COMPARATIVE STUDY OF MICROWAVE ASSISTED PRE-TREATMENT METHODS OF RICE HUSK FOR POTENTIAL ENERGY RECOVERY THROUGH ANAEROBIC DIGESTION

by

NADIA BINTI ABDUL JALIL

Dissertation submitted in partial fulfillment of

the requirements for the

Bachelor of Engineering (Hons)

(Civil Engineering)

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CERTIFICATION OF APPROVAL

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Approved by,

____

AP DR MOHAMED HASNAIN ISA

UNIVERSITI TEKNOLOGI PETRONAS
TRONOH, PERAK
SEPTEMBER 2013

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sourced or persons.

NADIA BINTI ABDUL JALIL

ABSTRACT

Rice husk is a major by-product of the rice-milling industries and it is abundantly available. It has been considered as a waste which causes disposal problems. Until today, open field burning that is often carried out after harvesting season is perhaps the most common practice of handling rice husk in many countries in Asia. Rice husk is commonly disposed via open burning in the field. Such practice leads to the energy being wasted and poses environmental health threats to the public. In the recent years, utilization of agricultural waste and residues for energy recovery has received a lot of attention. Ample availability of rice husk coupled with the continuous development of biomass energy conversion technologies have turned rice husk into a potential source of energy but due to its recalcitrant nature inhibits and slows the digestion of cellulose and hemicellulose, to be converted to fermentable sugars and biofuels. This lignocelluosic biomass is to be treated somehow in order to disrupt the lignin present and to digest the cellulose and hemicellulose in better percentage to get enhanced biofuel production. For this research, there are two objectives to be achieved which are to disrupt the lignin in order to get higher percentage of cellulose and hemicellulose for potential energy recovery and also to determine the best rice husk pre-treatment method for enhanced biofuel production. Four different chemical solutions, two acidic (dilute sulphuric acid and hydrogen peroxide) and two alkaline (dilute sodium hydroxide and sodium carbonate), of 2%, 3.5%, and 5% strength were used for pre-treatments of the biomass. Research conducted shows that the lignin was successfully disrupted after pre-treatment. Based on the results, quantitative analysis (CHNS, UV Visible Spectrophotometer & HPLC) had proven that NaOH with 3.5% concentration is the best chemical for the pre-treatment of rice husk for potential energy recovery. For untreated rice husk, the percentage of cellulose was 38.6% while the pre-treated rice husk with 3.5% concentration of NaOH gives a total of 59.3% of cellulose. From this result, it can be concluded that the best rice husk pre-treatment method for potential energy recovery is by using 3.5% concentration of Sodium Hydroxide (NaOH) where it gives the highest percentage of cellulose.

ACKNOWLEDGEMENT

First and Foremost, I am grateful to Allah S.W.T. for the blessing and strength that has provided me with the inspirations to pursue and finally, completed my final year project successfully.

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CHAPTER 1: INTRODUCTION

1.1 BACKGROUND OF STUDY

Fossil fuels are primary energy source that are being utilized nowadays. Due to concerns regarding depletion in supply, the world is now focusing on alternative sources for energy. Biofuels are good replacement of fossil fuels because of the easy availability of high volume agricultural biomass waste. Conversion of abundant lignocellulosic biomass to biofuels as transportation fuels presents a viable option for improving energy security and reducing greenhouse emissions. Unlike fossil fuels, which come from plants that grew millions of years ago, biofuels are produced from plants grown today. They are cleaner-burning than fossil fuels, and the short cycle of growing plants and burning fuel made from them does not add CO_2 to the atmosphere [1].

In general, agricultural wastes are biomass residues that can be divided into two categories namely the crop residues and the agro-industrial residues. Crop residues refer to plant residues that remain on the field after the collection of crops. The agro-industrial residues on the other hand are the by-products of the post-harvest processes that maybe generated from the process of cleaning, sieving, and milling. In Rice industry, a biomass residue that is commonly utilized for energy generation is rice husk. Rice husk is the outer layer of a rice seed. Rice husk is removed from the rice seed as a by-product during the milling process [2]. South and Southeast Asia account for over 90% of the world’s rice production. Rice husk is a major by-product of the rice-milling industries and is abundantly available. However, rice husks have been considered as waste, causing disposal problems. Like most other biomass materials, rice husk contains a high amount of organic volatiles. Thus, rice husk has been recognized as a potential source of energy [3].

It is estimated that only agriculture in the world leads to production of over 140 billion metric tons of biomass waste, if properly managed can produce huge amounts of energy, approximately equivalent to 50 billion tons of oil. The energy produced from the biomass is not only environment friendly and carbon neutral but it also reduces our dependencies on fossil fuels, thereby contributes efficiently to energy security and clean climate change mitigations [4].

Biogas production from various types of solid waste and residues like municipal solid waste and agricultural solid waste by anaerobic digestion method has been experimentally investigated and is considered to be one of the best future options available, as it is economically much feasible due to its smaller requirements and using waste or residues as feedstock [5,6].

1.2 PROBLEM STATEMENT

Lignocellulosic biomass waste is available in abundant quantities around the world, but due to its recalcitrant nature inhibits and slows the digestion of cellulose and hemicellulose, to be converted to fermentable sugars and biofuels. This lignocelluosic biomass is to be treated somehow in order to disrupt the lignin present and to digest the cellulose and hemicellulose in better percentage to get enhanced biofuel production [7-9].

Lignocellulosic biomass has been pretreated successfully by microwave assisted dilute acid pretreatment and microwave assisted alkali pretreatment for their enzymatic hydrolysis or liquid state anaerobic digestion [10,11]. Alkaline pretreatment has also given good results for the treatment of lignocellulosic. However a research study regarding combination of microwave assisted acidic and microwave assisted alkaline pretreatment of lignocellulosic biomass and their comparative effects is yet to be evaluated. This research study will be focusing on these areas, and will be providing a comparative analysis of the microwave assisted pretreatment methods on lignocellulosic biomass, for potential source of energy recovery.

1.3 OBJECTIVES

The main objectives of this research are as follow:-

1. To perform pre-treatment of rice husk for disruption of lignocellulosic biomass waste.
2. To compare the effects of each pre-treatment and to obtain the best pre-treatment method for potential energy recovery.

1.4 SCOPE OF STUDY

This research comprises of laboratory experiment involving the pre-treatment of agricultural biomass for energy recovery. The waste agricultural biomass chosen for this research is rice husk which is easily obtained in Malaysia. Rice husk which is also known as rice hull is the outermost layer of the paddy grain.

Prior to that, research and experiment is carried out to acquire sufficient knowledge about the pre-treatment of lignocellulosic biomass to get the best technique to conduct the experiment that contributes to the highest potential of energy recovery.

1.5 RELEVANCY OF PROJECT

South and Southeast Asia account for over 90% of the world's rice production. Rice husk is a major by-product of the rice-milling industries and is abundantly available. However, rice husk have been considered as a waste which causes disposal problems. Like other biomass materials, rice husk contains high amount of organic volatiles. It is also recognized as a potential source of energy. Hence, findings from this research will provide better understanding on the best pre-treatment method of rice husk for potential energy recovery.

1.6 FEASIBILITY OF THE PROJECT WITHIN THE SCOPE AND TIME FRAME

This research is a fundamental study of rice husk pre-treatment for potential energy recovery. This research is feasible in terms of materials availability and it is within time frame according to the schedule from the Gantt chart. The equipment required for this experiment is available in the laboratories in Universiti Teknologi PETRONAS. Prior to conducting the experiments, technical papers and journals are studied to enhance the knowledge on the pre-treatment of lignocellulosic biomass. This research has the potential to develop into diverse and wider scope for further research but it will require longer duration of study.

CHAPTER 2: LITERATURE REVIEW

2.1 PRE-TREATMENT OF LIGNOCELLULOSIC BIOMASS

Plant biomass is mainly composed of cellulose, hemicellulose and lignin along with smaller amounts of pectin, protein, extractives and inorganic minerals [12, 13]. Lignocellulose is the primary building block of plant cell walls and comprises a large fraction of municipal solid waste, crop residue, woodlot arising, forest residues and many dedicated energy crops [14].

Properties of biomass in term of proximate, ultimate and compositions are of great importance in any biomass-to-energy conversion process. In general, air-dried biomass typically contains 15-20% moisture. Remaining fraction of mass is total solids content present in biomass. The major part of biomass is carbon, oxygen and hydrogen. In general, biomass contains about 40-45% mass as oxygen and 35-50% mass as carbon on dry weight basis of biomass [15].

As shown in figure 2.1, the presence of lignin in lignocellulosic biomass leads to a protective barrier to the biomass and provide resistance to any chemical and biological degradation that prevents plant cell destruction by fungi, bacteria and enzymes.

Thus, the aim of pre-treatment is to break the impermeable/resistant layer of lignin so that cellulose and hemicellulose present in the biomass is hydrolyzed by the micro-organisms and converted into simple sugars. While conducting anaerobic digestion of lignocellulosic biomass, the hydrolysis is limited by a number of factors, the main of which are, crystallinity of cellulose, degree of polymerization, moisture content, available surface area, and lignin content [16].

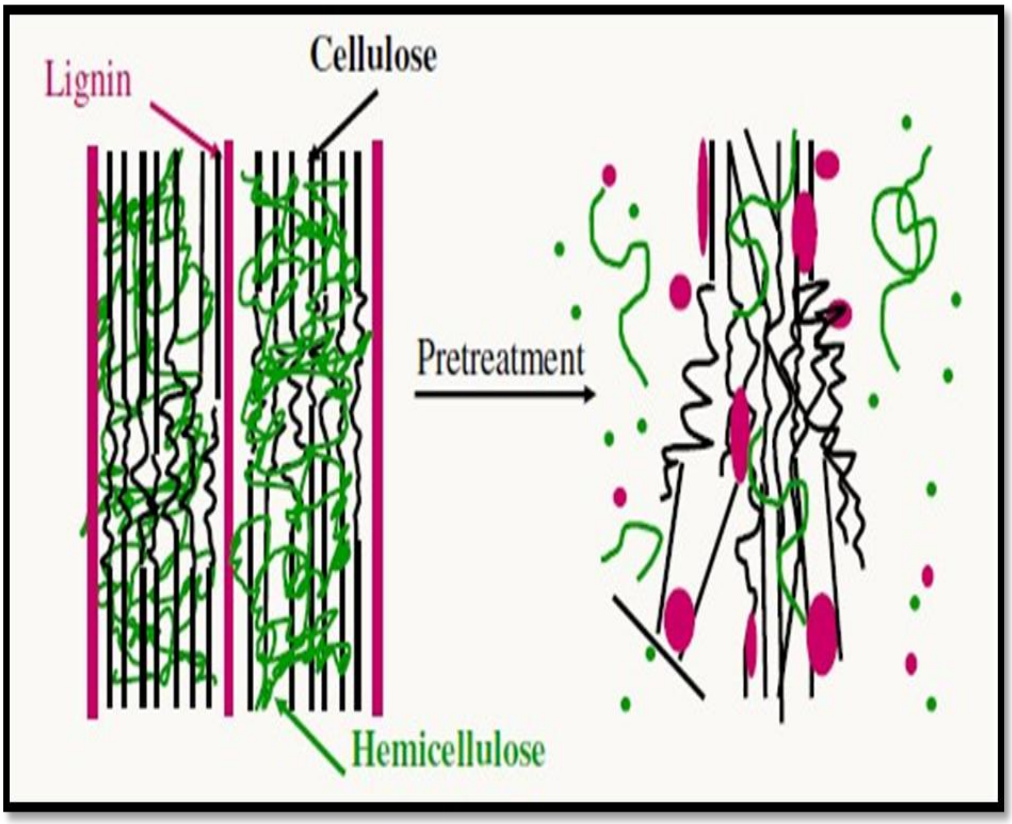


Figure 2.1: Simplified Impact of Pre-Treatment on Biomass

Numerous pre-treatment strategies have been developed to enhance the reactivity of cellulose and to increase the yield of fermentable sugars. Typical goals of pre-treatment includes:-

i. Production of highly digestible solids that enhances sugar yields during enzyme hydrolysis.

ii. Avoiding the degradation of sugars including those derived from hemicellulose.

iii. Minimizing the formation of inhibitors for subsequent fermentation steps.

iv. Recovery of lignin for conversion into valuable co-products.

v. To be cost effective by operating in reactors of moderate size and by minimizing heat and power requirements.

2.1.1 PRE-TREATMENT TECHNIQUES

Pre-treatment technologies are usually classified into physical, chemical, physicochemical and biological.

Brief descriptions of these technologies are discussed below.

- ***Physical Pre-Treatment***

This treatment is performed by applying one or more of the following techniques:-

- ✓ Milling/Grinding
- ✓ Irradiation
- ✓ Thermal

Physical pre-treatment aims at reducing the particle size and crystallinity, increasing the surface area, reducing the degree of polymerization, and shearing the biomass. Achieving these factors increases total hydrolysis yield of lignocellulose and reduce the digestion time. This treatment method cannot remove lignin, and requires high energy [17].

- ***Chemical & Physicochemical Pre-Treatment***

This treatment is performed by introducing one or more chemicals to chemically treat the lignocellulosic biomass. Some of the main techniques used in this treatment are;

A. Acidic Pre-treatment

This treatment is performed by adding concentrated or dilute acid in the lignocellulosic biomass to enhance the anaerobic digestibility. The objective of this technique is the solubilisation of hemicellulose for better accessibility to cellulose. This treatment causes the hydrolysis of hemicellulose, which are then results in the production of monomers and other products in acidic environments. This method results in increasing the accessible area of cellulose and hemicellulose, partial or nearly complete delignification, decreasing cellulose crystallinity and partial or complete hydrolysis of hemicellulose [18].

B. *Alkaline Pre-treatment*

This treatment is performed by mixing the lignocellulosic biomass with a strong or dilute base, or alkali. This treatment causes solvation and saphonication, which results in a swollen state of biomass, thus making it more accessible for enzymes and bacteria available. This method results in increasing the accessible area, partial or nearly complete delignification, decreasing cellulose crystallinity, decreasing degree of polymerization, and partial or complete hydrolysis of hemicellulose [18].

C. *Oxidizing Agents*

This treatment involves addition of an oxidizing compound like hydrogen peroxide or peracetic acid to the lignocellulosic biomass. The objectives of this treatment are to remove hemicellulose, and lignin to increase the accessibility to cellulose. This method performs treatment of lignocellulosic biomass by various reactions like, electrophilic substitution and displacements of side chains [19].

D. *Other Chemical Pre-treatments*

Different other chemical pre-treatments are available such as;

- Solvent extraction of lignin like ethanol-water, benzene-water, butanol-water, ethylene-glycol, and swelling agents.
- Gas treatment by Chlorine dioxide, Nitrogen dioxide, or Sulphur dioxide.
- Explosion Treatments like seam explosion, ammonia fibre explosion, carbon dioxide explosion, sulphur dioxide explosion [20].

❖ ***Biological Pre-Treatments***

This treatment is performed by introducing and mixing of lignocellulosic biomass with one or more of microorganism. The advantages of this process are low energy requirement, no chemical requirement, and mild environmental conditions, and disadvantage is very low treatment rate in most of the biological pre-treatment processes [21].

2.2 BIOFUELS PRODUCTION BY LIGNOCELLULOSIC MATERIAL

Any energy producing fuel obtained from biomass is termed as biofuels, regardless of its type, weather solid, liquid or gas. Biomass conversion to liquid and gaseous fuels is being preferred nowadays due to some advantages like abundant and easily accessible, non-polluting and environment friendly, sustainable and reliable. Studies have shown that high energy conversion efficiencies could be achieved by using integrated biomass gasification technology, and that could be used for future electricity generation from biomass [22]. Main reasons behind the popularity of biofuels are energy security, environmental concerns, and economics [23].

Depending upon the production technique, biofuels produced from biomass are classified into four groups as First generation biofuels (FGBs); second generation biofuels (SGBs); third generation biofuels (TGBs); and fourth generation biofuels. In this classification except third generation biofuels (which are produced from algae or oilgae), all other biofuels types are produced from lignocellulolosic biomass. Biofuels produced from sugar, starch, or vegetable oils by using conventional technology are considered as first generation biofuels. These are produced from seeds or grains, which are converted into starch, and its fermentation into bioethanol, or sunflower seeds, ultimately pressing them to produce vegetable oil, which could be used as biodiesel. Second generation biofuels are produced from non-food biomass waste like rice straw, wood and other energy crops. Third generation biofuels are produced from algae, as discussed. While the fourth generation biofuels uses most advanced technology to produce biogasolene from vegetables oil and biodiesel [24].

Depending upon the type these fuels can be categorized into two main categories like biorenewable liquid fuels and biorenewable gaseous fuels.

2.2.1 BIORENEWABLE LIQUID FUELS

Liquid biofuels derived from lignocellulosic biomass are mostly used for transportation, and these fuels are now being focused worldwide due to their availability, sustainability, regional development, rural manufacturing jobs, reduction of greenhouse gas emissions, and its biodegradability [25]. These fuels are further subdivided into these three types;

i. Biodiesels
ii. Bioalcohols
iii. Biosynthetic Oils

- *Biodiesels or Vegetable Oils*

  Biodiesels are the liquid fuels produced from animal fats and vegetable oils, but the production of biodiesel from vegetable oils and cooking oils will cause shortage in edible oils, and are insufficient compared to the demand. Biodiesel has also been studied to be produced from the microbial oils produced from lignocellulosic material and it seems the most suitable economic option for it [26], though research is currently ongoing to improve the pretreatment, saccharification and fermentation of lignocellulosic biomass economically to obtain maximum yield of microbial oil, and as a result maximum biodiesel [27].

- *Bioalcohols*

  Bioalcohols are the biomethanol and bioethanol production from lignocellulosic biomass which is used for the internal combustion engines as a replacement for gasoline, biomethanol is produced by gasification of biomass [28]. Bioethanol production is preferred from lignocellulosic material as it provides a significant portion of the raw materials for bioethanol production in the medium and long-term due to its low cost and high availability [29]. Lignocellulosic biomass contains major percentage of carbohydrate polymers like cellulose and hemicellulose, which are converted into simple sugars by hydrolysis before fermentation, this lignocellulosic hydrolysates contains different amounts xylose, arabinose, glucose, galactose, mannose, fucose, and rhamnose, which are then fermented into bioethanol by using different microorganisms [30]. Bioethanol is preferred to be used as transportation fuel due to some advantages over biomethanol like; it can be used directly in cars designed to run on pure ethanol or blended with gasoline to make ‘‘gasohol”. Bioethanol is an oxygenated fuel containing 35% oxygen, and as a result reducing particulate and NOx emissions from combustion. Bioethanol has a higher octane number (108), broader flammability limits, higher flame speeds and higher heats of vaporization than gasoline. These properties allow for a higher compression ratio, shorter burn time and leaner burn engine, which lead to theoretical efficiency advantages over gasoline in an internal combustion engine [31].

- *Biosynthetic Oils*

  Biosynthetic oil or bio oil is also a renewable liquid fuel obtained from biomass; it is usually produced by fast pyrolysis of biomass with relatively lower heating value as 16MJ/kg [32]. Pyrolysis is now considered to be a sound technique to obtain different chemicals and fuels from biomass. In this process, the organic matrix of biomass is thermally decomposed in the absence of oxygen, which results in producing an array of solid, liquid and gaseous products, the obtained products or fuels maybe used in engines and turbines for power generation purposes [33]. Bio oils are produced from techniques of pyrolysis depending upon the operating condition used, ranging from very slow to fast and flash. Fast pyrolysis is preferred due to higher liquid fuel production [34].

2.2.2 BIORENEWABLE GASEOUS FUELS

The gaseous fuels obtained from lignocellulosic biomass are the biogas by anaerobic digestion and biohydrogen by anaerobic fermentation.

- *Biogas*

  Biogas is considered to be most suitable renewable fuel to replace the conventional fossil fuels, in terms of availability, sustainability, reliability, and environmental concerns [35]. Biogas contains a mixture of methane and carbon dioxide with small amount of sulfuric compounds like hydrogen sulfide. A typical composition of biogas includes 55 to 70 % methane, 30 to 45 % carbon dioxide, 0 to 2% nitrogen, and about 0 to 500 ppm hydrogen sulfide [36]. Methane is the most important product obtained from biogas, to be used as fuel for cooking and transportation purposes. The energy contained in biogas methane is about 4800-6700 kcal/m^3 as compared to pure methane, which contains 8900 kcal/m^3 energy [37]. Anaerobic Digestion is the most commonly used method for biogas production due to high performance. In this method the organic biomass waste is degraded or biologically transformed by diverse microorganisms, and convert the biomass waste into biogas [38]. The biofuels resulted from the anaerobic digestion can then be utilized as a replacement for fossil fuels, and as these products are carbon neutral so they reduce carbon dioxide emissions to the environment, this process involves four main stages, these are hydrolysis, acidogenesis, acetogenesis, and methanogenesis [39].

- *Biohydrogen*

  Hydrogen production has been under investigation and experimentation since early 1980s and still different techniques are being used and modified to increase its efficiency [40]. One technique is to produce biohydrogen by using anaerobic digestion of different wastes like biomass, MSW, or wastewater sludge, but this process reduces hydrogen production efficiencies after continual use. Biohydrogen is also released by anaerobic and photosynthetic microorganisms using carbohydrate rich and non-toxic raw materials. Bio hydrogen is produced as a byproduct while the organic waste is converted into organic acids anaerobically; these organic acids are then used to produce methane. Biohydrogen is also produced by bacterial fermentation of sugars using bacteria such as Clostridia, under suitable conditions of temperature, pH control, reactor hydraulic retention time (HRT) and other treatment factors [41].

2.3 MICROWAVE PRE-TREATMENTS

During any pre-treatment method, hydrolysis of lignocellulosic biomass depends upon three main parameters, these are, chemical or reagent concentration, retention or residence time, and temperature. By fluctuating any of these parameters we can change the hydrolysis rate of lignocellulosic biomass. Studies have shown that the pre-treatments performed at high temperature have given successful results, in increasing the hydrolysis rate and product yields, while decreasing the residence time and reagent or chemical concentration required [42].

This temperature increment may be performed by conventional heating or by using microwave radiation, which has some advantages over the conventional heating like, superficial heat transfer, no direct contact of heating source and material, providing a volumetric and rapid heat and selective heating of more polar part and creating a hot spot with inhomogeneous materials [43]. Figure 2.2 shows a comparative analysis between conventional heating and microwave heating.

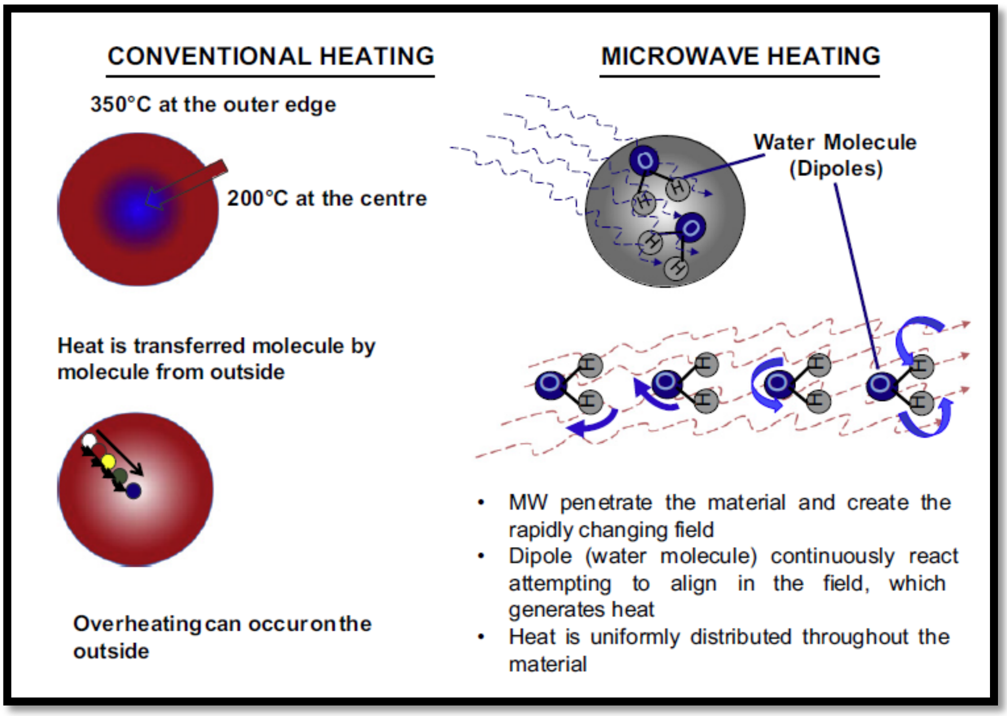


Figure 2.2: Difference between conventional heating and microwave heating

Microwaves are the electromagnetic waves between the frequency range of 300 MHz to 300 GHz, and most the microwave systems available for industrial and domestic purposes use 900 MHz to 2.45 GHz. Microwaves affect the material thermally and non-thermally. Thermally microwaves heat the material by interacting the molecules of material with electromagnetic field produced by microwave energy, non-thermally microwaves affect and interact the polar molecules and ions in the materials, causing physical, chemical, and biological reactions [44].

2.3.1 EFFECTS OF MICROWAVE PRE-TREATMENT

Microwave Irradiation effects on biomass and its modification have been studied since 1960’s and the modification of barley seeds by microwave treatment was evidenced and reported in 1969, but it was not until 1980’s when the application of microwave irradiation on lignocellulosic biomass for enhanced cellulose scarification was studied and proved useful in the processing of biofuels. From then the microwave irradiation technique has been used for efficient processing of biofuels, and it has since been studied for processing various waste types from sludge and municipal solid waste to biomass solid waste [45].

It has been investigated that the microwave pretreatment technique is very effective in reducing the lignin ratio in biomass, and resulting in an increase in the proportion of cellulose and hemicellulose.

2.4 COMBINATION OF MICROWAVE ASSISTED PRE-TREATMENTS AND THEIR EFFECTS

There have been several studies performed in the combination of microwave technique with other chemical techniques like, microwave assisted acidic pre-treatment and microwave assisted alkaline treatment. These studies have shown that the combination of microwave irradiation heating pre-treatment with chemical methods have given successful results. In these combined pre-treatments the lignocellulosic biomass is first mixed with chemical and then exposed to microwave radiation for some time while the reverse method, as initially exposing the lignocellulosic biomass to microwave radiation and then applying alkali treatment on it has also been studied, and shown good results, but the previous method is suggested as it is good to heat the sample after mixing with the chemical by microwave irradiation, which caused lignin disruption and increasing surface area of cellulose and hemicellulose, which also improves chemical technique, by providing better access to the cellulose and hemicellulose for pre-treatment [46].

CHAPTER 3: METHODOLOGY

3.1 RESEARCH METHODOLOGY

This research focused on performing microwave assisted acidic and alkaline pre-treatment of rice husk with different methods. Figure 3.1 summarizes the steps involved in pre-treatment of the biomass as explained below.

3.1.1 SAMPLE COLLECTION AND PREPARATION

a) Rice Husk was obtained from Bernas Sdn. Bhd. and used as biomass waste sample.

b) The samples were oven dried at a temperature of 105°C for 24h to remove the moisture content. The dried biomass was cut and ground to less than 40 mesh size (less than 0.42 mm).

c) The samples were placed in sealed plastic bags and stored in a desiccator at room temperature until the time for experimentation.

3.1.2 PRE-TREATMENT OF LIGNOCELLULOSIC BIOMASS WASTE

a) Four different chemical solutions, two acidic (dilute sulphuric acid and hydrogen peroxide) and two alkaline (dilute sodium hydroxide and sodium carbonate), of 2%, 3.5%, and 5% strength were prepared for pre-treatments of the biomass.

b) 1 g of each dried and ground biomass sample was immersed and soaked in 10 ml of each chemical solution. The mixture was subjected to irradiation in microwave oven at temperature of 170°C for 5 minutes. The sample was kept immersed in the chemical solution for 2h.

3.1.3 ANALYTICAL METHODS AND DATA ANALYSIS

a) Elemental Analysis (Carbon, Hydrogen, Nitrogen and Sulphur) of all the samples was performed by using LECO CHNS-932 to obtain C/N ratio.

b) The content of cellulose, hemicellulose and lignin was measured qualitatively by Fourier Transform Infrared (Perkin Elmer Spectrum One) and verified quantitatively by using UV Visible Spectrophotometer (Shimadzu UV-1601) and High Performance Liquid Chromatograph (Agilent 1100 Series).

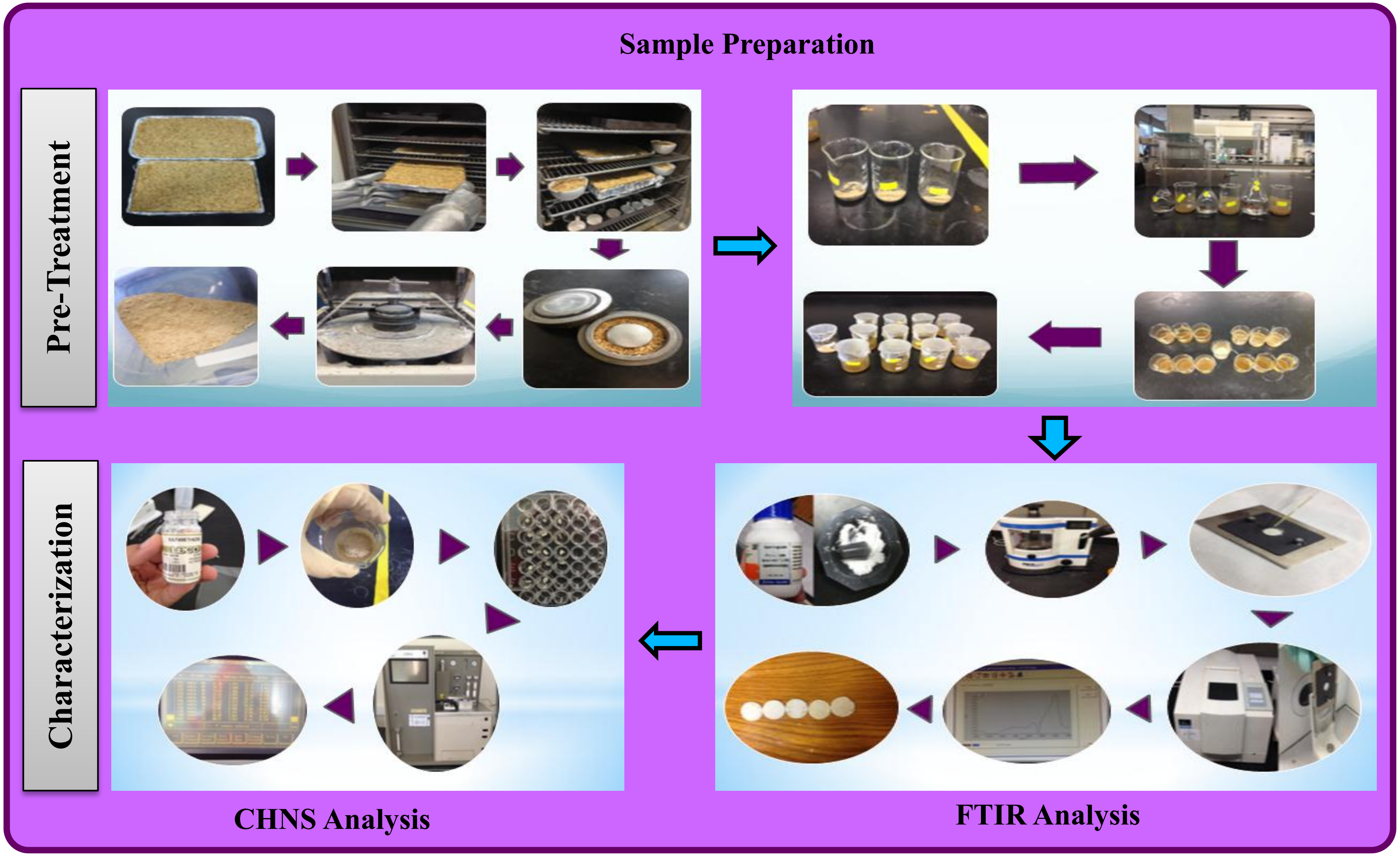


Figure 3.1: Methodology of Pre-Treatment and Characterization

3.2 KEY MILESTONE

Figure 3.2 shows the steps followed in this research.

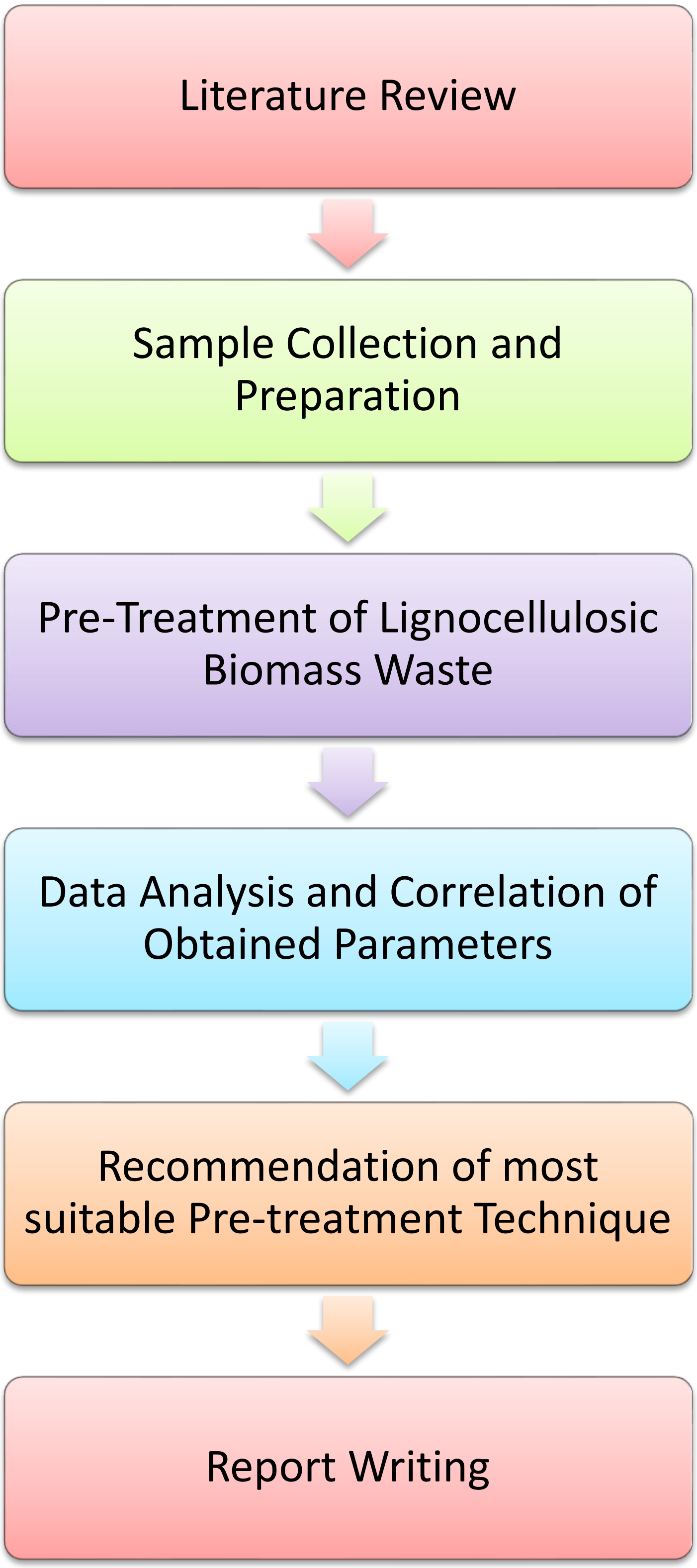
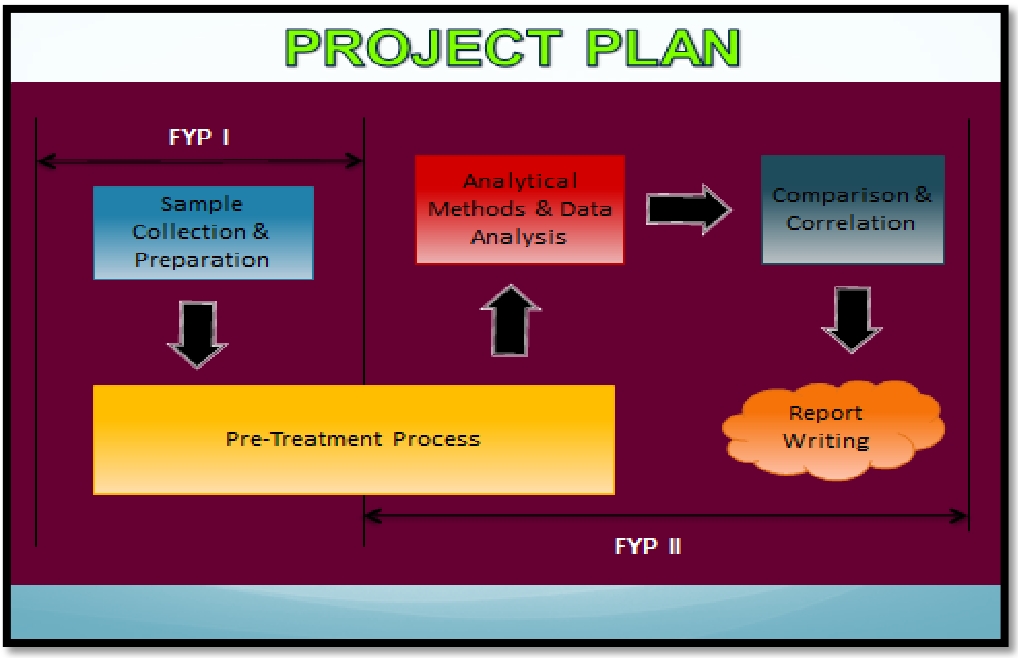


Figure 3.2: Research Flow Chart

3.3 PROJECT PLAN AND ACTIVITIES

Figure 3.3 shows the project plan and activities throughout the whole Final Year Project period.



PROJECT PLAN

FYP I

Sample Collection & Preparation

Pre-Treatment Process

Analytical Methods & Data Analysis

Comparison & Correlation

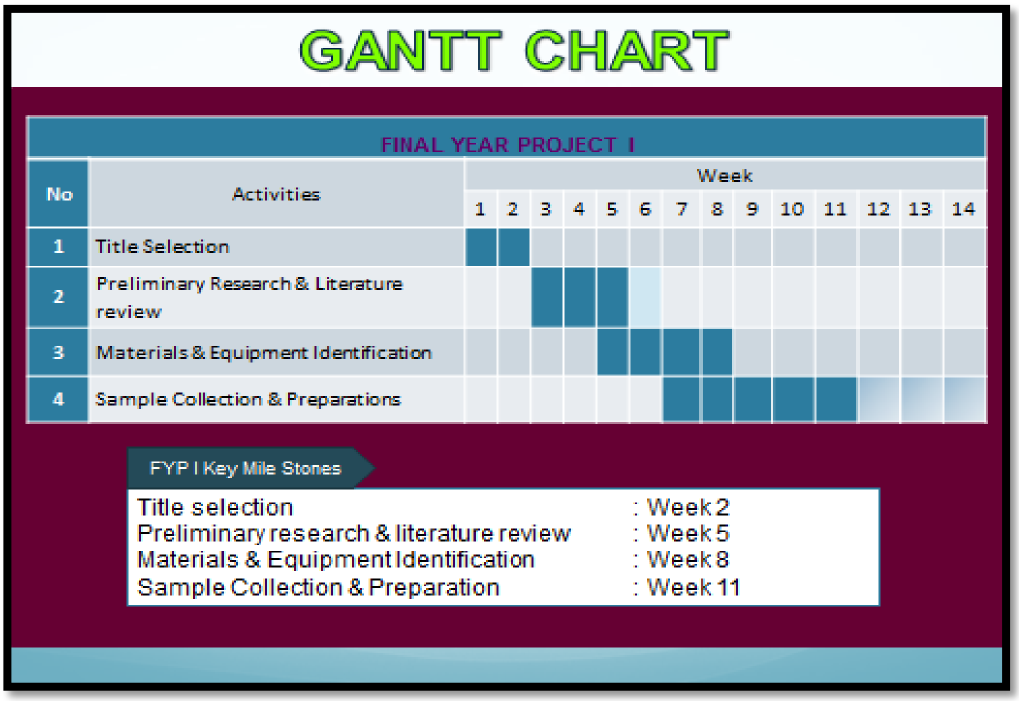
Report Writing

FYP II

Figure 3.3: Project Plan & Activities

3.4 GANTT CHART

Figure 3.4 shows the Final Year Project I Gantt Chart.



GANTT CHART

FINAL YEAR PROJECT I

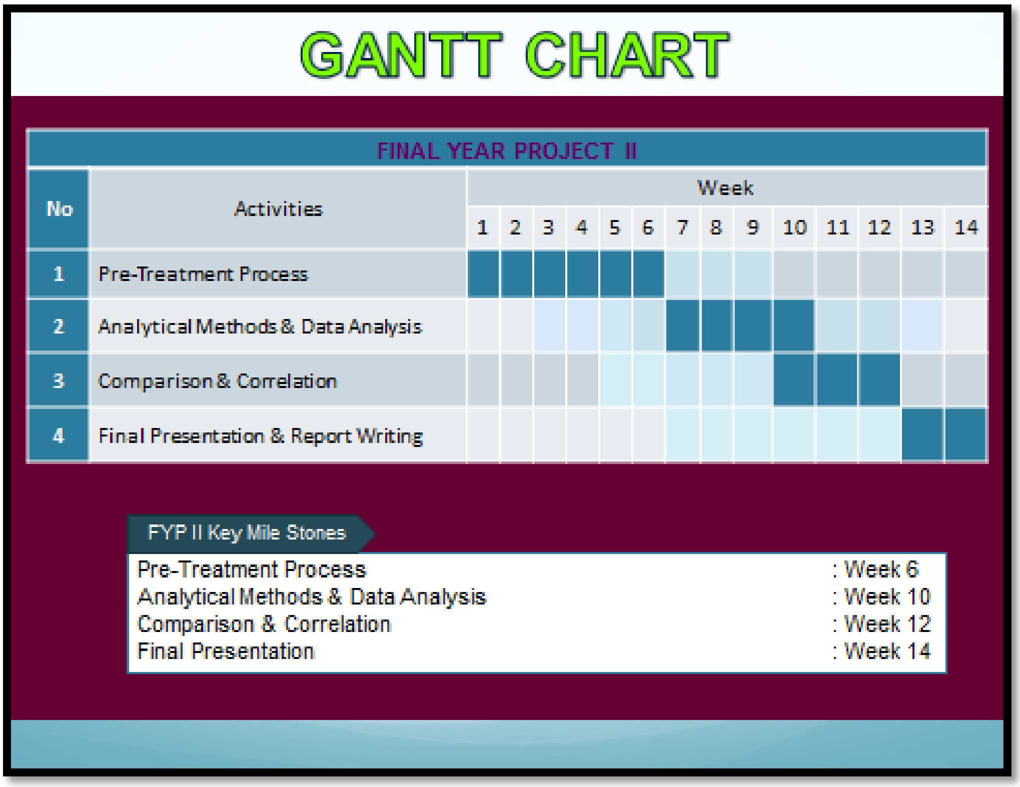
No	Activities	Week													
		1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	Title Selection	■	■												
2	Preliminary Research & Literature review			■	■	■	▨								
3	Materials & Equipment Identification					■	■	■	■						
4	Sample Collection & Preparations							■	■	■	■	■	▨	▨	▨

FYP I Key Mile Stones

Title selection : Week 2
Preliminary research & literature review : Week 5
Materials & Equipment Identification : Week 8
Sample Collection & Preparation : Week 11

Figure 3.4: Final Year Project I Gantt Chart

Figure 3.5 shows the Final Year Project II Gantt Chart.



GANTT CHART

FINAL YEAR PROJECT II

No	Activities	Week													
		1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	Pre-Treatment Process	■	■	■	■	■	■								
2	Analytical Methods & Data Analysis							■	■	■	■				
3	Comparison & Correlation										■	■	■		
4	Final Presentation & Report Writing													■	■

FYP II Key Mile Stones

Pre-Treatment Process	: Week 6
Analytical Methods & Data Analysis	: Week 10
Comparison & Correlation	: Week 12
Final Presentation	: Week 14

Figure 3.5: Final Year Project II Gantt Chart

3.5 MATERIALS REQUIRED

Table 3.1 presents the materials required for the research.

Table 3.1: Materials Required

MATERIALS	QUANTITY
Rice Husk	**500 g**
Sulphuric Acid (H_2SO_4)	**1000 ml**
Hydrogen Peroxide (H_2O_2)	**1000 ml**
Sodium Hydroxide (NaOH)	**1000 ml**
Sodium Bicarbonate (Na_2CO_3)	**1000 ml**

3.6 EQUIPMENT REQUIRED

Following is the list of equipment used in this research.

- Oven
- Hammer Mill
- Desiccator
- Centrifuge
- Microwave Oven
- Fourier Transform Infrared (Perkin Elmer Spectrum One)
- CHNS Elemental Analyser (LECO CHNS-932)
- UV Visible Spectrophotometer (Shimadzu UV-1600)
- High Performance Liquid Chromatograph (Agilent 1100 Series)

CHAPTER 4: RESULTS & DISCUSSION

4.1 FOURIER TRANSFORM INFRARED

Fourier Transform Infrared (FTIR) is the preferred method of infrared spectroscopy. Figure 4.1 shows the principle of work for FTIR.

FTIR can:-

- Identify unknown material
- Determine the quality or consistency of a sample
- Determine the amount of components in a mixture

Advantages of FTIR

- ✓ **Speed:** Because all of the components are measured simultaneously, most measurements by FTIR are made in a matter of seconds rather than several minutes.
- ✓ **Sensitivity:** Sensitivity is dramatically improved with FTIR for many reasons. The detectors employed are much more sensitive.
- ✓ **Internally Calibrated:** These instruments employ a HeNe laser as an internal wavelength calibration standard. The instruments are self-calibrating and never need to be calibrated by user.

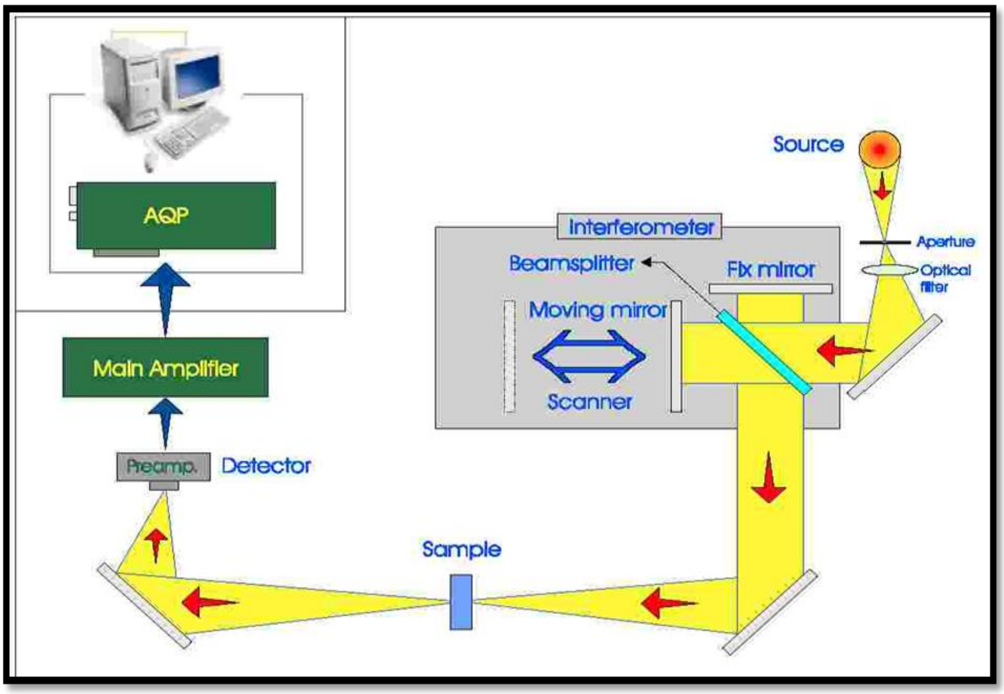


Figure 4.1: The Principle of Work

4.1.1 FTIR RESULTS

Figures 4.2 to 4.14 show the FTIR results for the blank (untreated) and pre-treated rice husk. The findings are as follows:-

As it was explained in the introduction, the organic part of the rice husk is mainly composed of cellulose, hemicellulose, lignin, and waxes, which most likely consist of alkene, esters, aromatics, ketones, and alcohols, with different oxygen-containing functional groups, e.g., OH stretching (3650 to 3200 cm^{-1}) and C=O stretching hemicelluloses (1732 cm^{-1}). Besides, some characteristic peaks of cellulose in RH can be observed at 1640 cm^{-1} (OH bending of adsorbed water), 1420 cm^{-1} (CH_2 strain), 1375 and 1270 cm^{-1} (CH bending). On the other hand, the vibrations of the aromatic rings can be seen at 1606 and 1515 cm^{-1} (aromatic ring vibrations), which can be only related to lignin. The inorganic part is characterized by three bands associated to Si-O-Si bonds (situated at frequencies of 1100-1070, 799, and 465 cm^{-1}). The previously mentioned bands will be used to evaluate the effectiveness of each chemical treatment on the preferential removal of different components [47].

For this research, the main interest is to see wavelength between 1000-1800 cm^{-1} because in this region, it usually contains a very complicated series of absorptions. These are mainly due to all manner of bending vibrations within the molecule. It is much more difficult to pick out individual bonds in this region than it is in the “cleaner” region at higher wavenumbers. The importance of setting this region is that each different compound produces a different pattern of troughs in this part of the spectrum [48].

From the results obtained, it was clearly shown that by conducting pre-treatment, the lignin was successfully removed. This shows that the first objective was achieved. It can be concluded that by performing pre-treatment of the rice husk, the lignin can be disrupted and this is a positive sign as by disrupting the lignin, cellulose and hemicellulose can be obtained at a higher percentage.

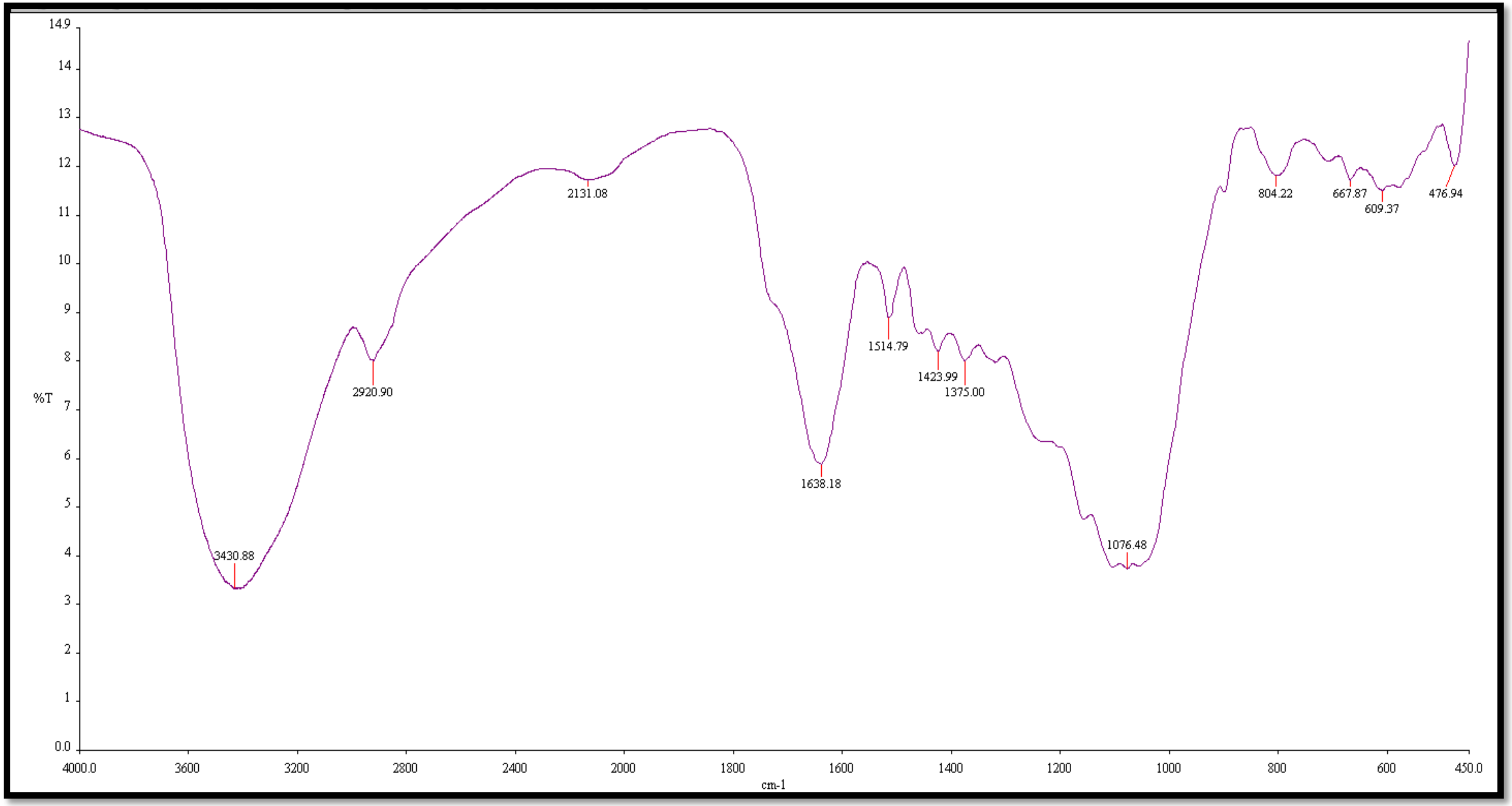


Figure 4.2: FTIR result for blank

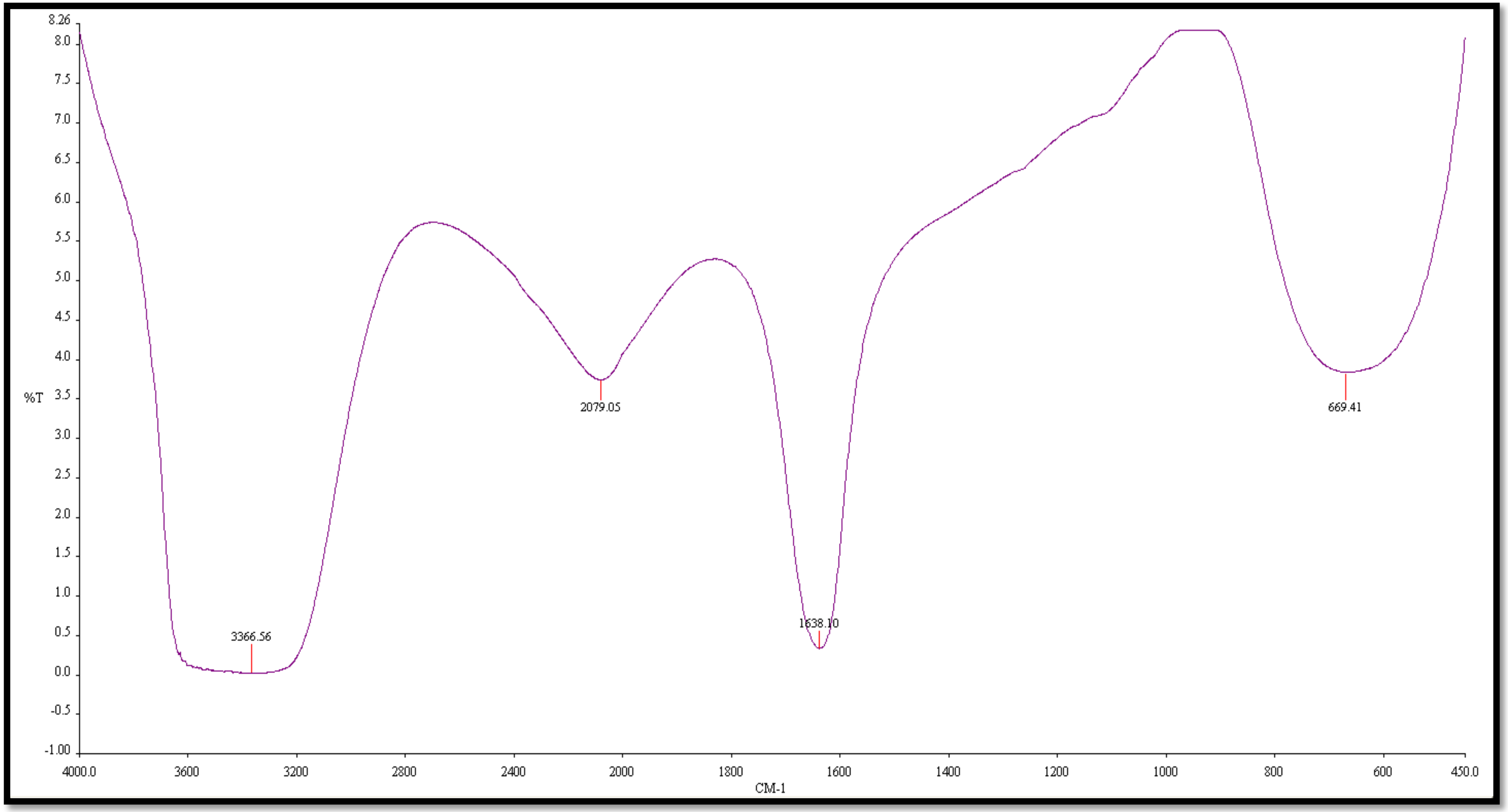


Figure 4.3: FTIR result for 2% NaOH

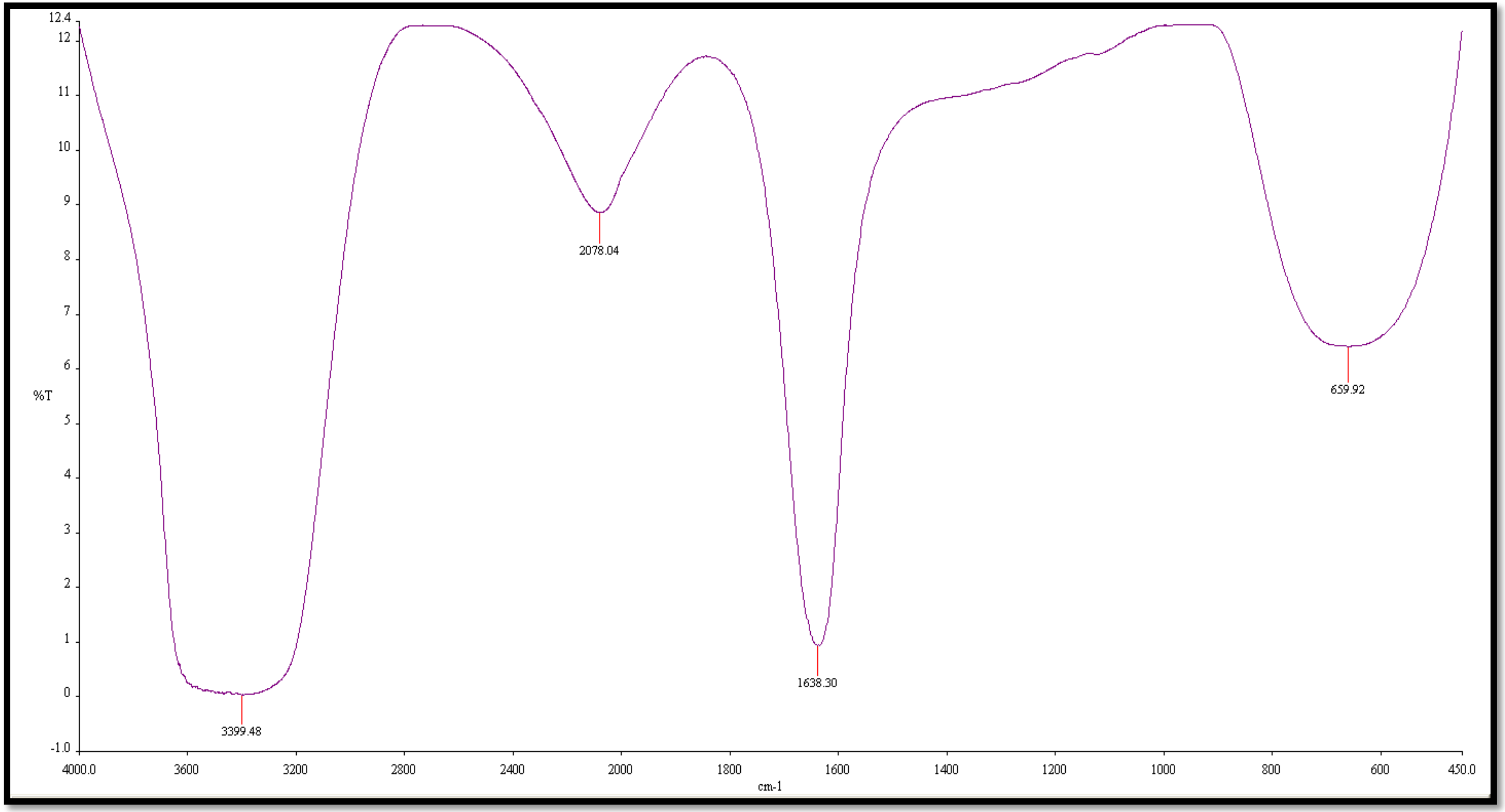


Figure 4.4: FTIR result for 3.5% NaOH

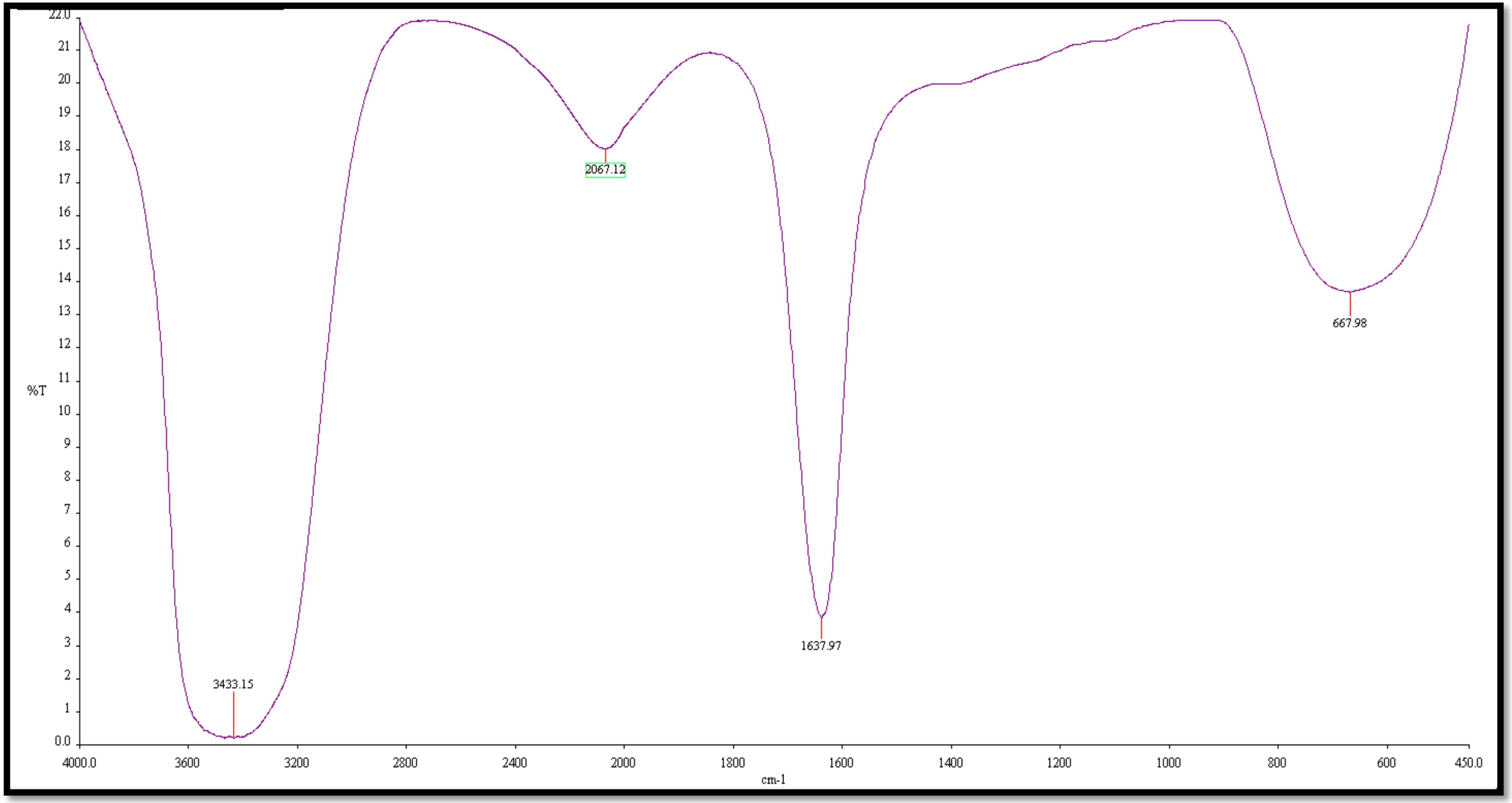


Figure 4.5: FTIR result for 5% NaOH

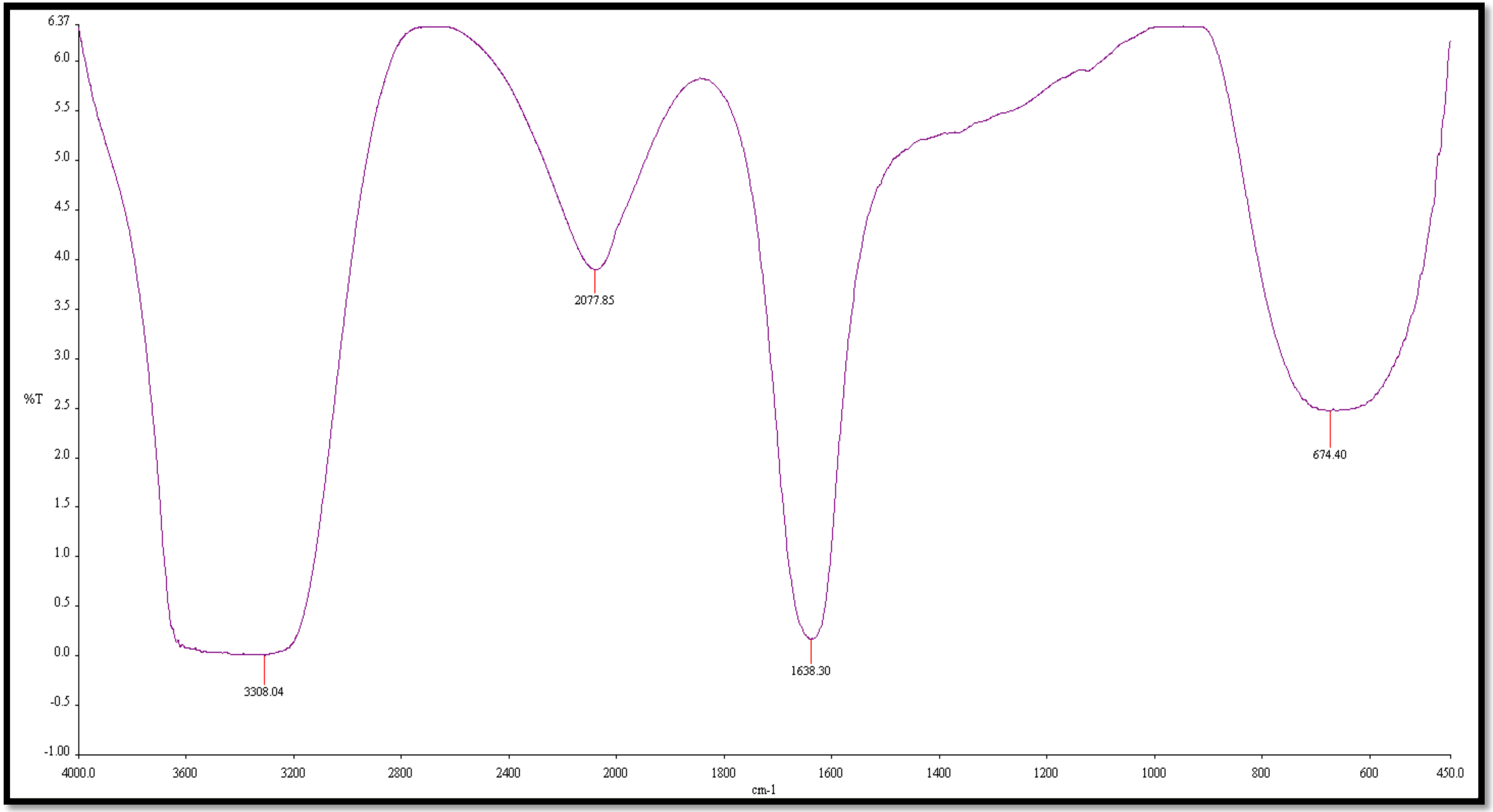


Figure 4.6: FTIR result for 2% Na_2CO_3

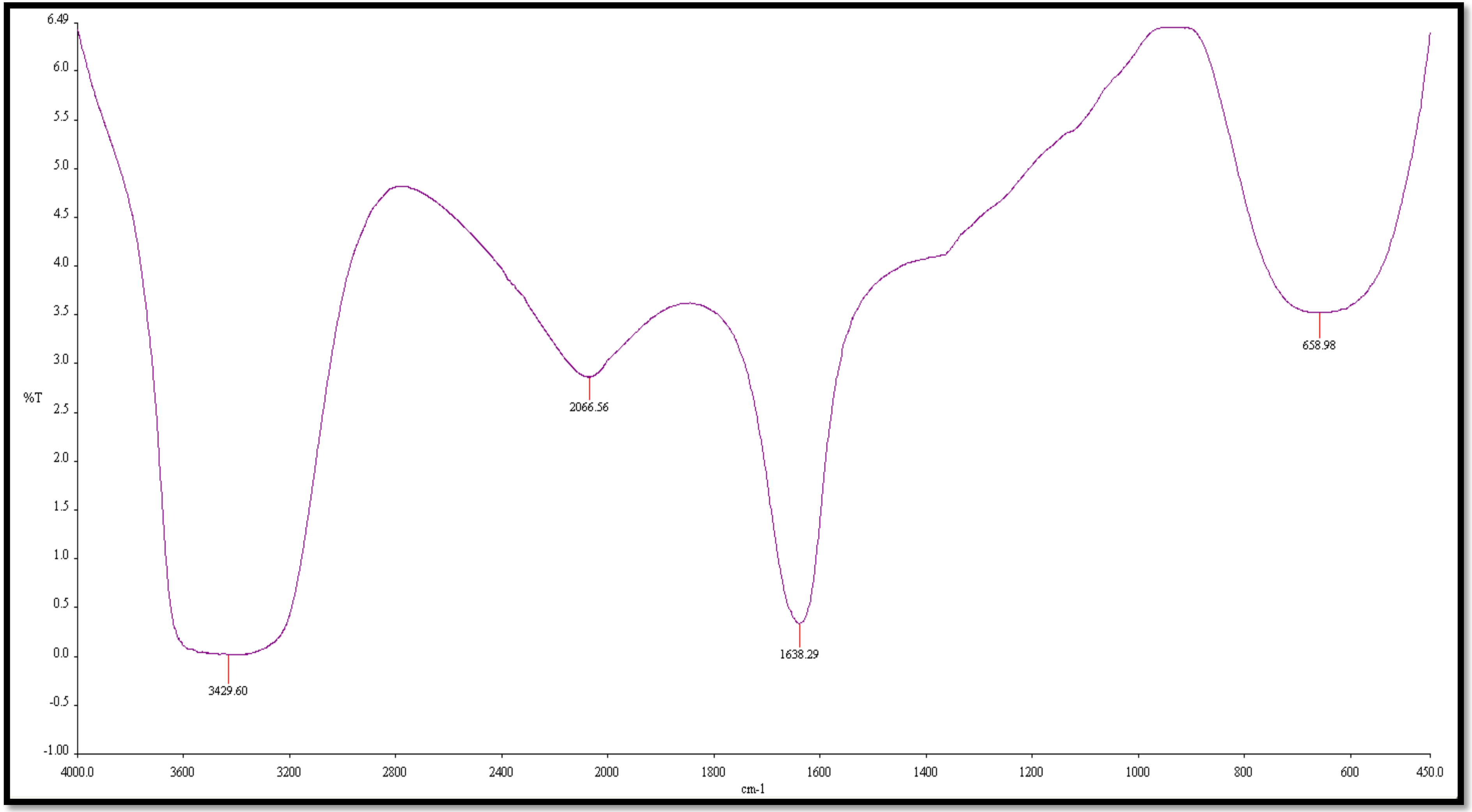


Figure 4.7: FTIR result for 3.5% Na_2CO_3

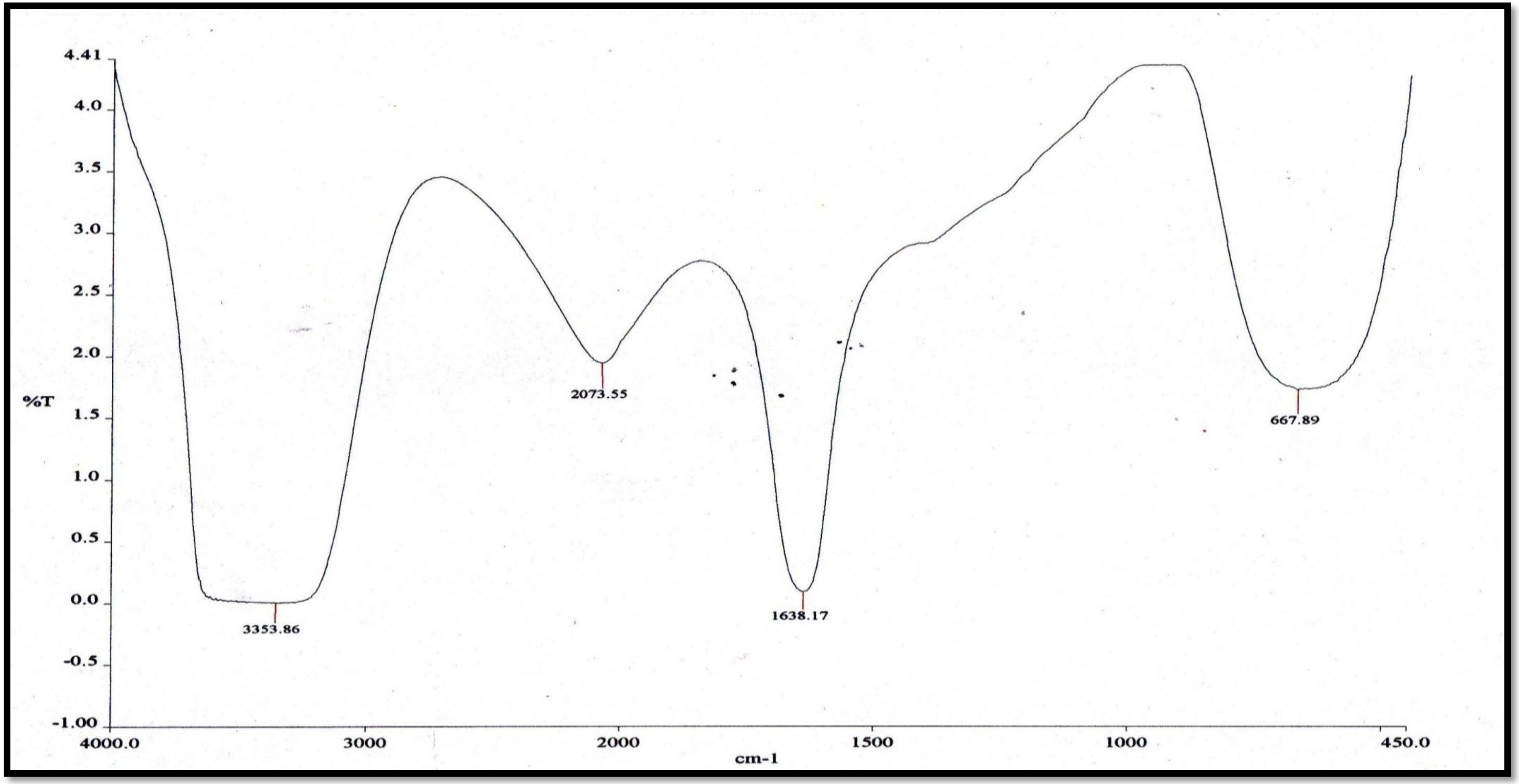


Figure 4.8: FTIR result for 5% Na_2CO_3

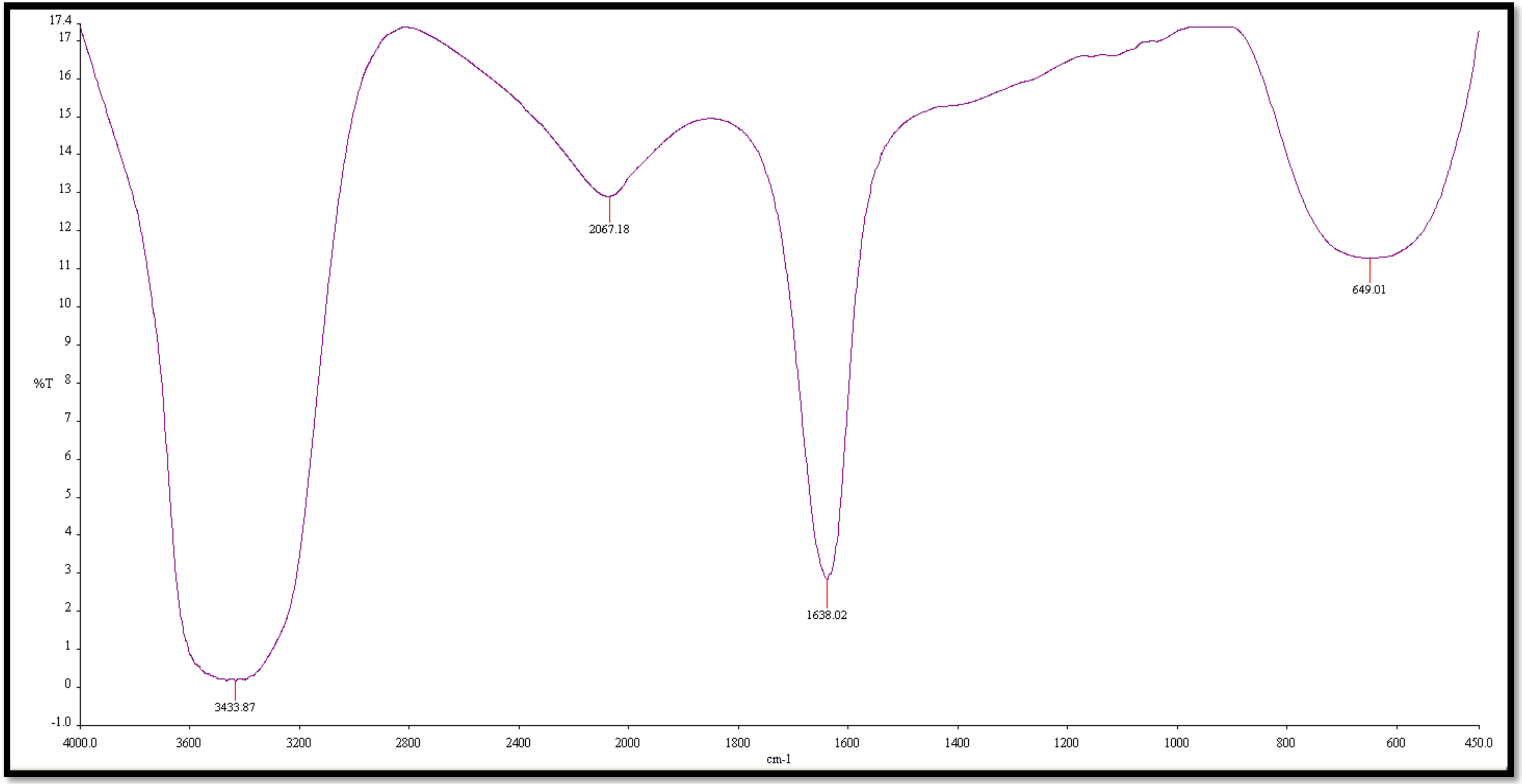


Figure 4.9: FTIR result for 2% H_2O_2

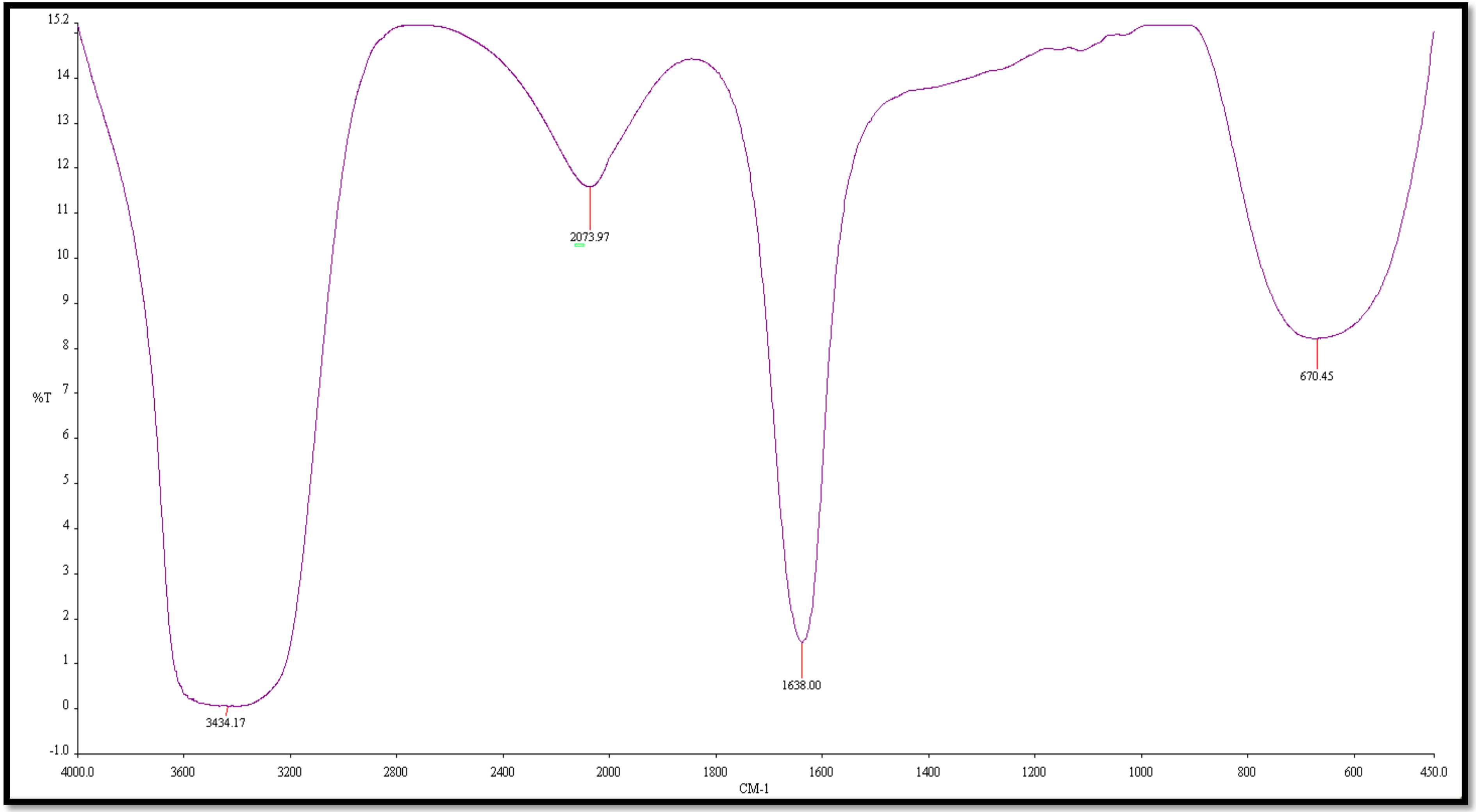


Figure 4.10: FTIR result for 3.5% H_2O_2

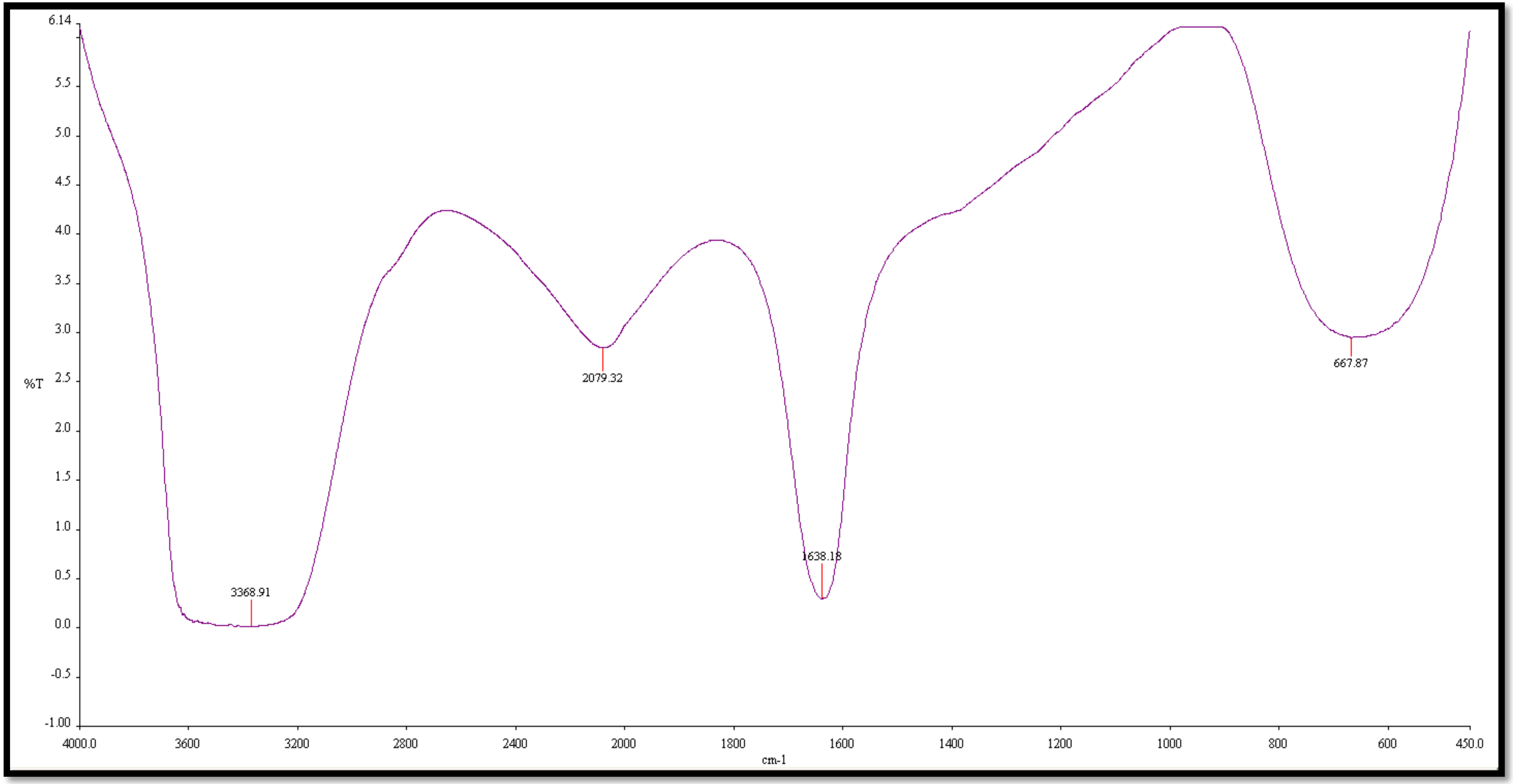


Figure 4.11: FTIR result for 5% H_2O_2

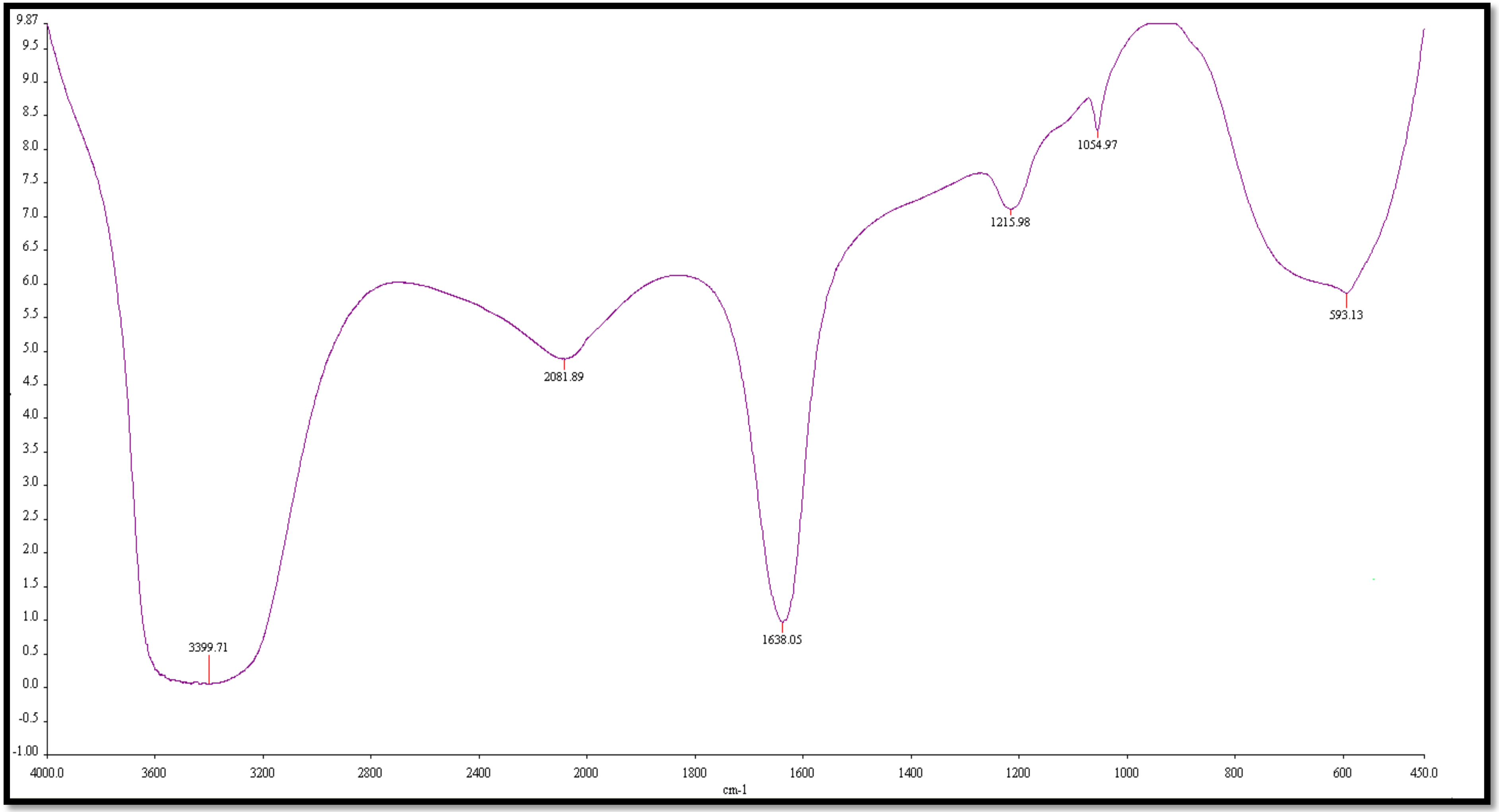


Figure 4.12: FTIR result for 2% H_2SO_4

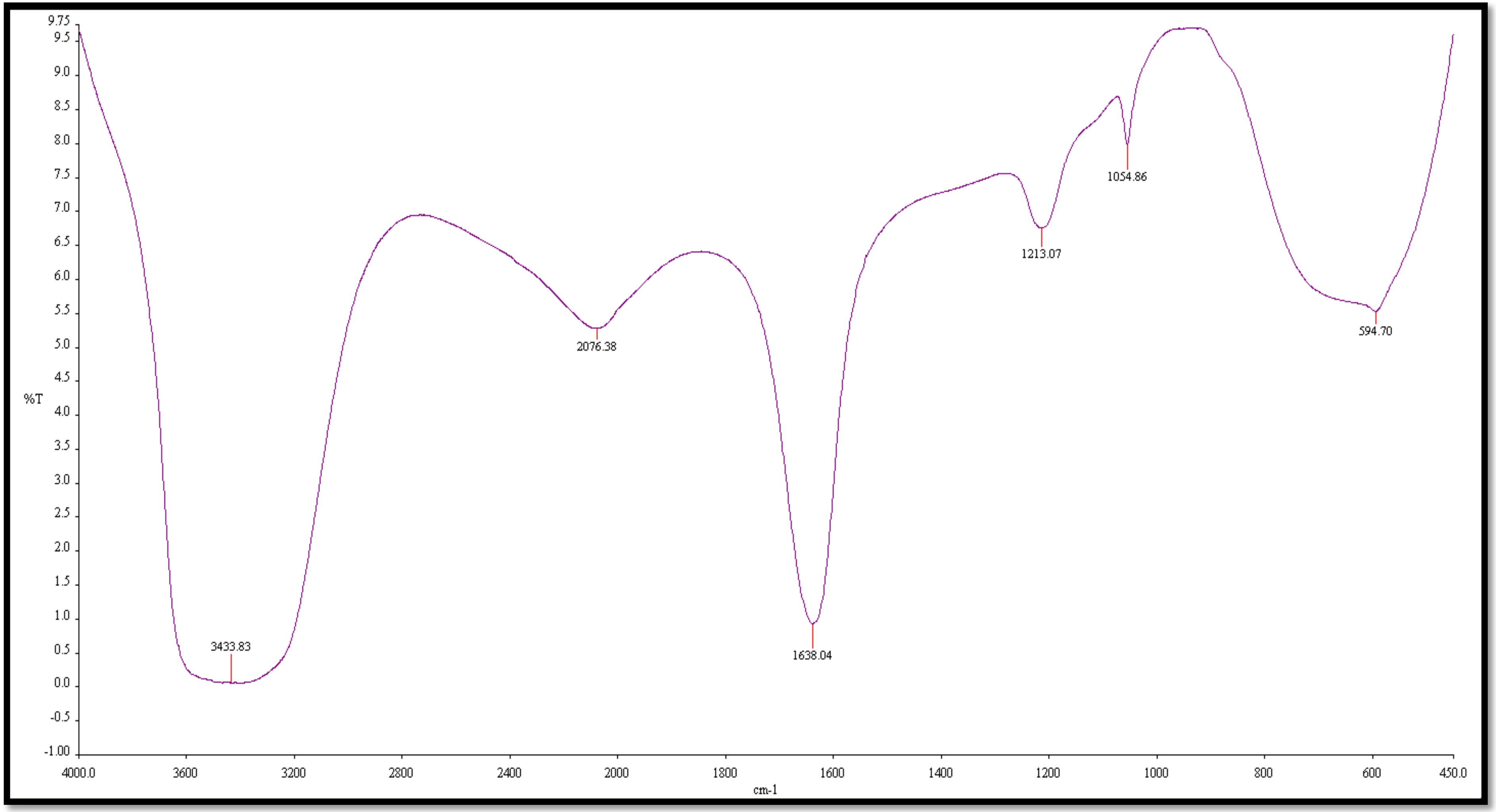


Figure 4.13: FTIR result for 3.5% H_2SO_4

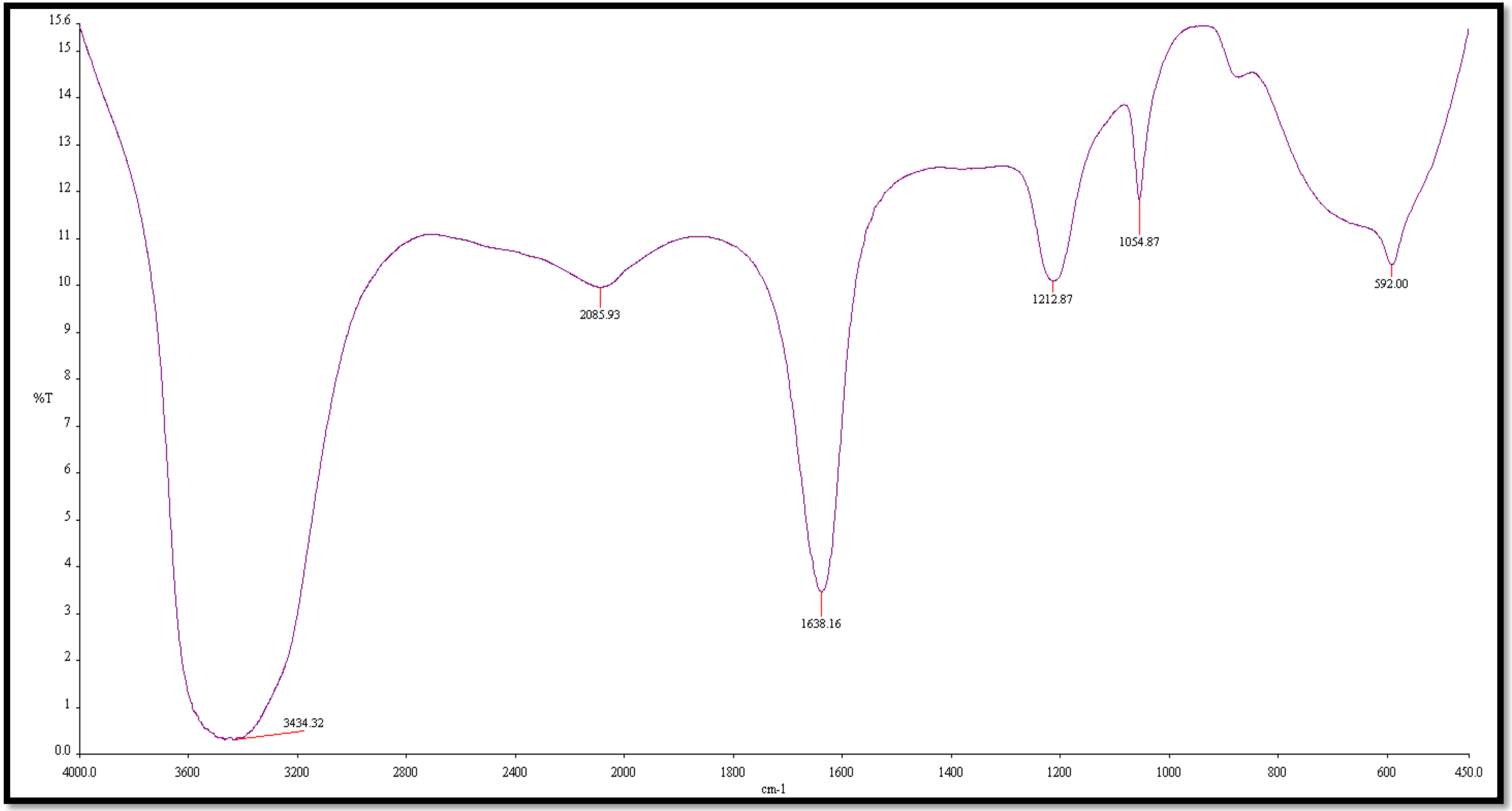


Figure 4.14: FTIR result for 5% H_2SO_4

4.1.2 CONVERSION OF TRANSMITTANCE TO ABSORBANCE

The FTIR graphs are plots of Transmittance vs Wavelength. Transmittance of the medium is the fraction of incident radiation transmitted by the medium. From the graph, the result is converted from transmittance to absorbance in order to see the trend of all chemicals with different concentrations to get the best result. Conversion of Transmittance to Absorbance is to show how much infrared had been absorbed by cellulose at wavelength 1640cm^{-1} and hemicellulose at 1075cm^{-1}.

Absorbance of a medium is defined by equation:-

$$A = \log 1/T$$

Table 4.1 and 4.2 shows the calculated absorbance for cellulose and hemicellulose respectively. An example of calculation pertaining to the blank is as follow:

$$\begin{aligned} A &= \log 1/0.058 \\ &= 1.23657 \end{aligned}$$

Table 4.1: Conversion of transmittance to absorbance for Cellulose

	Concentration %	Transmittance %	Transmittance	Absorbance
Blank	0	5.8	0.058	1.23657
H_2O_2	2	2.9	0.029	1.5376
	3.5	1.5	0.015	1.82391
	5	0.4	0.004	2.39794
H_2SO_4	2	1	0.01	2
	3.5	1.2	0.012	1.92082
	5	3.6	0.036	1.4437
NaOH	2	0.4	0.004	2.39794
	3.5	1	0.01	2
	5	4	0.04	1.39794
Na_2CO_3	2	0.2	0.002	2.69897
	3.5	0.3	0.003	2.52288
	5	0.1	0.001	3

Table 4.2: Conversion of transmittance to absorbance for Hemicellulose

	Concentration %	Transmittance %	Transmittance	Absorbance
Blank	0	4	0.04	1.39794
H_2O_2	2	16.5	0.165	0.78252
	3.5	14.6	0.146	0.83565
	5	5.5	0.055	1.25964
H_2SO_4	2	8.2	0.082	1.08619
	3.5	8	0.08	1.09691
	5	11.9	0.119	0.92445
NaOH	2	7.1	0.071	1.14874
	3.5	11.8	0.118	0.92812
	5	21.1	0.211	0.67572
Na_2CO_3	2	5.8	0.058	1.23657
	3.5	5.4	0.054	1.26761
	5	3.5	0.035	1.45593

- *Lignin*

Figures 4.2 to 4.14 show lignin was largely removed using all the four chemicals at all concentrations tested. Absence of the lignin peak at 1515cm^{-1} indicates that the first objective was achieved.

- *Cellulose*

As evidence from figures 4.2 to 4.14, cellulose percentage has increased for all pre-treated samples. Objective of this research is to get the best chemical and suitable concentration for the pre-treatment of the rice husk. Based on the graph, it clearly shown that the best chemical is Na_2CO_3 with 5% concentration where the percentage of cellulose gain was at the highest range compared to the others.

- *Hemicellulose*

For this part, as we could see from the figure 4.2 to 4.14, hemicellulose percentage was lower compared to before pre-treatment for all type of chemical pre-treatment except for Na_2CO_3 with 5% concentration.

Figures 4.15 and 4.16 show the absorbance obtained for cellulose and hemicellulose respectively, in the blank and pre-treated samples.

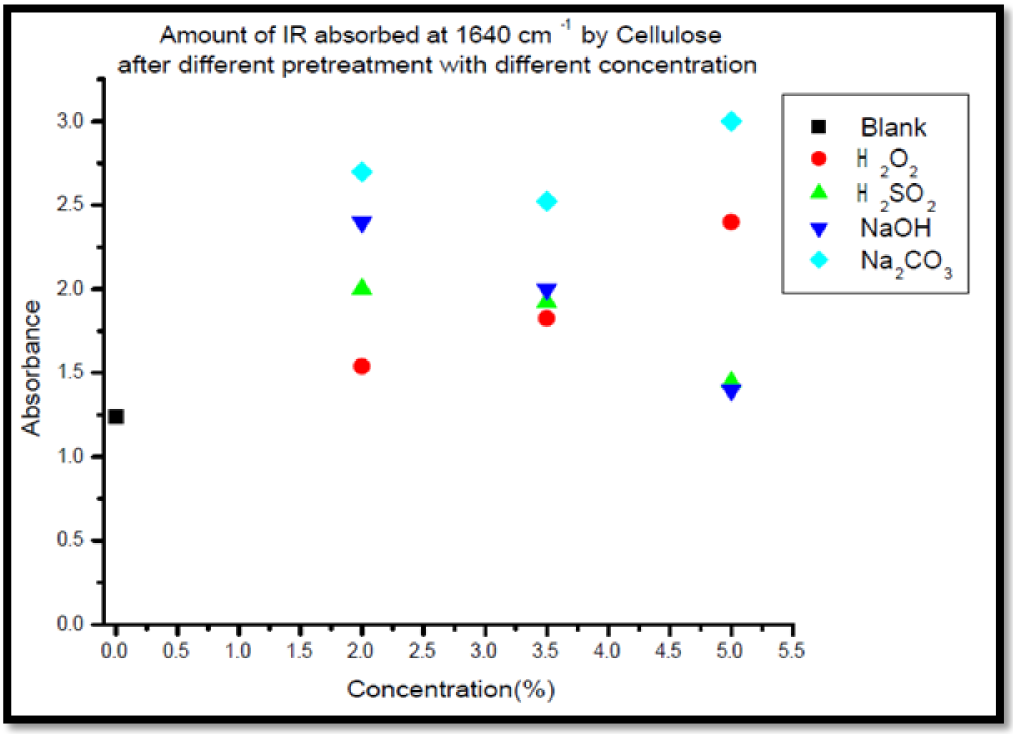


Figure 4.15: Absorbance of Cellulose

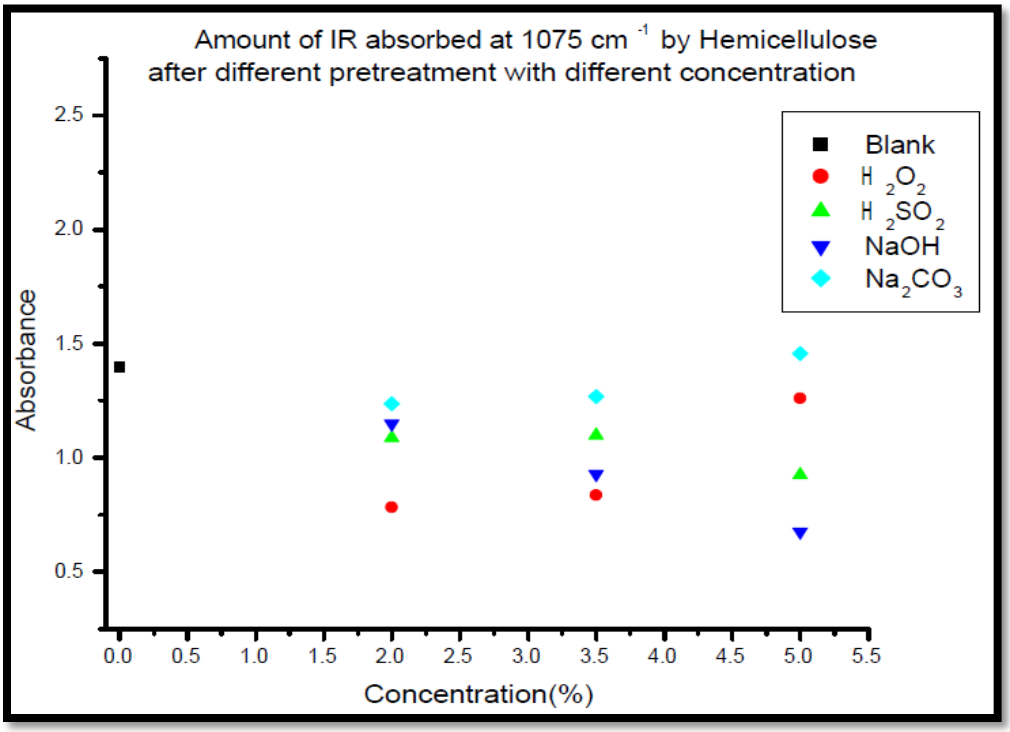


Figure 4.16: Absorbance of Hemicellulose

Based on the FTIR results, it shows that there are few pre-treated samples with high absorbance rate of more than 2 (for cellulose) and more than 1.3 (for hemicellulose). For cellulose, those pre-treated samples with higher absorbance rate are chemical solutions of 5% H_2O_2, 2% NaOH, 2% Na_2CO_3, 3.5% Na_2CO_3 and 5% Na_2CO_3. On the other hand, pre-treated sample with higher absorbance rate for hemicellulose is chemical solution of 5% Na_2CO_3. This is yet to be proven as FTIR gives only qualitative analysis. Quantitative analysis (CHNS, UV Spectrophotometer and HPLC) was done to verify the best result.

4.2 CHNS

A CHNS analyser is a scientific instrument which can determine the elemental composition of a sample. The name derives from the primary elements measured by the device which are Carbon (C), Hydrogen (H), Nitrogen (N) and Sulphur (S). This analyser uses a combustion process to break down substances into simple compounds which are then quantified [49].

This elemental analysis can be qualitative (determining what elements are present), and it can be quantitative (determining how much of each are present). Elemental analysis falls within the ambit of analytical chemistry, the set of instruments involved in deciphering the chemical nature of our world [50].

Table 4.3 presents the results obtained from CHNS analysis. These results were then plotted in graphs for better viewing as shown in figure 4.17 to 4.19. In order to get the best chemical solution for pre-treatment, Carbon to Nitrogen (C/N) ratio was calculated and presented in figure 4.20. As an indication, ratio in between 25-35 is the optimum range for enhanced biogas production [51]. From these findings, it can be concluded that NaOH with 3.5% concentration with C/N ration of 30.69 is the best chemical for the pre-treatment of rice husk for potential energy recovery.

Table 4.3: CHNS Results

	Concentration %	Carbon %	Hydrogen %	Nitrogen %	Sulphur %	C/N Ratio
Blank	0	40.60	3.84	1.64	0.25	24.71
NaOH	2	32.94	5.06	0.81	0.14	40.67
H_2SO_4	2	21.30	1.97	0.95	4.51	22.33
H_2O_2	2	24.32	2.99	1.07	0.54	22.84
Na_2CO_3	2	29.02	2.53	1.17	0.12	24.77
NaOH	3.5	36.72	3.33	1.20	0.12	30.69
H_2SO_4	3.5	18.13	1.85	1.27	5.96	14.25
H_2O_2	3.5	23.77	3.50	1.38	0.04	17.26
Na_2CO_3	3.5	25.07	4.38	1.38	0.22	18.16
NaOH	5	38.81	4.51	1.39	0.17	28.00
H_2SO_4	5	14.69	1.59	1.41	6.40	10.40
H_2O_2	5	22.37	1.97	1.69	0.05	13.21
Na_2CO_3	5	22.12	2.43	1.79	0.07	12.34

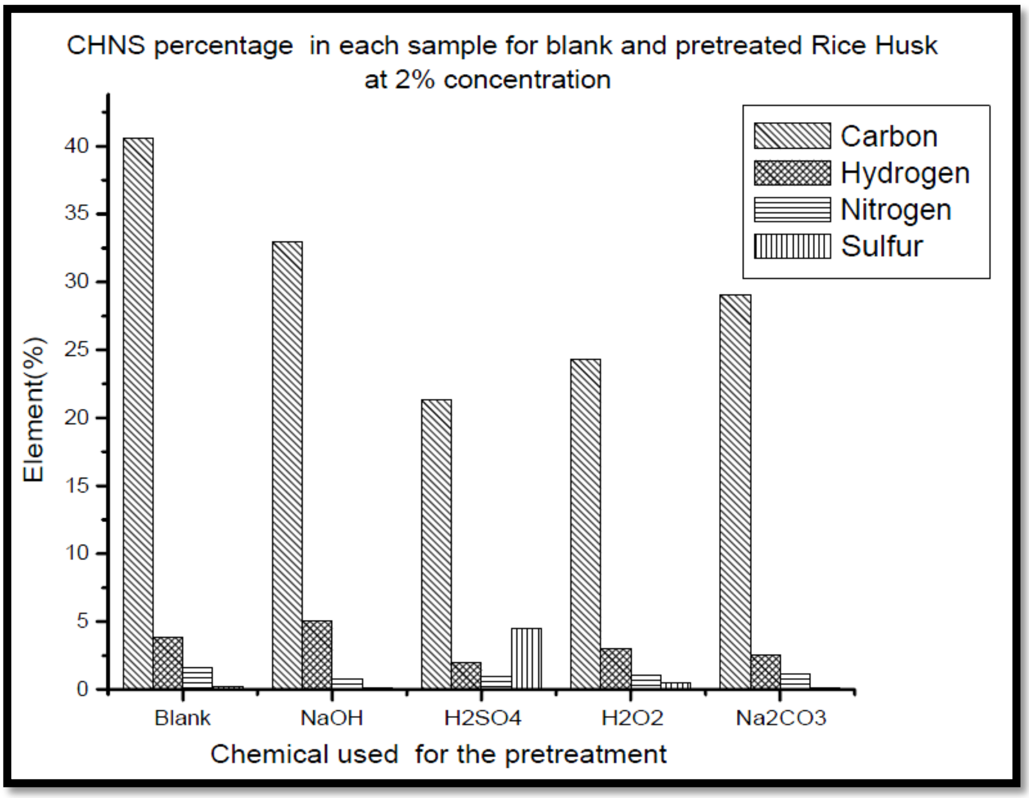


Figure 4.17: CHNS result for 2% concentration pre-treatment

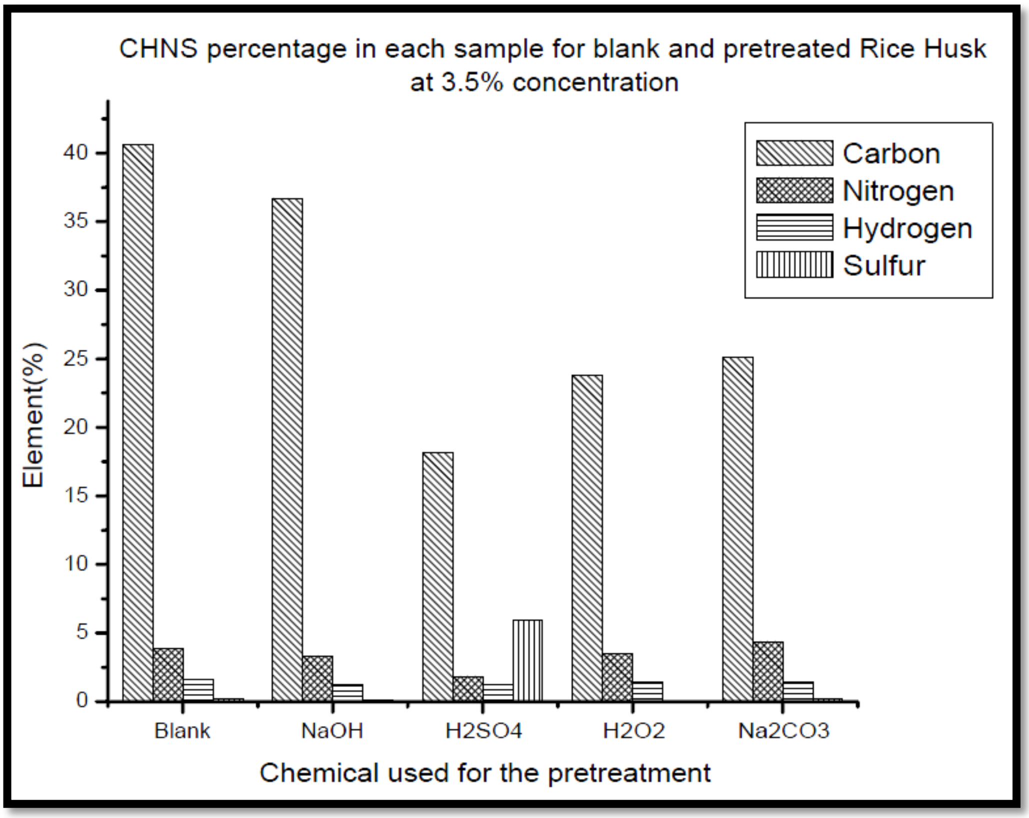


Figure 4.18: CHNS result for 3.5% concentration pre-treatment

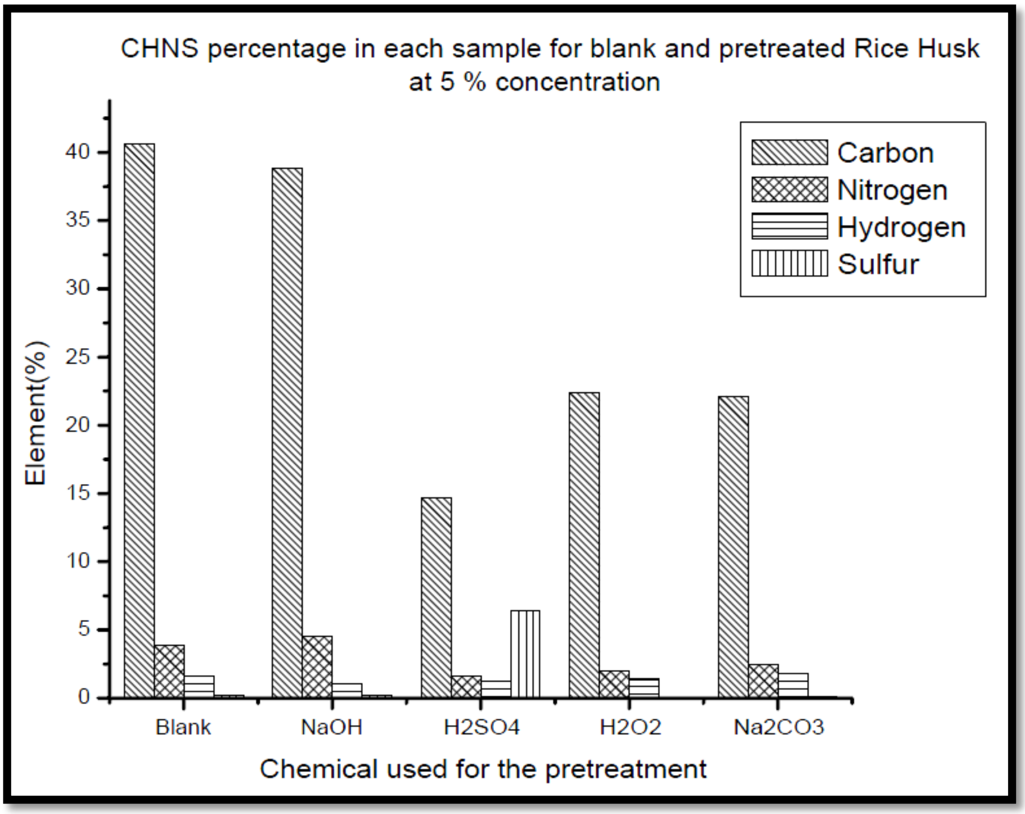


Figure 4.19: CHNS result for 5% concentration pre-treatment

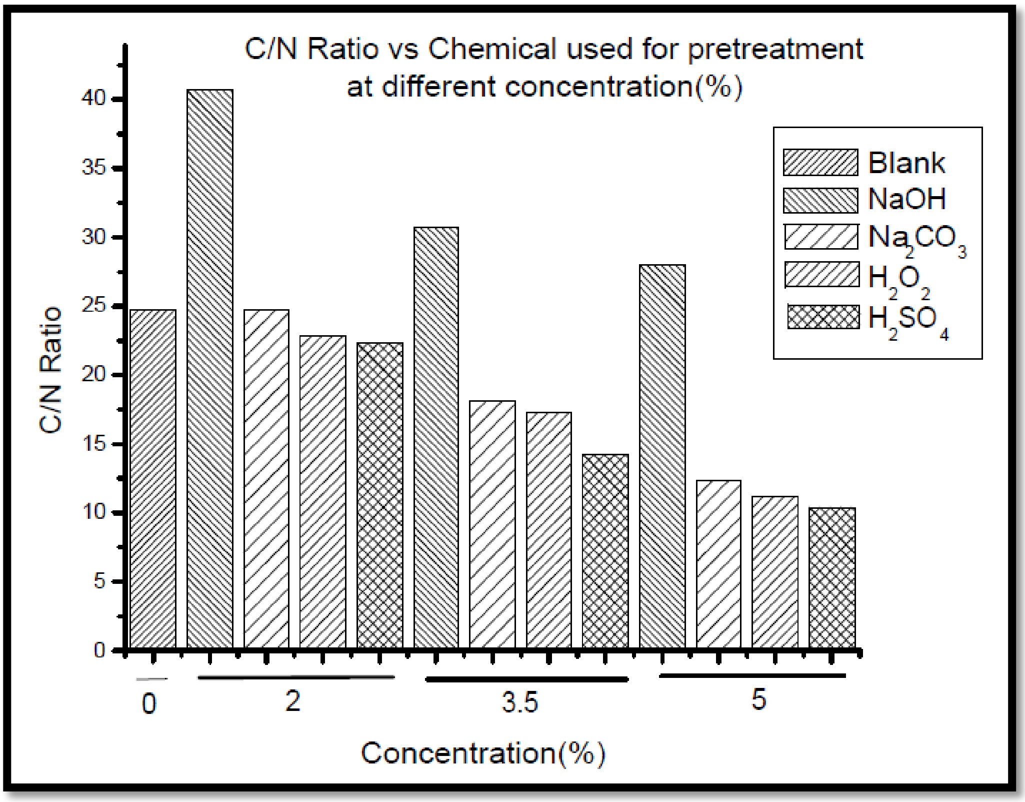


Figure 4.20: C/N ratio VS Chemical used for pre-treatment at different concentration

4.3 UV VISIBLE SPECTROPHOTOMETER AND HPLC ANALYSIS

These analyses are categorized as Quantitative Analysis whereby it could determine which chemical and which concentration is the best method for pre-treatment of rice husk. The composition of all the samples was determined by National Renewable Energy Laboratory (NREL) Standard Biomass Analytical Procedures [52].

Table 4.4 shows the results obtained from the two stage acid hydrolysis analysis. Based on the result, it shows that the pre-treated rice husk with 3.5% concentration of NaOH gives the highest cellulose yield of 59.3% compared to the other chemical solutions tested. Hence, 3.5% of NaOH is the best chemical solution for pre-treatment of rice husk for potential energy recovery.

Table 4.4: Results for Analysis by UV visible spectrophotometer and HPLC

Sample	Cellulose %	Hemicellulose %	Lignin %	Ash content %	Moisture %
Untreated Rice Husk	38.6	19.7	17.8	12.5	7.9
2% NaOH MW treated	51.6	13.7	11.3	13.6	6.3
3.5% NaOH MW treated	59.3	10.5	10.2	9.4	6.9
5% NaOH MW treated	57.4	9.3	12.4	11.2	6.4
2% Na_2CO_3 MW treated	40.3	18.9	16.4	14.9	6.1
3.5% Na_2CO_3 MW treated	42.6	18.4	15.7	13.3	6.7
5% Na_2CO_3 MW treated	44.5	17.6	14.5	13.7	6.2
2% H_2O_2 MW treated	44.3	17.8	15.2	12.8	7.2
3.5% H_2O_2 MW treated	47.2	16.1	14.6	11.2	7.4
5% H_2O_2 MW treated	48.3	13.6	14.1	13.3	7.2
2% H_2SO_4 MW treated	44.7	15.9	16.5	12.9	6.5
3.5% H_2SO_4 MW treated	54.2	11.4	14.8	10.3	6.4
5% H_2SO_4 MW treated	49.3	13.8	14.2	12.8	6.2

MW – Microwaved

❑ ***Energy Recovery from Cellulose***

Cellulose has a very high potential of energy, and has been successfully used for biofuel generation by ethanol or biogas, it has been reported that 100 grams of cellulose can produce up to 51.4 grams of ethanol and 48.6 grams of CO_2 [53], It has been also reported that theoretically we can recover 710 ml of biogas for each gram of cellulose, with 51 to 56% methane [54], nowadays cellulose while mixed with other nutrients, has energy efficiency of 52.1% to 83.6 % [55]

CHAPTER 5: CONCLUSIONS AND RECOMMENDATIONS

5.1 CONCLUSIONS

Based on the research done, for FTIR analysis, it was clearly shown that the lignin was largely removed (absence at the lignin peak 1515cm^{-1}). This shows that the first objective was achieved. From this result, it can be concluded that by doing pre-treatment of the rice husk, the lignin can be disrupted and this is a positive sign as by disrupting the lignin, cellulose and hemicellulose can be achieved at a higher percentage. FTIR analysis is qualitative based analysis hence quantitative analysis was done to achieve the second objective.

In order to achieve the second objective of this research, quantitative analysis was carried out. From the findings, it can be concluded that NaOH with 3.5% concentration with C/N ration of 30.69 is the best chemical for the pre-treatment of rice husk for potential energy recovery. To support this result, UV Visible Spectrophotometer and HPLC analysis was done and the results obtained were the same whereby 3.5% concentration of NaOH gives the highest cellulose yield among the chemicals solutions tested.

To put it in a nutshell, from the research done, for untreated rice husk, the percentage of cellulose was 38.6% while the pre-treated rice husk with 3.5% concentration of NaOH gives a total of 59.3% of cellulose. From this result, it can be concluded that the best rice husk pre-treatment method for potential energy recovery is by using 3.5% concentration of Sodium Hydroxide (NaOH) where it gives the highest percentage of cellulose.

5.2 RECOMMENDATIONS

There are a lot of improvement can be done on this research, some of the recommendation that can be considered are as follows:

1. Researcher can consider pre-treatment of various biomass wastes in order to diversify the utilization of waste material for potential energy recovery.
2. Other than using the 4 chemicals with different concentration, researcher can do comparative study on other chemicals with other different concentrations.
3. To perform solid state anaerobic digestion to determine the actual enhancement of biofuel production.

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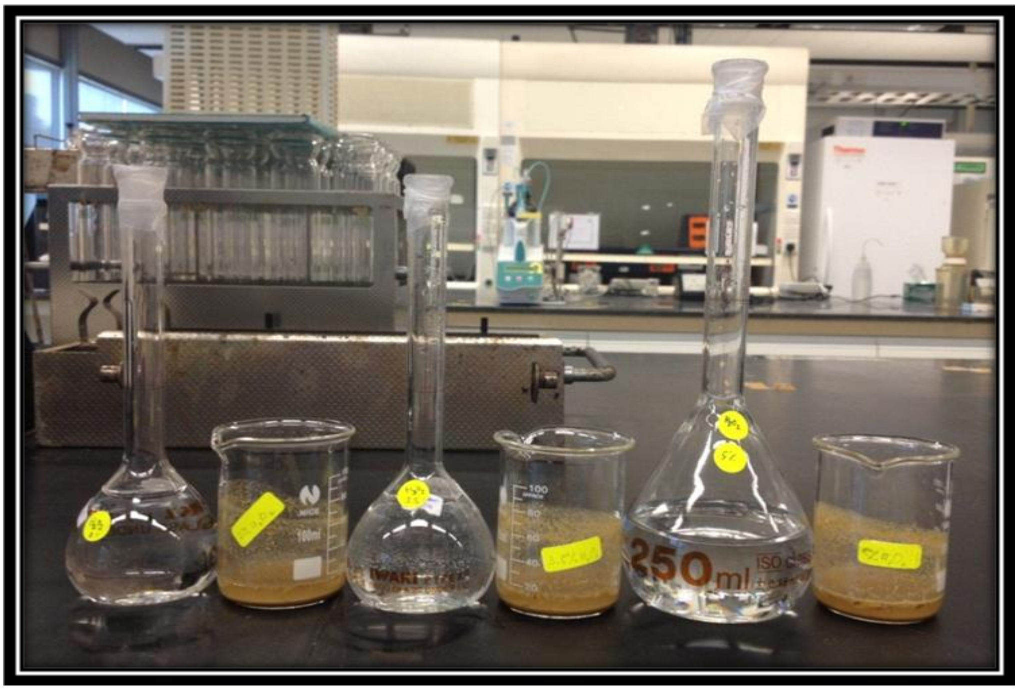
APPENDICES

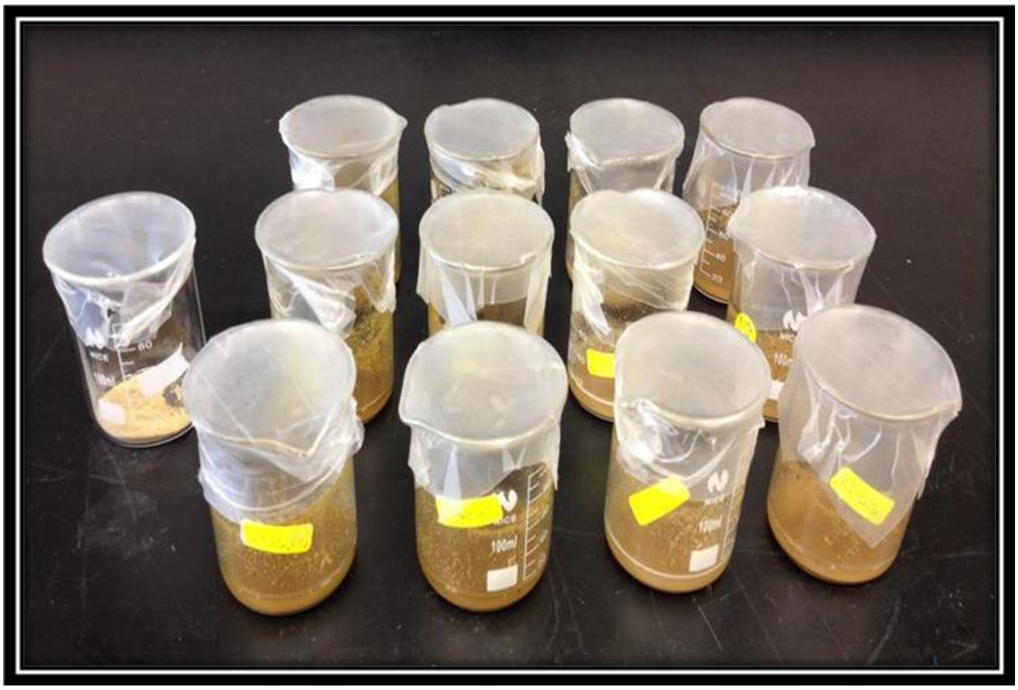
APPENDIX 1-1

PRE-TREATMENT PROCESS

Chemical Pre-treatment of rice husk



Pre-treated rice husk ready for analysis

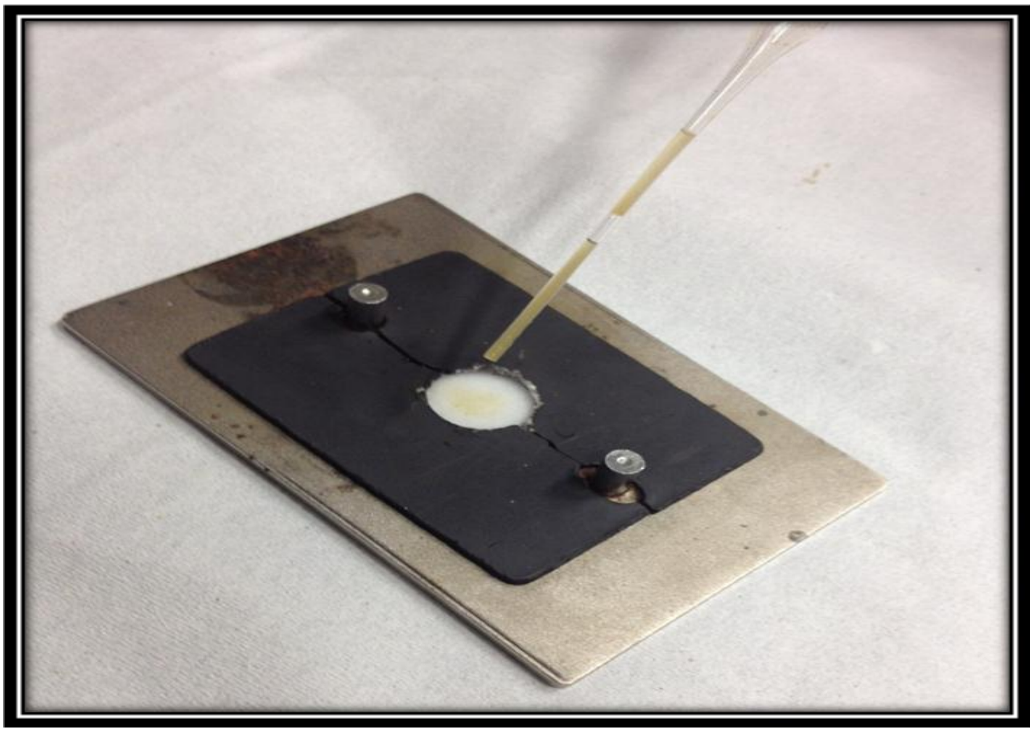


APPENDIX 1-2

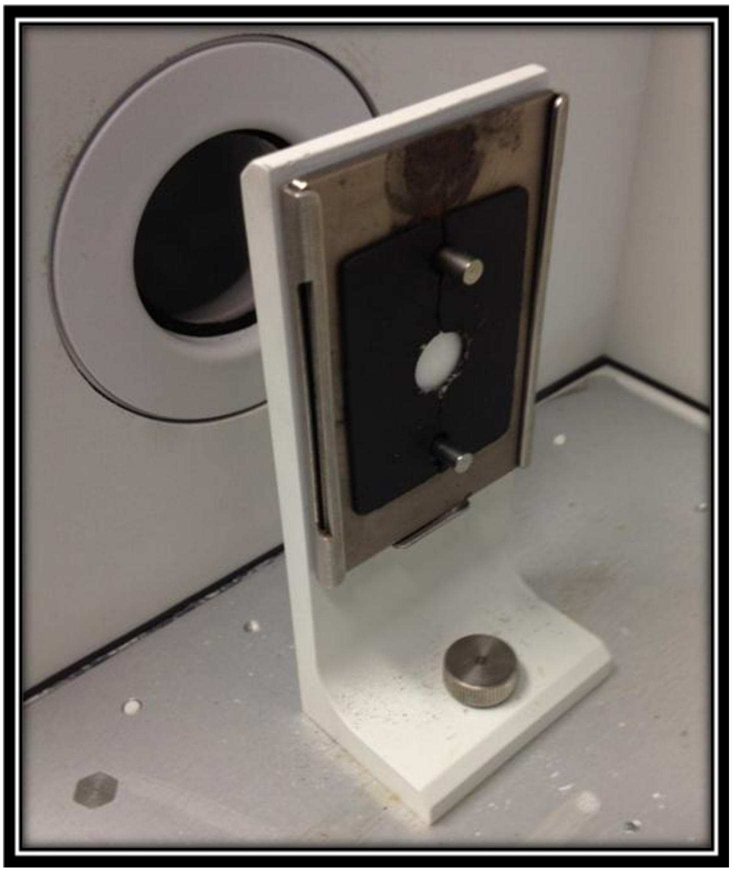
FTIR ANALYSIS

FTIR Analyser

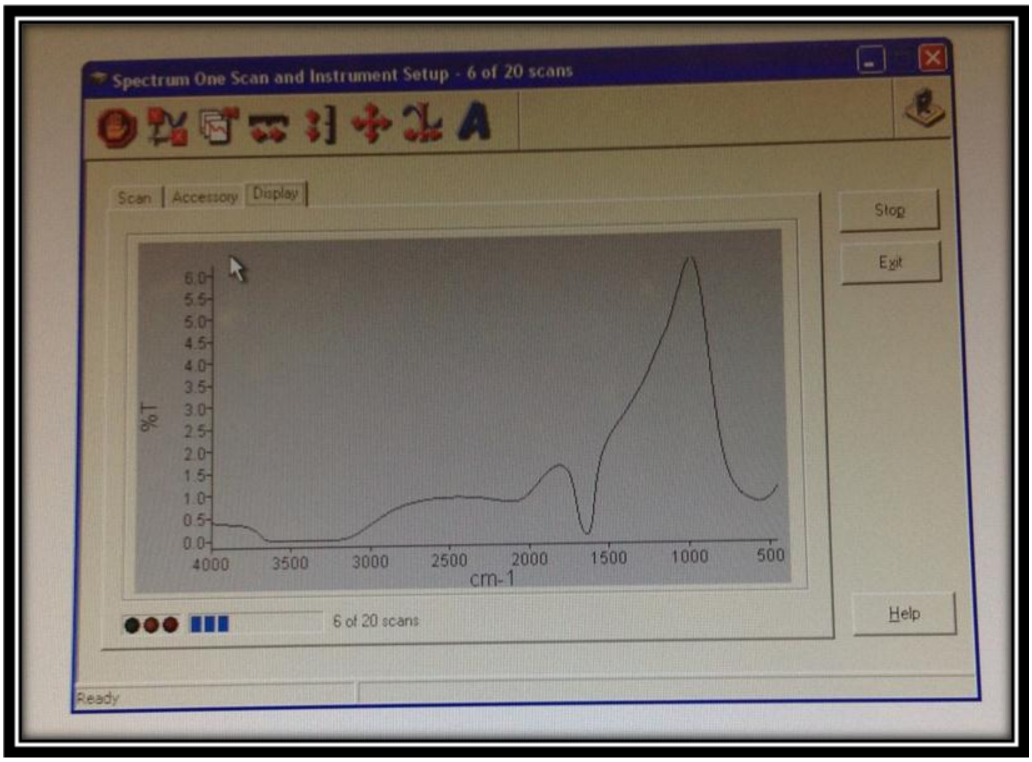
FTIR preparation



Sample ready for analysis



Analysing in progress



APPENDIX 1-3

CHNS ANALYSIS

CHNS Analyser

Sample ready to be analyse