DERIVATION OF NANOFIBRILLATED CELLULOSE FROM LOCALLY AVAILABLE RICE STRAW

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Degree of Master of Science

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Thesis submitted in partial fulfillment of the requirement for the Degree of Master of Science

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DECLARATION

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ABSTRACT

Cellulose has become a wonder material in the present context of research and development since it is fibrous and tough, hence biodegradable, biocompatible, and renewable natural polymer. Nowadays, rice straw as a cellulose source has gained momentum as rice is one of the major crops grown in most of the tropical and subtropical countries of the world where half of the world population consuming it as the major food source. Rice straw is the agricultural production residue from rice cultivation which is considered as an agricultural waste and cause decay related issues in the plantation. This biological waste material if utilized can be a renewable feedstock for the production of value added products for special applications. Sri Lanka being an agricultural country holds twentieth position in the worldwide rice production. However, a large amount of rice straw is generated per annum as a by-product of rice production in the country. Even though rice straw is utilized in various ways, there is a possibility for a value addition by extracting its constituents such as nanofibrillated cellulose from this commercially underutilized waste material and thereby embracing a bioeconomy approach in the country.

In this study, nanofibrillated cellulose (NFC) was extracted from Sri Lankan rice straw varieties BG352, Murunkan, Pachchaperumal and Moddaikaruppan in two distinct stages. Initially, rice straw was subjected to a series of chemical traetments to eliminate the non-cellulosic constituents. Then the obtained chemically extracted cellulose fibers were separated into nanofibers *via* high-intensity ultrasonication (HIUS) treatment. Structural, thermal and morphological characteristics of nanofibers and their intermediate products were determined. FTIR analysis confirmed that the chemical composition of nanofibers was mainly cellulose where amorphous natured hemicellulose and lignin were effectively removed during chemical treatments. Study revealed that around 25 - 38 percent cellulose was extracted from the four rice straw varieties *via* chemical process. From these chemically extracted cellulose fibers around 17 - 45 percent of nanofibrillated cellulose were extracted *via* high-intensity ultrasonication process. Morphology of rice straw during the extraction process was distinct when the non-cellulosic components were removed. Results indicated that the efficient multi-step treatment process yielded nanofibers with potential advanced applications.

Chemical extraction method is found to be the most efficient method for cellulose extraction from lignocellulosic biomass. Therefore, it is of paramount important to investigate the influence of parent materials on the synthesis process and the properties of the yield. Effect of particle size distribution of locally available traditional rice straw Murunkan on cellulose extraction was studied. Study revealed that after the series of chemical treatments rice straw with particle size distribution below 75 µm (Mu-75) yielded 27.19 ± 0.98 percent and rice straw with particle size distribution between 150 µm to 250 µm (Mu-250) yielded 38.31 ± 0.86 percent. Out of these cellulose fibers, around 63 percent of NFC was extracted from Mu-75 and around 55 percent of NFC from Mu-250. SEM images showed that the diameters of the extracted nanofibres from Mu-250 ranged from 75 to 200 nm whereas nanofibers from Mu-75 ranged between 27 – 104 nm. These findings will have profound influence upon extracting nanofibrillated cellulose from agricultural biomass.

Key words – Rice Straw, Nanofibrillated Cellulose, Chemical Extraction, High Intensity Ultrasonication, Bioeconomy

Table of Contents

List of Figures

List of Tables

List of Abbreviations

Abbreviation	Description
BC	Bacterial Cellulose
CPC	Chemically Purified Cellulose
CNC	Cellulose Nanocrystals
CNF	Cellulose Nanofibrils
DTA	Differential Thermal Analysis
DTG	Derivative Thermogravimetry
ECNF	Electrospun Cellulose Nanofibers
EDS	Energy-dispersive X-Ray Spectroscopy
FTIR	Fourier transform infrared spectroscopy
HIUS	High-Intensity Ultrasonication
HPH	High Pressure Homogenization
MFC	Microfibrillated Cellulose
NC	Nanocellulose
NCC	Nanocrystalline Cellulose
NFC	Nanofibrillated Cellulose
RRDI	Rice Research and Development Institute
RS	Rice straw
RSA	Rice straw ash
SEM	Scanning Electron Microscopy
TGA	Thermogravimetric Analysis
XRD	X-Ray Diffraction

List of Appendices

xi

CHAPTER 1: INTRODUCTION

1.1 Background

1.1.1 Agriculture Sector in Sri Lanka

Agriculture sector in Sri Lanka is significant in terms of land resource utilization as well as labor deployment. Although the country is moving towards industrialization, agricultural sector still contributes to foreign exchange earnings, around seven percent to the national Gross Domestic Product (GDP) and to government revenue. Wide ranges of crops are cultivated in their respective agro-ecological regions across the country[1]. Figure 1 shows the Land use and land cover of Sri Lanka. Out of the total land area, around forty two percent is devoted for the agricultural activities and approximately one third of the rural population engages in agricultural activities.

Rice, tea, rubber and coconut are the most important crops grown in Sri Lanka, where various other crops are grown on a medium and small scale in different agro-ecological regions[2]. During the production of these crops, tons of crop residues are generated in the country. These crop residues are used for different purposes on different scales in the country. However, there is no adequate estimate of the amount of annual crop residues produced and their use in Sri Lanka[3].

Nevertheless, the economic contribution from agriculture sector has steadily declined over the years and with a clear demonstration of yield deficiencies and low tech operations. Twenty first century is directing economies to go circular as well as embrace a bioeconomy approach. In that context the paddy production can be looked at in a complete different perspective and this research supports such a direction.

1.1.2 Agriculture Waste

Production activities always entail different types of pollution, such as solid waste, wastewater or gas. During thousands of years of planting, crop residues have been absorbed into the soil or used as animal feed, and returned the manure into the land in significant quantities which can be absorbed. However, these days' farms are getting

adapted to mechanized methods, synthetic pesticides and fertilizers. As a result of this, crop residues are considered as waste [4]–[7]. Disposal of this waste is a permanent problem for farmers around the world. Accumulation of this type of biomass in considerable quantity per annum causes deterioration of the environment as well as loss of potentially valuable materials that can be converted into value added products[8]–[11].
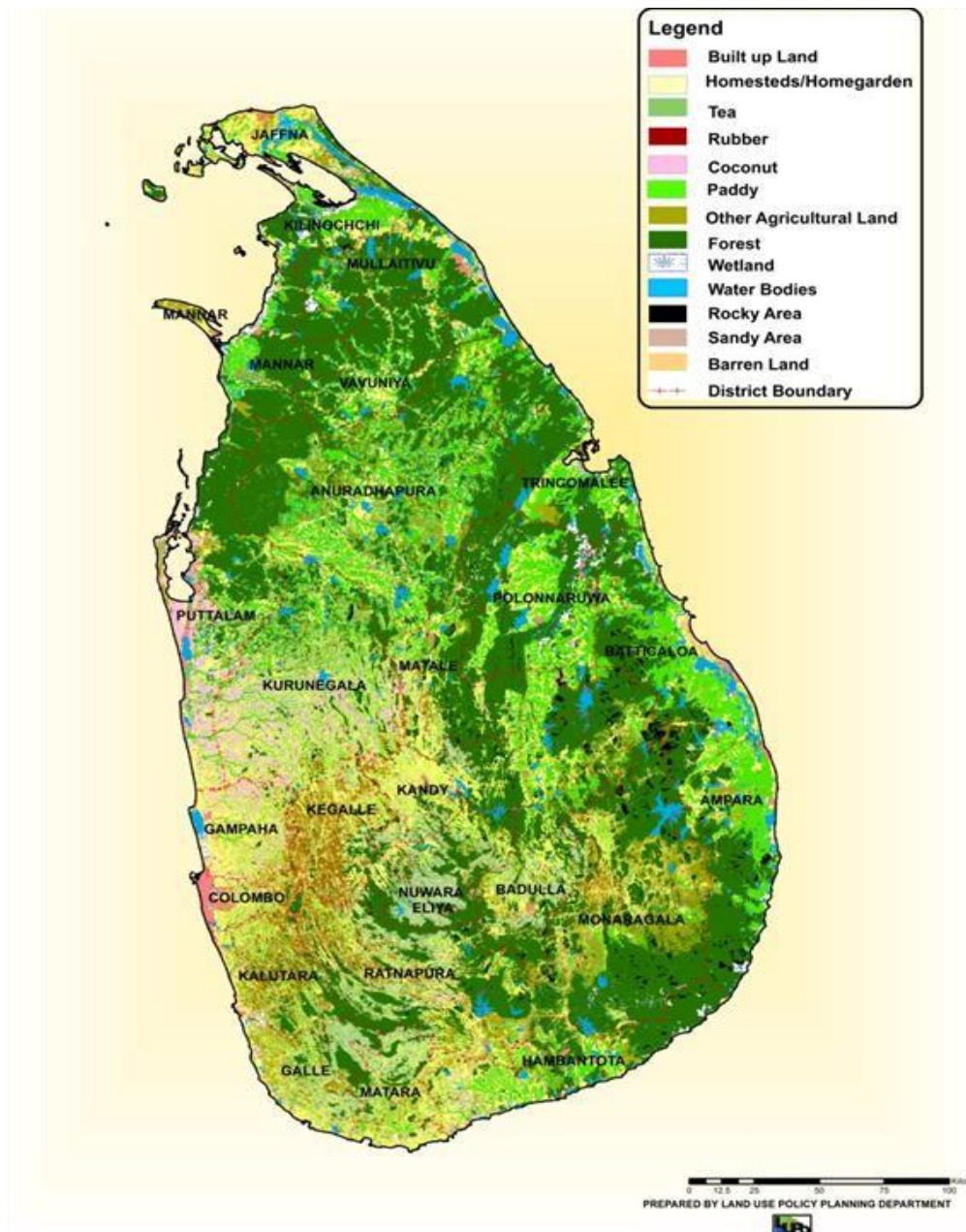
Figure 1.1: Land use and Land cover of Sri Lanka
(Source: Survey Department of Sri Lanka, 2018)

1.1.3   Agriculture Waste - Renewable Lignocellulosic Biomass

Renewable lignocellulosic constituents with slight variations in compositions are present in waste generated from agricultural production[12]–[14]. Cellulose and hemicellulose are the main components of these materials that can be considered as alternative sources of sustainable and renewable materials. These materials could potentially be used in various applications. Despite the excessive generation of agricultural waste, only a small fraction is utilized for some applications[15]–[18]. Natural fibers possess excellent properties. They have the potential to be utilized as reinforcing fillers in the matrix that can be used as alternative materials for hybrid and biocomposites. Natural-fiber-based polymer composites are gaining increasing demand in various commercial applications due to their low cost and potential global sustainability[19]–[21].

1.2 Objectives of the Study

Significant amount of rice straw is generated per annum from the rice production in Sri Lanka. Although rice straw is used in various ways, by extracting cellulose fibers and nanofibrillated cellulose, there is a potential for adding value to this commercially under-utilized waste.

The objectives of this study are to;

- extract cellulose fibers from four Sri Lankan Rice Straw varieties *via* a series chemical treatments.

- investigate the disintegration behavior of cellulose fibers with time during high-intensity ultrasonication (HIUS) treatment.

- isolate nanofibrillated cellulose (NFC) from the chemically extracted cellulose of four varieties *via* high-intensity ultrasonication (HIUS) treatment.

- study the effect of particle size distribution of parent material (rice straw) on cellulose and nanofibrillated cellulose (NFC) extraction.

Extracting nanofibrillated cellulose from locally available rice straw would be an ideal replacement to the synthetic fibers that are currently in use. The findings of this research will not only add value to the rice straw but also accentuate sustainable transition to a bioeconomy in the country.

CHAPTER 2: LITERATURE REVIEW

2.1 Paddy Cultivation in Sri Lanka

Rice being the staple food of Sri Lankans, the primary form of agriculture in the country is paddy production. Paddy is cultivated as a wetland crop in almost all parts of the country except at very high altitudes under rainfed, major and minor irrigation systems (District share of asweddumized paddy areas according to the mode of irrigation is presented in *Appendix A*).
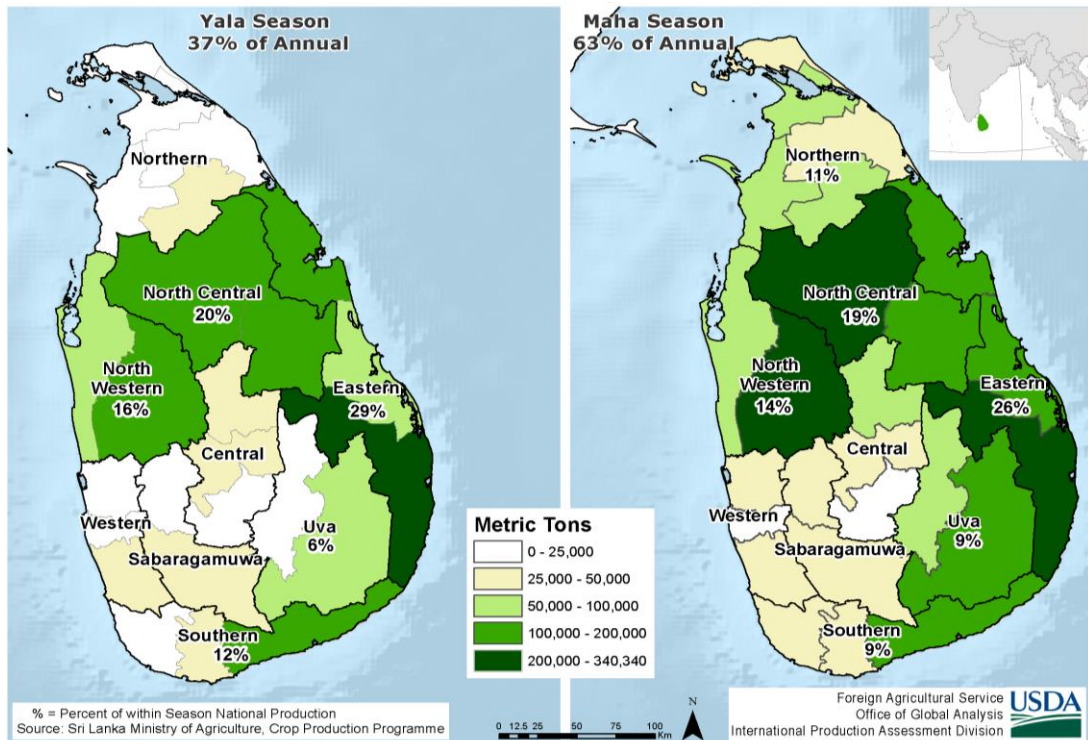
Figure 2.1: Rice Production by District
(Source: Department of Agriculture, Sri Lanka, 2016/2017)

As shown in Figure 2.1, there are two growing seasons in Sri Lanka. Yala which is effective from May to August during South-West monsoon and Maha which is effective from September to the following March during North-East monsoon. The total production and extent of land under paddy cultivation during both seasons in the years 2017/18 and 2018/19 are shown in Figure 2.2. In 2017/18, 2,383,153 metric tonnes of paddy over 791,679 hectares and in 2018/19, 3,929,831 metric tonnes from

1,040,954 hectares was harvested across the country (District level paddy cultivation and land extent are presented in *Appendix B*).
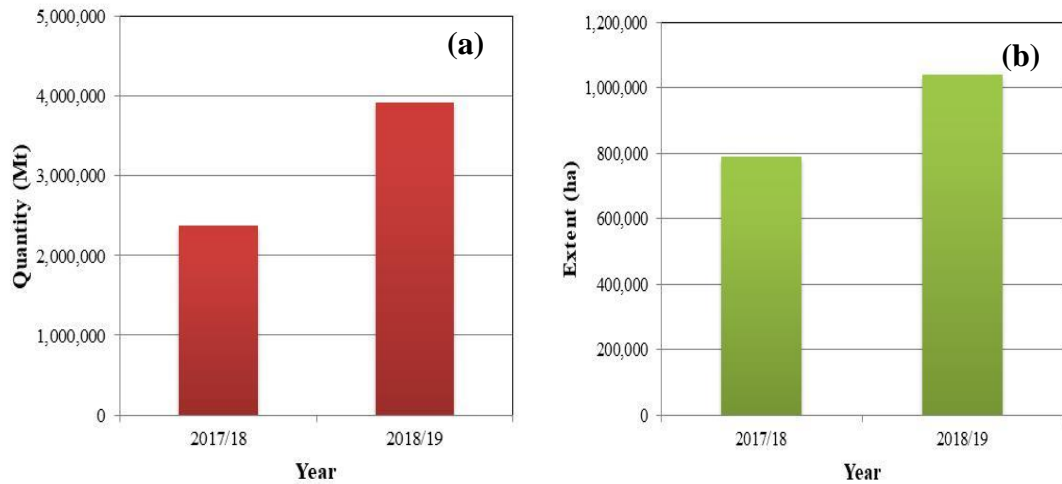
Figure 2.2: Paddy cultivation in Sri Lanka (a) production and
(b) land extent in the years 2017/18 and 2018/19
(Source: Department of Census and Statistics, Paddy Statistics, 2017/18 and 2018/19)

2.2 Rice Straw - by product from paddy cultivation and processing

On a global scale, rice wastes are generated in significant quantities. They are utilized in some regions. However, in most of the developing countries they are considered as wastes that causes pollution and has problems with proper disposal[22]. Stem of the rice plant is known as rice straw. It is identified as agricultural production residue removed during the rice harvest[23]–[27].
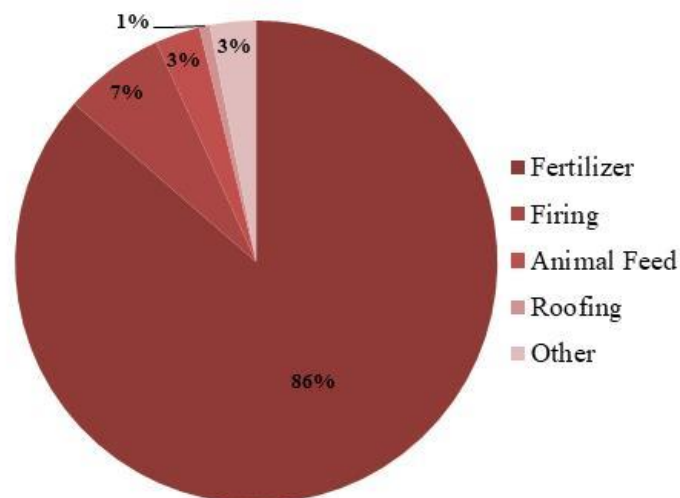
Figure 2.3: Uses of rice straw in Sri Lanka
(Source: Department of Census and Statistics, Paddy Statistics, 2014/15 Maha)

Generally, the grain to straw ratio is assumed as 1.0 to 1.1 where the straw value may vary between 0.7 - 1.4 depending on the rice variety, geographic location and climate of growth. As a result of this, rice straw is generated in significant quantities than the rice itself from paddy cultivation[28]–[30]. As per 2014/15 paddy statistics of Maha season (Figure 2.3) of Sri Lanka, rice straw is widely used as a feed for cattle, thatching roofs, fertilizer, etc. (District level sown area under paddy by use of straw is presented in *Appendix C*). However majority of the farmers' burn the rice straw at the threshing site when there is no alternate way of disposal.

2.3 Composition of Rice Straw

Rice straw is composed of both organic and inorganic matter. Cellulose, lignin, hemicellulose, some proteins and vitamins are the organic components while the major inorganic mineral component is silica[8], [31]–[33].
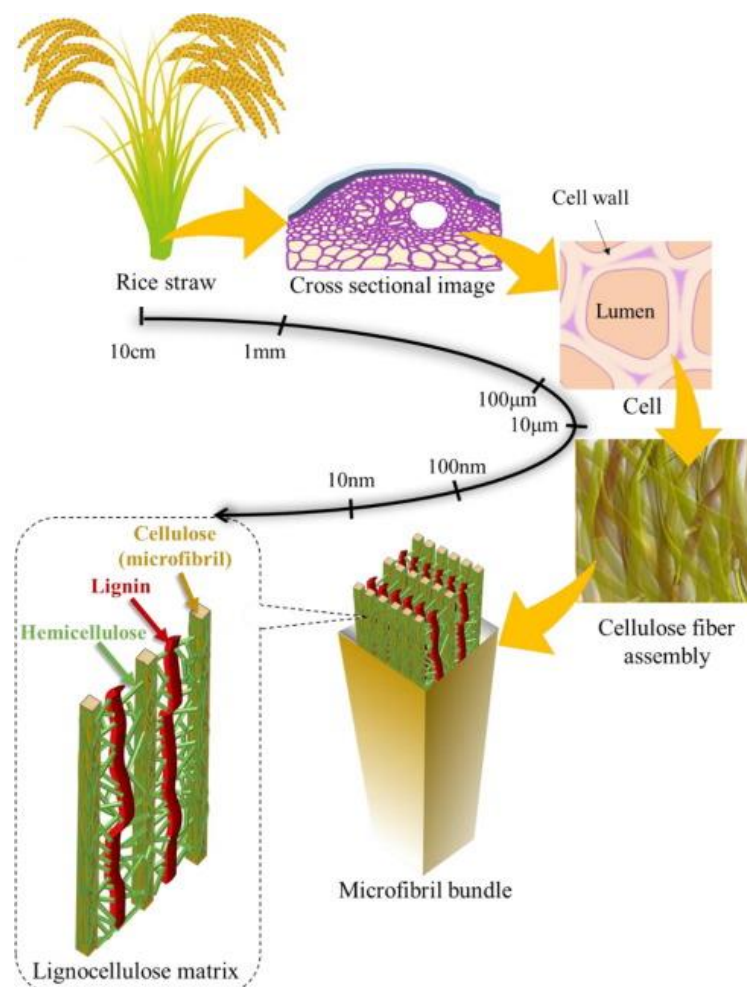
Figure 2.4: Hierarchical structure of rice straw [34]

Rice straw has a complex structure as shown in Figure 2.4 and 2.5 where the cellulose fibers are embedded in a hemicellulose and lignin organic polymer matrix. Rice straw has the composition of cellulose (22 - 47%), lignin (5 - 24%), hemicellulose (19 - 27%) and ash (13 - 20%)[35].
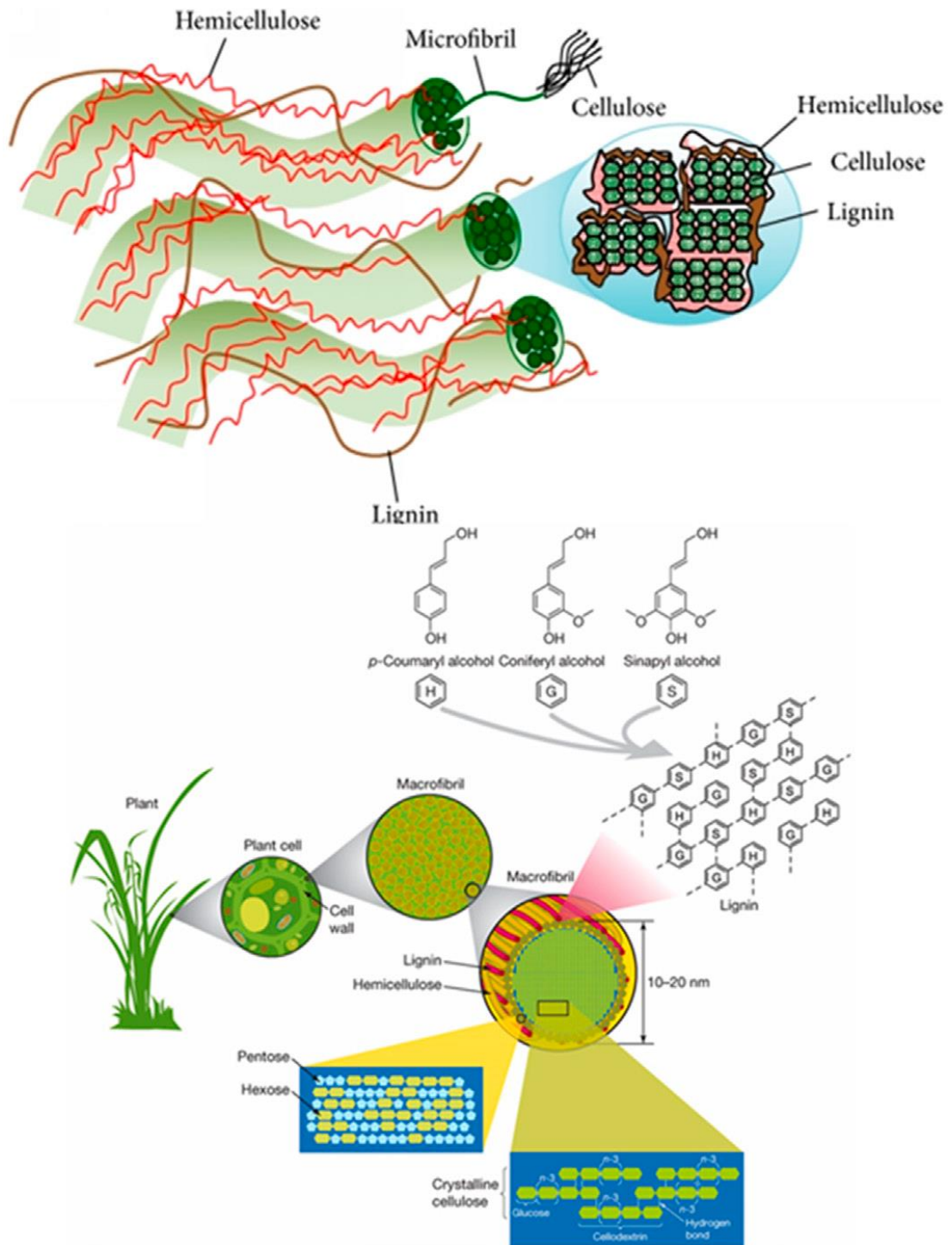
Figure 2.5: Schematic illustration of plant cell wall[35]

Cellulose acts as the structural component that provides reinforcement to the rice plant[16]. Apart from this, there is also a layer of wax made of complex mixture of various compounds which acts as a protective layer over the plant surface[36]–[40]. Therefore, a sophisticated method (Figure 2.6) should be employed to isolate cellulose fibers out from the plant with high purity.
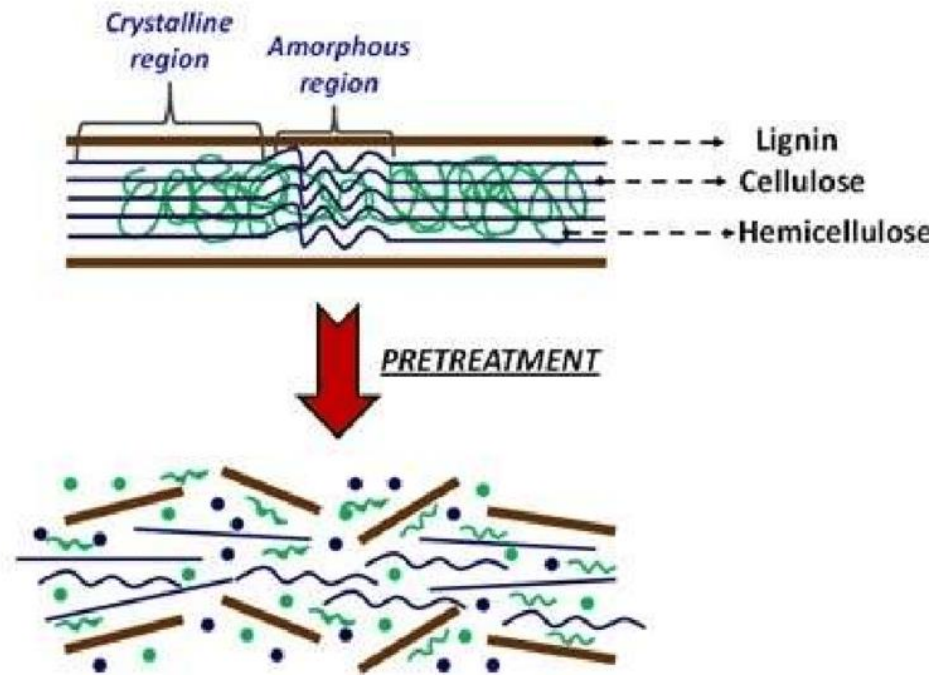
Figure 2.6: Deconstruction of lignocellulose [41]

Rice plants absorb silica from soil during growth and accumulate it in their structures. As shown in Figure 2.7, when burning at high temperature, absorbed silica gets concentrated. This concentrated silica in the ash makes it more valuable[42]–[46]. Among the agricultural waste, rice straw ash has very high potential to be utilized as filler in rubber compounds and as pozzolanic material in cementing systems due to its random availability, very high silica content and relatively low cost[47].
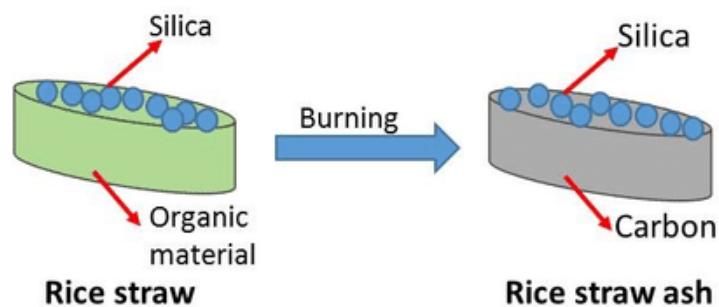
Figure 2.7: Illustration of silica in rice straw [42]

2.4 Natural Cellulose Fibers

Moving towards resource efficient society, natural fibers are renewable sources and can be revived by nature as well as human ingenuity. These natural fibers play an important role in the emerging bioeconomy as well as green economy[48]–[50]. Cellulose is a linear biopolymer that is present naturally in all plants. It is a vast source for biocompatible and environmentally friendly products.

Cellulose is the predominant component of lignocelluloses which has a long chain polysaccharide structure made of β (1,4) - linked glucose units. The chemical formula of the organic proportions of rice straw is $C_6H_{9.63}O_{4.57}N_{0.11}S_{0.02}$ which is very close to the chemical formula of cellulose monomer $(C_6H_{10}O_5)$[51],[52].. These linear structures are linked together to form planer sheet and bundled into microfibrils via various inter molecular bonds and intra molecular bonds as shown in Figure 2.7.
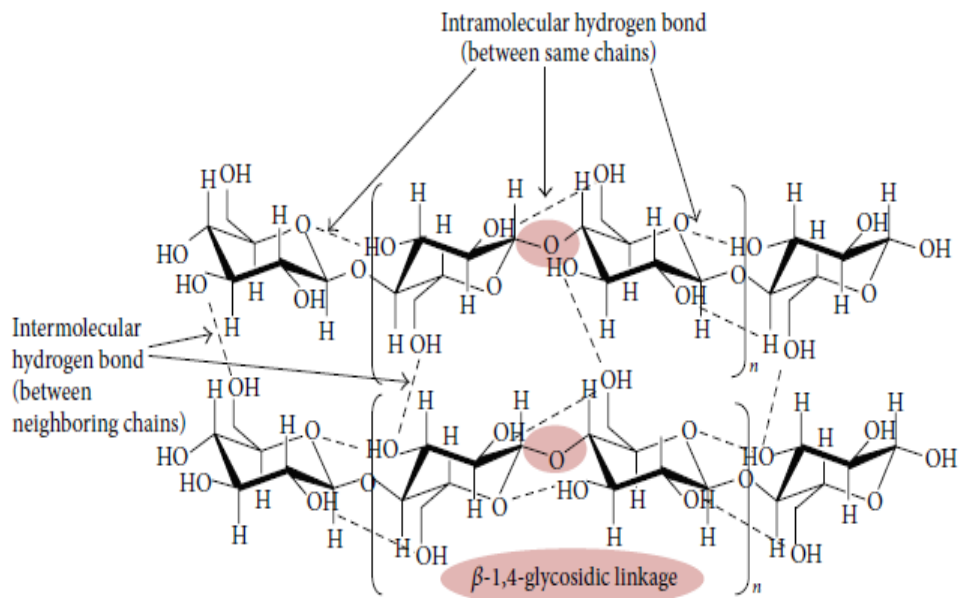
Figure 2.7: Chemical structure of cellulose [41]

Cellulose fibers acquire high axial rigidity due to inter-chain and intra-chain hydrogen bonding. Inside these cellulose fibers, there are domains which are composed of both highly ordered crystalline structures as well as low ordered

amorphous structures alternatively. Cellulose fibers which are comprised of well-ordered structure possess higher degree of crystallinity[16],[23].

2.4.1 Extraction of Cellulose Fibers from Agricultural Residue

Various efficient methods have been developed by researchers in order to isolate cellulose from cellulosic biomass. The cellulose extraction requires the removal of non-cellulosic materials such as hemicelluloses and lignin from agricultural residue[45],[53]. To achieve an economically viable method to utilize this biomass, its major fractions (cellulose, hemicelluloses, and lignin) must be extracted efficiently. Various treatment methods can be adapted to extract cellulosic and non-cellulosic components from agricultural residue.

2.4.1.1 Mechanical Treatment

Mechanical treatment methods that can be employed are chipping, milling or grinding. Surface/volume ratio is increased by means of reducing the particle size of the materials[54],[55]. However, effective separation of cellulose through this method is inefficient. Due to this, mechanical treatments are combined with other methods to achieve efficient cellulose extraction.

2.4.1.2 Chemical Treatment

Chemical treatments are effective in disrupting the cell of the agriculture residue. Some of the chemical treatment methods are alkaline hydrolysis, organosolv treatment, oxidation treatment and acid-alkaline treatment[36],[56].

2.4.1.3 Steam Explosion

Structure of the lignocellulosic biomass is broken through hydrothermal process. The ultimate effect of steam explosion on lignocellulose is a combination of physical and chemical. In this method, initially biomass is treated with high pressure steam around 14 – 16 bar for a short period of time within 20 seconds to 20 minutes at high temperature around 200 ˚C – 270 ˚C[55],[57]. Then pressure is quickly dropped to atmospheric pressure. This sudden drop in pressure breaks down the structure of biomass. Finally decomposed cellulosic and non-cellulosic fractions can be separated by employing standard extraction method.

2.4.1.4 Enzymatic Treatment

Enzymatic treatment is used to degrade the non-cellulosic components from the biomass while maintaining cellulose fibers. This treatment also facilitates selective hydrolysis as well as restrictive hydrolysis of definitive component in cellulose fibers[58]. Degradation of organic components present in cellulosic fibers cannot be done by a single enzyme. Therefore, a group of enzymes known as cellulases are used for the pretreatment of cellulose fibers.

2.4.2   Applications of Cellulose and Cellulose Derivatives

The fundamental chemistry of cellulose is similar to that of alcohols namely the formation of esters, ethers, etc. resembles the common derivatives of alcohols[45], [59]-[63] Due to the presence of inter and intra-chain hydrogen bonds within the structure of cellulose, it does not easily dissolve in common solvents. These aspects make cellulose ideal for industrial applications.

Cellulose in the form of cellulose acetate is widely utilized derivative in industrial applications[64]-[69]. Some of such applications include coatings, membranes, cigar filters, etc. Likewise, it is utilized in membrane production that is used in gas separation, reverse osmosis and hemodialysis[65]. Additionally, they are employed as an alternative for glass and moulding component, in certain fabrics and in photographic safety film. Furthermore, cellulose ethers are utilized in resins, soaps, adhesives and paper sizings[66].

2.5 Nanocellulose

Cellulose is referred to as nanocellulose when at least one dimension is in nanoscale. Process conditions influence the properties, dimensions and composition of nanocellulose. Based on the process parameters, nanocellulose can be categorized into two major classifications; nanocrystalline cellulose (NCC) and nanofibrillated cellulose (NFC)[68]-[70]. Though electrospun cellulose nanofibers (ECNF) and bacterial cellulose (BC) are considered as nanocellulose, large scale production of these two has its limitations[71]. NCC and NFC are produced by top-down process

by disintegrating cellulose fibers whereas electro spun cellulose nanofibres and bacterial cellulose are generated by bottom-up process by dissolving cellulose via electrospinning and by building up low molecular weight sugars via bacteria respectively. However, NCC and NFC found to be the common ones. Recently, nanofibrillated cellulose (NFCs) have gained much attention due to their strengthening effect, high aspect ratio, good optical and mechanical properties which make them ideal for many industrial applications in nanocomposites, gas barriers, security papers, coating additives and food packaging[48]. These applications can be considered as the second generation uses of cellulose.

2.5.1   Nanofibrillated Cellulose (NFC)

Nanofibrillated cellulose (NFC) is also known as cellulose nanofiber, cellulose nanofibrils (CNF) and microfrobrillated cellulose (MFC). NFC is composed of 10 - 50 mocrofibrils bundled together in alternating crystalline and amorphous domains and present a web like structure[63],[71]-[76]. The aspect ratio of NFC is high as the length of the fiber extends to few micrometers whilst the diameter is in the nanoscale. Due to this, NFC has a low percolation threshold and thereby exhibits a greater stability to form rigid network.

2.5.2   Extraction Methods of Nanofibrillated Cellulose

Several methods were used to extract nanofibers from lignocellulosic biomass. Depending on the disintegration process, different types of nanofibrillar materials are produced.

2.5.2.1 High Pressure Homogenization (HPH)

In HPH process, cellulose slurry is passed through a small nozzle into a vessel while maintaining high pressure. High hydrostatic pressures, shear and impact stresses, turbulent flow, cavitation as well as high temperatures generated result in the reduction of cellulose fibers into nano scale. One of the main disadvantages in this process is due to the small orifice size, final sample produced may tend to clog. Reducing the fiber size before the HPH process would facilitate to overcome the clogging problem[77].

2.5.2.2 Refining

Disk refiner is the most commonly used refiner type for NFC production. This contains two vertical disks with contoured surfaces where one disk rotates clockwise while the other remains stationary or rotates counter clockwise. Cellulose slurry is pumped between two disks through an inlet to the center of one disk. As the centrifugal force pushes fibers towards the circumference of the disk, fibers are subjected to abrasion forces which cut, soften rub and disperse the fiber to the degree required. Depending on the degree of refining required distance between the disks can be adjusted. Refining process can also be used as a mechanical pretreatment for HPH[69],[78].

2.5.2.3 Microfluidizer

When the cellulose slurry enters the inlet reservoir, the process will begin. High pressure is generated via an intensifier pump to accelerate cellulose slurry into the interaction chamber at high velocity. Inside this white chamber design, stream separates into micro-channels. Cellulose stream is then forced to collide upon itself. This produces forces of shear and impact of high magnitude. Advantage of using microfluidizer includes uniform particle size reduction and uniformity of results[65], [79].

2.5.2.4 Cryocrushing

In cryocrushing process, initially water absorbed cellulose fibers are immersed in liquid nitrogen. Then those immersed cellulose fibers are crushed using mortar and pestle. When high impact force is applied to the frozen cellulose fibers, pressure is exerted by the ice crystals. As a result of this, the cell wall get ruptured and thereby generates nanofibers[79].

2.5.2.5 High Intensity Ultrasonication

In high intensity ultrasonication (HIUS), ultrasound transmits into the liquid. Disintegration efficiency of this technique depends upon the fiber size and concentration, processing time, temperature and power. Depending on the applied

frequency, process results an alternative high (compression) and low (rarefaction) pressure cycles. Microscopic vaccum bubbles are created during the low pressure cycle. They get disintegrated intensely when these bubbles reach to a volume where they are unable to absorb more energy[80]-[82]. This intense destruction occurs during the high-pressure cycle. As shown in Figure 2.8, bubbles grow and eventually implode to produce hot spots that bring about acoustic cavitation[79].
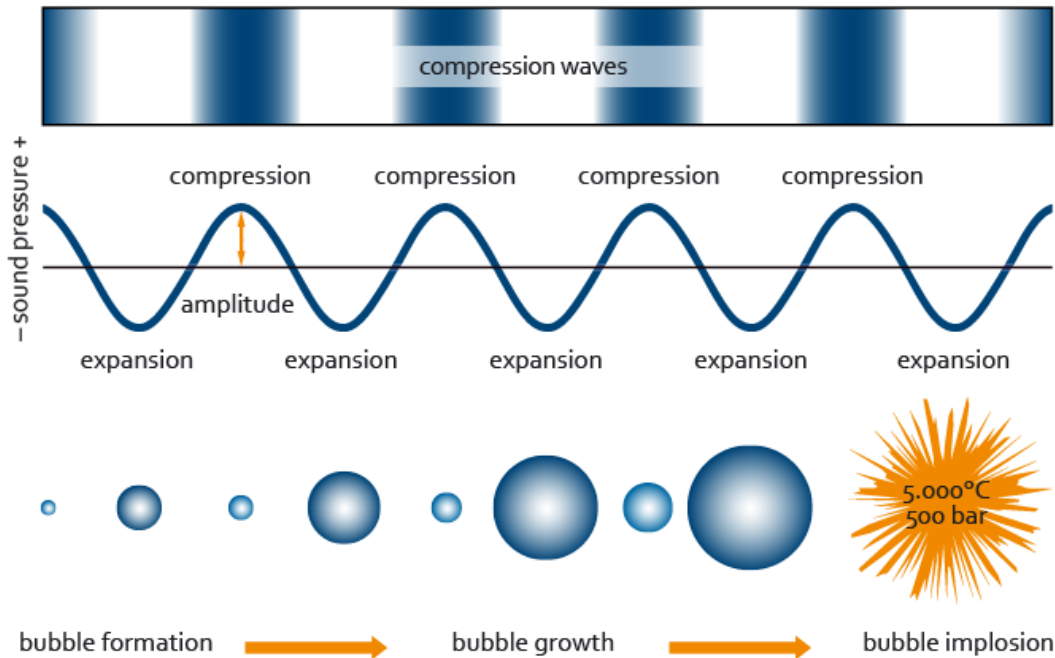
Figure 2.8: Cavitation process during high intensity ultrasonication[83]

Energy of this cavitation process is estimated as approximately 10–100 kJ/mol. This value is similar to that of the energy of hydrogen bond. HIUS treatment combined with chemical treatment is considered to be the efficient method in disintegrating nanofibrillated cellulose from lignocellulosic biomass.

2.5.3 Novel materials based on Cellulose Nanofibrils

Replacing traditional reinforcement materials with natural fibers provide several advantages. One such application is biodegradable composites. Incorporating nanocellulose to biodegradable polymers improves the mechanical properties, as well as accelerates the rate of biodegradation[84]-[89]. It can also be used for health care

applications like biomedicine, personal hygiene products and cosmetics as nanocellulose in its pure form is biocompatible. Further, dispersed nanocellulose can be utilized in stabilizing medical suspensions against sedimenting heavy ingredients and phase separation. Due to its nano size, it can act as carrier for immobilization of enzymes and other drugs where the carrier drug complex can penetrate through skin pores and treat skin diseases. And also it can be used as a peeling agent in cosmetics.

CHAPTER 3: MATERIALS AND METHODS

3.1 Materials

Analytical grade toluene ($C_6H_5CH_3$, $\geq$ 99.7 %), ethanol (C_2H_5OH, Min. 99.85 %,), acetic acid (CH_3COOH, $\geq$ 99.7 %), hydrochloric acid (HCl, $\geq$ 37.0 %), and sulfuric acid (H_2SO_4, 97.0 %) were procured from ACS, Sigma-Aldrich and hydrogen peroxide (6 % (w/v)), potassium hydroxide (KOH, $\geq$ 85.0 %) were obtained from MERCK Chemicals. Deionized water was prepared using Barnstead™ Smart2Pure™ Water Purification System (Thermo Fisher Scientific, Waltham, MA).

3.2 Collection of Rice Straw varieties

Technically modified variety BG352 (BG) and traditional varieties Murunkan (Mu), Pachchaperumal (Pa) and Moddaikaruppan (Mo) were used in this study. BG352 was collected after 2018 Yala seasonal harvest from Rice Research and Development Institute (RRDI), Bathalagoda whereas Murunkan, Pachchaperumal and Moddaikaruppan were collected after 2018/19 Maha seasonal harvest from Provincial Department of Agriculture, Jaffna.

3.3 Processing of Rice Straw

Stems of the aforementioned rice straw varieties were initially cut into 3 to 4 cm length pieces. These cut pieces were washed thoroughly using tap water until the washings became clean and colorless. These washed samples were air dried for 48 hours and oven dried for 5 hours at 60 ˚C. Finally the dried rice straw pieces of four varieties were milled separately to pass through 60 mesh aperture size screen. Obtained rice straw powder samples were stored in desiccators for further purification and investigation. Pictorial diagram of Moddaikaruppan rice straw processing is shown in Figure 3.1.
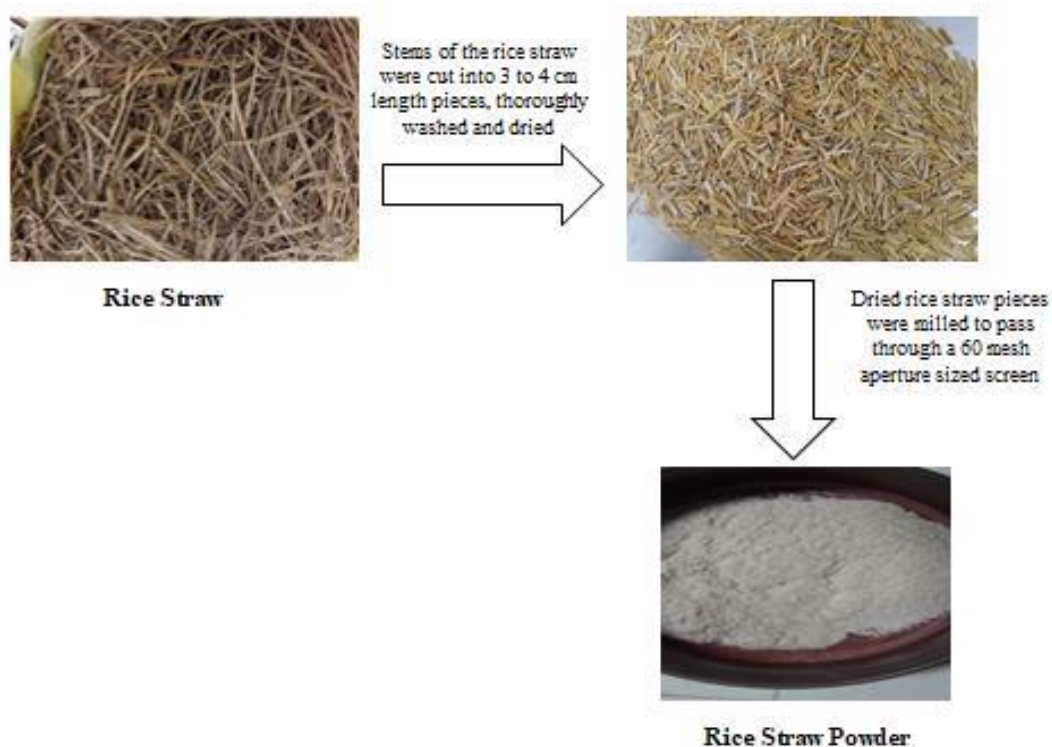
Figure 3.1: Processing of Moddaikaruppan rice straw

3.4 Preparation of Rice Straw Ash

Total ash content of four varieties was determined as residual weight after carbonizing each rice straw powder at 550 °C for 6 hours. Pictorial diagram of carbonization of Murunkan rice straw is presented in Figure 3.2. This process was performed in a chamber furnace (Nabertherm, Germany).
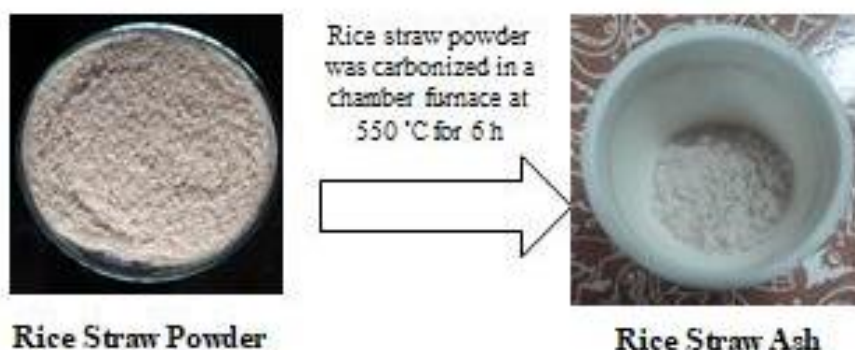
Figure 3.2: Carbonization of Murunkan rice straw

Obtained rice straw ash (RSA) was further treated with HCl and was filtered. The acid-insoluble residue that remained during the filtration process was washed with

ample amount of hot water until no chlorides were detected. Finally, remaining residue was dried and weighed as silicon rich residue. It is stated that acid leaching of rice straw ash helps to achieve relative pure silica with high specific surface area[90]. Three replications were carried out for the ash analysis, and the average is reported.

3.5 Cellulose Extraction

Rice straw powder of the four varieties was subjected to a series of chemical extraction and purification process to validate complete and smooth removal of non-cellulosic constituents[91]. Pictorial diagram of fiber extraction process is shown in Figure 3.3.

3.5.1 Removal of Wax

Wax acts as a protective layer on the plant surface. Removal of this protective layer is necessary to allow the chemicals used in the subsequent treatments to permeate into the plant cell. For this purpose, 10 g of rice straw powder was extracted with 2:1, v/v toluene/ethanol mixture (450 mL) for 15 hours in a Soxhlet apparatus.

3.5.2 Removal of Lignin

Oxidizing method known as peracetic acid treatment was carried out to remove lignin from rice straw. This process was conducted with a precise control of process parameters to degrade lignin at an optimum level without degrading the cellulose fibers. To achieve this, de-waxed rice straw powder was immersed in 3:10, v/v H_2O_2/CH_3COOH solution at 70 ˚C for 3 hours in a thermostatically controlled water bath using H_2SO_4 as catalyst. The reaction mixture was stirred continuously at 125 rpm.

3.5.3 Removal of Hemicellulose and Silica

Alkaline leaching was carried out to remove hemicellulose and silica. De-lignified rice straw powder was leached with 110 mL of 5 percent KOH for 24 hours at room temperature then for 2 hours at 90 ˚C. During this process, other inorganic residual materials were also leached.
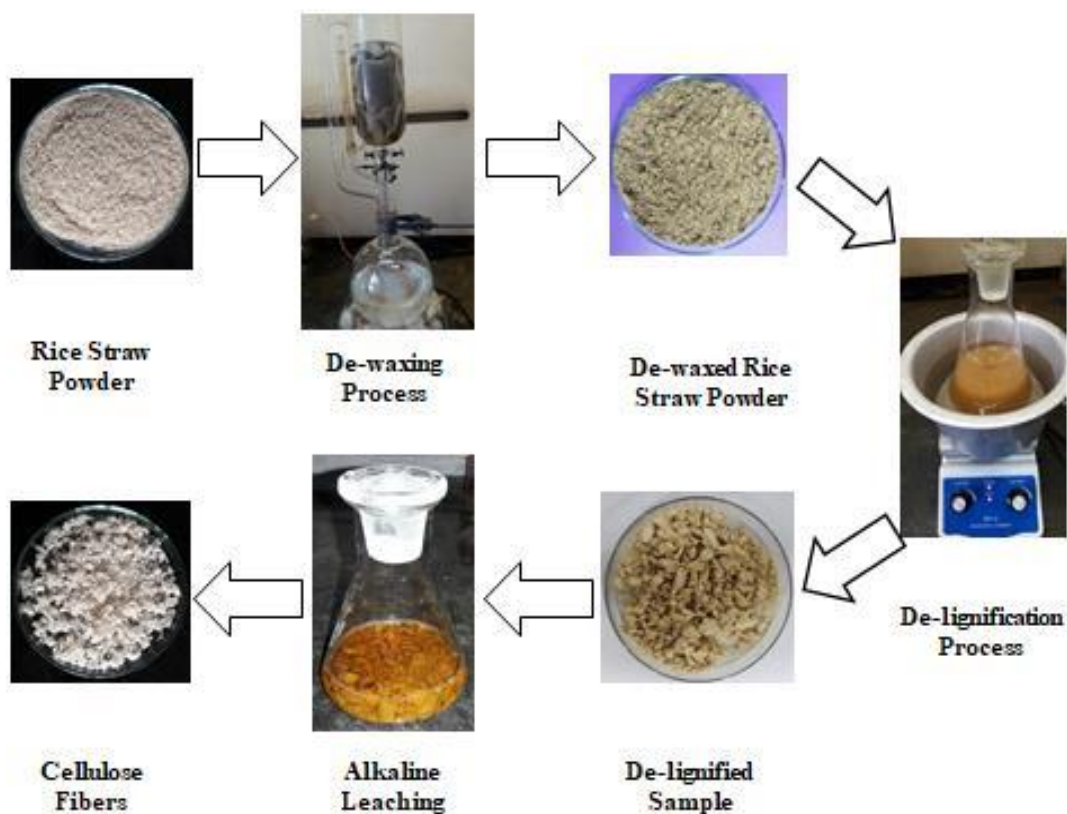
Figure 3.3: Cellulose fiber extraction process from BG352 rice straw variety

After each chemical treatment, samples were vacuum filtered and washed with copious amount of de-ionized water until filtrate reached neutral p^H and then oven dried at 60 ˚C. Finally, oven dried chemically extracted cellulose was collected and stored in desiccators for further investigation and characterization. Six replications were carried out for each compositional analysis for each rice straw variety, and the average is reported.

3.6 Isolation of Nanofibrillated Cellulose

1.0 (w/w)% concentration of chemically extracted cellulose fibers from four rice straw varieties were dispersed in 150 mL deionized water and was treated by high intensity ultrasonication (HIUS) (DC-400H, MRC ltd, Holon, Israel) at 500 W and 40 kHz. Sonication was performed for 90 minutes and the sonicated samples were collected at 15 minutes intervals to study the defibrillation effect of each variety. This process was carried out in ice/water bath to control the overheating of samples.

3.7 Effect of Particle Size Distribution of Rice Straw on Cellulose and Nanofibrillated Cellulose Extraction

In mechanical treatment methods, particle size of agricultural residue is reduced to increase the surface to volume ratio. This is achieved by employing methods such as chipping, milling, grinding, etc. However, effective separation of cellulose fibers from these methods is reported to be inefficient. Conversely, chemical treatment methods are found to be effective at disrupting the cell of the lignocellulosic biomass[2]. Thus, combination of these two methods would facilitate the removal of non-cellulosic components and promote effective separation of cellulose fibers and nanofibrillated cellulose from agricultural biomass.

This study is an attempt to analyze the effect of particle size of parent material rice straw on cellulose and nanofibrillated cellulose extraction. For this purpose, locally available traditional rice straw variety Murunkan was utilized. Initially, the straw was incised into small pieces, washed thoroughly, dried and milled. Then the milled rice straw powder was sieved using sieve shaker with 75 μm, 106 μm, 150 μm, and 250 μm aperture sized screens. Finally, the powdered rice straw sample with particle size distribution below 75 μm (Mu-75) and sample between 150 - 250 μm (Mu-250) were used for further investigation. Ash content of both the samples was determined.

Obtained rice straw powder (Mu-75 and Mu-250) was subjected a chemical process to remove non-cellulosic components.Acquired chemically extracted cellulose fibers were then mechanically disintegrated into nanofibers *via* HIUS with a process time of 90 minutes. Chemical composition, structural behavior, thermal properties and morphology of nanofibrillated cellulose and the intermediate products were characterized and compared.

3.8 Measurements and Characterization

Structural, morphological and thermal properties of rice straw, de-waxed rice straw, de-lignified rice straw, cellulose fibers, nanofibrillated cellulose and rice straw ash were studied.

3.8.1   Fourier transform infrared (FTIR) spectroscopy

Structures of the four varieties during the extraction process were studied from FTIR analysis. Samples mixed with 1:100, w/w KBr powder were used for FTIR analysis. The spectra was collected over $4000 - 600$ cm^{-1} range at 4 cm^{-1} resolution with an accumulation of 24 scans in transmittance mode. Testing was performed at ambient conditions on Bruker ALPHA spectrometer (Bruker Corporation, Billerica, MA).

3.8.2   X-Ray Diffraction (XRD)

Structural analysis was carried out using BRUKER D8 ADVANCE ECO X-ray diffractometer with Cu K$_\alpha$ radiation ($\lambda = 1.5406$ Å) at 40 kV and 25 mA. Rice straw, de-waxed rice straw, de-lignified rice straw and cellulose fiber samples were scanned and recorded the intensity in 2θ ranged from 5˚ to 45˚ (step size = 0.02˚, scanning rate = 2 seconds/step) whereas rice straw ash samples were scanned and recorded the intensity in 2θ ranging from 5˚ to 80˚ (step size = 0.02˚, scanning rate = 2 seconds/step). Data refinement and phase analysis were carried out using ICDD database.

3.8.3   Energy-dispersive X-Ray Spectroscopy (EDS)

Chemical composition and silicon mapping of ash derived from four rice straw varieties was conducted using EDAX Z1 Analyser.

3.8.4   Scanning Electron Microscopy (SEM)

Scanning electron microscopy was employed to observe morphology of the samples. Samples were gold sputter coated prior to observation and scrutinized with an accelerating voltage of 15 kV. The morphological analysis was carried out on EVO 18, Carl Zeiss AG, Germany, scanning electron microscopy.

3.8.5   Thermal Analysis

Thermal stability of each sample was determined using TGA SDT Q600 simultaneous thermal analyzer (TA instruments, Delaware, USA). Experiments were

performed with a heating rate of 10 ˚C/min from ambient temperature to 700 ˚C on rice straw, de-waxed rice straw, de-lignified rice straw, cellulose and nanofibrillated cellulose and 20 ˚C/min from ambient temperature to 1200 ˚C on rice straw ash under nitrogen (N_2) atmosphere.

3.8.6 Density Measurement

Density of cellulose fibers extracted from Mu-75 and Mu-250 was determined using pycnometer at 28 ˚C.

CHAPTER 4: RESULTS AND DISCUSSION

4.1 Characterization of Rice Straw Ash

4.1.1 Ash content in Rice Straw varieties

Ash component generally depend on type and variety rice, climate and geographic location of growth. Though rice straw is available in surplus amount, it has less or no immediate commercial value. Rice straw ash, which is rich in silica, is also not commercially utilized yet.
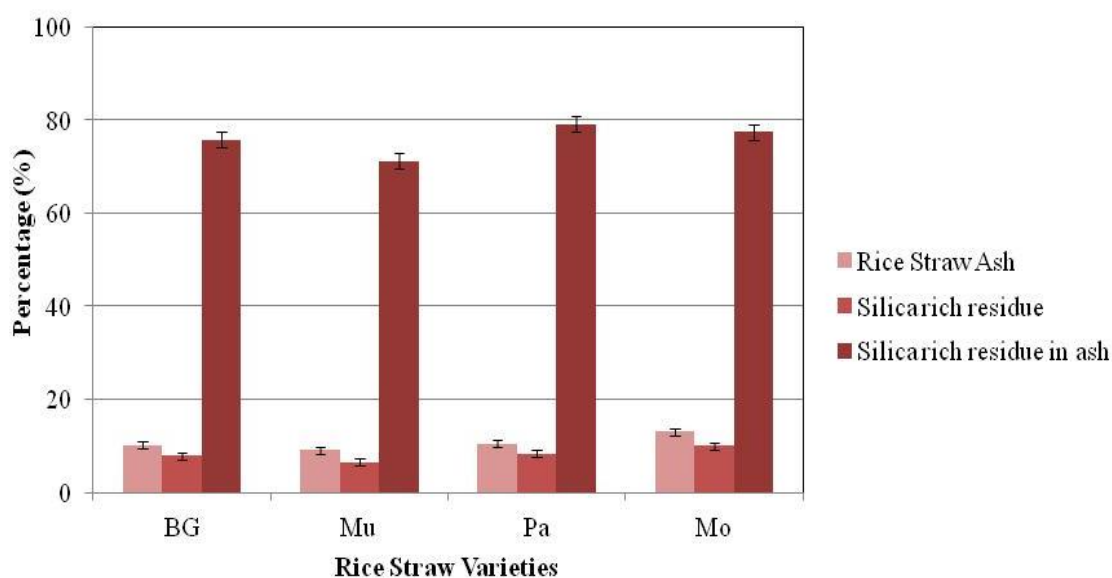
Figure 4.1: Percentage of ash and silica rich residue in ash in Sri Lankan rice straw varieties

Ash content and amount of silica rich residue in of the four rice straw varieties are presented in Figure 4.1. BG352 (BG) had the ash content 10.15 ± 0.44 percent, Murunkan (Mu) had 9.10 ± 0.36 percent, Pachchaperumal (Pa) had 10.49 ± 0.34 and Moddaikaruppan (Mo) had 13.00 ± 0.41. 75.7 percent, 71.2 percent, 79.1 percent and 77.4 percent of each ash contained silica rich residue respectively. Silica rich residue content is also reported as percentage of ash.

Major component of inorganic minerals in rice straw is silica. The actual composition of rice straw varies with the type of paddy, geographical conditions, crop season, samples preparation and relative humidity. During the plant growth, silica is

absorbed from the ground and congregated in the straw where it forms a structure and is filled with cellulose[52]. When burned, it leaves a silica rich residue.

The above results show that content of silica rich residue in the rice straw varieties ranges between 71 - 79 percent. However, the observed difference may be due to the difference in rice varieties and soil condition in different locations.

4.1.2 FTIR Analysis of Rice Straw Ash

FTIR spectra of rice straw and rice straw ash of BG352 variety is presented in Figure 4.2. In Figure 4.2, two important regions were observed in the FTIR spectra of BG352 rice straw ash. Bands above ~1100 cm^{-1} correspond to organic functional groups whereas bands below 1100 cm^{-1} correspond to inorganic functional groups.
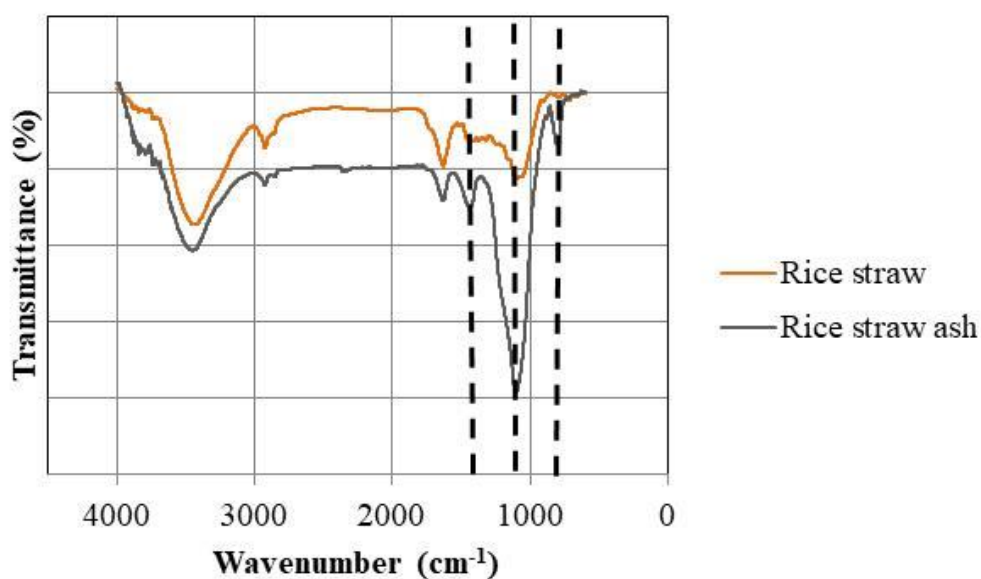
Figure 4.2: FTIR spectra of rice straw and rice straw ash of BG352 variety

Figure 4.3 shows the FTIR spectra of ash derived from rice straw varieties BG352 (BG), Murunkan (Mu), Pachchaperumal (Pa) and Moddaikaruppan (Mo). Three important bands are accentuated in the inorganic region related to the SiO_2. Most importantly band located around 1070 cm^{-1} indicates the presence of tetramers of

cyclic siloxanes in the four varieties[8]. Presence of these tetramers in all four varieties is confirmed by the band located around 800 cm^{-1}.
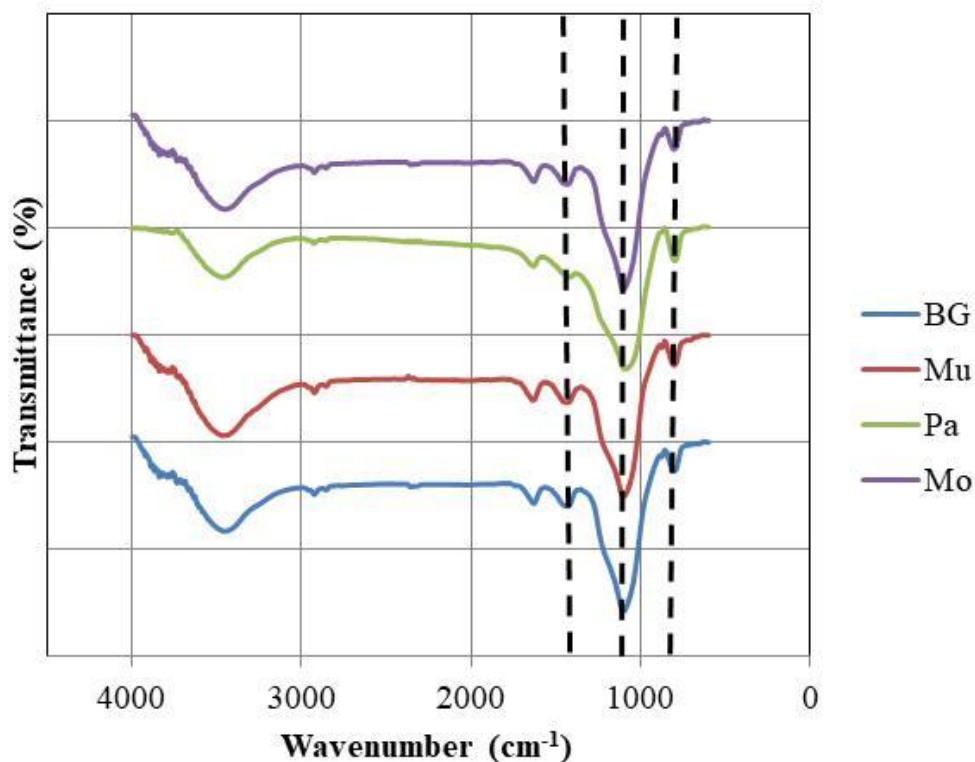
Figure 4.3: FTIR spectra of ash from rice straw varieties BG352 (BG), Murunkan (Mu), Pachchaperumal (Pa) and Moddaikaruppan (Mo)

4.1.3 Structural Analysis of Rice Straw Ash

Figure 4.4 shows the EDS analysis and Si mapping of ash derived from the four rice straw varieties. Under the same carbonizing conditions, fiber structure of all four rice straw varieties were easily damaged. Broken ash particles were clearly observed in Figure 4.4 (a_1, a_2, a_3 and a_4). EDS analysis shows (Figure 4.4 (c_1, c_2, c_3 and c_4) the major elements present in ash are Si, O and K whereas Na, Mg, Ca and Fe were present as trace elements. Si mapping shown in figure 4.4 (b) confirms silica as the predominant element present in ash surface of all four varieties. However, element K was less present in BG352 (Figure 4.4[1]) and Moddaikaruppan (Figure 4.4[2]) than other two varieties.
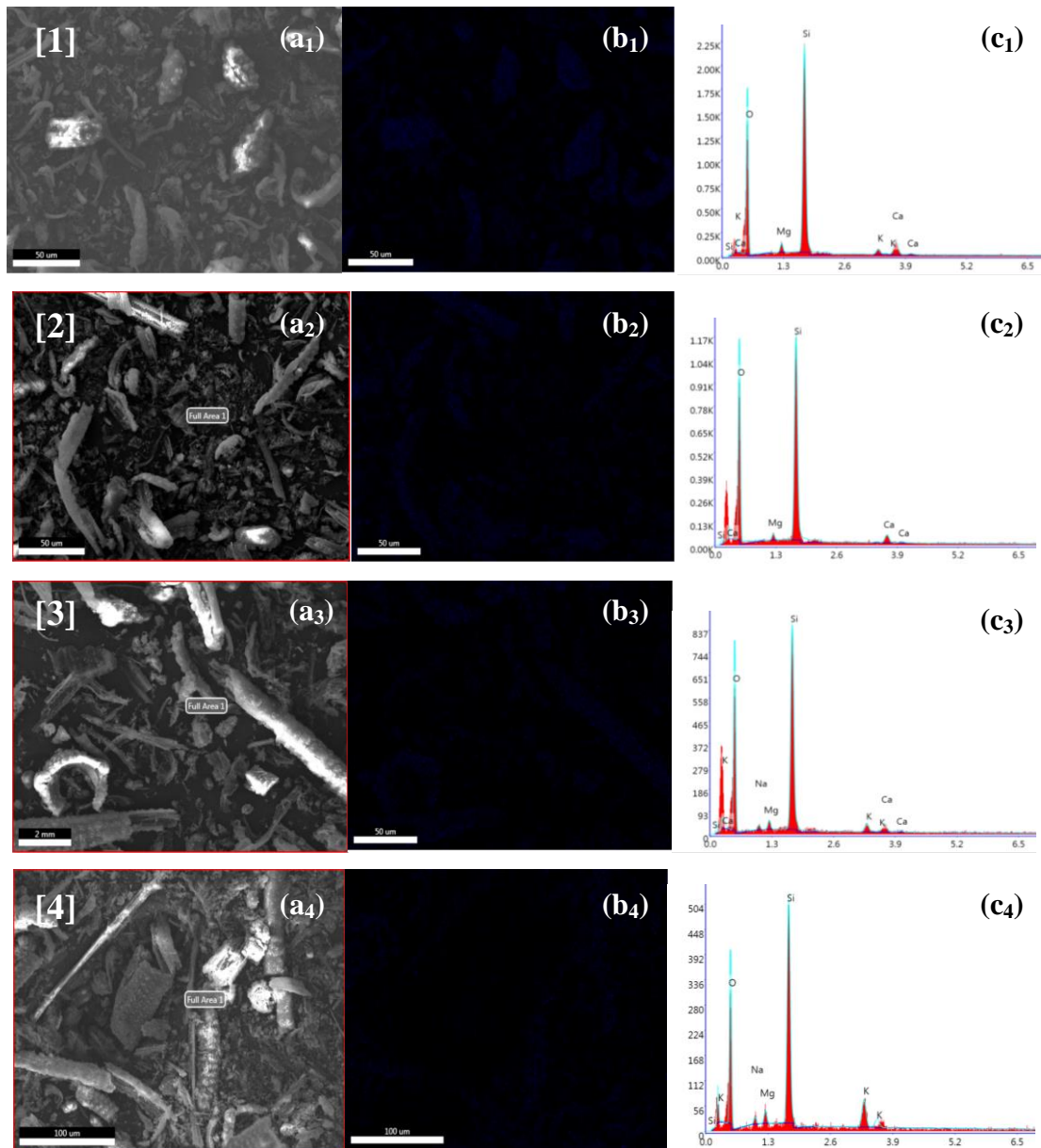
Figure 4.4: (a$_1$-a$_4$) SEM images; (b$_1$-b$_4$) Si mapping and (c$_1$-c$_4$) EDS spectra of [1] BG352, [2] Murunkan, [3] Pachchaperumal and [4] Moddaikaruppan variety

Figure 4.5 shows the XRD patterns of rice straw ash where the presence of sylvite, calcite, quartz and arcanite are denoted as S, C, Q and A respectively. Amorphous silica is observed as a baseline peak in the range of 2θ = 15 - 30° whereas traces of quartz observed could be due to the soil contamination of the rice straw.
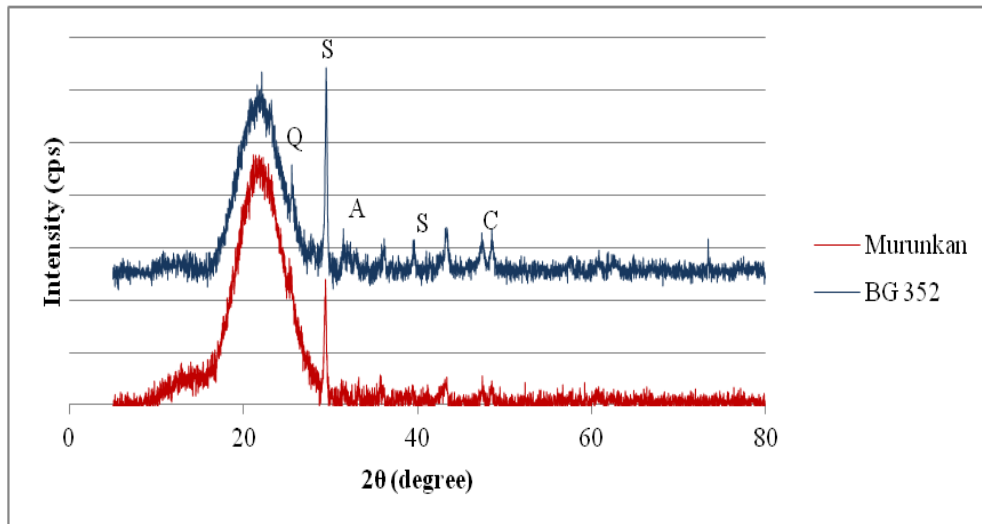
Figure 4.5: XRD spectra of BG352 and Murunkan rice straw ash

Presence of cristobalite and trydimite was not observed in XRD spectra of rice straw ash (Figure 4.5) confirms that carbonization of rice straw into ash at 550 ˚C did not facilitate the crystallization of silica[8]. This makes rice straw ash a better pozzolanic material. Diffraction pattern in Figure 4.5 shows high-intensity peaks at $2\theta = 28.3º$ and $40.4º$ which correspond to sylvite (KCl) and secondary minerals such as arcanite (K_2SO_4) and calcite ($CaCO_3$).

Table 4.1: Percent crystallinity of rice straw and rice straw ash

Rice Straw Variety	Percent Crystallinity	
	Rice Straw	**Rice Straw Ash**
BG352	51.8 ± 2.61	24.3 ± 3.52
Murunkan	61.4 ± 2.33	34.2 ± 3.04
Pachchaperumal	64.0 ± 2.15	36.9 ± 3.15
Moddaikaruppan	55.4 ± 2.86	27.6 ± 3.87

It is also noted that rice straw ash is amorphous which is an important factor for pozzolanic reactivity. This is because crystalline phases do not react easily towards calcium hydroxide (CH), whereas amorphous silica reacts at room temperature in wet conditions[9]. Amorphous nature of silica is confirmed by the drop in percent crystallinity clearly observed (Table 4.1) from rice straw to rice straw ash in all four varieties.

4.1.4 Morphology of Rice Straw Ash

Morphology and topography of the surface of rice straw ash was determined using scanning electron spectroscopy. Micrographs of rice straw ash derived from four varieties are presented in Figure 4.6.
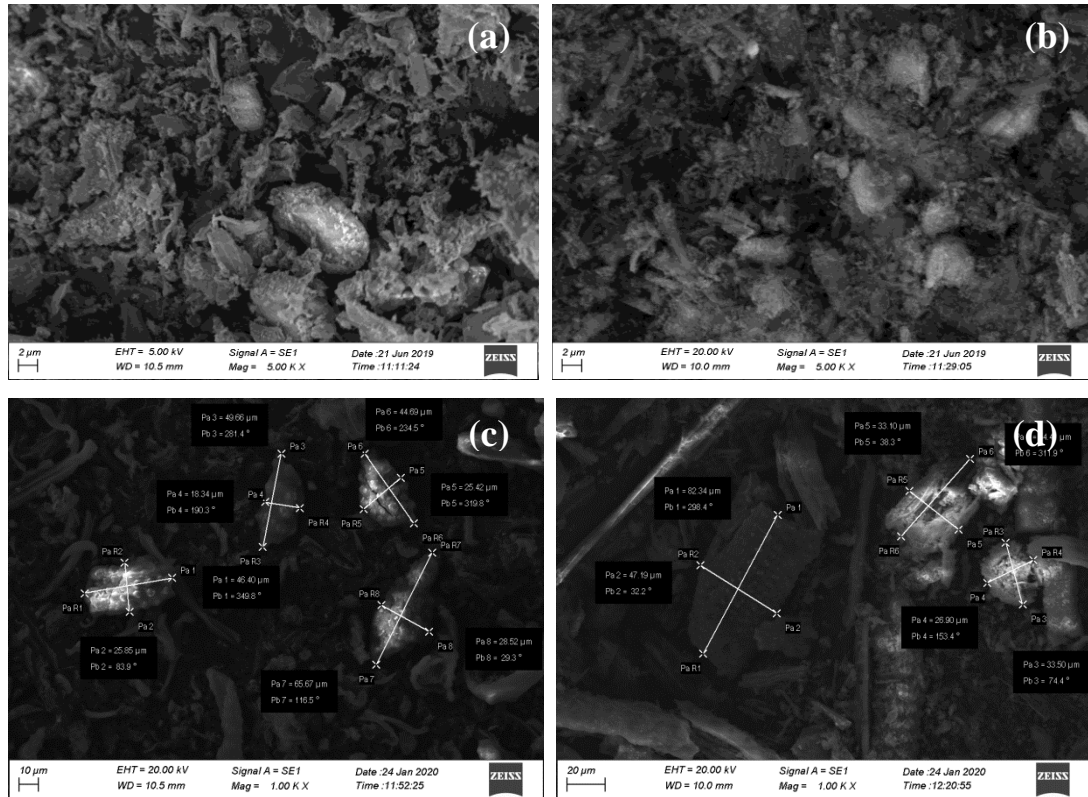
Figure 4.6: SEM images of rice straw ash (a) BG352, (b) Murunkan, (c) Pachchaperumal and (d) Moddaikaruppan

In the above SEM micrographs (Figure 4.6), grooves and grains are observed on the surface of rice straw ash which gives a rough appearance. Ash shows porous and tracery surface morphology, with a high surface area due to the release of volatile substances present in rice straw (Figure 4.6 (a) and (b)). Further, the grains observed in rice straw ash (Figure 4.6 (a) – (d)) correspond to silicon compounds dispersed across the surface. These make them suitable for specific applications such as construction material, special ceramics material, filler for rubber compounds or catalyst support[43],[46].

4.1.5 Thermal behaviour of Rice Straw Ash

A graphical illustration of the relationship between TGA curves and temperature of BG352 rice straw ash is demonstrated in Figure 4.7.
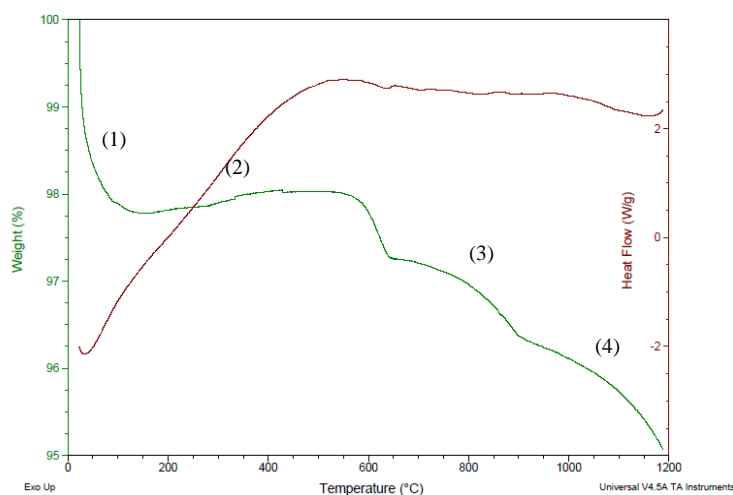
Figure 4.7: TGA/DTA curves of rice straw ash BG352

Four endothermic peaks of each ash sample were observed. The first peak is due to the loss of hygroscopic moisture and very light volatiles, second peak corresponds to the emission of volatiles, third peak located between 600 - 850 ˚C is attributed to the amorphous silica while the fourth peak is due to the degradation of secondary minerals which are present in crystalline form[9],[44]. When the weight loss at the final peak increases, the crystallinity of rice straw ash decreases which indicates higher crystallinity.

4.2 Characterization of Cellulose Fibers

4.2.1 Visual Inspection

Rice straw varieties BG352, Murunkan, Pachchaperumal and Moddaikaruppan were subjected to a series of chemical treatments to validate the complete and smooth removal of the non-cellulosic constituents. Waxy substances in rice straw were initially removed using toluene/ethanol mixture *via* soxhlet extraction. This removal of protective layers allowed the permeation of other chemicals into the plant cell in subsequent treatments. Then a low environmental impact oxidizing method known as peracetic acid treatment utilized to remove lignin, required a precise process control of process parameters to achieve an optimum level of delignification and bleaching

without degrading the cellulose structure. Hemicellulose, silica and other residual inorganic materials were leached through alkaline treatment. Finally cellulose with high purity was extracted successfully from the locally available rice straw varieties BG352 (BG), Murunkan (Mu), Pachchaperumal (Pa) and Moddaikaruppan (Mo). It was observed that pale brown colour of rice straw from the four varieties as shown in Table 4.2, gradually reduced with each step and finally turned to white which is the characteristic colour of cellulose.

Table 4.2: Colour change of rice straw varieties during chemical extraction process

Compone-nt	Rice Straw Variety			
	BG	**Mu**	**Pa**	**Mo**
Rice Straw				
De-waxed Rice Straw				
De-Lignified Rice Straw				
Cellulose				

4.2.2 Composition of Rice Straw Varieties

After the series of chemical treatments rice straw variety BG352 yielded 25.35 ± 0.91 percent cellulose, Murunkan yielded 33.68 ± 0.68 percent cellulose, Pachchaperumal yielded 33.63 ± 0.10 percent cellulose and Moddaikarupan yielded 38.31 ± 0.86 percent cellulose. Figure 4.8 summarizes the amount of cellulose, hemicellulose, lignin, wax, and ash present in the three traditional rice straw varieties.
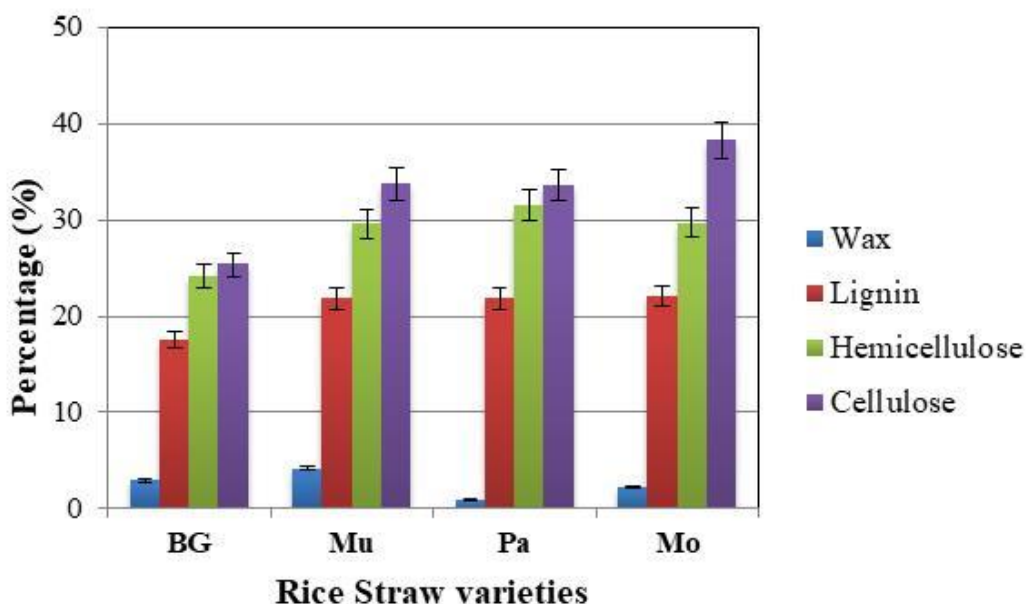
Figure 4.8: Chemical Composition of Sri Lankan Rice Straw Varieties

Above results show that amount of cellulose fibers present in four rice straw varieties ranges between 25 - 38 percent. It is reported that the cellulose content in rice straw varies between 28 - 36 percent[24] and cellulose content in BG352 variety as 29.3 percent[5] in the previously reported studies. Nevertheless, cellulose content in three traditional varieties was determined for the first time in the country. The observed difference between the traditional and technically modified varieties may be due to the difference in rice varieties and soil condition in different locations.

4.2.3 FTIR Analysis

FTIR spectrum of Moddaikaruppan rice straw variety during the extraction process is shown in Figure 4.9. After the successful extraction from chemical treatments, the end-product was confirmed as cellulose.
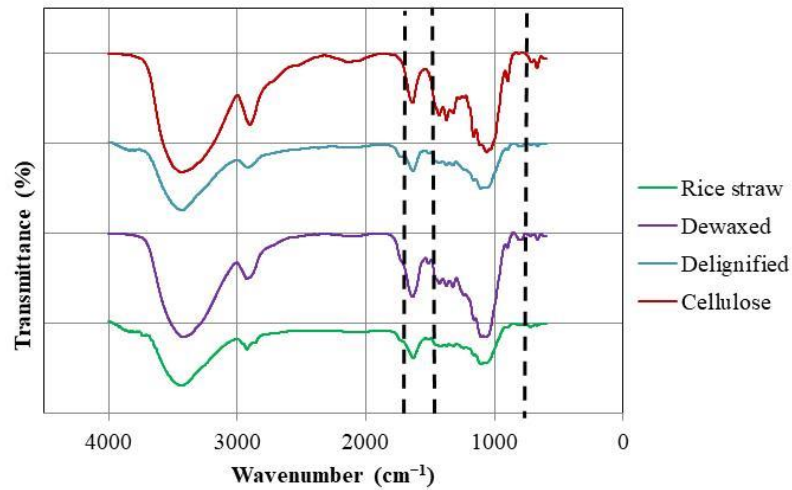
Figure 4.9: FTIR spectra of Moddaikaruppan during chemical extraction process

The sequential and complete removal of lignin (1516 cm^{-1}, aromatic skeletal vibrations) in de-lignification and leaching of hemicellulose (1729 cm^{-1}, carbonyl stretching) and silica (796 cm^{-1}, Si–O–Si stretching) in the third step can be clearly observed[7]. The dominant peaks between 1200 and 900 cm^{-1} are related to C—O stretching bonds. Enhanced peak intensity around 960 cm^{-1} after chemical treatment implies that a typical structure of cellulose became more dominant compared to the raw materials.
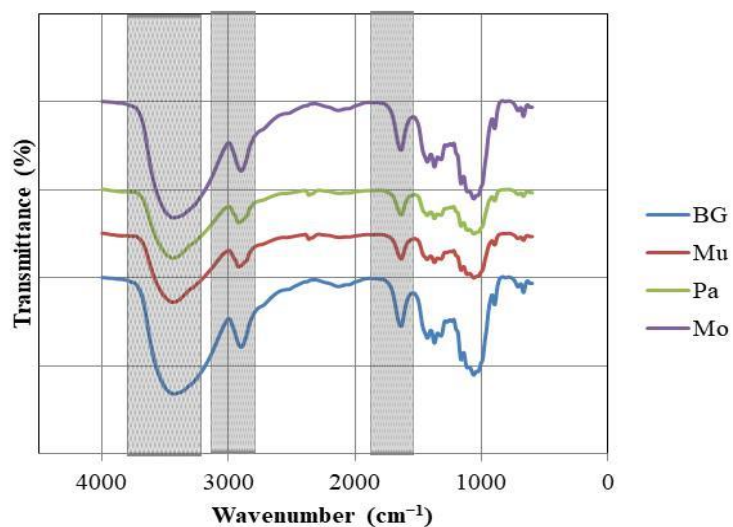
Figure 4.10: FTIR spectra of cellulose fibers extracted from BG352(BG), Murunkan(Mu), Pachchaperumal(Pa) and Moddaikaruppan(Mo)

Figure 4.10 shows the FTIR spectrum of cellulose fibers extracted from BG352, Murunkan, Pachchaperumal and Moddaikaruppan rice straw varieties. The dominant peak around 2900 cm^{-1} is associated with CH-stretching vibrations. It can be observed that intensity of this peak after chemical treatment has remarkably increased. The broad absorption band in the range of 3500– 3000 cm^{-1} is attributed to OH-stretching vibrations[32]. Due to enhancement of the surface moisture absorption of fiber samples, the increase in the intensity of this peak after chemical treatment is observed. The broad absorption band related to -OH stretching mode is prominent for BG352 and Moddaikaruppan than Murunkan and Pachchaperumal. This is probably due to a large number of hydroxyl groups in both BG352 and Moddaikaruppan which may be associated with an increase in the number of hydrogen bonds formed.

4.2.4   Structural Analysis of Cellulose Fibers

XRD analysis was performed on rice straw after each chemical treatment to study the effect of chemical treatments on the crystalline structure of fibers. The peak around 22.2° attribute to the typical crystal lattice of I$_\beta$ which indicates that both rice straw and cellulose exhibit the diffuse characteristics pattern of an amorphous phase[32]. Shoulder peak at 16.4° and weak peak at 34.7° in Figure 4.11 indicates the removal of lignin and hemicellulose from rice straw.
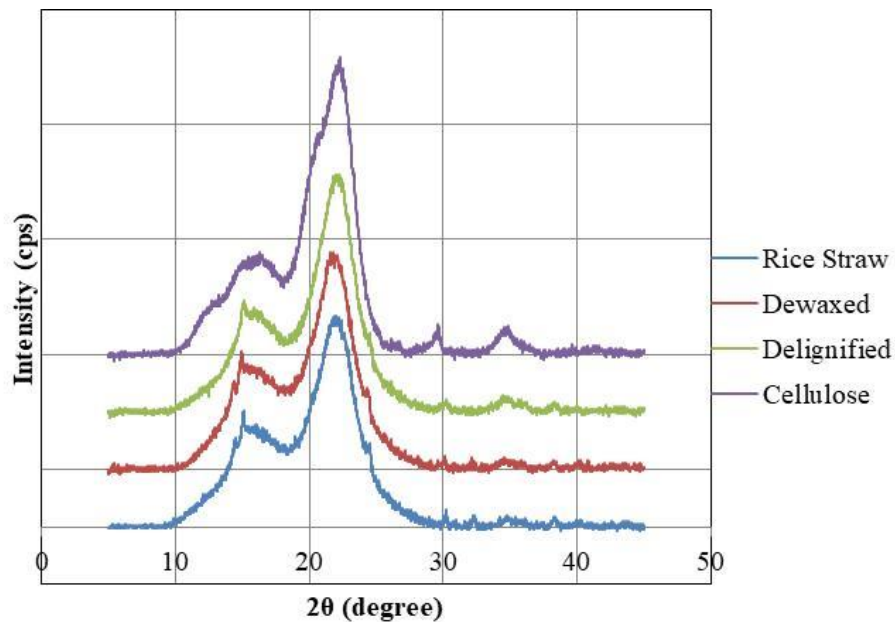
Figure 4.11: XRD spectra of BG352 during chemical extraction process

The series of chemical treatments on rice straw had a significant effect on the crystallization of the cellulose fibers. Sharper diffraction peak around 22.2˚ observed in Figure 4.12 indicates higher degree of cryatallinity in the extracted cellulose fibers. Murunkan and Pachchaperumal exhibit sharper peaks than BG352 and Moddaikaruppan. Higher crystallinity observed in the cellulose correlates with higher tensile strength of the fibers.
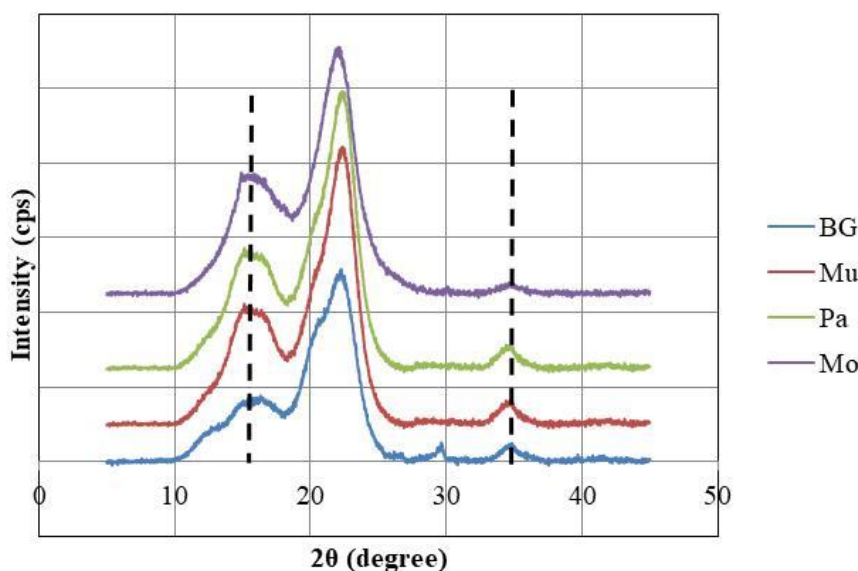
Figure 4.12: XRD spectra of cellulose fibers extracted from rice straw varieties BG352(BG), Murunkan(Mu), Pachchaperumal(Pa) and Moddaikaruppan(Mo)

The crystalline parameters of rice straw fibers in terms of the percent crystallinity are given in Table 4.3. The significantly higher crystallinity of cellulose is ascribed mainly due to the removal of amorphous cellulose during the chemical treatment.

Table 4.3: Percent crystallinity of untreated and treated rice straw

Component	Percent crystallinity			
	BG	**Mu**	**Pa**	**Mo**
Rice straw	51.8 ± 2.61	61.4 ± 2.33	64.0 ± 2.15	55.4 ± 2.86
Dewaxed rice straw	56.2 ± 2.54	62.8 ± 2.15	66.2 ± 2.62	58.1 ± 2.94
Delignified sample	59.7 ± 2.95	65.3 ± 2.45	67.1 ± 2.62	61.6 ± 2.46
Cellulose	62.3 ± 3.76	69.6 ± 3.34	69.9 ± 3.12	64.7 ± 3.82

Hemicellulose and lignin present in rice straw are amorphous while cellulose is crystalline in nature. Above results illustrated that removal of amorphous parts (lignin and hemicellulose) of the rice straw.

4.2.5 Morphology of Untreated and Treated Rice Straw

Fibers acquired from rice straw are a bundle of single cells bound together by lignin and other binding materials. SEM images of rice straw variety BG352 during the chemical extraction process are shown in Figure 4.13 and 4.14 Murunkan are shown in Figure 4.15, Pachchaperumal are shown in Figure 4.16 and Moddaikaruppan are shown in 4.17.
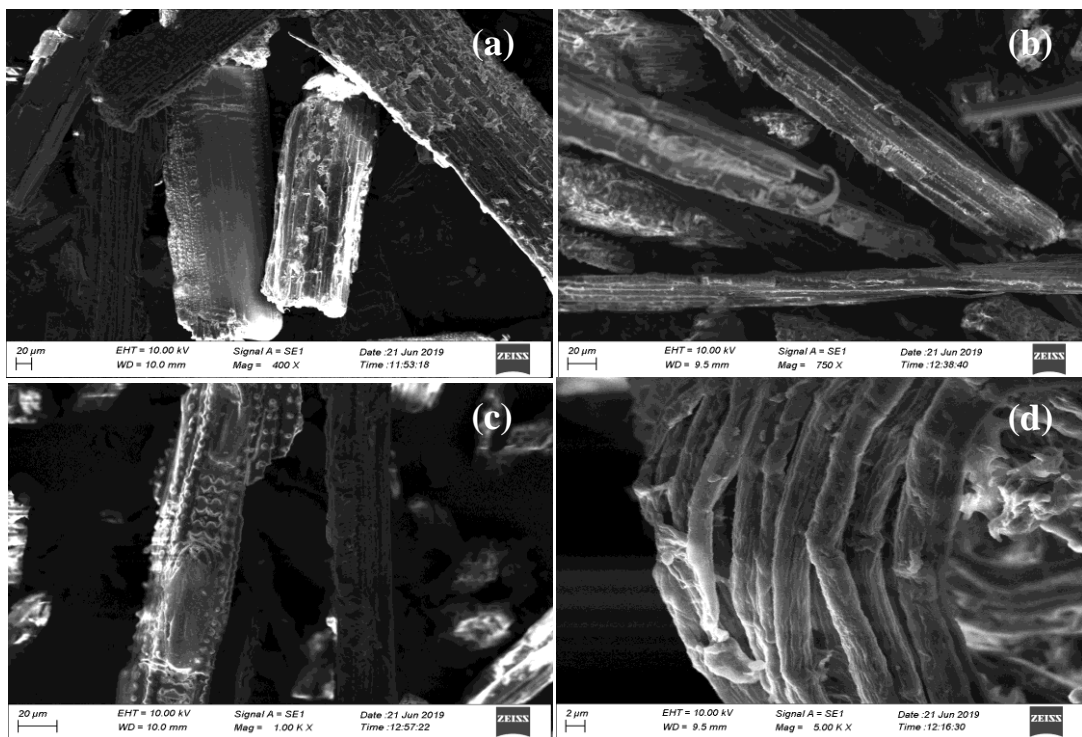
Figure 4.13: Wide view of BG352 during extraction process (a) rice straw, (b) de-waxed rice straw, (c) de-lignified rice straw and (d) cellulose fibers

Grooves and grains are present on the surface of rice straw (Figure 4.13(a) 4.14(a), 4.15(a), 4.16(a) and 4.17(a)) which gives a rough appearance. Morphologies of untreated and treated rice straw are conspicuous when the extractive substances were removed from rice straw. Some parts of dense lignin and hemicelluloses can be observed (Figure 4.13(a), 4.13(b), 4.14(a), 4.14(b), 4.15(a), 4.15(b) 4.16(a), 4.16(b),

4.17(a) and 4.17(b)) around the fibers of untreated rice straw. Figure 4.13(d), 4.15(d), 4.16(d) and 4.17(d) shows the chemically purified cellulose to be mostly in the form of fibers and they were separated into individual micro-sized fibers to a greater extent after the chemical isolation and purification treatments.
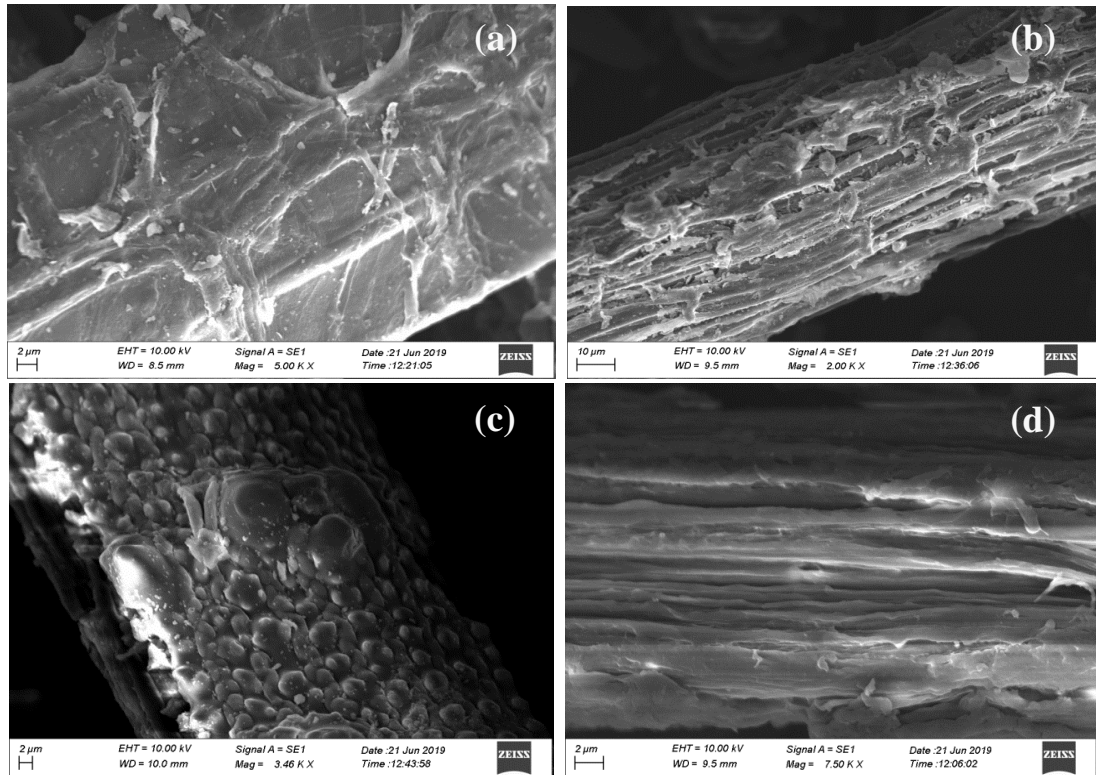
Figure 4.14: Detailed view of BG352 during extraction process (a) rice straw, (b) de-waxed rice straw, (c) de-lignified rice straw and (d) cellulose fibers

After the removal of lignin, phytoliths was revealed. Some of them observed to be dumbbell shaped whereas some of them appeared to be in small and large globular shaped (Figure 4.14(c), 4.16(c) and 4.17(c)). Evidently, shape of phytoliths is not homogeneous across the de-lignified sample.
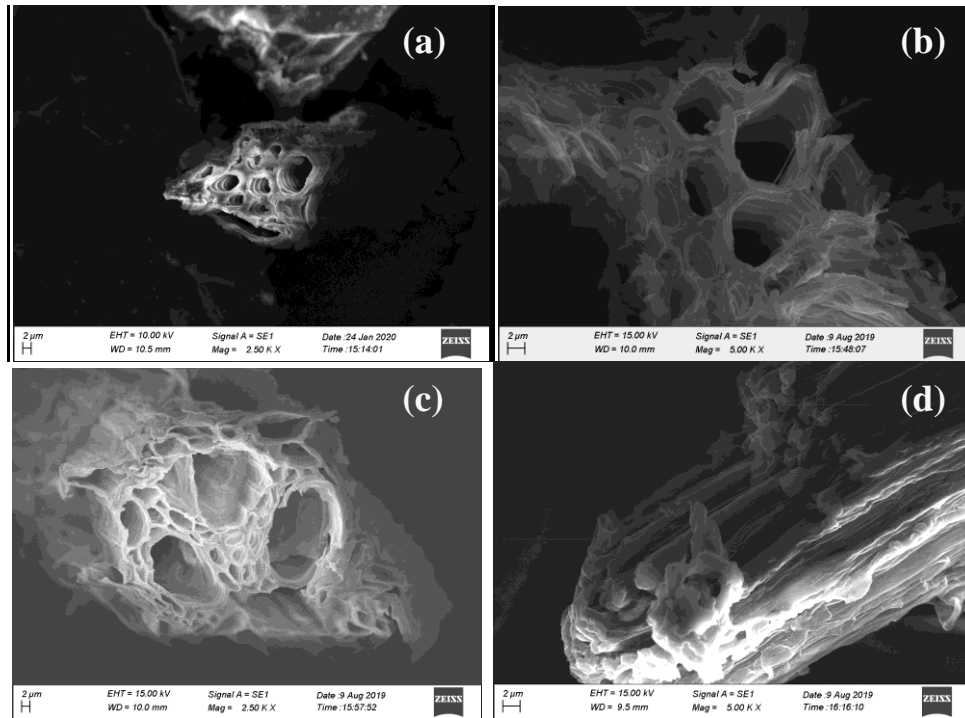
Figure 4.15: Cross sectional view of Murunkan during extraction process
(a) rice straw, (b) de-waxed rice straw, (c) de-lignified rice straw and
(d) cellulose fibers
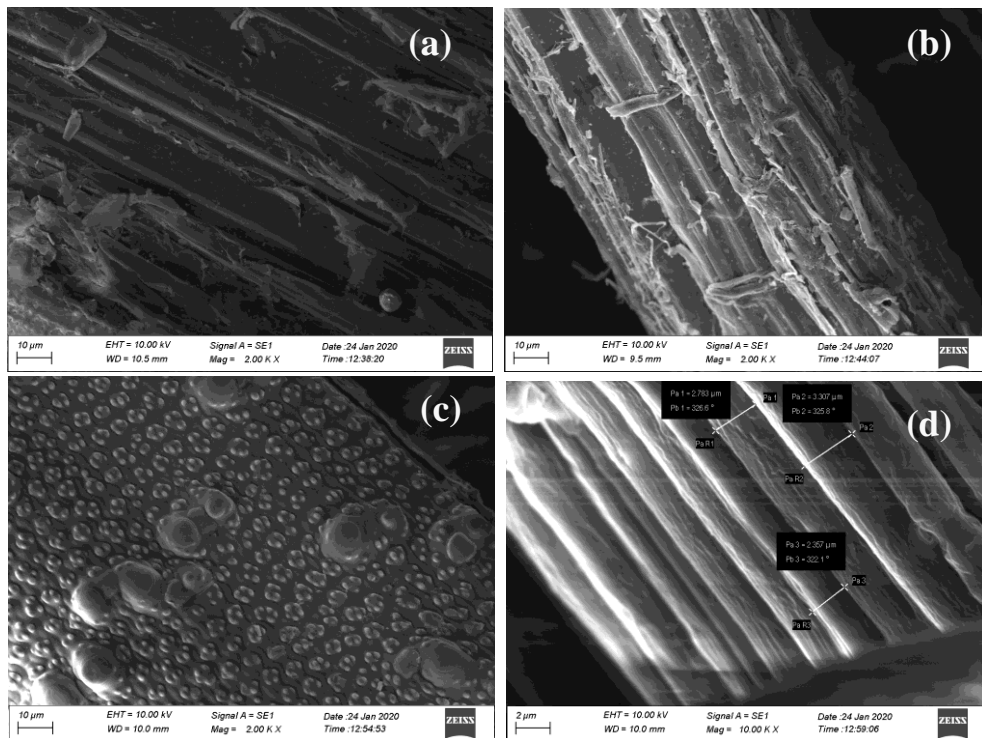
Figure 4.16: Detailed view of Pachchaperumal during extraction process
(a) rice straw, (b) de-waxed rice straw, (c) de-lignified rice straw and
(d) cellulose fibers

Morphologies of untreated and chemically treated rice straw are observed to be greatly different. Some parts of dense lignin, hemicelluloses, and ashes have surrounded the untreated fibers. Apparently, the surface of cellulose fibers looks smoother with the removal of amorphous natured lignin and hemicelluloses. The surface morphology of all the rice straw varieties significantly varied during the processing. However, all four rice straw varieties (Figure 4.13 to 4.17) exhibited similar type of morphological structures during the extraction process.
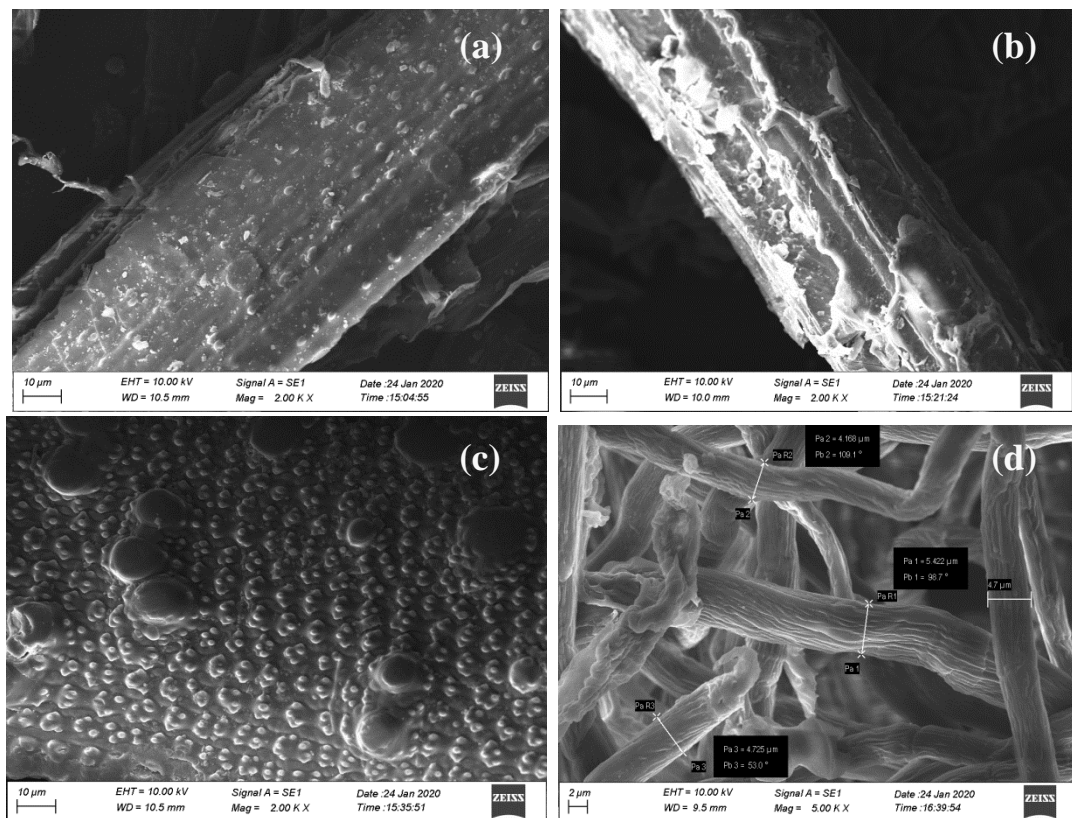
Figure 4.17: Detailed view of Moddaikaruppan during extraction process (a) rice straw, (b) de-waxed rice straw, (c) de-lignified rice straw and (d) cellulose fibers

4.2.6 Thermal Analysis of Untreated and Treated Rice Straw

Thermal stability of cellulose fibers are of paramount importance in identifying their applications. Thermal degradation of cellulose occurs due to a pyrolytic fragmentation which leads to aromatized entities and finally to a highly cross linked carbon skeleton.

Figure 4.18 shows the thermal degradation behaviour of Pachchaperumal variety during the chemical extraction process whereas Figure 4.19 depicts the derivative thermogravimetry of Pachchaperumal variety during the extraction process.
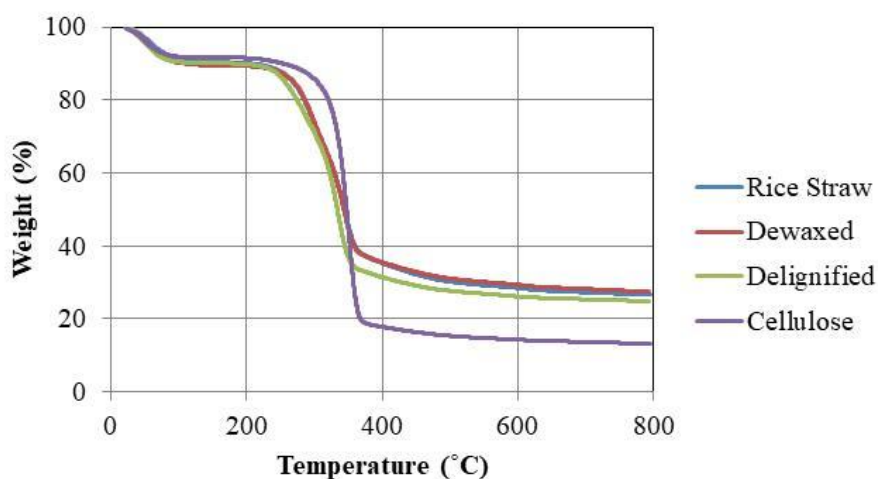
Figure 4.18: TG curves of Pachchaperumal during chemical extraction process
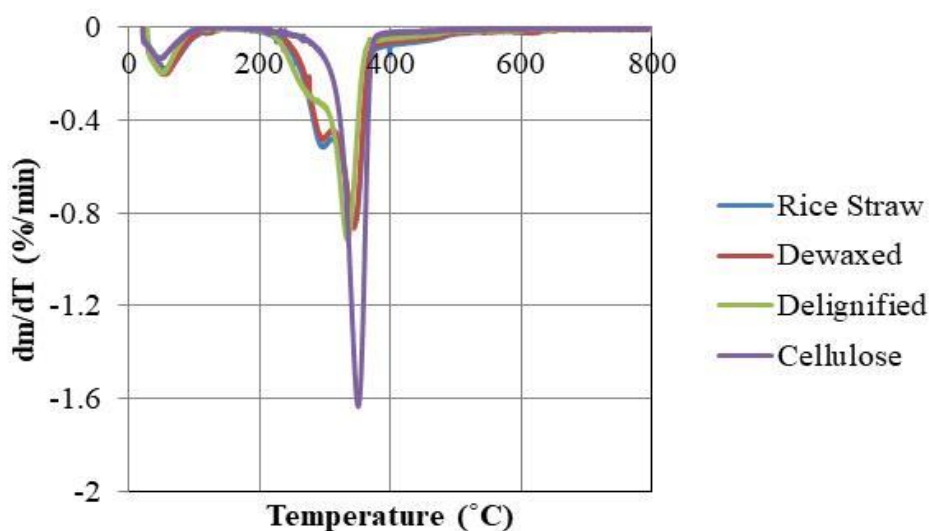
Figure 4.19: DTG curves of Pachchaperumal during chemical extraction process

Thermal degradation of rice straw variety Pachchaperumal exhibited a stepwise mechanism which consists of three steps. Similar behaviour was observed in other three varieties as well during the chemical extraction process. Initially a small weight loss was observed around 100 ˚C. This was due to the loss of hygroscopic moisture

and low volatile molecules. Then a major weight loss was observed within the range 210 ˚C to 400 ˚C which was a result of the degradation of hemicellulose and the cleavage of glycocidic linkages of cellulose. When the thermally unstable hemicellulose was degraded, a resistant increase in cellulose was visibly observed[92]. Finally, slow pyrolysis of lignin started around 250 ˚C and persisted till 700 ˚C[93],[94].
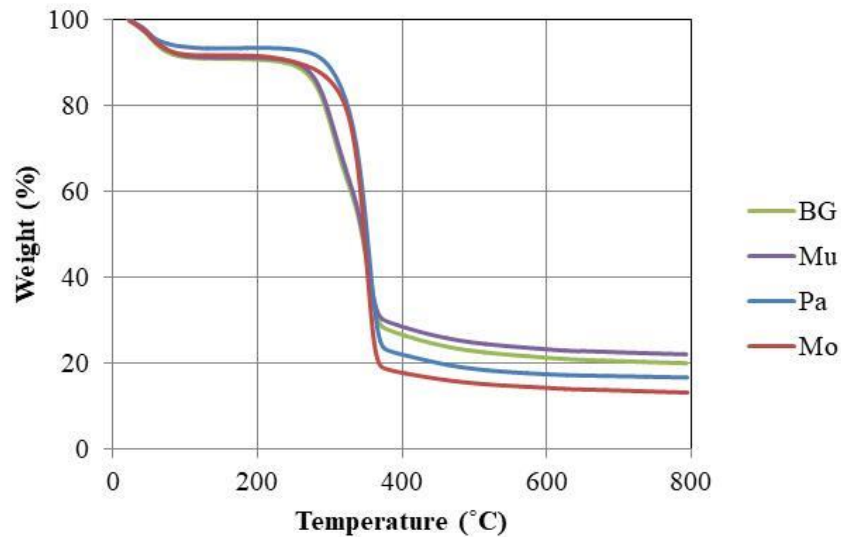
Figure 4.20: TG curves of cellulose fibers extracted from BG352(BG), Murunkan(Mu), Pachchaperumal(Pa) and Moddaikaruppan(Mo) varieties

Figure 4.20 shows the thermal degradation behaviour of cellulose fibers extracted from the four rice straw varieties. The resistant increase in cellulose observed is due to the removal of almost all hemicelluloses from rice straw. Though cellulose fibers extracted from all four rice straw varieties showed similar thermal degradation behaviour, as summarized in Table 4.4, a significant difference between the contents of the residues remained after pyrolysis was observed. This indicates that the thermal stability of cellulose is visibly improved.

Table 4.4: Degradation temperature of cellulose fibers extracted from Rice Straw

Cellulose	Degradation Temperature (˚C)	Residue at 800 ˚C (%)
BG352	351.2 ± 2.41	13.2 ± 0.12
Murunkan	354.2 ± 2.94	16.7 ± 0.23
Pachchaperumal	365.1 ± 3.23	17.1 ± 0.26
Moddaikaruppan	351.7 ± 2.62	14.5 ± 0.14

4.3 Characterization of Nanofibrillated Cellulose

4.3.1   Influence of treatment time on defibrillation of cellulose fibers

Ultrasonication is an important step which influences the disintegration of cellulose fibers. Ultrasonic energy is generally applied to disperse the nanoparticles. Cavitation bubbles develop and grow when high intensity ultrasound is applied. During the collapse of these bubbles, a considerable amount of energy is released. This creates a mechanical shock wave effect thus leads to the disruption of agglomerated particles[80].

High intensity ultrasonication treatment (HIUS) was applied for time periods ranging from 15 min to 90 min on cellulose fibers extracted from the four rice straw varieties. The weight reduction with time was calculated, and the results are presented in Figure 4.21. As shown in Figure 4.21, the sonication time had a significant effect. The observed weight loss depicts the disintegration process on cellulose fibers.
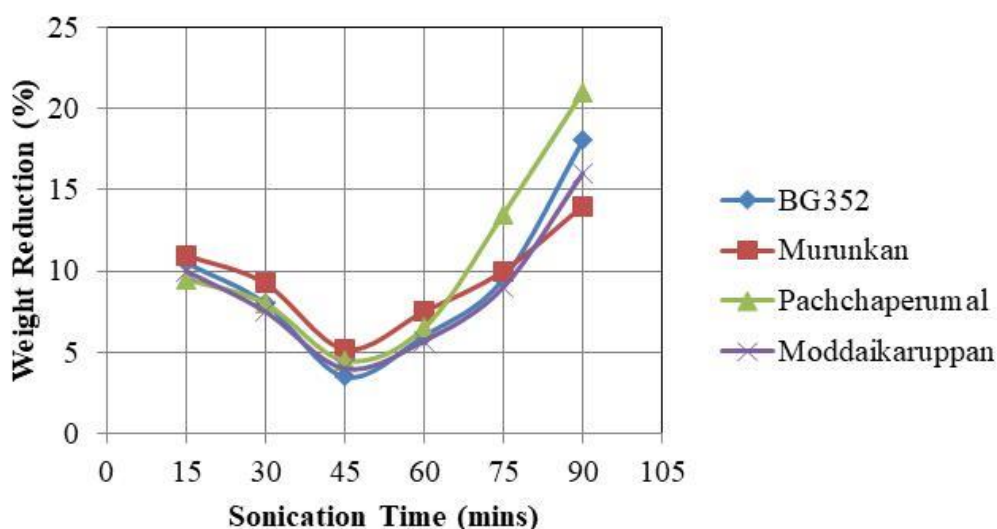
Figure 4.21: Effect of ultrasonication time on cellulose fibers

Time demonstrates the quality of dispersion. Longer sonication time facilitates the defibrillation of cellulose fibers and thereby increases the yield of Nanofibrillated cellulose (NFC)[83]. If the sonication time is long, more NFCs will be disintegrated, which may lead to a change in morphology of NFCs into nanowhiskers. However, 90 minutes of ultrasonication facilitated more weight reduction, which implies the

efficiency of disintegration of cellulose. All four varieties behaved in a similar way with the sonication time. However, comparatively BG352 and Moddaikaruppan showed more weight reduction with time than Murunkan and Pachchaperumal varieties.

4.3.2 Yield of Nanofibrillated Cellulose from High Intensity Ultrasonication

Figure 4.22 shows the amount of nanofibrillated cellulose extracted from chemically extracted cellulose of the four varieties. It was observed that highest amount of NFCs were extracted from BG352 cellulose fibers whereas lowest amount was recorded from Murunkan cellulose fibers. It is noted that a significant amount of NFC remained in the colloidal suspension. Though highest yield was recorded with Moddaikaruppan variety, it was also observed that maximum amount of NFCs were disintegrated and distributed in the colloidal suspension of this variety.
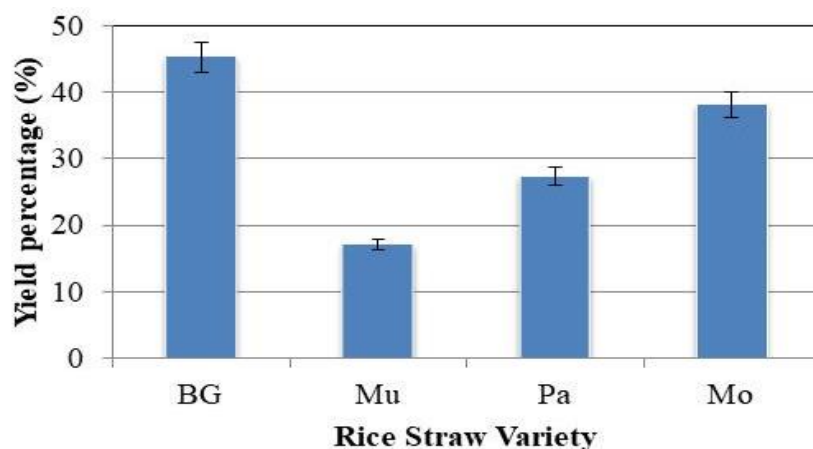
Figure 4.22: Yield percentage of nanofibrillated cellulose
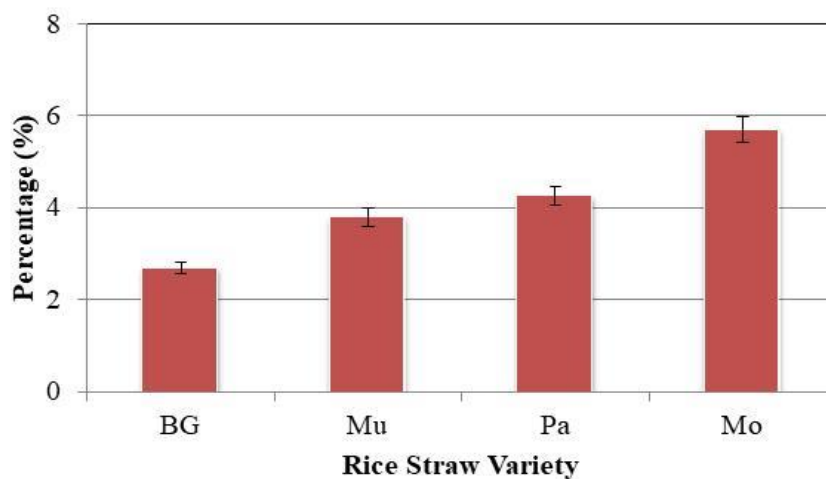
Figure 4.23: Amount of NFC remained in the colloidal suspension

4.3.3 FTIR Analysis of Nanofibrillated cellulose

FTIR of nanofibrillated cellulose derived from the chemically purified cellulose of four varieties are shown in Figure 4.24. NFCs extracted from all four varieties showed the same cellulose characteristic FTIR peaks at 3400 cm^{-1} of O-H stretching vibrations and at 2900 cm^{-1} of -CH stretching vibrations. Peak associated with O-H bending vibration of absorbed water at 1640 cm^{-1} that was evident in cellulose fibers was more pronounced for cellulose nanofibres[79]. Small peak in the anomeric region (950 – 700 cm^{-1}) at 897 cm^{-1} represents the glycosidic -C_1-O-C_4 deformation characteristic peak of the β-glycosidic link in cellulose[13]. This was observed to be weaker for cellulose nanofibres which indicate a scission of β-glycosidic link in cellulose by high intensity ultrasonication (HIUS) treatment. Essentially, cellulose nanofibres isolated by HIUS showed little chemical alteration as observed in FTIR analysis.
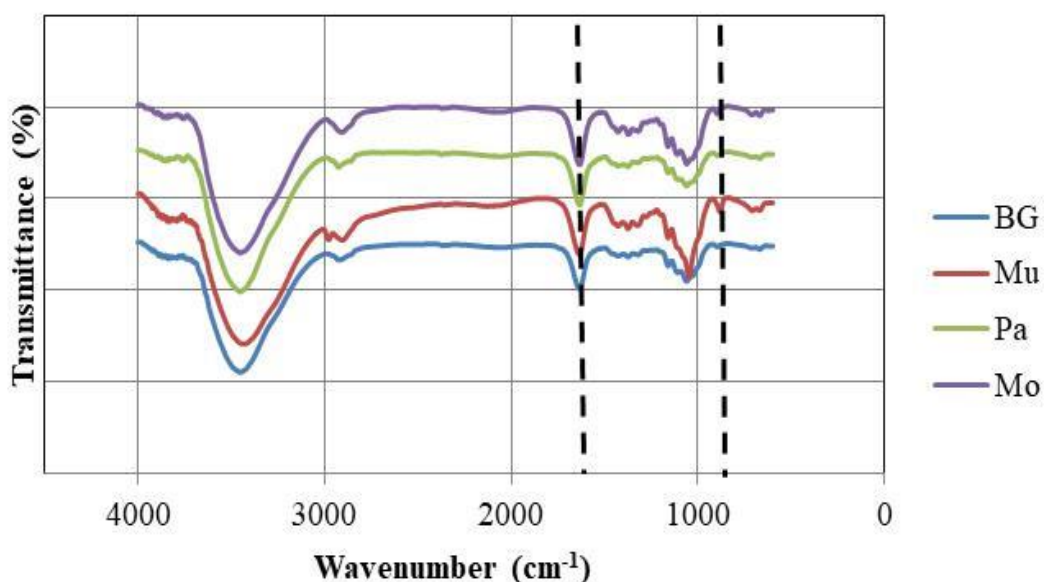
Figure 4.24: FTIR spectra of nanofibrillated cellulose from Sri Lankan rice straw varieties

4.3.4 Morphological study of cellulose fibers during HIUS treatment

Diameter of the disintegrated cellulose fibers was observed via scanning electron microscopy during the HIUS treatment and the images obtained throughout the treatment are presented in Figure 4.25.
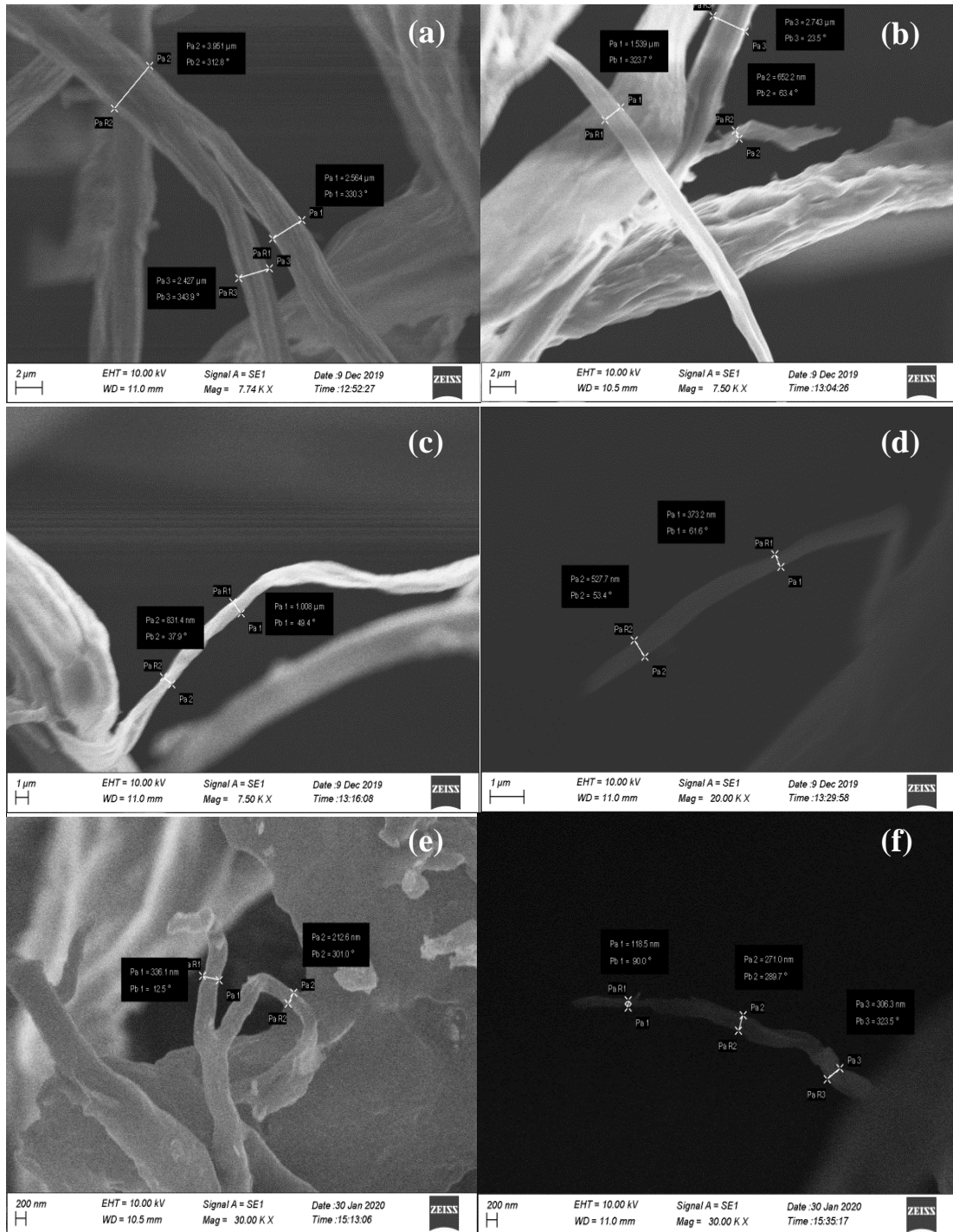
Figure 4.25: SEM images during the HIUS treatment (a) 15 mins,
(b) 30 mins, (c) 45 mins, (d) 60 mins, (e) 75 mins and (f) 90 mins

After 15 minutes of sonication, defibrillation process of cellulose fiber was observed
as presented in Figure 4.25(a). From this image, it was evident that the HIUS has a
significant effect on disintegration of cellulose fibers. After 45 minutes of sonication

as shown in Figure 4.25(c), both nanofibrillated cellulose as well as the unfibrillated chemically extracted cellulose fibers were observed. This exhibits that the disintegration process is still happening even after 45 minutes. Figure 4.25(d) exhibits that after 60 minutes the diameter of chemically extracted cellulose fibers were greatly reduced and more defibrillated cellulose fibers were observed. The lengths of the fibers were observed to be in micrometer range which varied from 140 µm to more than 300 µm. After 75 minutes of HIUS treatment, diameter of the disintegrated fibers was observed to be greatly reduced.
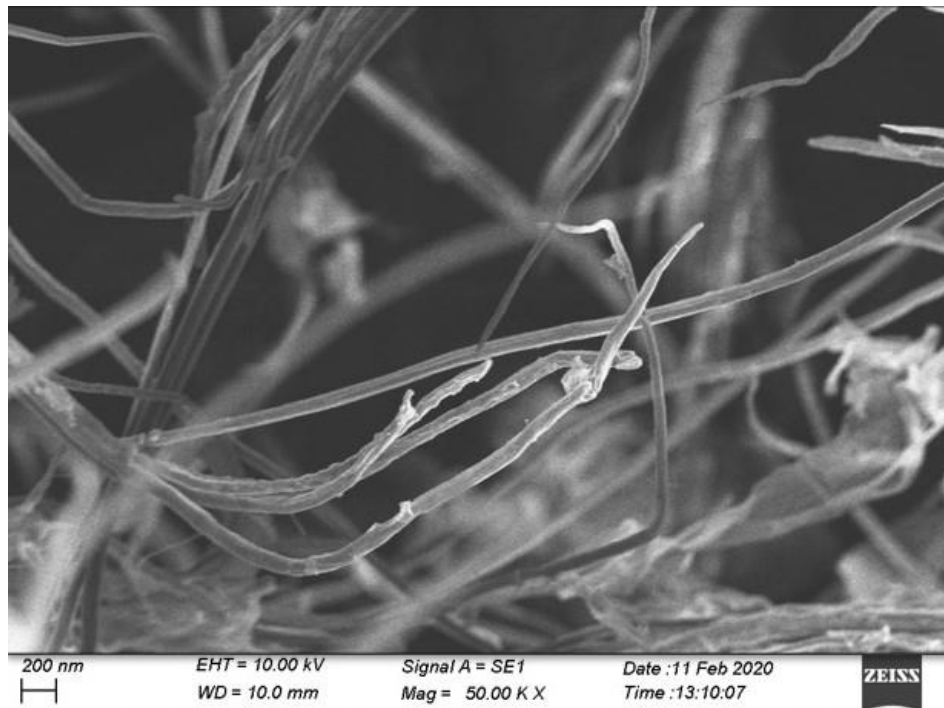
Figure 4.26: SEM image of nanofibrillated cellulose from BG352 variety

After 90 minutes treatment, fibrils with diameter in nanometer range were obtained (Figure 4.25(f) and 4.26). This proves that the HIUS is efficient in disintegrating nanofibrillated cellulose from chemically extracted cellulose fibers. However, it is also noteworthy that the fibrils in the colloidal suspension may contain fibrils less than this observed diameter. Further continuing the HIUS with longer treatment time may facilitate the defibrillation, hence the energy consumption of this process would be comparatively high. Nevertheless, HIUS can be utilized for the effective separation of nanofibrillated cellulose from locally available rice straw.

4.3.5 Thermal Analysis of Nanofibrillated cellulose

Analysis of thermal properties of nanofibrillated cellulose is essential to ascertain their suitability in bio-composite processing. Figure 4.27 shows the TG curves of nanofibrillated cellulose of four varieties obtained after 90 minutes of ultrasonic treatments.
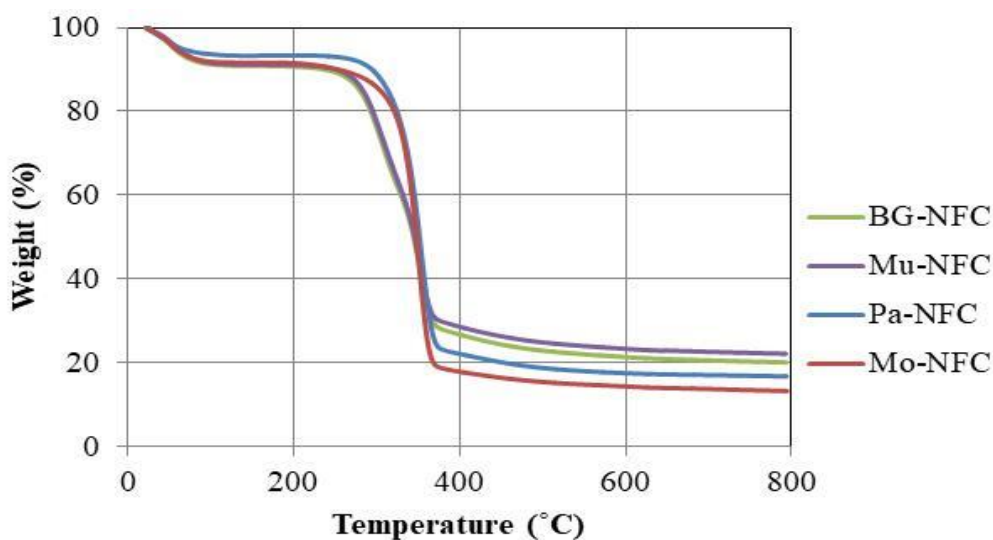
Figure 4.27: Thermal analysis of nanofibrillated cellulose

The nanofibrillated cellulose obtained after HIUS treatment showed similar degradation behaviour to that of chemically extracted cellulose fibers. Decomposition temperature of NFCs from all four varieties started approximately at 355 ˚C. This indicates that high intensity ultrasonication treatment had little effect the thermal degradation of NFCs except the structural changes. These results are in accordance with the FTIR results obtained.

4.4 Effect of Particle size distribution of Rice straw on Cellulose and Nanofibrillated cellulose

Chemical extraction and purification method is found to be the most efficient method for cellulose extraction from lignocellulosic biomass. Therefore, it is of paramount important to investigate the influence of parent materials on the extraction process and the properties of the yield[95]. In this study, effect of particle size distribution on cellulose and nanofibrillated cellulose extraction from locally available traditional rice straw variety Murunkan was studied. Powdered rice straw sample of Murunkan variety with particle size distribution below 75 µm (Mu-75) and between 150 - 250 µm (Mu-250) were utilized in this study.

4.4.1 FTIR Analysis

FTIR spectrum of Mu-250 during the chemical extraction and purification process is presented in Figure 4.28. After the successful extraction from chemical treatments, the final product was confirmed as cellulose. Similar analysis was carried out for Mu-75 as well.
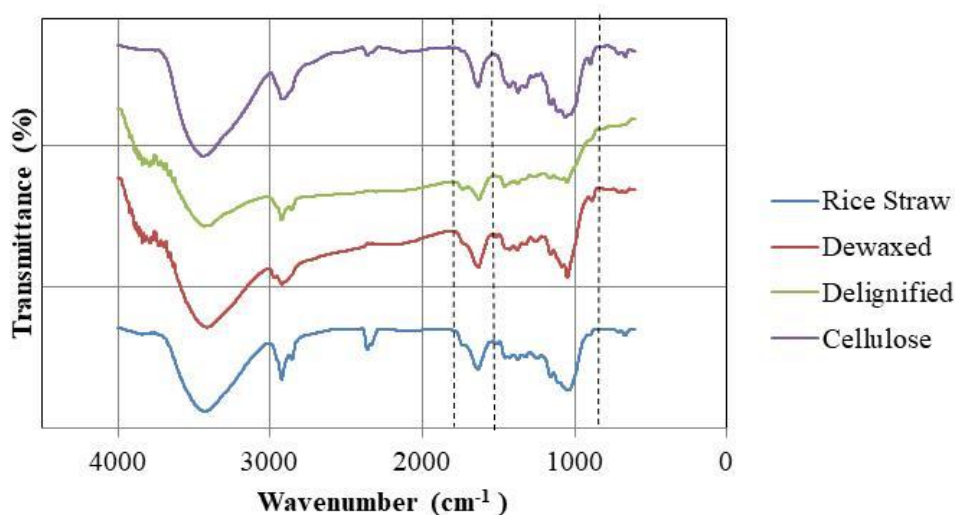
Figure 4.28: FTIR analysis of Mu-250 during chemical extraction process

Initially, removal of lignin was confirmed by the removal of aromatic skeletal vibrations at 1516 cm^{-1}. Then the removal of carbonyl stretching at 1729 cm^{-1} confirmed the removal of hemicellulose. Finally Si-O-Si stretching at 796 cm^{-1} confirmed the removal of silica[55].
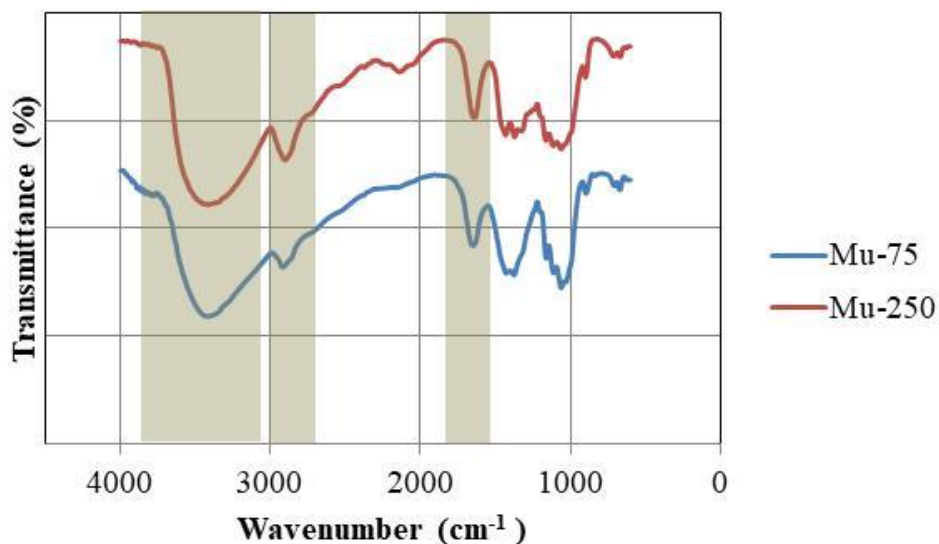
Figure 4.29: FTIR analysis of cellulose fibers extracted from
Mu-75 and Mu-250

FTIR spectrum of cellulose fibers extracted from Mu-75 and Mu-250 is shown in Figure 4.29 and nanofibrillated cellulose is shown in Figure 4.30. Peak observed around 2900 cm^{-1} is assigned for the stretching of asymmetric and symmetric methyl and methylene groups[54]. In Figure 4.28, it was observed that intensity of this peak has increased after the chemical treatments. In Figure 4.29 the intensity of this peak is high for Mu-250 than Mu-75.
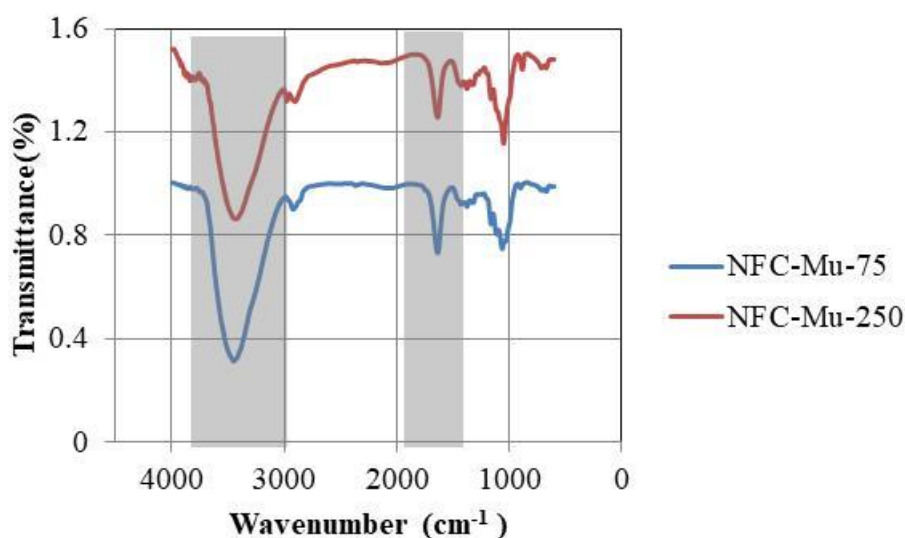
Figure 4.30: FTIR analysis of nanofibrillated cellulose extracted from
Mu-75 and Mu-250

48

The broad peak observed around 3400 cm^{-1} (Figure 4.28, 4.29 and 4.30) is attributed to -OH stretching vibrations. This peak was observed in the spectra of all the fibers which exhibit the hydrophilic nature of the fibers[79]. However, the intensity of this peak was observed to be higher in NFC than cellulose particularly in NFC-Mu-75. This may be due to a large number of hydroxyl groups in the particle size below 75 µm and thereby associated with an increase in the number of hydrogen bonds formed. From Figure 4.30, it is evident that NFC is more hydrophilic than cellulose. Therefore, surface modification may need to be performed depending upon the applications.

4.4.2 Compositional Analysis

After the series of chemical treatments Mu-75 yielded 27.19 ± 0.98 percent cellulose, whereas Mu-250 yielded 38.31 ± 0.86 percent cellulose. Subsequently ash contents from these rice straw samples were 8.83 ± 0.24 percent from Mu-75 and 10.17 ± 0.24 percent from Mu-250. Figure 4.31 shows the amount of cellulose, hemicellulose, lignin, wax and ash present in rice straw samples Mu-75 and Mu-250. Though both the rice straw samples yielded cellulose between 27 - 38 percent, highest yield was reported in Mu-250 sample where the particle size distribution varied between 150 µm - 250 µm. From these results, it is evident that the particle size of the raw material has a direct impact on the yield.
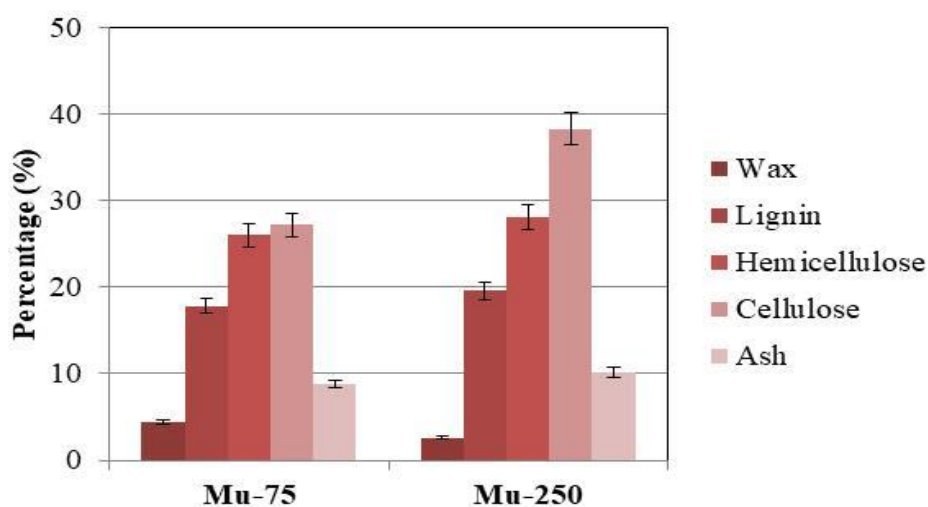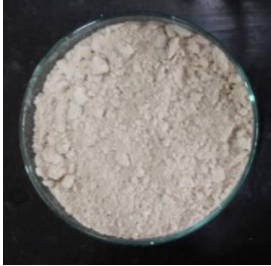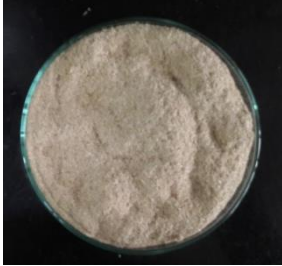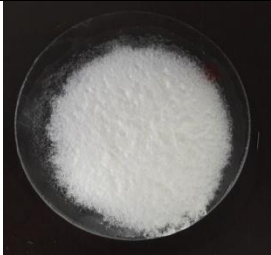
Figure 4.31: Composition of rice straw samples Mu-75 and Mu-250

Table 4.5: Mu-75 and Mu250 samples during cellulose and nanocellulose extraction

Components	Mu-75	Mu-250
Rice Straw		
Delignifies rice straw		
Cellulose		
Nanofibrillated Cellulose		

Mu-75 and Mu-250 samples during the chemical and HIUS extraction process are presented in Table 4.5. Gradual decrease in colour was observed with the chemical and mechanical treatments. Yield of nanofibrillated cellulose from Mu-75 cellulose was calculated as 63.84 ± 0.93 percent whreras yield percentage of nanofibrillated cellulose from Mu-250 cellulose was 54.94 ± 0.87. It was also observed around 12 percent of NFC-Mu-75 and around 1 percent of NFC-Mu-250 remained in the colloidal suspension. These values demonstrates a reciprocal relationship between particle size of the parent material and the yield percentage.

Density of the chemically extracted cellulose samples of Mu-75 and Mu-250 was determined using pycnometer. Calculated density values for both the cellulose samples are summarized in Table 4.6.

Table 4.6: Density of cellulose fibers extracted from Mu-75 and Mu-250

Sample	Density (g/cm³)
Mu - 75	$1.1419 \pm 8.165 \times 10^{-5}$
Mu - 250	$1.1368 \pm 4.714 \times 10^{-5}$

Fiber density has a direct impact on the strength. So, it is important to find out the density of cellulose in determining its application. Studies report that low density fibers are preferred for fiber-reinforced composites. Even though the density values for both the samples are similar, comparatively Mu-250 can be considered as lower dense fiber than Mu-75.

4.4.3 Thermal Analysis

In order to determine the significant impact of particle size, thermal behaviour of native and treated samples were analyzed[96]. Figure 4.32 presents the chemically extracted cellulose fibers from Mu-75 and Mu-250 whereas Figure 4.33 presents the NFC extracted from cellulose fibers of Mu-75 and Mu-250.
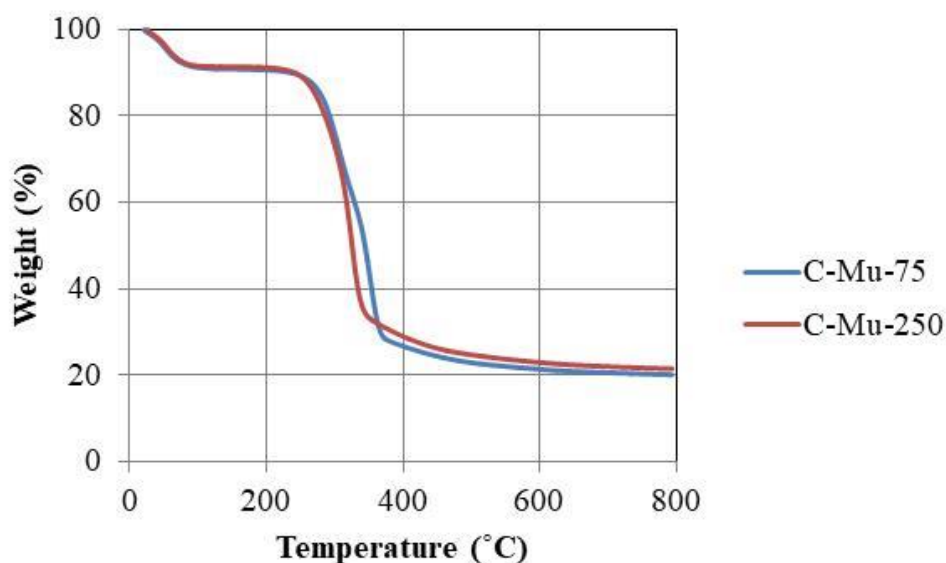
Figure 4.32: Thermal analysis of cellulose fibers extracted from
Mu-75 and Mu-250

51

Both Mu-75 and Mu-250 showed similar degradation behaviour as other rice straw varieties during the chemical extraction process.
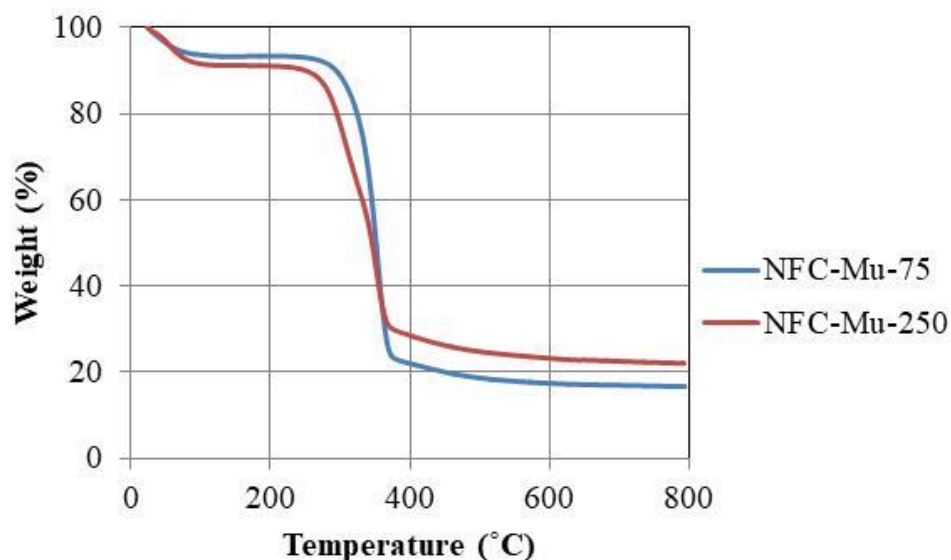
Figure 4.33: Thermal analysis of nanofibrillated cellulose extracted from Mu-75 and Mu-250

Degradation temperature of Mu-75 cellulose was observed as 322.4 ˚C with 24 percent residue at 800 ˚C and degradation temperature of Mu-250 cellulose was 334.7 ˚C with 18.4 percent residue at 800 ˚C. However the degradation temperature of both nanofibrillated cellulose exhibited highly similar degradation pattern to that of their respective chemically extracted cellulose fibers.

4.4.4   Morphological Analysis

SEM images of Mu-75 during the chemical and HIUS extraction process are presented in Figure 4.34 and the SEM images of Mu-250 are presented in Figure 4.35. Grooves and grains are observed on the surface of rice straw (Figure 4.34(a,b) and 4.35(a,b)). Morphologies are discernible when the extractive components were eradicated from rice straw *via* the series of chemical treatments. Some of dense lignin and hemicelluloses are observed (Figure 4.34(a,b,c) and 4.35(a,b,c)) around the fibers of rice straw. After the removal of lignin, the shape of the phytoliths was revealed. Apparently, the shape of phytoliths is not observed to be homogeneous within the delignified sample (Figure 4.34(d) and 4.35(d)).
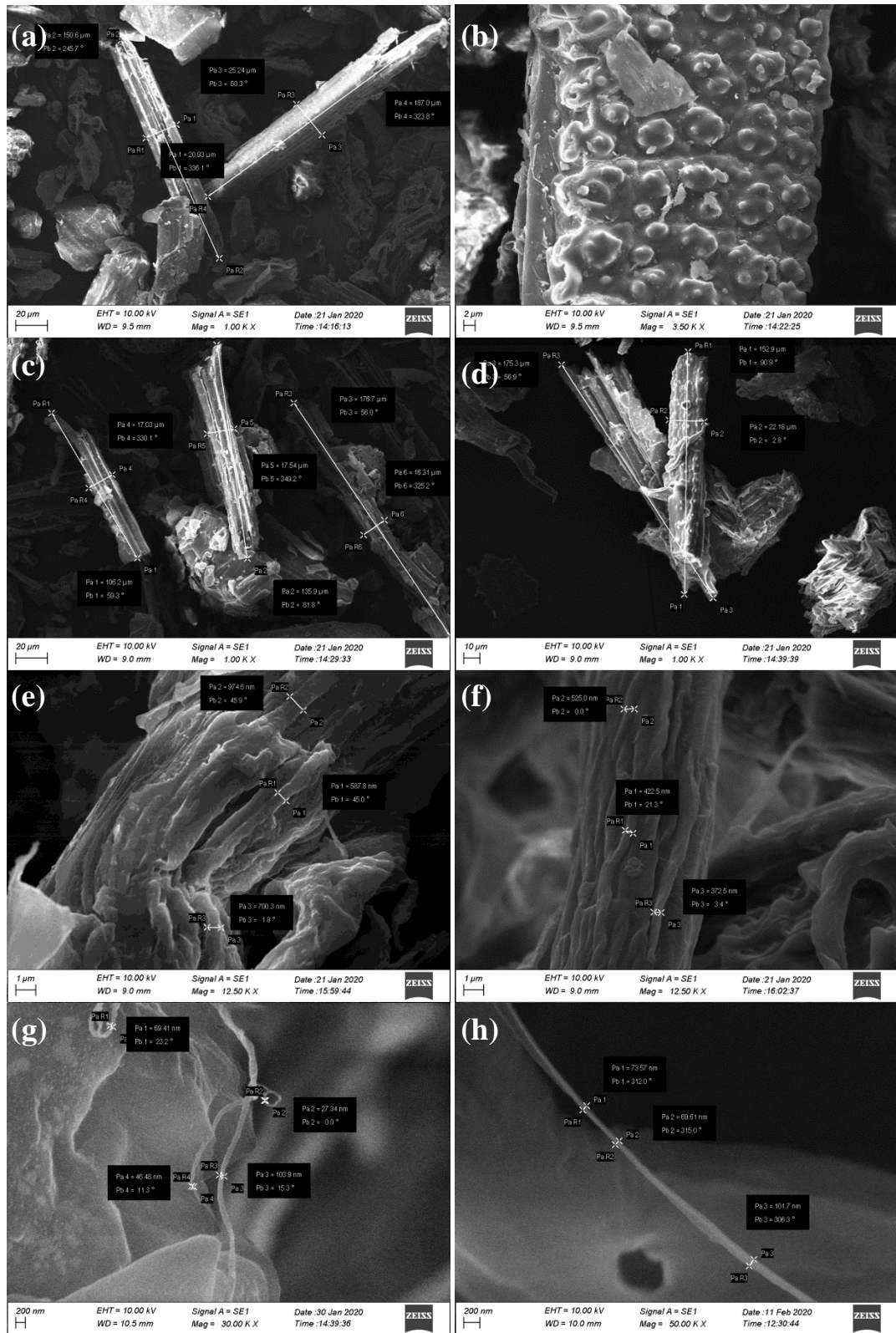
Figure 4.33: SEM images of Mu-75 during chemical and HIUS treatment (a,b) rice straw, (c) dewaxed, (d) delignified, (e,f) cellulose fibers and (g,h) nanofibrillated cellulose
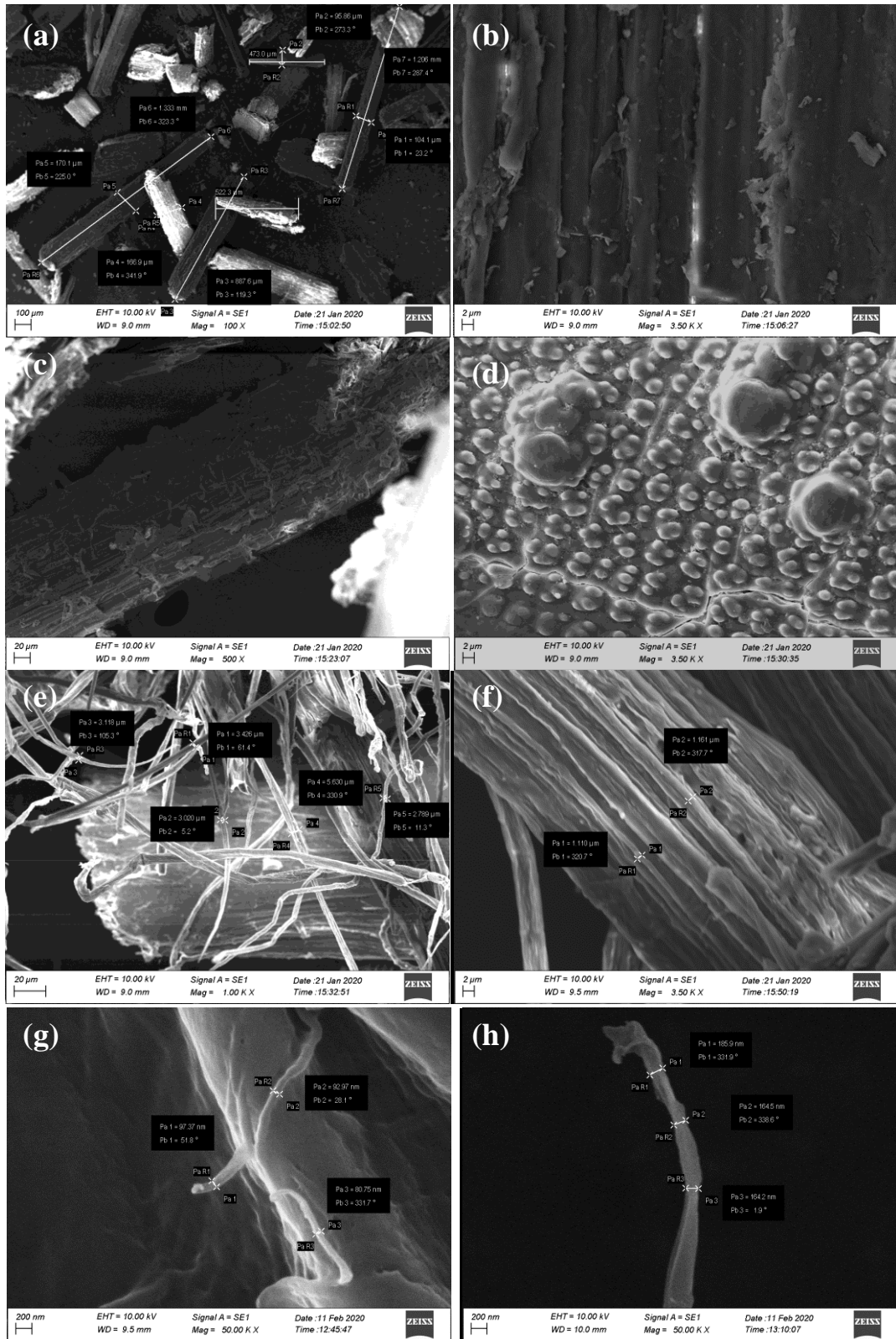
Figure 4.34: SEM images of Mu-250 during chemical and HIUS treatment (a,b) rice straw, (c) dewaxed, (d) delignified, (e,f) cellulose fibers and (g,h) nanofibrillated cellulose

However, in Mu-75, phytoliths were visible even in rice straw (Figure 4.34(b)). This proves that milling process has ruptured the rice straw surface to a greater extent. Individualized fiber bundles were observed on the surface of single micro-sized fiber in Figure 4.34(e,f) and 4.35(e,f). While these single fibers maintained their initial structure, the widths of those individualized fibers were observed to be in micro to nanometers. Figure 4.34(e,f) and 4.35(e,f) shows the chemically extracted cellulose to be mostly in the form of fibers. They were separated into individual micro-sized fibers to a greater extent. Hence, the diameter of Mu-250 cellulose was found to be within 90 nm to 200 nm and the Mu-75 nanofibrillated cellulose marked the lowest width which was around 27 nm. The effect of particle size on cellulose and nanofibrillated cellulose extraction was well exhibited in the above SEM images.

CHAPTER 5: CONCLUSIONS

Sri Lanka being an agricultural country generates equal amount of waste from paddy production. Even though rice straw is utilized in various ways, there is a possibility to do value addition by extracting the cellulose fibers and nanofibrillated cellulose out of this underutilized waste material, thus adopting a sustainable bioeconomy in the country.

Rice straw ash derived from four locally available rice straw varieties was analyzed for its properties. The study revealed that there is no significant difference between the compositions of rice straw ash derived from these four rice straw varieties. Silica protrusions and grains observed on the surface of the rice straw leaves a silicon rich rice straw ash during carbonization which varied between 71 - 79 percent of the ash content. Thermal analysis exhibited greater weight loss with lower crystallinity. All four samples exhibited better pozzolanic behaviour. Rice straw ash from locally available rice straw can be explored as silica rich source in industrial applications.

Nanofibrillated cellulose (NFCs) was extracted from four Sri Lankan rice straw varieties BG352, Murunkan, Pachchaperumal and Moddaikaruppan in two distinct stages. FTIR and SEM analysis confirmed that the chemical composition of nanofibers was mainly cellulose where hemicelluloses and lignin were effectively removed during chemical treatments. Study revealed that around 25 - 38 percent cellulose was extracted from the four rice straw varieties *via* chemical process. Further, higher amount of cellulose fibers were extracted from traditional varieties Moddaikarupan (38.31 ± 0.86 percent), Murunkan (33.68 ± 0.68 percent) and Pachchaperumal (33.63 ± 0.10 percent) than the technically modified variety BG352 (25.35 ± 0.91 percent). Out of these cellulose fibers around 17 - 45 percent of nanofibrillated cellulose were extracted *via* high-intensity ultrasonication process. It was noted that that highest amount of NFCs were extracted from BG352 cellulose fibers whereas lowest amount was recorded from Murunkan cellulose fibers. SEM images displayed that the diameters of the nanofibers extracted in nanometer range

where the lengths were observed to be micrometer range. Results indicated that the efficient multi-step treatment process yielded nanofibrillated cellulose with potential advanced applications.

Effect of particle size distribution of rice straw on cellulose and nanofibrillated cellulose was also studied. Traditional rice straw variety Murunkan with two different particle size distribution (below 75 μm (Mu-75) and between 150 μm - 250 μm (Mu-250) was used for this study. These samples were also subjected to the same physiochemical process and the results were compared. Study revealed that around 63 percent of NFCs were extracted from Mu-75 cellulose and around 55 percent of NFCs were extracted from Mu-250 cellulose. Effect of particle size on nanofibrillated cellulose extraction was well exhibited in the SEM images. In addition, it was also observed that cellulose fibers from Mu-75 were mostly in the form of short fibers whereas cellulose from Mu-250 were found to be in fibrillar network like structure with long fibers. This study reveals that the particle size distribution of rice straw has a considerable effect on yield and properties of cellulose and nanofibrillated cellulose extraction.

CHAPTER 6: RECOMMENDATIONS

6.1 Study on other varieties

Experiments were performed on four locally available rice straw varieties BG352, Murunkan, Pachchaperumaal and Moddaikaruppan in this study. Sri Lanka being an agricultural country produces wide range of rice varieties. Future research is suggested to extend this study to other varieties as well as to explore the possibilities of extracting cellulose and nanofibrillated cellulose fibers from a mixture of locally available varieties.

6.2 Investigation of disintegration behavior of cellulose fibers with different frequencies

Experimental results showed that sonication time had a significant effect on disintegration behaviour of chemically extracted cellulose fibers. Accordingly, study on the effect of frequencies during the high intensity ultrasonication process in achieving nanofibrillated cellulose is recommended.

6.3 Scale-up framework to extract cellulose and nanofibrillated cellulose from locally available rice straw

Laboratory scale experiments showed consistent results during cellulose and nanofibrillated cellulose extraction. Scaling up this process would add value to this commercially under-utilized waste and also accentuate sustainable transition to a bioeconomy in the country.

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APPENDIX A

District share of asweddumized paddy areas according to the mode of irrigation
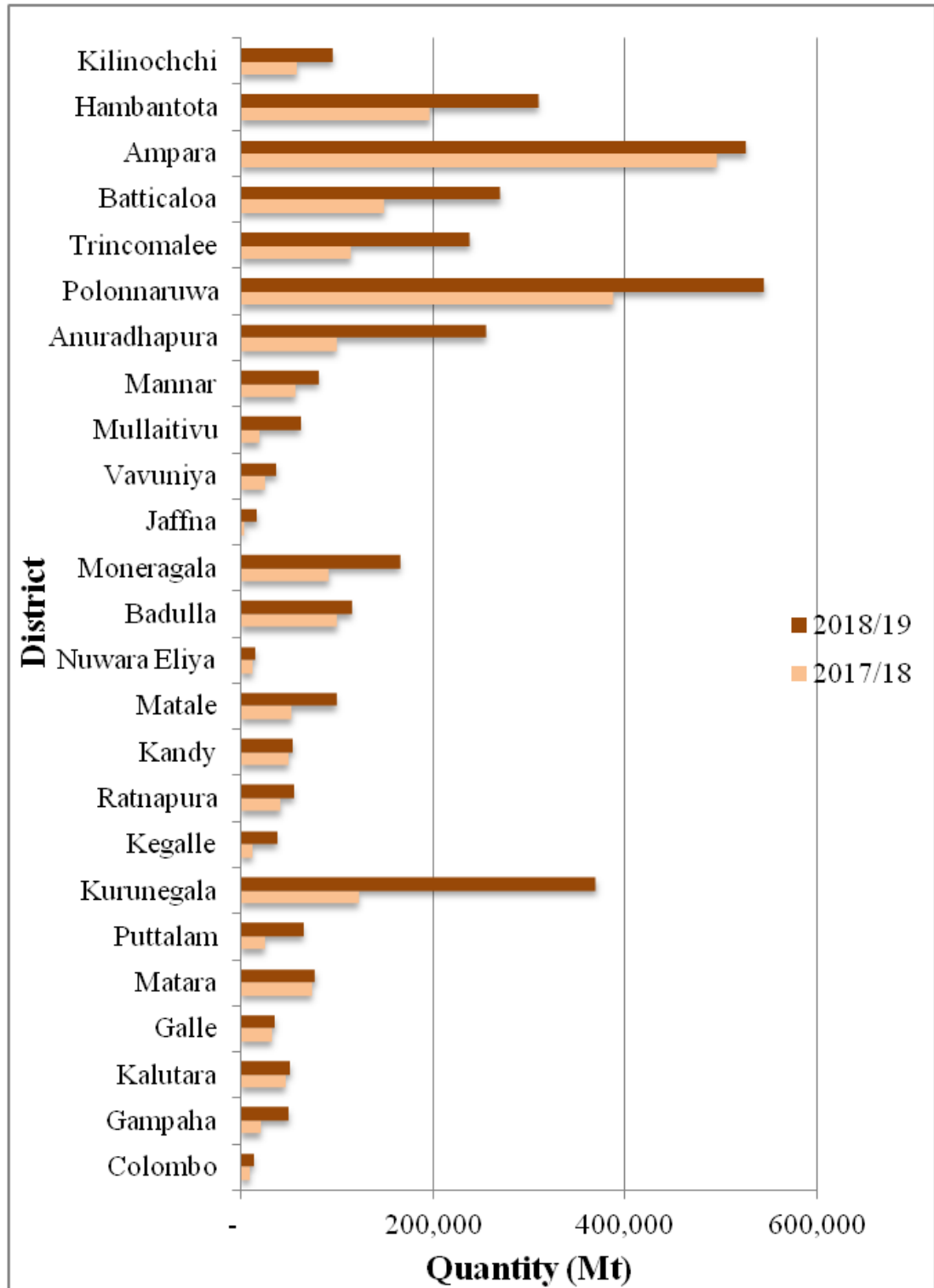
(Source: Survey Department of Sri Lanka, 2018)
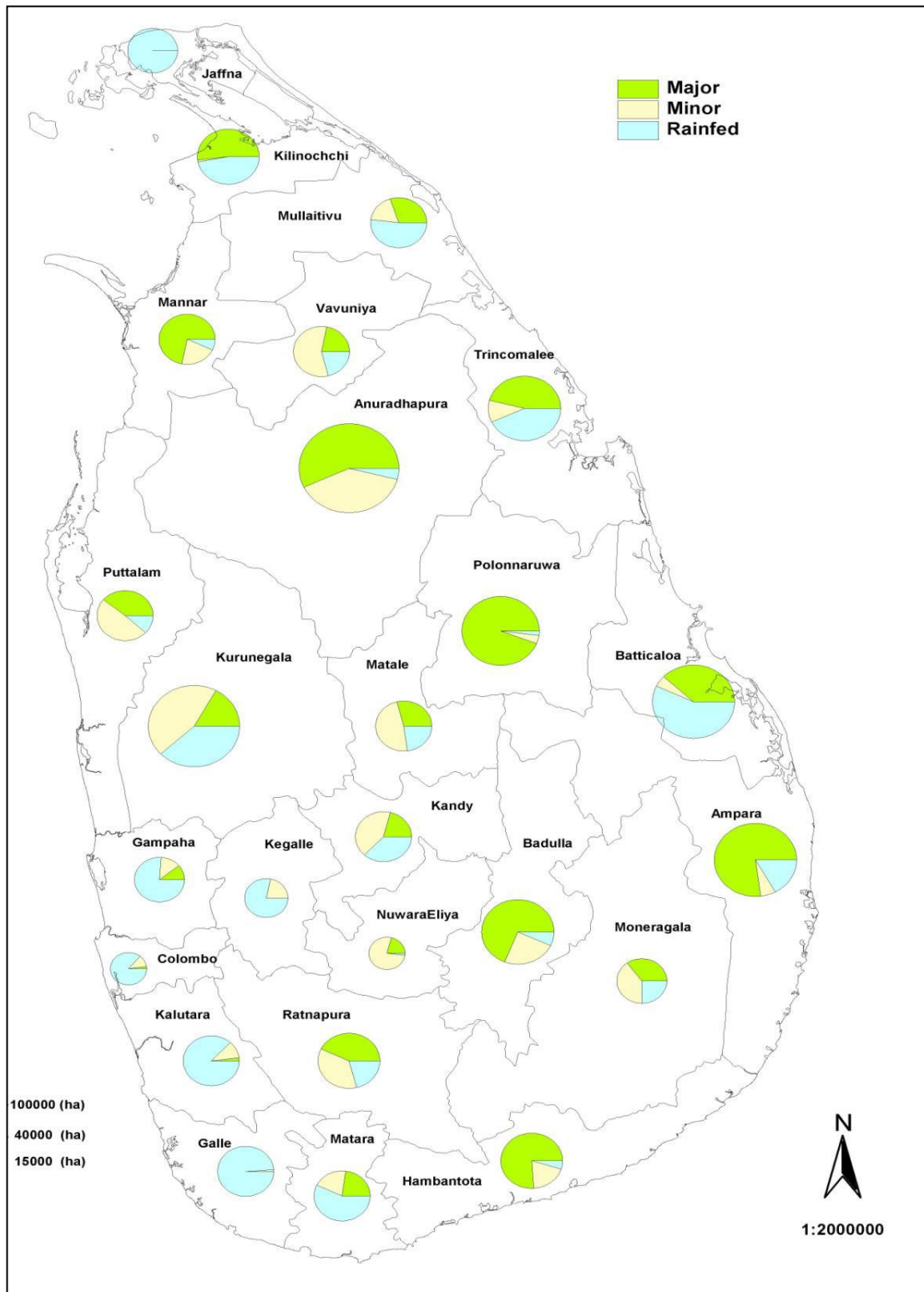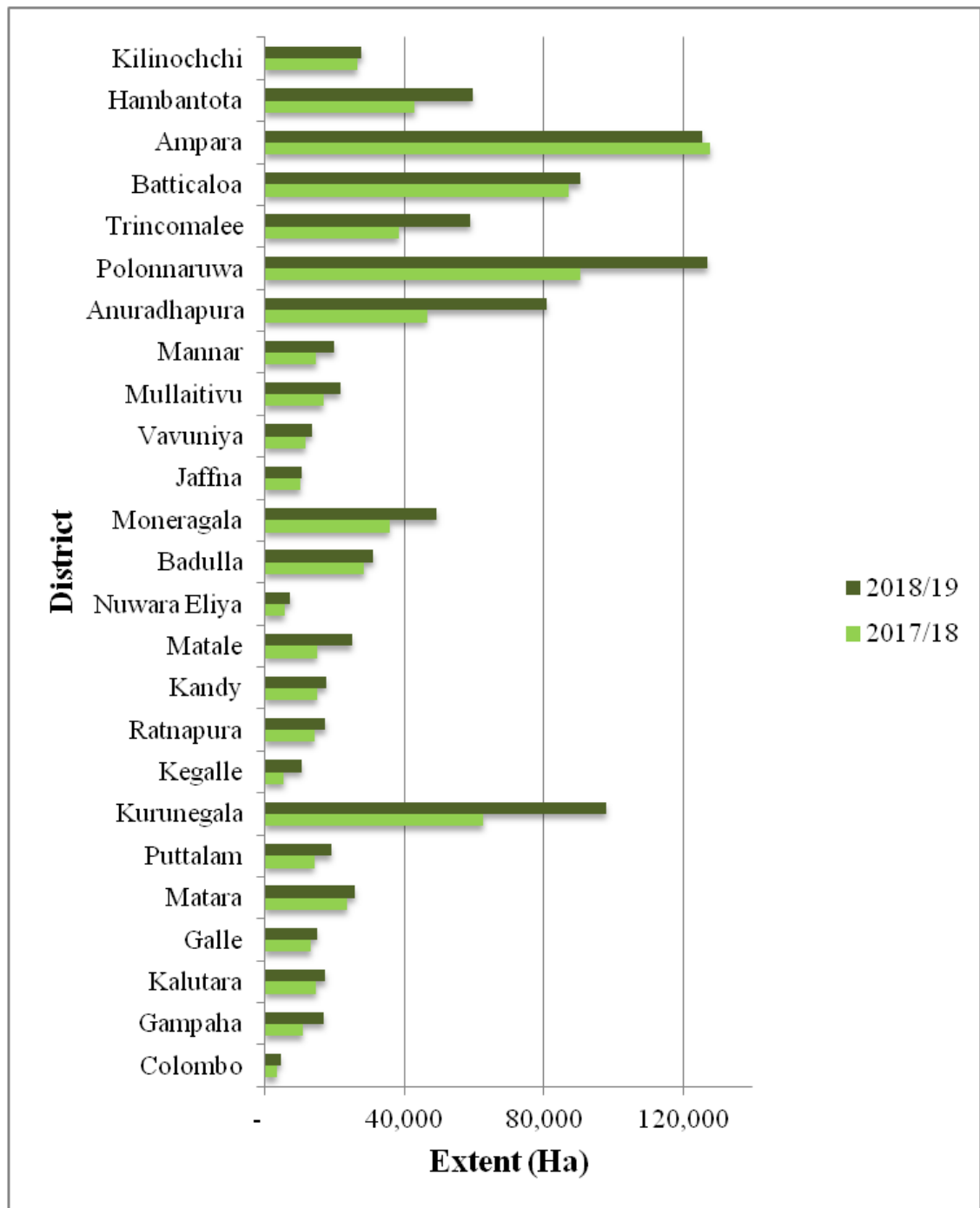
APPENDIX B

B1. District level paddy cultivation during 2017/18 and 2018/19

(Source: Department of Census and Statistics, Paddy Statistics, 2017/18 and 2018/19)

B2. District level paddy extent during 2017/18 and 2018/19

(Source: Department of Census and Statistics, Paddy Statistics, 2017/18 and 2018/19)

APPENDIX C

District level sown area under paddy by use of straw

(Source: Department of Census and Statistics, Paddy Statistics, 2014/15 Maha)

District	Total Sown Area (Ha)	Apply for Fertilizer (%)	Firing (%)	For Animal Feed (%)	For Roofing (%)	Other (%)
Colombo	3,484	73.9	4.5	10.1		11.5
Gampaha	11,154	93.6	4.6	0.2	0.1	1.5
Kalutara	13,020	77.3	2.6	1.1	0.2	18.8
Kandy	12,135	88.1	2.9	1.2	3.9	3.9
Matale	20,365	94.4	3.5	0.3		1.8
Nuwara Eliya	5,237	94.7		5.3		
Galle	13,130	78.1	4.6	3.7		13.6
Matara	14,447	90.7	5.1	0.5		3.7
Hambantota	27,175	97.3	2.1	0		0.6
Jaffna	10,038	19.1	2.7	75.9	0.3	2
Mannar	17,321	79.2	1	0	4.1	15.7
Vavuniya	16,841	91.4	1.1	7.3	0	0.2
Mullaitivu	14,613	98.7			1.3	
Kilinochchi	23,675	86.2	8.7	5.1		
Batticaloa	61,014	90.2	1.1	7.6		1.1
Ampara	83,133	85.5	9.7	2.4	0.1	2.3
Trincomalee	34,470	84.2	0.2	5.1	10.5	
Kurunegala	79,375	88.7	8.7	0.9	0.1	1.6
Puttalam	20,116	93.5	5.5	0.9		0.1
Anuradhapura	99,814	75.3	17.4	0.6		6.7
Polonnaruwa	74,766	86.5	10.5	1.6		1.4
Badulla	27,057	96.5	2.2		0.6	0.7
Monaragala	36,038	94.6	3.5	0.4	0.4	1.1
Ratnapura	11,751	91.2	3.8			5
Kegalle	6,240	70.6	7.2		4.1	18.1
Uda walawe	12,366	98.6	0.4	0.4		0.6
Mahaweli 'H'	23,851	91.4	5.9			2.7
Sri Lanka	**772,626**	**86.3**	**6.8**	**3**	**0.7**	**3.1**