ISOLATION OF MICROCRYSTALLINE CELLULOSE FROM OIL PALM EMPTY FRUIT BUNCH BLEACHED PULP: STATISTICAL OPTIMIZATION OF ACID HYDROLYSIS AND CHARACTERIZATION

TUAN MUHAMAD HASSAN BIN TUAN HAMZAH

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by

TUAN MUHAMAD HASSAN BIN TUAN HAMZAH

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LIST OF ABBREVIATIONS

ANOVA	Analysis of Variance
C.V.	Coefficient of Variation
CCD	Central composite design
CMCC	Commercial Microcrystalline Cellulose
CCRD	Central Composite Rotatable design
CPO	Crude palm oil
DoE	Design of Experiment
df	Degree of Freedom
DP	Degree of polymerization
Eq.	Equation
FTIR	Fourier transform infrared
FFB	Fresh Fruit Bunch
MCC	Microcrystalline cellulose
MF	Mesofiber
MPOB	Malaysian Palm Oil Board
OD	Dry weight
OPEFB	Oil palm empty fruit bunch
OPF	Oil Palm Fronds
OPT	Oil Palm Trunk
OPEFB-pulp	Bleach pulp from OPEFB
OPEFB-MCC	Microcrystalline from OPEFB
OPEFB-DP	Dissolving pulp (DP) from OPEFB
SEM	Scanning Electron Microscope
R^2_{Adj}	Adjusted R-Squared

R^2_{Pred}	Predicted R-Squared
RSM	Response Surface Methodology
TEM	Transmission electron microscopy
TCF	Total chlorine free
TGA	Thermogravimetric analysis
XRD	X-ray diffraction

LIST OF SYMBOLS

%	Percentage
ºC	Degree Celsius
g	Gram
g/cm^3	Gram per cubic centimetre
g/mol	Molar mass
ml	Mililiters
L	Liters
N	Normality
HCl	Hydrochloric acid
H_2SO_4	Sulfuric acid
H_2O_2	Hydrogen peroxide
H_3O^+	Hydronium
KBr	Potassium bromide
KI	Potassium iodide
$MgSO_4.7H_2O$	Magnesium sulphate heptahydrate
NaOH	Sodium hydroxide
NH_4OH	Ammonia solution
OH	Hydroxide

PENGASINGAN SELULOSA MIKRO BERHABLUR DARIPADA PULPA TERLUNTUR TANDAN BUAH KOSONG KELAPA SAWIT : PENGOPTIMUMAN STATISTIK HIDROLISIS ASID DAN PENCIRIAN.

ABSTRAK

Pengoptimuman parameter proses hidrolisis asid bagi pengeluaran selulosa microcrystalline (MCC) daripada tandan kosong buah kelapa sawit (OPEFB) yang dinilai dengan menggunakan kaedah sambutan permukaan melalui reka bentuk komposit memusat. Sebelum proses hydrolysis, proses pemulpaan yang mesra alam dan turutan pelunturan dilakukan terhadap OPEFB untuk menghasilkan pulpa yang bebas klorin. Sementara untuk pengoptimuman, satu set eksperimen dilakukan dengan menggunakan tiga faktor yang berbeza, iaitu masa, suhu dan kepekatan asid. Dalam julat 10 hingga 30 min, 80 hingga 130 ºC dan 1.5 hingga 3.5 N telah digunakan untuk pembolehubah. Sementara itu, hasil %, kestabilan termal dan indeks penghabluran dari OPEFB-MCC yang dihasilkan telah dinilai sebagai tindak balas dan dibandingkan dengan nilai yang diramalkan. Berdasarkan keadaan proses pengoptimuman untuk pengeluaran MCC pada masa hidrolisis = 20 min, suhu = 106 ºC dan kepekatan asid = 2.5 N, masing-masing. MCC dengan hasil yang tinggi (92.2 %), kestabilan haba yang baik (335.33 ºC) dan indeks penghabluran (72.88 %) diperoleh melalui keadaan ini. Keputusan MCC dari keadaan yang dioptimumkan kemudian dicirikan dengan menggunakan morfologi, fizikokimia, indeks crystallinity dan kajian termal dengan menggunakan spektroskopi tranformasi Fourier-inframerah (FTIR), mikroskop elektron pengimbasan (SEM), Brunauer-Emett-Teller (BET), analisi belauan sinar-X (XRD), dan analisis termogravimetri (TGA). Spektrum FTIR menunjukkan bahawa urutan pulpa dan pelunturan yang digunakan dapat menghilangkan komponen lignin dan hemiselulosa di dalam OPEFB. Ini terbukti dengan kehilangan puncak pada 1514 cm^{-1} untuk lignin dan 1735 cm^{-1} untuk hemiselulosa dalam pulpa TCF berbanding OPEFB. Struktur morfologi bagaimanapun, dapat menyebabkan morfologi permukaan MCC di bawah pemerhatian SEM menunjukkan bahawa struktur MCC kasar dan padat selepas proses hidrolisis asid. Menarik untuk ambil perhatian bahawa, bentuk analisis BET MCC dipaparkan saiz mesopores (2.22 nm) struktur berliang. Indeks penghabluran meningkat (43.14 %) selepas bahan hidrolisis asid yang mula OPEFB menjadi OPEFB-MCC. Keadaan optimum OPEFB-MCC menunjukkan indeks penghabluran tertinggi berbanding dengan keadaan lain iaitu 72.88 %. TGA menunjukkan bahawa OPEFB-MCC yang diperoleh pada keadaan optimum menunjukkan kestabilan terma yang lebih baik di $T_{20\%}$, $T_{50\%}$ serta T_{max} pada 334.66 ºC, 341.83 ºC dan 350 ºC masing-masing berbanding dengan keadaan lain. Secara keseluruhannya, dapat disimpulkan bahawa proses hidrolisis pada 20 min pada suhu 106 ºC menggunakan 2.5 N asid adalah keadaan ideal untuk pengeluaran OPEFB-MCC dengan hasil yang tinggi, penghabluran yang tinggi dan kestabilan haba yang lebih baik. Penghasilan MCC yang optimum adalah berpotensi dijadikan sebagai pengisi bahan penguat berteknologi hijau dalam bahan komposit.

ISOLATION OF MICROCRYSTALLINE CELLULOSE FROM OIL PALM EMPTY FRUIT BUNCH BLEACHED PULP: STATISTICAL OPTIMIZATION OF ACID HYDROLYSIS AND CHARACTERIZATION.

ABSTRACT

The optimization the acid hydrolysis process parameters condition for the production of microcrystalline cellulose (MCC) from oil palm empty fruit bunch (OPEFB) evaluated by using response surface methodology via central composite design. The OPEFB was first subjected to the environmental friendly pulping and bleaching sequence for the production of total chlorine free pulp prior to the acid hydrolysis process. Meanwhile for the optimization, a set of experiment was performed using three different factors which are time, temperature and acid concentration were carried out. The range of 10 to 30 min, 80 to 130 ºC and 1.5 to 3.5 N have been used for the variable. Meanwhile, yield %, thermal stability and crystallinity index of the resultant OPEFB-MCC were evaluated as the responses and were compared with the predicted values. Based on the optimization process conditions for MCC production were at hydrolysis time= 20 min, temperature= 106 ºC and acid concentration= 2.5 N, respectively. The OPEFB-MCC with high yield (92.2 %), good thermal stability (335.33 ºC) and crystallinity index (72.88 %) were obtained through this condition. The resultant OPEFB-MCC from optimized condition was then characterized by means of morphological, physiccochemical, crystallinity index and thermal study by using Fourier transform infrared (FTIR) spectroscopy, scanning electron microscopy (SEM), Brunauer–Emett–Teller (BET), X-ray diffraction (XRD) analysis, and thermogravimetric analysis (TGA). The FTIR spectra showed that the pulping and bleaching sequence used were able to remove lignin and hemicellulose component inside OPEFB. This proven by the disappearance of peak at 1514 cm^{-1} for lignin and 1735 cm^{-1} for hemicellulose in the TCF pulp as compared to OPEFB. The morphological structure however, get effected the surface morphology of OPEFB MCC under SEM observation showed that OPEFB-MCC rough and compact structure after the acid hydrolysis process. Interesting to note that, form BET analysis MCC displayed mesopores size (2.22 nm) of porous structure. From XRD analysis revealed that the crystallinity index was increased (43.14 %) after acid hydrolysis starting material OPEFB to resultant OPEFB-MCC. The optimum condition of OPEFB-MCC shows the highest crystallinity index as compared to other condition which is 72.88 %. The TGA showed that the obtained OPEFB-MCC at optimum condition displayed a better thermal stability at $T_{20\%}$, $T_{50\%}$ as well as T_{max} at 334.66 ºC, 341.83 ºC and 350 ºC respectively as compared to other condition. Overall, it can be concluded that the hydrolysis process at 20 min at 106 ºC using 2.5 N acids is the ideal condition for production of OPEFB-MCC with high yield, crystallinity and better thermal stability. The obtained OPEFB-MCC from this optimum condition has a potential to be used as a reinforcement filler for the production of green composite material.

CHAPTER 1

INTRODUCTION

The oil palm is one of the main agricultural commodities in Malaysia, and now Malaysia is one of the biggest producers and exporters of palm oil in the world (Awalludin *et al.*, 2015; Hashim *et al.*, 2010). In 2012, more than 5.39 million hectares of land in Malaysia have been planted with oil palm tree, and produced 17.73 million metric tonnes of palm oil annually (MPOB, 2012). From palm oil industry, oil represents only about 10 % of oil production while the rest 90 % represents as a biomass waste such as oil palm trunk, oil palm fronds, oil palm empty fruit bunch (OPEFB), palm kernel shell and mesocarp fibre (Awalludin *et al.*, 2015; Basiron *et al.*, 2004). It was estimated 83 million tonnes (dry weight) was produced in 2012 and is expected to reach 100 million tonnes dry weight by 2020 (Umar *et al.*, 2013).

The main source of fibre from oil palm tree is OPEFB, the residue obtained after stripping fruits from the fresh fruit bunch, producing more than 73 % of fibre. Among these biomass, OPEFB was the largest amount of waste generated and was estimated more than 7.0 million tonnes in dry per year (F. Y. Ng *et al.*, 2012; Shinoj *et al.*, 2011). OPEFB is considered as valuable biomass that has a good potential to be converted not only to energy but also as a raw material for the production of high value added materials of such as panels and composites, fine chemicals, pulp and paper, regenerated cellulose, cellulose derivatives as well as compost and bio-fertilizers (Haafiz, Eichhorn, *et al.*, 2013; Mahjoub *et al.*, 2013). The OPEFB are comprised of 60.6 % of cellulose, 24.15 % of hemicellulose, and 16.92 % of lignin

(Wanrosli *et al.*, 2004). Due to its renewability, cheap, abundantly available and non-toxic, made this material is a great raw material for the isolation and production of the cellulose based products (Wanrosli *et al.*, 2004).

Cellulose is the most abundant biopolymer in nature, it can be isolated from wood, and non-wood such as cotton, kenaf, bagasse, oil palm fibre and other plant-based materials and it also can be produced from algae, tunicates as well as microorganisms (Klemm *et al.*, 2005; Siró *et al.*, 2010). Cellulose is a linear homopolymer of glucose $(C_6H_{10}O_5)_n$ with repeating units containing D-glucose in the $^4C_1$ conformation, which can be decomposed by microbial and fungal enzymes, but unable to be dissolved in water (Haafiz, Eichhorn, *et al.*, 2013; R. Li *et al.*, 2009). Nowadays, cellulose or cellulose based product has been used in various industries, such as in the paper industry, pharmaceutical industry and also in the automotive industry. Cellulose is the main material for the production of pulp and paper and has been used as the starting material for the production of microcrystalline cellulose (MCC), regenerated cellulose fibers such as rayon, and other cellulose derivatives, especially ester and ether (Sixta, 2006).

In plant cells, cellulose chain molecules are self-assembled by hydrogen bonding into microfibrils, which are contains crystalline and amorphous regions (Fernandes *et al.*, 2011; Nishiyama, 2009). They are four different types of cellulose polymorphs, called as cellulose type I, II, III and IV (Hussin *et al.*, 2016; Isogai *et al.*, 1989; Kontturi *et al.*, 2006). Meanwhile lignin and hemicellulose have only amorphous region in their composition (Rosnah *et al.*, 2009; Zickler *et al.*, 2007). The acid hydrolysis technique refer as a heterogeneous process which has been employed in order to remove the amorphous region and leave behind the insoluble crystalline region referred as microcrystalline cellulose (MCC) (Adel *et al.*, 2011;

Haafiz, Eichhorn, *et al.*, 2013). Acid hydrolysis treatment is able to eliminate and removed the amorphous region in cellulose which consequently increased the crystalline index of MCC without alter the chemical structure and the cellulose composition (Haafiz, Eichhorn, *et al.*, 2013; Trache *et al.*, 2016).

MCC is a white, fine odourless, biodegradable crystalline powder, which is can be effectively isolated through hydrolysis technique from the lignocellulosic fiber materials (Haafiz, Eichhorn, *et al.*, 2013; Hussin *et al.*, 2016). MCC is insoluble in water, dilute acid, renewability and organic solvents as well as good hydroscopicity (J. Li *et al.*, 2014; Merci *et al.*, 2015; Trache *et al.*, 2016). MCC has been used as a suspension stabilizer and water retaining in several dairy compounds, binder and filler in the food, reinforcing agent in polymer and medical Tablets in pharmaceutical industry (Chuayjuljit *et al.*, 2010; El-Sakhawy *et al.*, 2007; Haafiz, Eichhorn, *et al.*, 2013; Trache *et al.*, 2016). MCC displayed high crystallinity index, the crystallization index of MCC was reported as through X-ray diffraction (XRD) analysis of 55 to 80 % (Chuayjuljit *et al.*, 2010; Haafiz, Eichhorn, *et al.*, 2013).

In recent years, MCC has attracted researcher's attention to be used as a potential starting material into cellulose reinforced nanocomposites (de Menezes *et al.*, 2009). Numerous studies have been conducted in order to isolate MCC from various sources which included the extraction of cellulose fibres was carried out from rice husk by alkali and bleaching treatments, which were subsequently converted to nanocrystals using a sulphuric acid (H_2SO_4) hydrolysis treatment (Mathew *et al.*, 2005). Isolation of microcrystalline cellulose has been carried out from jute cellulose by using the same acid hydrolysis (H_2SO_4) approach by Jahan *et al.* (2011). In addition to these isolation studies, characterization of microcrystalline cellulose from oil palm biomass residue has been reported by Haafiz, Eichhorn, *et al.*

(2013). Moreover, the studies shows that acid concentration, fiber to acid ratio, temperature, treatment time and the origin of raw materials are influences the MCC isolation yield as well as overall characteristics (Hussin *et al.*, 2016; Jahan *et al.*, 2011). To date, there is little information have been reported on the optimization of process parameters to produce MCC isolate from OPEFB. The optimization in the experiment is refers to improving the performance of a system, a process, or a product in order to obtain the best system performance without increasing the cost (Bezerra *et al.*, 2008; Salim *et al.*, 2012). Since, there are many variables affecting the process of isolation of MCC, a quantitative assessment of their efficiency is required. In the context of study the optimization of process parameters in producing MCC, response surface methodology (RSM) is one the best approach.

RSM is a collection of mathematical and statistical techniques, which are utilized for creating, enhancing, displaying and investigation of the response, which affected by a few input variables, with the target of optimizing the response (Baş *et al.*, 2007; Bezerra *et al.*, 2008; Myers *et al.*, 2016; Salim *et al.*, 2012). RSM is such a successful statistical method to examine the behaviour of any procedure to assess the impact of a few factors at the same time (Baş *et al.*, 2007; Hossain *et al.*, 2015). The main advantages of this techniques is reduced the number of experiment as well as reduce the cost needed to evaluate multiple parameters and their interactions (Kincl *et al.*, 2005; Salim *et al.*, 2012).

The optimization of acid hydrolysis process parameters focus on achieving the maximum yield of OPEFB-MCC produced with good crystallinity and thermal stability. Several analytical methods such as Scanning Electron Microscope (SEM), Fourier transform infrared spectroscopy (FTIR), Thermogravimetric analysis (TGA), X-ray diffraction (XRD) and Brunauer–Emett–Teller (BET) were utilized to analysed morphological, chemical and thermal properties of the isolated OPEFB-MCC at optimized experimental conditions of the acid hydrolysis process. The optimization of the acid hydrolysis is crucially important for the production of MCC from OPEFB in turn the obtained material has a potential to be used as a green filler for the composite manufacture, consequently will able to reduce the waste produced from oil palm industry especially waste from OPEFB.

1.1 Objectives:

The objectives of this research are:

1. To evaluate the influence of acid concentrations, temperatures and times on yield, thermal stability and crystallinity of MCC isolate from OPEFB by using RSM.

2. To obtain the acid hydrolysis optimum condition of MCC through the RSM.

3. To compare the physicochemical, morphological and thermal stability of optimized MCC with C-MCC.

1.2 Problem statements

1. The production of MCC from OPEFB have been studies before, however there is no information reported on the acid hydrolysis concentration, temperature and time. The aforementioned variables will affect the overall characterization of mcc include yield, thermal stability as well as crystallinity.
2. Therefore the optimization process is required, since there are many variables. RSM is one of the best approach to reduce the number of experiment as well as the cost. It also will help to provide the optimum condition in isolation of MCC.

CHAPTER 2

LITERATURE REVIEW

2.1 Oil palm tree

The oil palm tree (*Elaeis guineensis*) is one of the largest agriculture plants in Malaysia. It's originated from West Africa where it was growing and later developed into an agricultural crop (Hashim *et al.*, 2010). Climatic conditions which are hot and humid throughout the year make oil palm cultivation suitable in Malaysia. The climatic condition was important factor in growing oil palm, because oil palm tree need high-rainfall, low-lying areas, a zone naturally occupied by moist tropical forest, wet and humid tropical conditions with high rainfall rate (2.0 mm) the most biologically diverse terrestrial ecosystem on Earth (Chuah *et al.*, 2006; Fitzherbert *et al.*, 2008; Yusoff, 2006).

Figure 2.1 The Oil Palm Tree

Oil palm trees consist of two different species which is *Elaeis guineensis* and *Elaeis oleifera* (Baudouin *et al.*, 1997). *Elaeis guineensis* are mainly grown in oil palm plantations in Malaysia. It is a monecious species belonging to the palm subfamily Arecoideae. The variety is mainly a combination between the dura and pisifera, also known as tenera range (Awalludin *et al.*, 2015; H. Zulkifli *et al.*, 2010). This plant has both male and female functions flowers on the same plant in the alternating cycle. In the way, opportunities for self-pollination can be reduced (Adam *et al.*, 2011; Awalludin *et al.*, 2015). In term of morphology, similar to other palm species, palm trees is the height of a single plant. The stems can reach up to 20-30m in mature (Edem, 2002). The oil palm classification was summarized in Table 2.1.

Table 2.1 Oil palm tree classification

Kingdom	Plantae
Sub-kingdom	Tracheopionta
Division	Angiospermae
Class	Monocotyledons
Subclass	Arecidae
Order	Arecales
Family	Arecaceae
Genus	Elaeis

Oil palm tree was first introduced to Malaysia in early 1870's, as an ornamental plant by British during those days reported by Basiron (2007) and the first commercial oil palm estate in Malaysia was set up at Tennamaran Estate, Selangor in 1917, laying the foundations for the industry in Malaysia. (Basiron *et al.*, 2004; Sulaiman *et al.*, 2012). In early the 1960s, the cultivation of oil palm quickly increased in the beginning of sixties under the government's agricultural diversification program which was established to lessen the country's economic dependence on rubber and tin sources.

In late the 1960s, the government introduced land settlement schemes for planting oil palms as a means to eradicate poverty for the landless farmers and smallholders. The oil palm plantations in Malaysia are based on the estate management system and smallholders' scheme. The Malaysian government decided to penalize the export of crude palm oil (CPO) with high export price in late 1970, and it improves the profitability of the refining sector (Awalludin *et al.*, 2015).

Figure 2.2 The empty fruit bunch oil palm fiber

The statistics showed that Malaysia has only 54,000 hectares of oil palm plantations in 1960. To date, the total area under oil palm cultivation is over 5.39 million hectares was recorded in 2014. It increased 11.0 % from the previous total area under oil palm cultivation in 2010 which is 4.85 million hectares as shown in Figure 2.3. The oil palm tree plantation cover more than 16 % of the land in Malaysia, since total landmass in Malaysia is 32.98 million (Awalludin *et al.*, 2015; Basiron *et al.*, 2004; Shafie *et al.*, 2011)

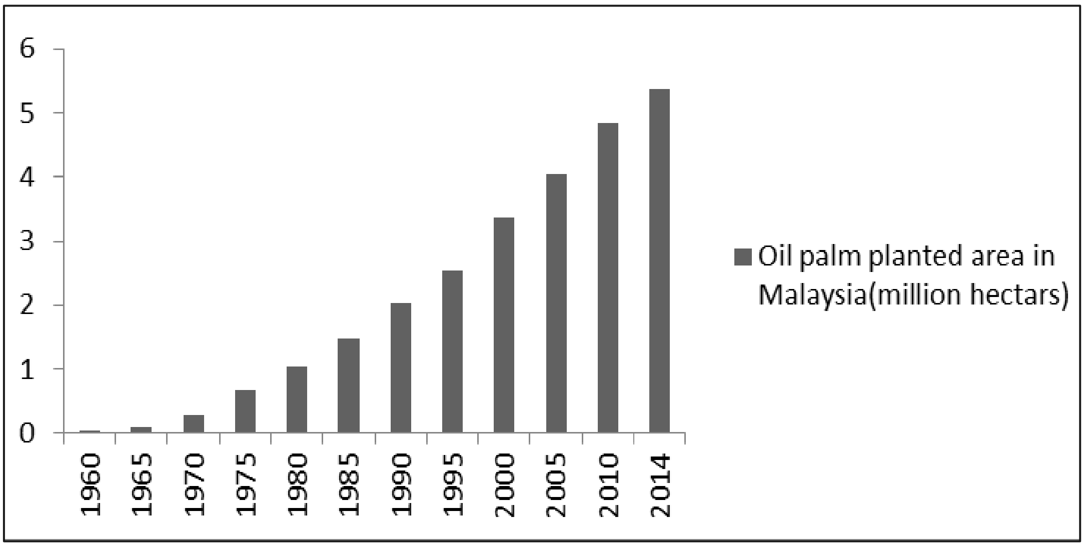

Figure 2.3 The expansion of oil palm cultivation area in Malaysia from 1960 until 2014 (Awalludin *et al.*, 2015)

2.2 Oil palm in Malaysia

In 1971 the oil palm tree (*Elaeis guineesis*) was introduced as a the main agricultural crop in Malaysia and has become the key crop to the national economic expansion (Awalludin *et al.*, 2015; Hashim *et al.*, 2010). Malaysia is one of the countries that are favourable benefit from the palm oil industry and responsible for the rise of this industry globally through huge contributions and continuous commitment. For decades, Malaysia has held title as one of the most productive of palm oil producers (Sayer *et al.*, 2012). However in 2007, Indonesia overtook Malaysia due to the rapid expansion of oil palm plantations in the region. Even so, Malaysia still holds the title as the world's leading crude palm oil exporter (Awalludin *et al.*, 2015). The sum of palm oil supplied by Malaysia and Indonesia is more than 80 % of the global annual oil supply (Amiruddin *et al.*, 2005; Mazaheri *et al.*, 2010).

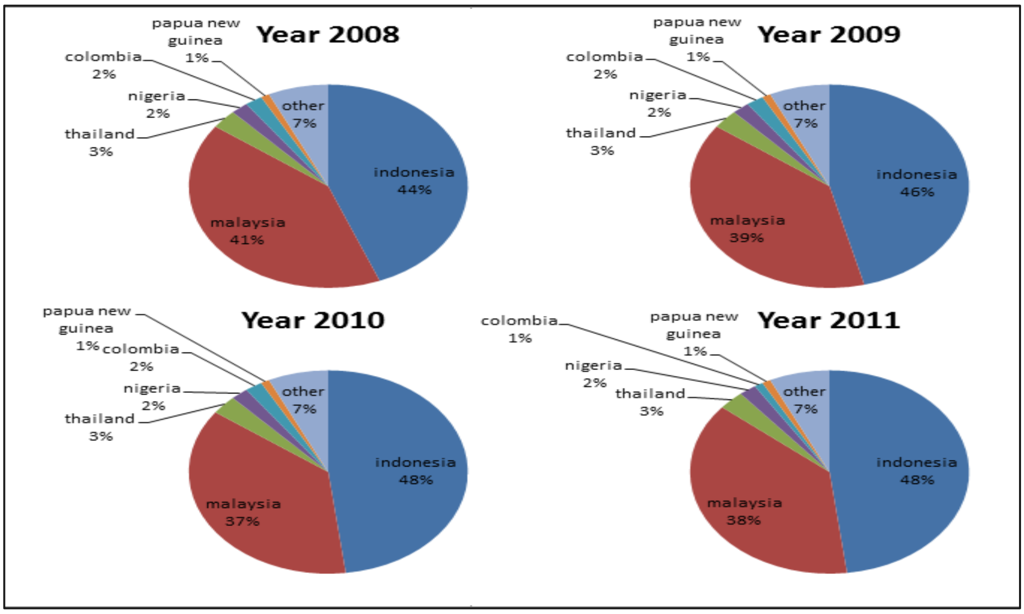

Figure 2. 4 World's top palm oil producers from 2008 to 2011 (Awalludin *et al.*, 2015; Sulaiman *et al.*, 2012)

The Figure 2.4 shows the distribution of world's largest palm oil producers from 2008 until 2011. The estimated world productions of palm oil in 2008 to 2011 were 42.9, 45.3, 45.9 and 49.9 million tonnes respectively (Sulaiman *et al.*, 2012). Overall, Malaysia recorded an increase in palm oil production regardless of several years of drop in the total output of palm oil production compared to the previous years. The amounts of palm oil produced in Malaysia between the year of 2000 and 2014 as shown in Figure 2.5. From 2000 to 2014 the production of oil palm increase at 8.84 %.

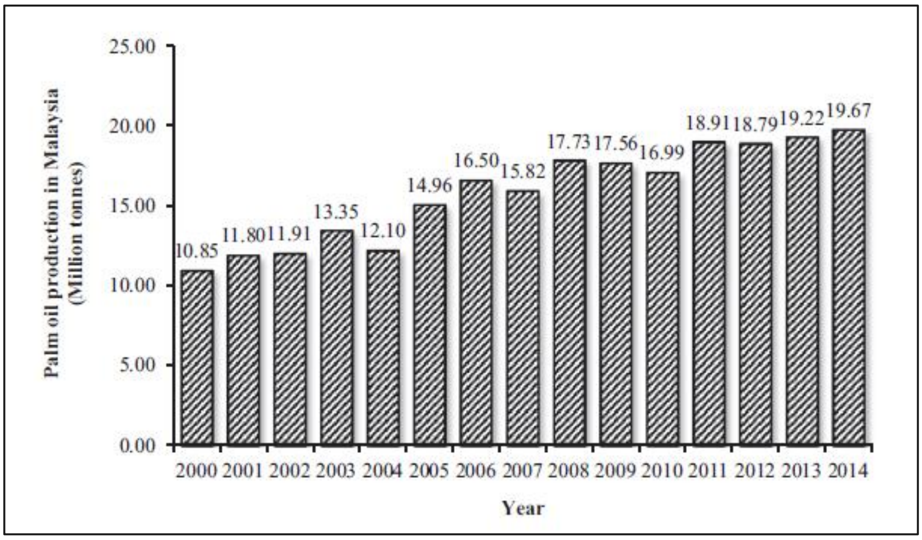

Figure 2.5 Palm oil production in Malaysia (Awalludin *et al.*, 2015)

2.2.1 The oil palm biomass

The economic life span of oil palm trees is about 25 years before the trees are cut for replanting process. During the replanting huge amount of oil palm biomass waste is generated (Salim *et al.*, 2012). In the case of the oil palm industry, the solid biomass wastes are generated in two ways (Awalludin *et al.*, 2015). First, it comes from the oil palm plantations where the wastes are in the form of harvested trunks and pruned fronds. Oil palm fronds (OPF) are available continuously as a result of pruning activity during fruit harvesting; while oil palm trunks (OPT) are available during replanting process. Second, it comes from the palm oil extraction mills, which included oil palm empty fruit bunch (OPEFB), mesocarp fiber (MF) and palm kernel shell (PKS). The OPEFB are generated after the fresh fruit bunches have been pressurized cooked and stripped from the bunch for the oil extraction purpose. The MF is produced during the palm oil extraction process, while the PKS are obtained after the process of nut separation from its kernel.

From the Figure 2.6, it show in the palm oil mill, oil consist only 10 % of the total biomass and the rest was discarded as biomass wastes (Awalludin *et al.*, 2015). In average, to produce one tonne of crude palm oil, it required five tonnes of fresh fruit bunches as reported by Stichnothe *et al.* (2011). According to Shuit *et al.* (2009), 50-70 tonnes of biomass waste can produced from 1 hectare of oil palm plantation. In 2009, it was estimated about 77.3 million tonnes of oil palm biomass were generated by Malaysian oil palm industry (F. Y. Ng *et al.*, 2012).

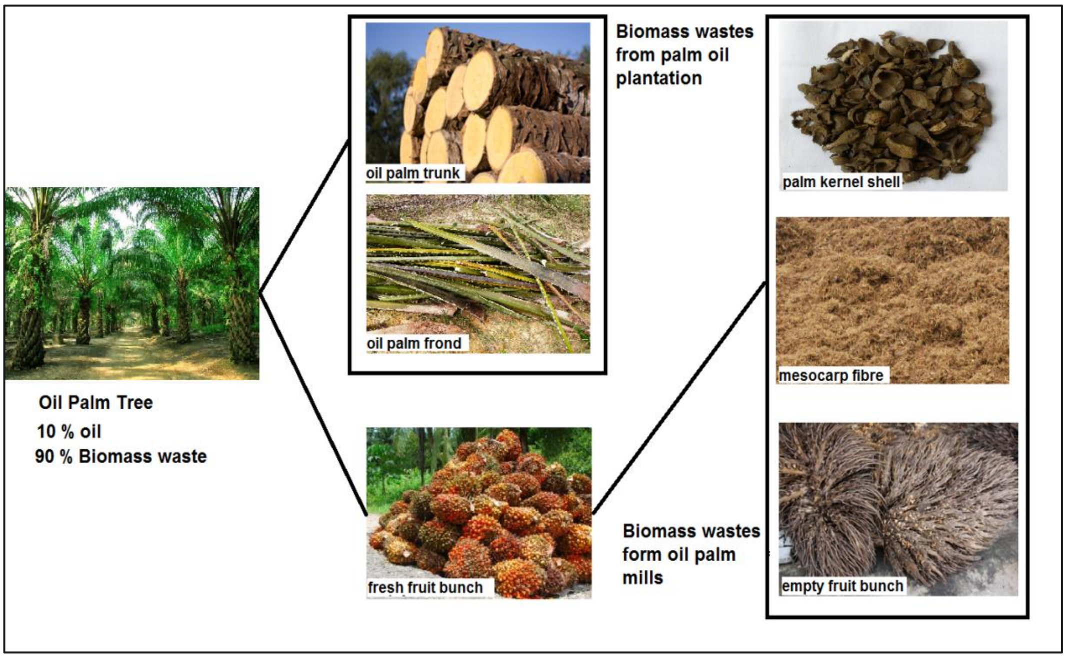

Figure 2.6 The oil palm biomass (Awalludin *et al.*, 2015)

The availability of dry oil palm biomass in Malaysia in 2009 is shown in Figure 2.7. It shows that the fronds contribute the highest amount of dry weight followed by trunks, oil palm and shells, and empty fruit bunches which are 44.8, 13.9, 11.6, and 7.0 million tonnes respectively. The OPEFB are available in a lower amount as compared to other biomass, however the cellulose content in OPEFB is the highest. Due to the high cellulose content, it has been used as a raw material in many research related to the cellulose product industry. The by-products from palm oil, if not able to be utilised and managed properly, will impose the disposal problem to the oil palm mill. In 1980, depending on the type of residue, oil palm residues were used as much, boiler fuel, or as fertiliser in the fields to reduce the environment impact paving the way toward a zero-waste policy (Abdul Khalil *et al.*, 2008).

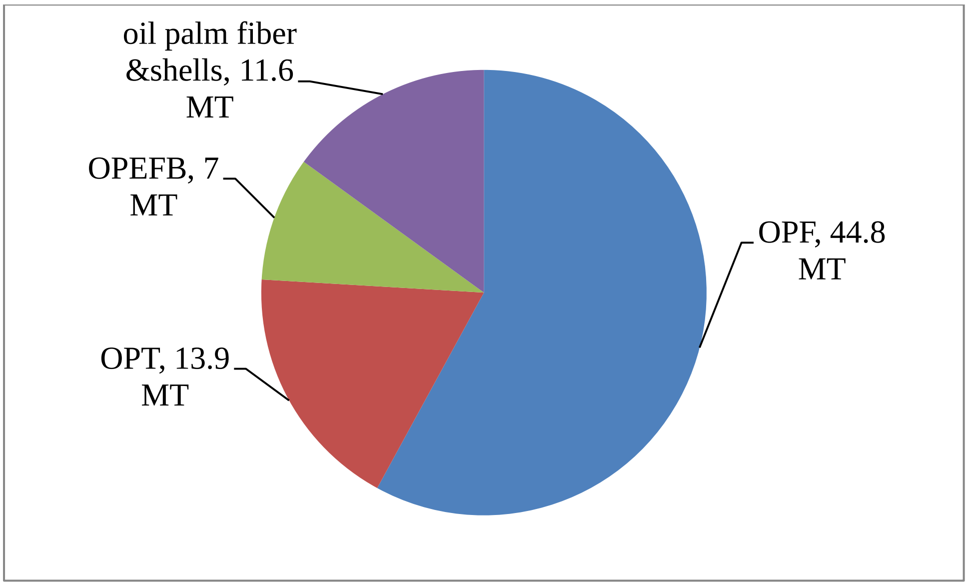

Figure 2.7 Availability of dry oil palm biomass in Malaysia in 2009 (MT= Million Tonnes) (F. Y. Ng *et al.*, 2012)

The economic life cycle of the oil palm tree is about 25 years. However, the main economic criteria for felling (with the purpose for replanting) are the height of palm which reaches 13 m and above and annually yield of bunches falling below 10 to 12 tonne per hectare. This felling activity under the project of replanting produces a large quantity of lignocellulosic by-product, in the form of stem, as well as frond (Sumathi *et al.*, 2008).

The oil palm tree is classified as a carbon neutral element, because it produces the same amount of carbon released with the amount of carbon absorbed in lifetime if it been utilized through combustion or decompose (Awalludin *et al.*, 2015). As it is known, 90 % from palm oil mill are discarded as a waste. The lack of technology use to utilize the oil palm waste make the remaining wastes can worsen the biomass overload problem. This problem is not only happen in Malaysia but in all state have oil palm plantation, over than 190 million tonnes of liquid and solid residues are being produced by palm oil industry in the world case (Lee *et al.*, 2013).

2.2.2 Oil palm empty fruit bunch (OPEFB)

OPEFB is one of the by-products produced from oil palm factory after palm oil has been extracted. OPEFB is a lignocellulosic source which is available for the in cellulose production. OPEFB is usually being burned in incinerators of palm oil mills and it will cause environmental pollution (Rahman *et al.*, 2007). This material is available in abundance as fibrous material from purely biological origin. OPEFB is considered as a valuable biomass residue which can be converted not only into energy (which is currently its major use), but also as a raw material for the product on of higher value product such as panelling and composites, fine chemicals, pulp and paper as well as compost and bio-fertilizer (Wanrosli *et al.*, 2004). OPEFB contains neither chemical nor mineral additives, and depending on proper handling operations at the mill, it is free from distant elements such as gravel, nails, wood residues, waste etc. However, it is saturated with water due to the biological growth combined with the steam sterilization at the mill. Since the moisture content in OPEFB is around 67 %, pre-processing is necessary before OPEFB can be considered as a good fuel (Anonymous, 2015b). OPEFB have three larger components which make up of 16.92 % lignin, 60.6 % cellulose and 24.15 % hemicellulose (Wanrosli *et al.*, 2004).

In general, utilization of biomass in lignocellulosic composite might attribute to several advantages such as having low density, greater deformability, less abrasiveness to equipment, biodegradable and low cost (Rozman *et al.*, 2004). Through the initial review it is believed as a profitable method in producing innovative products, from OPEFB. Now there are varieties products produced from

OPEFB, such as in food packaging, pulp, fertilizer and medium density fiber board and for energy purpose such as ethanol, and biodiesel bio-methane (Basiron *et al.*, 2004). One of the reasons for the utilization of this material is due to the highest cellulose contains as well as lignin and hemicellulose.

2.3 Cellulose

Cellulose (Figure 2.8) is ubiquitous and renewable natural biopolymer, which is considered as one of the most important organic compounds produced in the biosphere. It is biosynthesized by a number of living organisms ranging from lower to higher plants, sea animals, bacteria and fungi (Brinchi *et al.*, 2013; Klemm *et al.*, 2011; Lavoine *et al.*, 2012; Ummartyotin *et al.*, 2015). Its remarkable reinforcing capability, excellent mechanical properties, low density and environmental benefits have drawn the attention of scientists to utilize cellulose to develop environmentally friendly polymer composites or green composites (Eichhorn *et al.*, 2010). cellulose is a linear homopolymer of glucose $(C_6H_{10}O_5)_n$ with repeating units consisting of d-glucose in a $^4C_1$ conformation, which is insoluble in water but degradable by microbial and fungal enzymes (R. Li *et al.*, 2009).

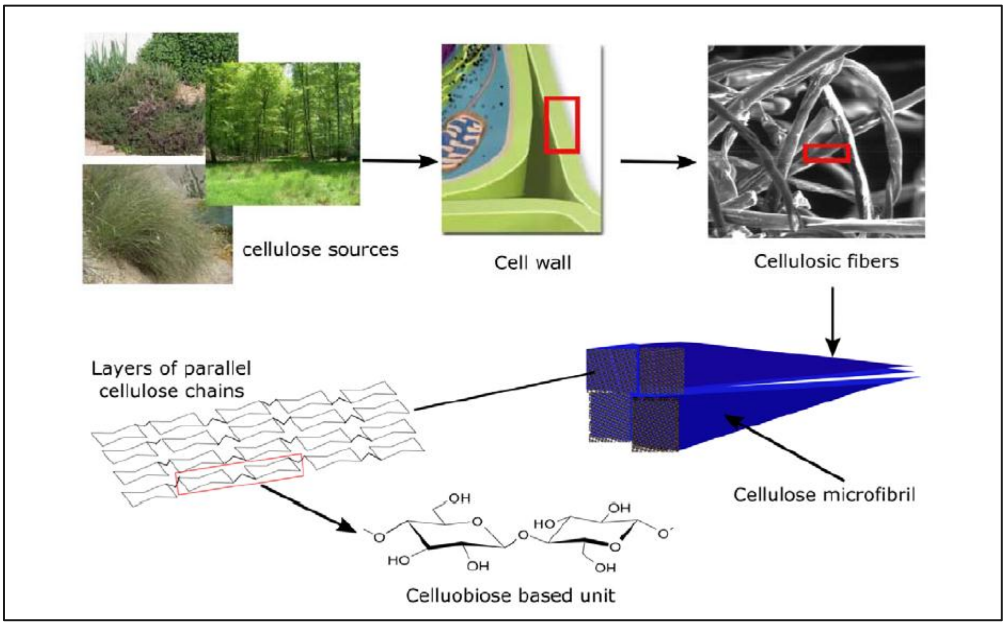

Figure 2. 8 The schematic diagram of cellulose: From the source to structure molecule (Trache *et al.*, 2016)

In nature, cellulose molecular chains are biosynthesized and self-assembled into microfibrils, which are composed of crystalline and amorphous domains (Fernandes *et al.*, 2011; Nishiyama, 2009). Cellulose is mainly used to produce paperboard and paper. Smaller quantities are converted into a wide variety of derivative products such as cellophane and rayon. Conversion of cellulose from energy crops into biofuels such as cellulosic ethanol as an alternative fuel source. For industrial use cellulose is mainly obtained from wood pulp and cotton material (Klemm *et al.*, 2005).

Cellulose can be effectively obtained from a top-down approach, in which wood, cotton, annual plant or other agricultural residues can be used to produce a desired size of cellulose; or from a bottom-up approach, where cellulose is biosynthesized from glucose using bacteria such as Acetobacter Xylinum. The amounts and the properties of cellulose depend on the extraction process, the origin and the lifetime of the natural source (Trache *et al.*, 2016). Commonly, these sources are composed of cellulose, hemicellulose, lignin, extractives and trace elements. In their cell walls, the spirally oriented cellulose plays the role of reinforcements in a soft hemicellulose and lignin matrix. An effective removal process of hemicellulose, lignin and other impurities will generate pure cellulose. As it is well known, cellulose has no taste, hydrophobic, odourless, chiral, renewable and biodegradable. However due to insoluble in water and in most organic solvents, which leads to a limitation in its reactivity and process ability for utilization of cellulose materials (Azeh *et al.*, 2012).

2.3.1 Cellulose chemistry

This biopolymer gained a remarkable place in the annals of polymers. As early as 1839, the French Chemist Anselme Payen coined the name “cellulose” for a white powder that he isolated from plan tissue (Habibi *et al.*, 2010; Siqueira *et al.*, 2010). In 1920, the chemical structure of cellulose was determinated by Hermann Staudinger (Borges *et al.*, 2014; Hokkanen *et al.*, 2016). The cellulose is a linear carbohydrate polymer with long chains of β-(1→4)-linked D-anhydroglucopyranose moieties repeat units (Figure 2.9). It is called as a polysaccharide because cellulose was made up of sugar monomers (Klemm *et al.*, 2005).

The size of cellulose molecules is commonly conveyed as degree of polymerization (DP), which states size as terms of the number of anhydroglucose units per cellulose chain. In nature, the DP of cellulose chains ranges from 100 for microcrystalline cellulose (MCC) to 15,000 in native cotton in relation to their isolation method (Klemm *et al.*, 2005). Each monomeric unit, in cellulosic chain, contains three hydroxyl groups, primary hydroxyl in the methylol group (–CH_2OH) at C-6 and secondary hydroxyl groups (–OH) at C-2 and C-3 of the anhydroglucose unit (O'Connell *et al.*, 2008).

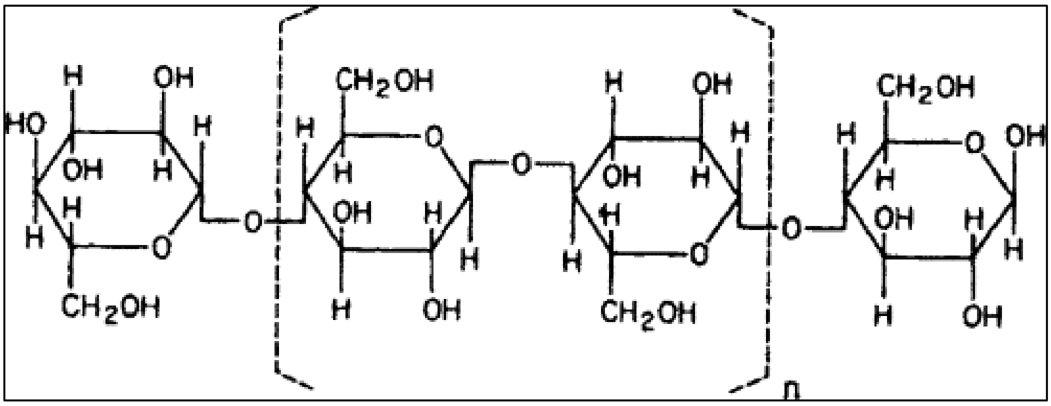

Figure 2. 9 Chemical structure of cellulose chain

The ability of these OH groups to form hydrogen bonds plays a key role in controlling the physicochemical properties and also directing the ultrastructure of cellulose. The cellulosic chains (20–300) are bundled together to generate microfibrils, which are jointly grouped to form cellulose fibers. Each polymeric chain is asymmetric possessing two different end-units, a reducing and a non-reducing end. The reducing end has carbonyl functionality, and the non-reducing end features a supplementary OH-group in position C-4. Hydrogen bonds within a cellulose chain hinder the free rotation of the rings along their linking glycoside bonds, resulting in stiffening of the chain (Trache *et al.*, 2016; Yaman, 2004).

The inter chain hydrogen bonds and the van der Waals interactions lead to the ordered (crystalline) or the disordered regions (amorphous) of the cellulose structure. This biopolymer exists in different polymorphs, differing in unit cell dimensions, in geometry, in chains orientation and polarity (Klemm *et al.*, 2005; Wertz *et al.*, 2010; Yaman, 2004). Cellulose has four different polymorphs, named cellulose type I, II, III and IV (Hussin *et al.*, 2016). In nature, cellulose is established in the crystalline form cellulose I, consisting of a mixture of cellulose Iα (triclinic structure) and Iβ (monoclinic structure). It can be transformed irreversibly into the thermodynamically most stable cellulose II polymorph using a mercerization process (e.g. treatment with concentrated sodium hydroxide solution) or precipitated (regenerated) from solution. Four other crystal polymorphs of cellulose (II_{II}, III_{II}, IV_{I} and IV), in addition to the cellulose I and cellulose II, can be produced by different treatments. Within the framework of this review, only native cellulose I is considered. This semi crystalline fibrillar structure is the main source of microcrystalline cellulose and responsible for the mechanical properties due to its high modulus and crystallinity (Trache *et al.*, 2016).

2.4 Microcrystalline cellulose (MCC)

Microcrystalline cellulose (MCC) is a fine, white, odourless, crystalline powder and biodegradable material that can be isolated from cellulose (Haafiz, Eichhorn, *et al.*, 2013). MCC can be isolated from any type of fibre with high cellulose content (Trache *et al.*, 2016). The isolation of microcrystalline cellulose particles can be done via mechanical treatments (Hanna *et al.*, 2001), biological treatments (Adel *et al.*, 2011) and chemical treatments; for example acid hydrolysis (Haafiz, Eichhorn, *et al.*, 2013; Hussin *et al.*, 2016; Trache *et al.*, 2014). MCC showed a high degree of crystallinity as determined by X-Ray diffraction (XRD) which is typically from range 55 to 80 % (Chuayjuljit *et al.*, 2010). It was said that MCC obtained from different origins and hydrolysis conditions would differ in their crystallinity, moisture content, surface area, porous structure, particle size and molecular weight (de Menezes *et al.*, 2009). Due to its excellent properties, MCC has generated much attention and interest during these few last decades in both academic and industrial fields. MCC has great applications for examples as a water-retainer in medical industries (El-Sakhawy *et al.*, 2007), a direct compressor in development of tablets and soluble drugs in pharmaceutical field (Chamsai *et al.*, 2013), a stabilizer, emulsifier in several dairy compounds (Galal *et al.*, 2010), a reinforcing agent in polymers (H.-M. Ng *et al.*, 2015) and a green adsorbent (Hussin *et al.*, 2016).

Features like lightness, stiffness, strength, fibrous nature, non-toxicity, water insolubility, crystallinity, biodegradability and renewability make MCC more attractive to be used in various industrial fields (Haafiz, Hassan, *et al.*, 2013; Ma *et al.*, 2008; Merci *et al.*, 2015; N. I. Zulkifli *et al.*, 2015).

2.4.1 Sources of Microcrystalline cellulose

MCC can be isolated from any cellulosic material especially material high with cellulose content (Trache *et al.*, 2016). Wood and cotton are the main industrial sources and the important feedstock in MCC production (Leppänen *et al.*, 2009; Shcherbakova *et al.*, 2012; Thoorens *et al.*, 2014). However, competition between various fields such as furniture, pulp and paper, building products and burning wood for energy and the production of cotton for textiles industry, causing them challenging to provide all sectors with the required quantity of wood and cotton with an appropriate price (Trache *et al.*, 2016). In addition, wood and cotton are not available in many regions, thus tuning options for non-woody cellulose. Usually, the non-woody plants comprise less lignin than wood and it can influence the cost of production because less chemical use in bleaching process and energy demanding during production. MCC obtained from different type of cellulose source and hydrolysis condition commonly differ in their crystallinity, particle size, moisture content, surface area, porous structure and molecular weight (de Menezes *et al.*, 2009; Trache *et al.*, 2014). The sources and crystallinity index of MCC from different source was summarize in Table 2.2.

Table 2.2 The sources of MCC and crystallinity index

Sources	Reflection at 2θ (˚)	CrI (%)	L(nm)	References
Baggsse-MCC	18.26	76	4.42	(El-Sakhawy *et al.*, 2007)
Rice straw - MCC	18.26	78	3.97	(El-Sakhawy *et al.*, 2007)
Cotton stalk - MCC	18.26	77	5.31	(El-Sakhawy *et al.*, 2007)
Commercial-MCC	18.26	78	5.52	(El-Sakhawy *et al.*, 2007)
Jute-MCC	13.17,21.31	83	N/A	(Das *et al.*, 2010)
Cotton silver - MCC	3.51, 22.6	80	N/A	(Das *et al.*, 2010)
Rice hulls-MCC	18.26	87	5.77	(Adel *et al.*, 2011)
Bean hulls - MCC	18.26	90	9.07	(Adel *et al.*, 2011)
Commercial-MCC (cotton)	18.26	85	7.94	(Adel *et al.*, 2011)
Jute-MCC	22	74	N/A	(Jahan *et al.*, 2011)
Cotton linters-MCC	15.2, 22.6	77	N/A	(Terinte *et al.*, 2011)
Corn cob-MCC	12.5, 20.4	73	N/A	(Azubuike *et al.*, 2012)
Groundnut shell -MCC	15.0, 16.6, 22.4	74	N/A	(Azubuike, 2012)
OPEFB-MCC	19, 22.6	87	N/A	(Haafiz, Eichhorn, *et al.*, 2013)
Oil palm frond-MCC	16, 21.7	71	N/A	(Hussin *et al.*, 2016)
Commercial-MCC (cotton)	19, 22.6	79	N/A	(Haafiz, Eichhorn, *et al.*, 2013)
Fodder grass - MCC	20.35, 22.3	80	N/A	(Kalita *et al.*, 2013)
Alfa-MCC	15.2, 16.8, 22.6	73	5.02	(Trache *et al.*, 2014)
Commercial-MCC (cotton)	15.2, 16.8, 22.6	81	5.25	(Trache *et al.*, 2014)

2.4.2 Isolation process of microcrystalline cellulose

There are various methods that can be used for the extraction of cellulose from plants by using chemical, physical, and biological processes combined (Trache *et al.,* 2016). Generally, the hydrolysis treatment is the common method used to isolate MCC from cellulose, this treatment generally followed by neutralization, washing and drying processes. For lignocellulosic materials, it involves firstly the removal of lignin, hemicellulose, etc. and isolation of cellulosic fibers. Secondly, a controlled hydrolysis treatment (generally acid hydrolysis) to remove the amorphous regions of the cellulose polymer; and finally, post-treatments were performed to recover the final MCC product. Besides that, several processes can be used for isolation of MCC, such as alkali hydrolysis, steam explosion, extrusion and radiation-enzymatic(Haafiz, Eichhorn, *et al.*, 2013; Trache *et al.*, 2016). It is well known that the physicochemical, mechanical and morphology properties of MCC exhibit according to the origin of the raw material and isolation process (Hussin *et al.,* 2016).

Among the isolation process acid hydrolysis is the most common method for industrial microcrystalline production because of a lower in price and a higher degree of crystallinity as compared to other isolation method (Haafiz, Eichhorn, *et al.*, 2013; J. Li *et al.*, 2014; Trache *et al.*, 2016).

2.4.2(a) Acid hydrolysis

The typical process widely used for the isolation of crystalline region from cellulose in the form of MCC is by using acid hydrolysis because it requires less reaction time as compared to other technique such as alkali hydrolysis, steam explosion, extrusion and radiation-enzymatic (Trache *et al.*, 2016). The preparation of MCC was first reported and patented by Battista and Smith under American Viscose Corporation (Battista, 1950). They had isolated MCC fibers by controlled acid hydrolysis of cellulosic fibers to a level-off degree of polymerization (LODP). The principle of national approach was to pass dilute cellulosic pulp-water suspension through a mechanical homogenizer, in which small fragments of the agglomerated microcrystals were finally obtained.

Broadly, cellulose microfibrils are composed of crystalline regions and amorphous domains located at the surface and along their main axis. Upon contact with acidic solutions, the amorphous regions are preferentially cleaved; whereas the crystalline domains that have a higher resistance to acid attack remain essentially intact (Pääkkö *et al.*, 2007; Trache *et al.*, 2016). It is worth mentioning that the diameter of these MCC fibers which usually varies from around 30 nm to 20 μm in diameter and up to hundred microns in length is widely determined by their source and the isolation process (de Menezes *et al.*, 2009; Hussin *et al.*, 2016; Trache *et al.*, 2016). The schematic diagram of MCC separation during acid hydrolysis was show in Figure 2.10. During acid hydrolysis, acid solution either hydrochloric acid (HCl) or sulphuric acid (H_2SO_4) penetrates the disordered amorphous region prior to crystalline region and cleaves the glycosidic bond. As a result, the proportion of highly organized crystalline regions and crystal dimensions increased apparently (Adel *et al.*, 2010).

Numerous researchers had investigated the influence of processing conditions on the physicochemical, thermal and mechanical properties. The temperature and time of hydrolysis procedure, nature and concentration of acid as well as the fiber-to-acid ratio play the important roles in the particle size, morphology, crystallinity, thermal stability and mechanical properties of MCC (Adel *et al.*, 2011; El-Sakhawy *et al.*, 2007; Hussin *et al.*, 2016).

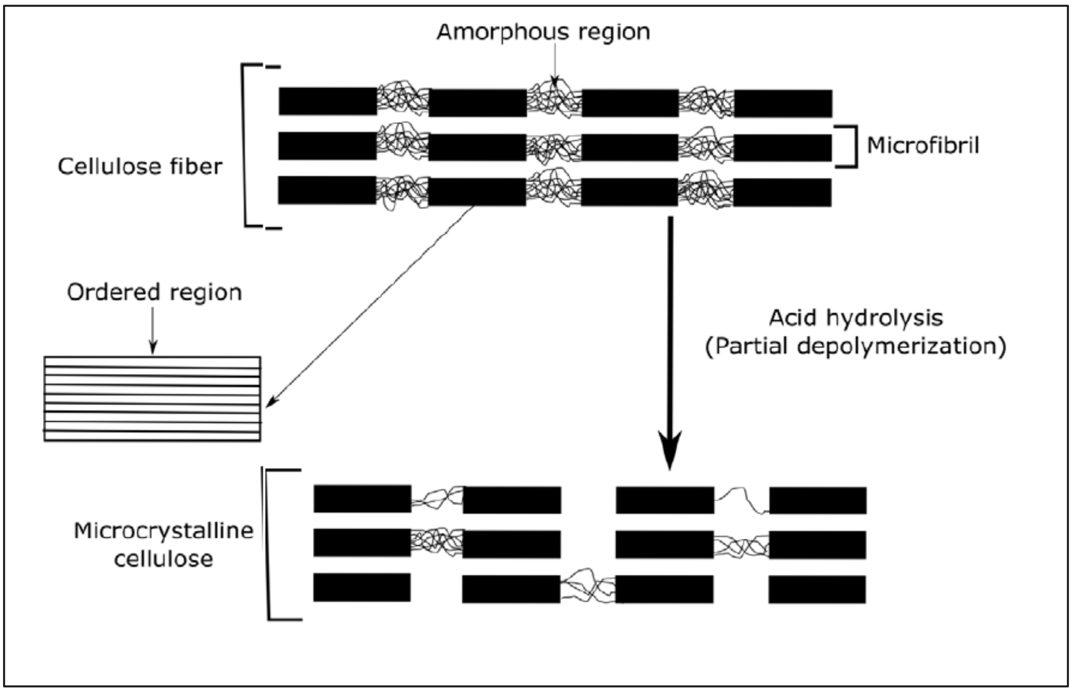

Figure 2.10 Schematic diagram of microcrystalline cellulose separation during acid hydrolysis (Trache *et al.*, 2016)

2.4.2(b) Alkali hydrolysis

Alkali hydrolysis is the second used in delignification method of lignocellulosic materials (Kaith *et al.*, 2011; Miao *et al.*, 2013). This method was applied to remove the lignin structure and to make separation of the linkages between lignin and carbohydrates. Some researcher uses the alkali hydrolysis to produce MCC in order to overcome some problem caused by acid hydrolysis process (Trusovs, 2002). This process does not involve high temperature or high pressure application and it produce MCC economically effective manner utilizing readily available chemical and cellulose material. A few years later, the alkali process was joined with acid treatment (Nguyen, 2006). This method employs less alkali and acid than previous processes and it is a simple, economical and environmentally friendly process. However, it is important to note that the employment of this process needs to be carefully controlled to avoid undesirable cellulose degradation so that intact MCC can be isolated (Trache *et al.*, 2016).

2.4.2(c) Stem explosion

The steam explosion process has been and has always been widely investigated as a promising mechanical pulping technique. It offers many attractive features compared to other technologies for examples lower capital investment, lower environmental impact, fewer hazardous process chemicals and conditions, and more potential for energy efficiency. In 1927, this process was invented by Mason as a process to produce fibers for board production. This process was treated lignocellulose raw material in the steam explosion in two steps, within the steam-treated lignocellulose from the first step is being extracted to recover a low degree of polymerization cellulose and during the second steam process, it was saturated with strong mineral acid to obtain MCC.

The method was patented by Ha and Landi in 1998 was a very interesting process using an only one-step steam explosion treatment process without the need for conventional acid hydrolysis as a supplement to steam treatment (Ha *et al.*, 1998). In this process, MCC was obtained by introducing a cellulose source material into a pressurized reactor; subjecting the cellulosic material to a steam explosion treatment under controlled conditions. As reported earlier by other researcher that the steam explosion allows to breakdown the lignocellulosic material components by steam heating, shearing forces owing to the expansion of the moisture and hydrolysis of glycosidic bonds by an organic acid formed during the process (Jacquet *et al.*, 2012).