentieth century brought about a surge in this by-product's volumes [1]. Practically, nearly 180 kg of cobs is generated from an average ton of shelled corn with Nigeria as the second-biggest corn consumer in Africa sub-region, following South Africa, with approximately 10.79 million Metric tonnes in 2014[1][2]. In Nigeria, the significant amounts of corn are grown in the Northern region of Kaduna, Borno, Niger, and Taraba and with the South-Western areas like Ogun, Ondo, and Oyo [2]. Corn cobs are a heavily fibrous agro-based commodity, with several uses industrially. Technically, with their low nutritional benefits, they are applied as fuel, litter for chickens and other animals, mulch, and soil conditioner and as a feed for ruminants [1]. Their absorbency and abrasiveness qualify them for a range of industrial purposes as a sorbent for fluids, water in industrial applications, and oil clean up with both industrial and environmental oil spills [1]. In animal feed, they are amazing media for vitamins and antibiotics, and in lawn care products like herbicides and pesticides [1]. They are used in the manufacture of chemicals such as furfural, or xylitol sugar substitution and as a blast polishing agent with jewelry, nuts, and a very cheap viable route of renewable energy generation [1]. The cobs would be of significant economic advantage when processed into furfural as it is commonly used as petro based solvent, lubricants, and production of nylon [3]. Moreover, it functions as an intermediate product for the preparation of tetrahydrofuran, furfuryl alcohol, pharmaceutical products, fragrance, and herbicides [3]. Corn Cobs produces 30-32 percent pentosan, a form of polysaccharide that is a feedstock in furfural production [3]. The use of maize cobs as the raw materials for furfural production is very advantageous as maize cobs retain the highest level of pentosan amongst other recognized agro-based biomass for furfural production [3]. In general, forestry and agricultural waste has overtime been identified as feedstocks for the synthesis of valuable chemicals, as biomass conversion processes are particularly suitable for the generation of valuable products. The integrated processing plants which can handle various feedstocks and make efficient use of process residues are required for the efficiency and economy of product recovery [4]. The processing of furfural through agro-wastes biomass has been established from 1830 when furfural was invented by Dobereiner and widely documented in the literature [5].It is developed by the hydrolysis of pentosans in wastes like corncobs to xylose as furfural. Tetrahydrofuran (THF), or oxolane, is a natural compound with the chemical formula $(CH_2)_4O$. It is a liquid heterocyclic ether with colorless, water-mixable, with low viscosity [6]. The commonly applied industrial procedure requires the acid-catalyzed dehydration of 1, 4-butanediol, a process equivalent to ethanol-based diethyl ether [6]. DuPont introduced a strategy for the development of Tetrahydrofuran with the oxidization of n-butane to yield crude maleic anhydride, supported by catalytic hydrogenation. THF can as well be processed to furan via catalyzed hydrogenation, as it encourages some carbohydrates to be processed to THF through acid-catalyzed hydrolysis into furfural and decarboxylation towards furan. Sensitive applications via the polymerization reaction transform THF into a linear dimensional polymer as poly tetramethylene ether glycol (PTMEG) in the presence of strong acids. This is a polymer that is used mainly to produce elastomeric polyurethane fibers. It is also an aprotic solvent for the industrial preparation of poly-vinyl chloride and lacquers. It possesses the dielectric value of 7.6 with a mild polarity that dissolves a broad variety of polar and non - polar chemicals. THF is water soluble with the formation of solid hydrated clathrate complexes at low temperatures [6]. THF was investigated as a miscible co-solvent in an aqueous system in the delignification and liquefaction of plant lignocellulosic materials to generate sustainable substrate chemicals and carbohydrates as an alternative to biofuels. Diluted THF facilitates the chemical conversion of biomass glycans and disintegrates the bulk of lignocellulosic materials rendering it an excellent agent for pretreatment of the biomass. It is typically adopted in polymer science as it dissolves PVC with gel permeation chromatography, liquefy old PVC plastic, and to degrease metal parts industrially. It is as well a component of the mobile phase with the reversed-phase liquid chromatography [6]. It possesses a greater tolerance with elution than acetonitrile or methanol but used less frequently. Through the use of PLA plastics, THF is used extensively as a solvent in 3D Printing technology, cleaning the clogged 3D printer parts, removal of extruder lines, and shines finished prints. Additionally, THF is often used as a mixed solvent with lithium metal batteries lately, enhancing the stability of the metal anode. THF is a common solution solvent in the laboratory as the miscibility with water is neutral with most reactions with organometallic compounds like Grignard reagents and organolithium. In the meantime, industrial THF contains significant water to be extracted for critical operations like organometallic compounds [6]. In this context, furfural was recovered from discarded corncobs salvaging environmental nuisance under organic and inorganic acidic catalyzed hydrolysis as a starting feedstock for the synthesis of tetrahydrofuran.

## 2.0 MATERIALS AND METHODS

Corncobs, mortar and pestle, blender, sieve shaker, distilled water, concentrated sulphuric acid, acetic acid, round bottomed flask, sodium chloride, quick fit distillation set, heating mantle,

**2.1 Feedstock Preparation**
locally obtained corncobs were dried, pulverized and sieved to uniform particle size of 150 mesh [7]

**2.2 Mineral and organic hydrolysis of Corn cobs (pentosan) and distillation of furfural**
50 grams of corncobs powder were hydrolyzed and simultaneous dehydrated with 1.5L of 1M $H_2SO_4$ in the presence of NaCl as a catalyst and with $CH_3COOH$ at the same conditions separately. The reactions were conducted in a stirred refluxed reactor equipped with thermometer and condenser at a temperature of $100^{O}C$ for some hours at atmospheric pressure and steam distilled at $162^{o}C$ obtaining some colorless distillates in each case [7].




**2.3 Furfural Classical Identification**
The obtained furfural was analyzed qualitatively using aniline-acetic anhydride Analysis was done qualitatively by adding reagent to the obtained furfural sample. The reagent used to analyze furfural was mixed of acetic acid and aniline at 1:1. If the sample contains furfural, the colour changed to red [7].

**2.4 GCMS Analysis of furfurals**
GC-MS was done to identify the sample component in each cases [8].

**2.5 Physicochemical properties of furfural.**
Boiling point [9], density [10], refractive index [11], water solubility [12], dielectric constant [13], viscosity [14] and surface tension [15] were determined accordingly.

**2.6 Yield determination of furfural**
The recovered solid cake was thoroughly drained with de-ionized water to a constant pH with the filtrate, then dried at 50°C for 12h. The weight losses of this residue was determined [7].

**2.7 Synthesis of THF with Furfural pathway**
THF can be produced by decarboxylation of furfural to furan under reductive conditions and then subsequently hydrogenated to tetrahydrofuran (THF)

**International Journal of Academic and Applied Research (IJAAR)**
**ISSN: 2643-9603**
**Vol. 4, Issue 8, August – 2020, Pages: 27-32**

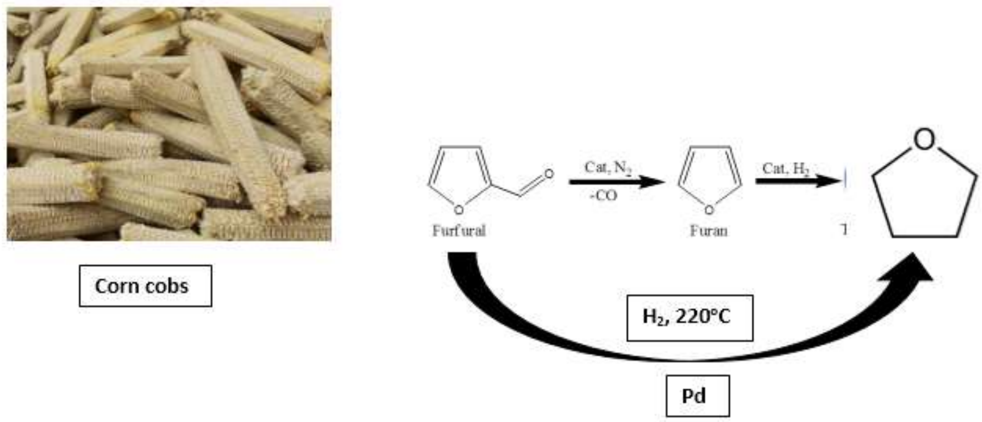



Figure 1. Synthetic pathway of tetrahydrofuran from agro waste biomass derived furfural

## 3.0 RESULTS AND DISCUSSION

Table 1. Furfural classical test

| Test | Sulphuric acid | Acetic acid |
|---|---|---|
| Aniline-acetic anhydride Analysis | positive | positive |

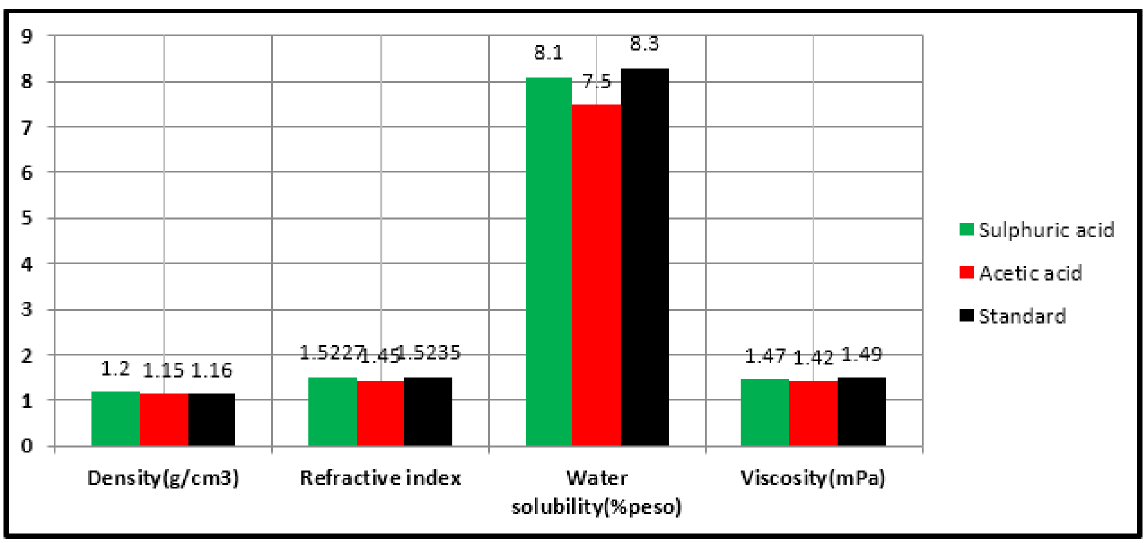



Figure 2.Physicochemical parameters of the extracted furfural against standard.

**International Journal of Academic and Applied Research (IJAAR)**
**ISSN: 2643-9603**
**Vol. 4, Issue 8, August – 2020, Pages: 27-32**

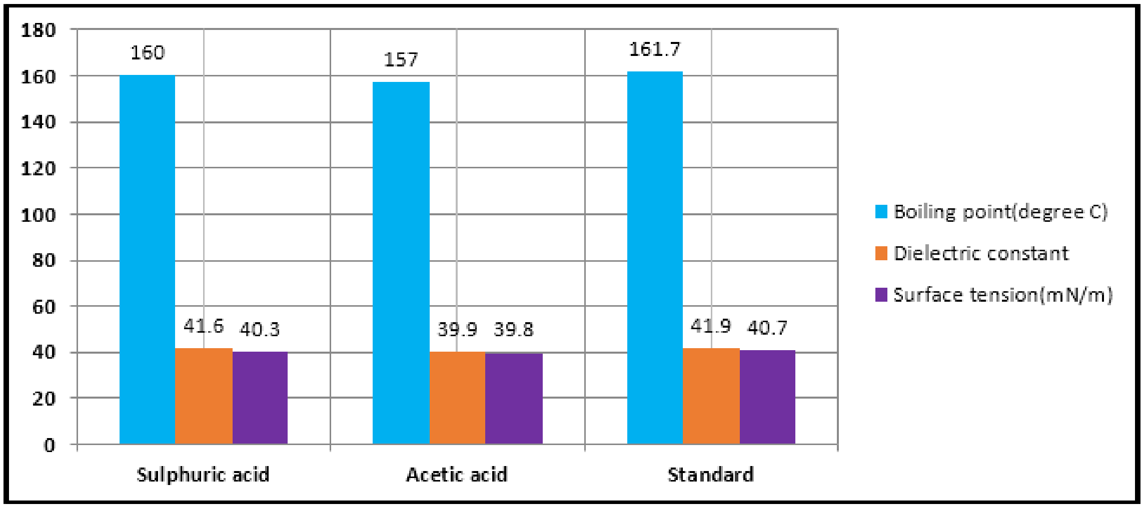



Figure 3. Physicochemical parameters of the extracted furfural against standard.

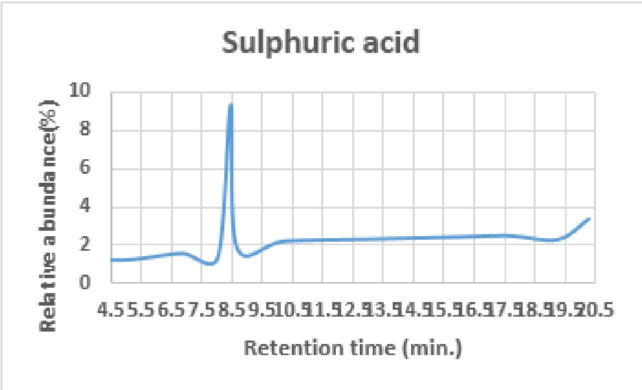



Figure 4. GCMS of furfural from 1M sulphuric acid hydrolysis of corn cobs

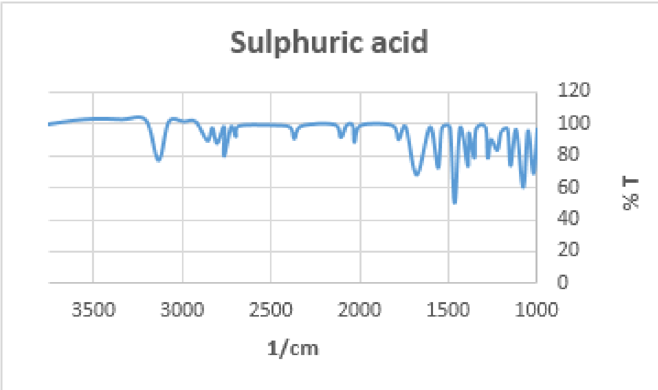



Figure 5.FTIR of furfural from 1M sulphuric acid hydrolysis of corn cobs

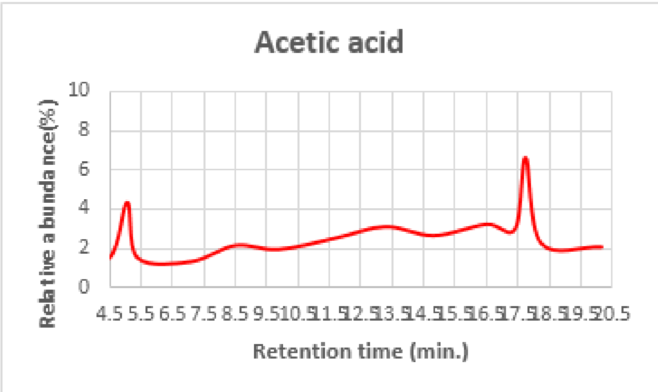



Figure 6.GCMS of furfural from 1M Acetic acid hydrolysis of corn cobs

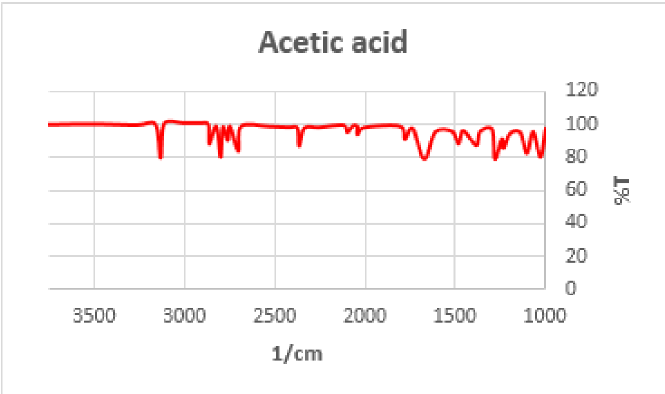



Figure 7. FTIR of furfural from 1M acetic acid hydrolysis of corn cobs

Table 2. FTIR spectrum analysis of sulphuric acid hydrolyzed furfural

| Wavelength($cm^{-1}$) | Class | Structure | Assignment |
|---|---|---|---|
| 3135.92 | Alkenes | RCH=CH2 | =C−H stretch |
| 2766.59 | Aldehydes | RHCO | −C−H stretch |
| 1680.83 | Aldehydes | C=CCHO | −C=O stretch |
| 1560.68 | Alkenes | 4 rings | C=C stretch |
| 1467.23 | Aromatics | C−C ring | Ar C−C stretch |
| 1080.10 | Ethers | R−O−R | C−O stretch |

Table 3. FTIR spectrum analysis of acetic acid hydrolyzed furfural

| Wavelength($cm^{-1}$) | Class | Structure | Assignment |
|---|---|---|---|
| 3135.20 | Alkenes | RCH=CH2 | =C−H stretch |
| 2802.06 | Aldehydes | RHCO | −C−H stretch |
| 1673.50 | Alkenes | Cis RCH=CHR | C=C stretch |
| 1483.30 | Aromatics | C−C | Ar C−C stretch |

Table 4. The yields of furfural

| Hydrolysis | Initial weight of the corncobs(g) | Final volume of the furfural(ml) | Final weight of the furfural(g) | Yield (%) |
|---|---|---|---|---|
| Sulphuric acid | 50.00 | 45.00 | 21.00 | 42 |
| Acetic acid | 50.00 | 38.00 | 17.50 | 35 |

The acidic hydrolysis ($H_2SO_4$ and $CH_3COOH$) of pentosans with the simultaneous conversion of pentoses into furfural as a starting feedstock for the synthesis of tetrahydrofuran were achieved. The products obtained were initially colorless to final yellowish liquids. They were tested for an aldehyde functional group by using aniline-acetic anhydride to the formation of a red precipitate. The yield of furfural according to table 4 implies the better reactivity and selectivity of sulphuric acid than to acetic acid under similar experimental conditions. As well, the high level of boiling point with sulphuric acid that can be due to the residual sulfates allows and enhances complete ionization processes compare to acetic acid with only one ionizable proton with incomplete ionization[7]. The selected physicochemical properties of the furfural through 1M sulphuric acid tend to closer to standard values than to that of acetic acid [16]. The Chromatograms as presented in Figures 4 and 6 revealed dominant peaks that are indications of a single component with the distilled products at 8.47 and 17.75 minutes with sulphuric acid and acetic acid respectively. The presence of aldehydes (furfural) was established by the IR spectrum on Tables 2 and 3 with the existence of six peaks with sulphuric acid hydrolyzed furfural and four with the acetic acid hydrolyzed furfural.

## 4.0 CONCLUSION

Furfural, value addition from discarded corn cobs has been synthesized comparatively with inorganic (sulphuric acid) and organic-based acid (acetic acid) using sodium chloride as a catalyst at the same conditions experimentally. Furfural as a cheap feedstock to the preparation of tetrahydrofuran is an encouraged and viable synthetic pathway that can add value extensively in the area of waste management with corn cobs.

## 5.0 REFERENCE

1. Feedipedia - Animal Feed Resources Information System - INRA CIRAD AFZ and FAO (2019).Feedipedia.org.
2. Sahelcp.com (2017). http://sahelcp.com/wp-content/uploads/2017/06/Sahel-Newsletter-Volume-14.pdf.
3. Nurul Hidayat et al (2019). Preliminary Design of Corncob based Furfural Plant .AIP Conference Proceedings 2062, 020048 (2019); https://doi.org/10.1063/1.5086595.
4. Ullah, K.et al (2015). Assessing the lignocellulosic biomass resources potential in developing countries: A critical review. Renewable and Sustainable Energy Reviews, 51, 682–698. doi:10.1016/j.rser.2015.06.044
5. Riera, F. A.et al (2007). Production of furfural by acid hydrolysis of corncobs. Journal of Chemical Technology & Biotechnology, 50(2), 149–155. doi:10.1002/jctb.280500202
6. Tetrahydrofuran. En.wikipedia.org. (2020). https://en.wikipedia.org/wiki/Tetrahydrofuran.

7. Widyastuti, Catur R.and Istiqomah Istiqomah (2014).Production of Furfural from Corncobs Agricultural Waste by Acid Hydrolysis at Atmospheric Pressure." Journal Bahan Alam Terbarukan, vol. 3, no. 2, 1 Dec. 2014, pp. 71-75, doi:10.15294/jbat.v3i2.5765.
8. Elvira M.S.M. Gaspar and João F. Lopes (2009). Simple gas chromatographic method for furfural analysis. Journal of Chromatography A, 1216 (2009) 2762–2767.
9. CBSE, S. (2016). Determination of Boiling point - Learn CBSE. Learn CBSE.https://www.learncbse.in/determination-boiling-point/.
10. How to Measure the Density of Liquids. Sciencing. (2020).https://sciencing.com/measure-density-liquids-5815427.html.
11. Refractometry: Analyzing Results. (2003). http://www2.ups.edu/faculty/hanson/labtechniques/refractometry/interpret.htm.
12. How to Calculate Solubilities. Sciencing. (2020).https://sciencing.com/calculate-solubilities-5179123.html.
13. diksha105. (2020). Determine the dielectric constant of the given liquid. https://www.slideshare.net/diksha105/determine-the-dielectric-constant-of-the-given-liquid.
14. Determination of viscosity of liquid using Ostwald viscometer (2020). https://labmonk.com/determination-of-viscosity-of-liquid-using-ostwald-viscometer.
15. Determination of surface tension (2020). https://mafiadoc.com/experiment-5-determination-of-surface-tension-by-_59c6abf01723ddb571da0373.html.
16. Ambalka, VU and MI Talib (2012) International Journal of Engineering and Sciences.**1** 30-36.