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DEVELOPMENT OF OIL SORBENTS FROM CELLULOSE BY ACETYLATION

Miss Thitima Tanosawan

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ปัญหาน้ำมันหกรั่วไหลส่งผลกระทบต่อสิ่งแวดล้อม สิ่งมีชีวิต และเศรษฐกิจเป็นอย่างมาก ในงานวิจัยนี้จึงศึกษาการพัฒนาวัสดุดูดซับน้ำมัน โดยการนำไส้ของหญ้าปล้องและเส้นใยนุ่นมาทำปฏิกิริยาแอเซทิเลชันกับอะซิติกแอนไฮไดรด์ ในสภาวะซึ่งปราศจากตัวทำละลาย ขอบเขตของปฏิกิริยาแอเซทิเลชันถูกตรวจวัดด้วยค่าความสามารถในการแทนที่ โดยตัวแปรที่ต้องการศึกษา ได้แก่ ปริมาณอะซิติกแอนไฮไดรด์ ปริมาณตัวเร่งปฏิกิริยา อุณหภูมิ และระยะเวลาที่ใช้ในการทำปฏิกิริยา จากการศึกษาพบว่าสภาวะสำหรับการทำปฏิกิริยาแอเซทิเลชันไส้หญ้าปล้องและเส้นใยนุ่นที่ให้ค่าความสามารถในการแทนที่สูงสุด (2.79 และ 2.59) คือที่ปริมาณการใช้อะซิติกแอนไฮไดรด์ 40 และ 80 มิลลิลิตร โดยใช้ 1.5% เอนโบรโมซักซินิไมด์ เป็นตัวเร่งปฏิกิริยาที่อุณหภูมิของการทำปฏิกิริยา 80 องศาเซลเซียส ระยะเวลา 2 ชั่วโมง ตามลำดับ พิสูจน์เอกลักษณ์ของผลิตภัณฑ์ที่ผ่านการแอเซทิเลชันด้วยเทคนิคสแกนนิ่งอิเล็กตรอนไมโครสโกปี อินฟราเรดสเปกโทรสโกปี คาร์บอนแมกเนติกเรโซแนนท์สเปกโทรสโกปี และเทอร์มอลสเปกโทรสโกปี ผลิตภัณฑ์ที่ผ่านการทำปฏิกิริยาแอเซทิเลชันมีความสามารถในการดูดซับน้ำมันมากกว่าผลิตภัณฑ์ที่ยังไม่ได้ผ่านการทำปฏิกิริยา โดยไส้หญ้าปล้องที่ผ่านการทำปฏิกิริยาแล้วมีความสามารถในการดูดซับน้ำมัน 7.46, 7.61 และ 7.70 กรัมน้ำมันต่อกรัมวัสดุดูดซับ สำหรับน้ำมันจักร น้ำมันเครื่องยนต์และน้ำมันบังเกอร์ซี ตามลำดับ ซึ่งมีค่าใกล้เคียงกับวัสดุดูดซับตามท้องตลาด ในขณะที่เส้นใยนุ่นหลังทำปฏิกิริยามีความสามารถในการดูดซับน้ำมันมากที่สุดที่ 76.72, 76.74 และ 79.89 กรัมน้ำมันต่อกรัมวัสดุดูดซับ ดังนั้นจากการศึกษานี้แสดงให้เห็นว่าวัสดุดูดซับน้ำมันดังกล่าวนี้สามารถใช้แทนที่วัสดุดูดซับน้ำมันที่ไม่สามารถย่อยสลายทางธรรมชาติได้ สำหรับการทำความสะอาดน้ำมันที่หกรั่วไหล

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THITIMA TANOSAWAN: DEVELOPMENT OF OIL SORBENTS FROM CELLULOSE BY ACETYLATION. ADVISOR: ASSOC. PROF. SUPAWAN TANTAYANON, Ph.D., 79 pp

Oil spills impose a global impact on the environment, living organisms and economy. This study attempted to develop materials for oil spill cleanup from acetylation of jointed grass pith and kapok fiber with acetic anhydride in solvent free system. The extent of acetylation was quantitatively determined using the degree of substitution (DS), which varied acetic anhydride content, amount of catalyst, reaction temperature and reaction time. The results showed that acetylated jointed grass pith and acetylated kapok fiber with high degree of substitution (DS=2.79 and 2.59) were achieved with 40 and 80 mL of acetic anhydride, 80°C, 2.0 hours of reaction time using 1.5% *N*-bromosuccinimide (NBS) as a catalyst. The characterization of the acetylated products was evaluated by SEM, FT-IR, ^{13}C-NMR and TGA. The acetylated product showed high sorption capacity than the non-acetylated ones. The acetylated jointed grass pith had the same oil sorption capacity as commercial sorbent at 7.46, 7.61 and 7.70 g oil/g sample for machine oil, motor oil and Bunker C, respectively. While acetylated kapok had much higher oil sorption capacity at 76.72, 76.74 and 79.89 g oil/g sample. Accordingly, the acetylated kapok fiber can be the alternative oil sorbent to substitute the non-biodegradable materials for oil spill clean up.

Field of Student: Petrochemistry and Polymer Science Student's Signature..........................
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LIST OF ABBREVIATIONS

°C : Degree Celsius

h : Hour

g : Gram

mg : Milligram

cm^{-1} : Wavenumber

cP : CentiPoise

S_0 : Initial dry sorbent sample weight

S_W : net water sorption

S_{WT} : weight of sorbent sample at end of water test

S_S : Net oil sorption

S_{ST} : Weight of sorbent sample at end of oil test

CHAPTER I

INTRODUCTION

1.1 Introduction

Oil is one of the most important energy sources in the world. Nowadays the oil demand is rising. This results in continued development of oil industry. There is always a risk of oil spillage to land, river and ocean due to accidents, equipment and tanker breaking, human's intention, wars or natural disasters (such as hurricanes or earthquakes) when oil is explored, refined, transported, stored and used. Oil spill into ocean is a major environmental problem. Oil covering on ocean surface can cause significant environmental impact. Oil pollution affects marine and coastal ecosystem, natural resources and tourism. Therefore, it is necessary to remove the spilled oil as quickly as possible. There are several approaches for oil spilled management, however, those methods are expensive, complicated and sometimes have an impact on the environment, for example using chemicals such as oil dispersant, oil gelling agent, oil spills skimmers or oil spills boom. Generally the popular method for cleanups and collecting the spilled oils is to use oil sorbents because they are inexpensive, easy to used and have a quick uptake property.

Oil sorbent materials can be classified into three types which are inorganic mineral products, organic synthetic products and organic natural products. Synthetic sorbents such as polypropylenes (PP) are the most popular oil sorbent materials among other types. However, there is a disadvantage of this type of material, these materials degrade very slowly or sometimes non-degradable which can cause the environmental problem.

In recent years, biodegradable or organic natural products such as rice husk, sawdust, corn cob, sugarcane bagasse, straw, bark, milkweed, kenaf, and kapok [1-3] are of interest to use as oil sorbents. These materials are agricultural residues which are accessible and inexpensive. Among these materials, rice straw, corn cob, and wood fiber have poor oil sorption capacity while milkweed, cotton and kapok have greater oil sorption capacity.

The main component of these agricultural products is cellulose. The polar hydroxyl groups on the surface of cellulose materials have forming a well hydrogen bonds with water, leads to high water absorption. Thus, to develop materials to reduced hydrophilicity of the surface are of our research interest. There are various method to improve hydrophobic properties, such as treatment with organic solvent [4,5], methylation [6,7] and acetylation [8-12]. However, the use of surface treatments has the disadvantage of increasing the overall cost of the final product. Chemical modification by mean of acetylation are interest. Acetylation with acetic anhydride, substitutes the cell wall hydroxyl groups with acetyl groups, rendering the surface more hydrophobic, and thus, increase oil sorption capacity than non-acetylated sorbent.

This study focuses on the modification of cellulose from jointed grass and kapok by acetylation for the preparation of a new oil sorbent material. We want to optimize the reaction conditions for cellulose acetylation by varying sample sizes, acetic anhydride content, amounts of catalyst used, reaction temperatures and reaction time which would help to increase oil sorption capacity. Oil sorption capacity of products will be altered while varying reaction conditions and changing the starting materials (jointed grass and kapok). This is to develop an effective oil absorbance material from natural products which are environmental friendly, inexpensive and also to add value to them. In addition, these biodegradable materials can be used to replace the commercially available synthetic sorbents.

1.2 Objectives of Research

The objectives of this research work are:

1. To synthesize and investigate acetylated cellulose by the acetylation of jointed grass and kapok.
2. To obtain the optimum condition of acetylation of jointed grass and kapok with acetic anhydride.
3. To develop low cost and biodegradable oil sorbents from cellulose by acetylation.

1.3 Scope of Research

The stepwise investigation was gone through as follows:

1. Survey literature for related research work.
2. Synthesize the acetylated cellulose by the acetylation. The reaction conditions were varied, 20 to 120 ml of acetic anhydride, amounts of catalyst used from 0 to 3.0% *N*-bromosuccinimide, the temperature from 70 to 100°C and time from 1 to 3 h. FT-IR, ^{13}C-NMR and TGA.
3. Investigate the influence of volume of acetic anhydride, amounts of catalyst used, temperature and time on the degree of substitution value of the acetylated of joints grass piths and acetylated kapok.
4. Examine oil sorption capacity of acetylated joints grass piths and acetylated kapok.
5. Summarize the results.

CHAPTER II

THEORY AND LITERATURE REVIEWS

2.1 Theory

2.1.1 Petroleum

Petroleum is a mixture of hundreds of organic compounds deriving from decomposition of fossils deposited within the stratum under a static circumstance without oxygen for a long time. Most petroleum composes of saturated hydrocarbon with the main composition of carbon and hydrogen. The rests are organic compounds with other non-metals mixing in the molecular structure such as sulfur, oxygen, and nitrogen at an inconstant amount. Diversity of compositions leads to different colors of petroleum such as yellow, green, brown and black. Petroleum can be found either as thin as water, or as viscous as asphalt. State of petroleum depends on composites, temperature and pressure of petroleum storing environment. It can be classified into two states, crude oil and natural gas. Before applying crude oil, a procedure of compounds separation called refining is needed. Petroleum is classified as inflammable compound. When fractional distillation is performed, it will yield various products at different boiling points, such as liquid propane gas, benzene, kerosene, diesel, fuel oil and asphalt. Some of the products obtained by fractional distillation are important substances in lubricating oil and grease production, including some chemicals, for instance, plastic and synthetic rubber [13].

2.1.2 Oil spill situation

Rapidly increasing needs of energy provoke more oil shipping importation from abroad, which always comes along with oil leakage into the sea, although the prevention policy has been applied. This oil leakage affects marine ecosystem, natural resources even traveling business and aquaculture within the oil-contaminated area and causes a large value of damage to economy, society and environment. Besides, the increase of oil drilling, exploration, production and marine transportation may affect the environment and traveling places, as it had occurred in foreign countries. Some causes of oil leakage are as following:

2.1.2.1 Defective instruments

Defects of instruments may occur during oil production, storing or transferring process, for instance, leakage or breakage of crude oil delivery line or oil hose under the sea.

2.1.2.2 Accidents

Oil cargo ships or other kinds of ships leakage or wreckage accident often causes oil contamination into water sources, especially the water traffic routes which may expose to high risk of accidents. For example, the ships crash on each other, on the submerged rocks or being on fire with any reasons.

2.1.2.3 Human deeds

Human deed that causes oil leakage into the water the most is piratical disposing. Due to changing new products after freighting, it is necessary to wash the storing containers so that a lot of waste water is produced. The ships that have no equipment to deal with this waste water often dispose it into the water source. Moreover, the waste water from the ballast tanks which is used water from the cleaning process and get contaminated with oil also causes water contamination. Waste water disposed from the industries and urban areas also get contaminated with oil.

2.1.2.4 Oil transfer

Oil transfer between the ship and the port can sometimes cause such oil leakage, however, it is not severe because port areas are usually controlled by the government. Oil transfer between the ship and the ship can easily cause oil leakage and difficulties for the government to control. Some cargo ships are too huge to enter the port due to shallow water bottom, therefore, transferring from the cargo ship to another small one cannot be avoided.

2.1.2.5 Marine petroleum drilling and exploration

Marine petroleum drilling and exploration, infiltration can happen from drilling platforms during the drilling process.

2.1.2.6 Natural leakage

Oil leakage from its storage can occur from all ground areas in the seas and the oceans over the world

2.1.3 Oil spill impact [14]

Oil spill into the land, the rivers or the oceans severely affects ecosystem, natural resources, wildlife and even coastal businesses. Severity level depends on different factors such as type of oil, amount of the leak, type and abundance of environmental resources, area geography, hydrology situation, water source oceanography, and meteorology situation. Effects of oil spill into water sources can be summarized as following:

2.1.3.1 Physical impact

Oil has less specific gravity than water, when the leakage occurs oil will float on water surface and obstructs the sunlight from shining through the water thoroughly. This suppresses the photosynthesis process of plant planktons, algaes, and other water plants, which are food production sources for the next consumers in the food chain. This results in changes some bacteria’s digestion potential, reduces water pH rate, oxygen in the air cannot dissolve into the water, as the covering oil slick acts like a barrier between water and air and makes water temperature higher.

Besides, oil leakage also affects creatures, those are small aquatic animals e.g. fish, small animal planktons, crustaceans, sea fowls, penguins, sea otters, seals, sea lions. But what get the most critical effect with the highest death rate are water birds. When their feathers are soaked with oil, it will coagulate and lets the water leak into their skin and makes them unable to maintain body temperature and overheated. They will be so hot or cold and eventually die or get drowned. Moreover, oil may block their mouths, nose or may even irritate their eyes. The oil covering their skin will be absorbed into their bodies to suppress reproduction and growth by reducing incubation rate.

Figure 2.1 Oil spill impact.

2.1.3.2 Biological impact

Biological impacts are the consequence of physical impacts. That is to say, reduction of planktons and photosynthesis of algae affects eating behavior and survival of aquatic animals. Because oil is toxic, it can damage skin tissues and causes wounds and gastrointestinal bleeding. Additionally, it also has long-term effects on reproduction. Oil can get into creatures' body through respiration (vapor), leaking into creatures' skin, through the mouth (by eating contaminated food or their behavior of preening oil-contaminated feathers). Toxic substances in oil can get into creatures' body. By these means, the creature houses toxin in their body and when it is eaten by a predator, the predator will succeed the toxin. This is the toxin succession process in the food chain, from the primary consumers (i.e. planktons, fish) to the top consumers, including human.

When oil is blown into the mangrove areas, it affects spawning ground and vegetation in the areas. Remaining oil mixed with sediments and clay invalidates the growth of the seeds and block mangrove tree roots' respiration.

2.1.3.3 Economic and social impact

Economic and social impacts are the consequences of physical and biological impacts. Oil pollution worsens water quality and affects directly to fishery and coastal aquaculture. Due to contamination in aquatic animals' tissues, the products are reduced in quantity and may result in product shortage, which raises the price up. When oil slicks and oil sediments are blown into traveling places, e.g. beaches, coral reefs, mangrove forests, they become dirty and stinky. Beauty and aesthetics of the traveling place will be worsened and traveling industry will be seriously damaged.

2.1.4 Elimination of oil spill

There are many methods to eliminate oil slicks. The efficiency of each method depends on different specific areas and type of oil. Therefore, it is necessary to consider the appropriate method in order to help control and eliminate oil slicks successfully. Concerning information, such as type of oil, volume of leaking oil, direction and velocity of tidal and wind currents, weather, geographical appearance, must be gathered and considered before determining in picking one of these methods or applying an integration of multiple methods. Methods of eliminating oil slicks are as followings:

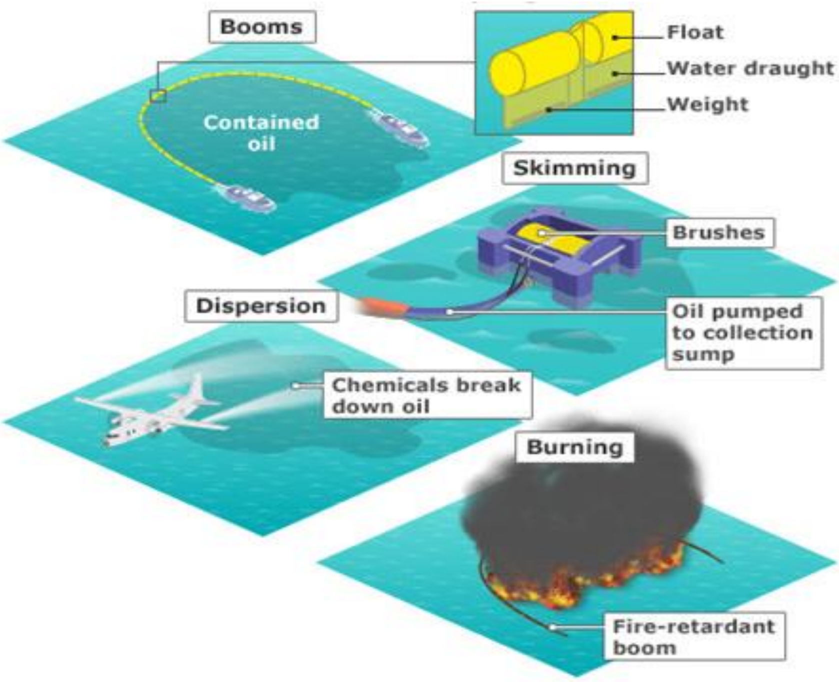


Figure 2.2 Elimination of oil spill.

2.1.4.1 Natural decomposition

Natural decomposition is suitable in case of a small volume of oil leakage (no more than 20 ton liters) and if the leaking oil can decompose itself naturally. This includes leakage that is not harmful to water resources and coastal areas which are important to economy and environment such as diesel.

2.1.4.2 Booming and skimming

This method aims to skim and absorb oil slicks that are floating on the water surface especially, with a coordination of boom and skimmer. Boom limits oil dispersion and increases density of the oil on water surface. After that, skimmer or absorbent is applied to eliminate contaminating oil from water surface. This is the best method as it does not have effects on environment. The only one constraint is the wind current during operation.

2.1.4.3 Chemical treatment

This method works effectively in a short time. Chemical substance is injected on the oil-contaminated area. However, this method should only be applied in case where other methods are ineffective. The substance applied in the process must not affect aquatic ecosystem and must be permitted by concerning administrative agency. For example, some kind of bio-surfactants manufactured from micro-organisms or bacterias, e.g. rhamnolipid from bacteria *Pseudomonas sp.*, emulsan from bacteria *Acinetaobacter sp.*, glycolipid from bacteria *Rhodococcus sp.* These substances can be used to decrease oil surface tension until it disperses into the water to activate natural decomposition process. In case of the chronic leakage, this method should not be applied, as it would remain non-evaporable substances.

2.1.4.4 Combustion

Combustion can work only before the physical and chemical change of the oil occurs. Oil slicks must be over 3 mm. thick. It will be limited with special fire-resistant oil boom i.e. ceramic type boom. This method requires special expertise and a careful check whether the oil has been completely separated from other areas before combustion. Otherwise it may cause danger or damage.

2.1.4.5 Coast cleaning

This is the last method in case where other methods do not work properly. When the oil slicks are blown to the coast area, operators and tools will be gathered to collect the contaminating oil. Some example tools for collecting oil coagulated and contaminating with wastes are spades, shovels, hods, and plastic bags.

2.1.5 Oil-sorbent materials

Oil sorbent materials can be categorized into three major classes, including inorganic mineral products, organic synthetic products and organic vegetable products.

2.1.5.1 Inorganic mineral products [5,15]

Mineral products include perlite, vermiculites, sorbent clay, and diatomite. These materials do not show adequate buoyancy retention and their oil sorption capacity is generally low.

2.1.5.2 Organic synthetic products [5]

Synthetic sorbents such as polypropylene and polyurethane are the most commonly used commercial sorbents in oil-spill cleanup, owing to their oleophilic and hydrophobic characteristics [14]. A major disadvantage of these materials is that they are non-biodegradable.

2.1.5.3 Organic vegetable products [5,17]

Organic vegetable products such as straw, corn cob, and wood fiber showed greater oil sorption capacities than synthetic sorbents, but they often do not absorb water well, which is a disadvantage when use in marine environments.

2.1.6 Jointed grass

Jointed grass is classified into the same family as grass. It has wide range of distribution areas, as it is an endemic plant of southern Asia (India and Sri Lanka), Indochina (Burma and Thailand), Indonesia, Malaysia and Papua New Guinea. It distributes around the tropical area, such as America, Africa, Asia and northern Australia. Its distribution in Thailand can be seen in many regions, especially at the waterside areas, unoccupied areas, or agricultural areas such as in the paddy field.

Figure 2.3 Jointed grass trunk and cross section of jointed grass trunk.

Jointed grass trunks are comprised of internodes. It has 15-30 cm. long with straight leaves and is generally between 60-120 cm. high. It has light porous sponge-like tissues with a lot of fiber that it can float on the water surface. Jointed grass is usually used to feed the animals and in the field of conservation. It helps prevent soil collapse and loosen soil impaction as a kind of ground cover.

Jointed grass cellular physical organ that affects liquid absorption, such as water and oil, is aerenchyma. Aerenchyma is developed from decomposition of Parenchyma cells, in order to produce large sponge-like air spaces in its roots, trunks or leaves. This may be a genetic character or natural adaptation to cope with stressful circumstances, for instance, to improve the efficiency of the internal air circulation within the hypoxia condition or to help improve the plants endurance to environment aground and in the water.

2.1.7 Kapok

Kapok is also an agricultural product cultivated in Southeast Asia, Malaysia, Sri Lanka, other parts of East Asia and Africa [18].

Figure 2.4 Kapok tree and kapok seed.

Kapok fiber is a silky plant fiber that clothes the seeds of the tree (Figure 2.4). The kapok fiber is fluffy, lightweight, non-allergic, non-toxic, resistant to rot, inelastic, brittle and odorless. It has rich oiliness and is inelastic to be spun. It is conventionally used as stuffing for bedding, upholstery, life preservers and other water-safety equipment because of its excellent buoyancy, and for insulation against sound and heat because of its air-filled lumen [19,20]. It has high oil absorbency characteristics but exhibits good water repellency because of its waxy on the fiber surface [21,22].

In Thailand, kapok fiber is found in the northeastern, central and the southern regions, such as Prachuap Khiri Khan, Kanchanaburi, and Nakorn Sri Thammarat. Kapok fiber has been used mainly as a stuffing material for beds and pillows because of its availability and low agricultural product price. Approximatly 120-150 seeds of kapok give 1 kilogram of kapok fiber andit can be sold 8-10 baht per kilogram, while the kapok fiber without seeds can cost 30-35 baht per kilogram.

2.1.8 Natural products

Natural products are high molecular weight polymers. Natural fibers are obtained from either plant or animal. Fibers like wool and silk obtained from animals are proteins, and so they are formed from amino acids joined together by many amide linkages. Cotton and linen, on the other hand, are derived from plants and so they are carbohydrates having the general structure of cellulose, formed from glucose monomers [23]. General structures for these polymers are shown in Figure 2.5.

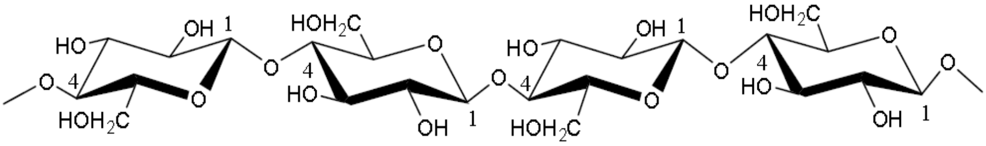


Figure 2.5 Chemical structure of cellulose chain.

Cellulose is probably the single most abundant organic compound that exists on the earth. It is the chief structural component of plant cell wall. For example, it comprises 10-20% of the dry weight of leaves, about 50% of the weight of tree wood and bark, and about 90% of the weight of cotton fibers, from which pure cellulose is most easily obtained. Filter paper is a source of almost pure cellulose in the laboratory. Cellulose is an example of the simpler class of polysaccharide; these are called homopolysaccharides because they contain only one kind of monosaccharide unit [24]. In the case of cellulose, this unit is glucose linked at positions β-1, 4-glycosidic bond, containing about 3,000 molecules of glucose units as a polymer and having a molecular weight of about 500,000. Cellulose molecular configuration has a linear shape with no branches. General chemical formula for cellulose is $(C_6H_{10}O_5)_n$, when n represents the number of glucose units that comprise cellulose.

The linear arrangement of β-linked glucose nits in cellulose presents a uniform distribution of OH groups on the outside of each chain. When two or more cellulose chains make contact, the hydroxyl groups are ideally situated to “zip” the chains together by forming hydrogen bonds (Figure 2.6). Zipping many cellulose chains together in this way gives a highly insoluble, rigid, and fibrous polymer that is ideal as cell-wall material for plants. Cellulose has been a popular substance for centuries. Because it can be difficultly dissolved into other organic solvents. Due to its high qualities of hardness and crystallization, cellulose could be applied in various fields, such as in the field of chemistry or engineering. It can be modified in many ways of use [25].

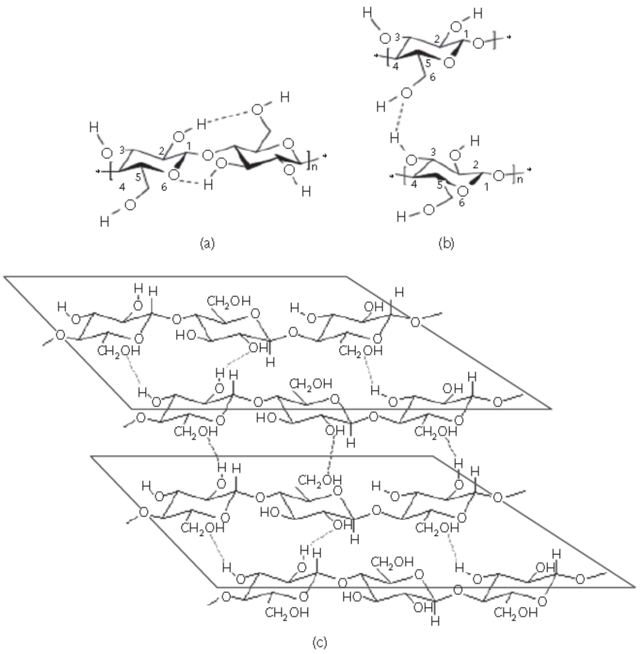
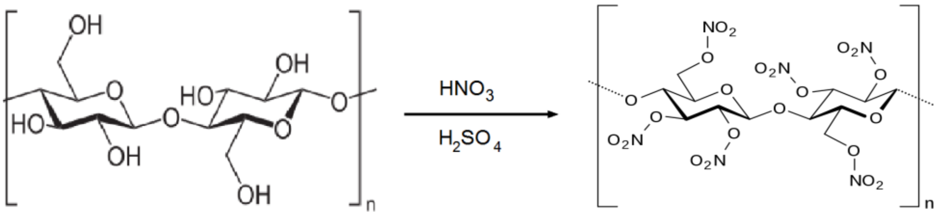


Figure 2.6 Cellulose structure (a) the intramolecular hydrogen bonding between C2-OH, C6-OH and C3-OH, (b) the intermolecular bonding between C3-OH and C6-OH, and (c) the intermolecular bonding between C2-OH and C6-OH and C3-OH [26].

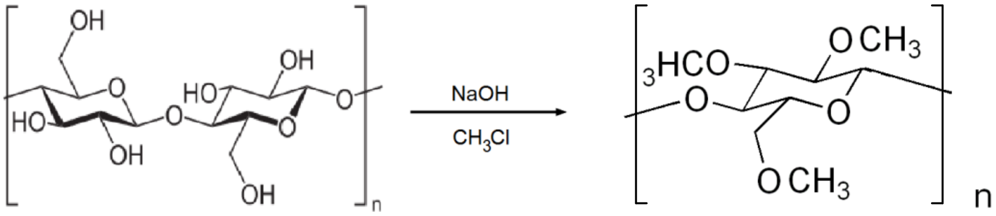
2.1.9 Cellulose derivatives [25]

Several derivatives of cellulose are used commercially. Most of these are compounds in which two or three of the free hydroxyl groups of each glucose unit have been converted to an ester or an ether, with various reagents. This conversion substantially alters the physical properties of the material, making it more soluble in organic solvent and allowing it to be made into fibers and films, for example cellulose nitrate, methylcellulose or cellulose acetate. Cellulose nitrate, also called ‘gun cotton’ or ‘nitrocellulose’, is used in explosives and film forming material.



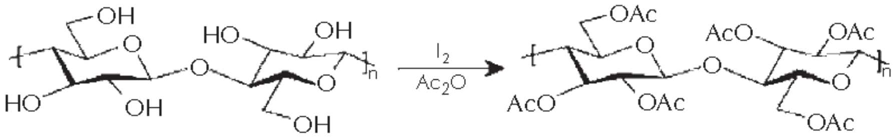
Scheme 2.1 Conversion of cellulose to nitrocellulose.

Methylcellulose has an extremely wide range of uses such as thickener, emulsifier, construction materials, paper and textile.



Scheme 2.2 Conversion of cellulose to methylcellulose.

Treating cellulose with acetic anhydride produces the triacetate known as ‘Arnel’ or ‘acetate’, used widely in the textile industry.



Scheme 2.3 Conversion of cellulose to cellulose triacetate [26].

These reaction is acetylation, a chemical reaction that is called ethanoylation in the IUPAC nomenclature. It describes a reaction that introduces an acetyl functional group (CH_3CO) into a chemical compound. The opposite chemical reaction is called deacetylation it is the removal of the acetyl group [27,28].

Derivatives of cellulose are derived from the substitution reaction of hydroxyl group with other substitute groups. The degree of substitution (DS), which is the mean value of cellulose substituted by other substitute groups, will show the highest value at 3, as each anhydroglucose unit contains hydroxyl, which can react with 3 groups.

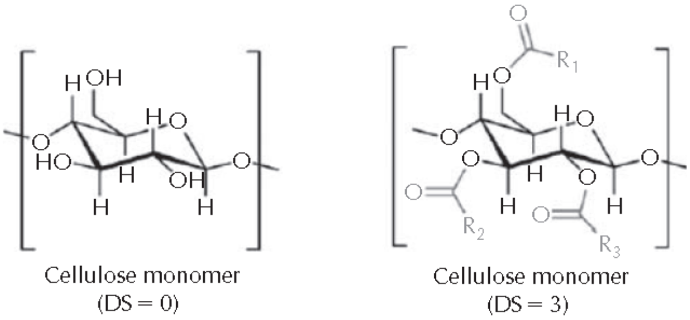


Figure 2.7 Structures of cellulose monomer and related cellulose triacetate [26].

2.2 Literature Reviews

In 2004, Khan *et al*. [18] studied 7 types of biomass absorbents, i.e. kapok fibers, paddies, cat-tail fibers, coconut fibers, duck weeds, saw dust and bagasse. Oil sorption and desorption tests of these absorbents were performed and compared to synthetic polyester absorbents. Engine oil and tap water were used in this oil sorption and desorption test. The result revealed that absorbent tested could absorb more than 70% of the oil, except coconut fiber and bagasse that could absorb only 32% and 20%, respectively. Duck weed could absorb nearly as much oil as polyester. According to oil desorption test, biomasses desorbed less than 1.5% while polyester desorbed about 4% of the absorbed oil.

In 1992, Chol *et al*. [15] investigated the oil sorption capacity of three sorbents such as milkweed, kenaf and polypropylene from the surface of an artificial sea water containing crude oil. The results revealed that milkweed could absorb 40 g of crude oil/g of fiber, higher than the other two sorbents and could be reused at least three times.

In 2005, Annuciado *et al*. [41] investigated the oil sorption capacity of various vegetable fibers such as mixed leaves residues, mixed sawdust, sisal (*Agave sisalana*), coir fiber (*Cocos nucifera*), sponge-grourd (*Lufa cylindrica*) and silk-floss. Three commercial systems such as static system, dynamic system and dry system, developed to control these spills. The results revealed the sorption capacity further increased by reducing granulometry. The silk-floss showed high oil sorption capacity at 85 g oil/g sorbent for 24 hours while other sorbents showed around 5.5-8.0 g oil/g sorbent in the dynamic system.

In 2003, Saito *et al*. [29] investigated the oil absorption performance of Sugi bark and compared to that of polypropylene absorbents. Five kinds of oil were used, Bunker A, Bunker B, Bunker C, bio oil and motor oil. The results revealed that Sugi bark could absorb more oil than polypropylene, especially Bunker C which could absorb as much as 16.5 times their own weight, while polypropylene could absorb only 1.2 times. Only Bunker A could absorb approximately at 13.4 and 15.0 times, respectively. They found that sheet materials could absorb oil effectively and easy to apply for oil absorption material.

In 2006, Perachula *et al*. [30] studied oil absorbency of the piths of Ya-Plong (Hymenachne acutigluma) and compared to that non-woven polypropylene absorbent web. Four kinds of oil were used, crude oil, fuel oil, diesel oil, and lubricating oil. The results revealed that Ya-Plong could absorb these oils at 54.6, 87.7, 51.3, and 80.1 g oil/g sorbent, respectively. The web could absorb at 5.7, 7.0, 6.2, and 6.1 g oil/g sorbent so, respectively. While water absorbency of two absorbents were not much different.

In 2009, Abdullah *et al*. [1] studied kapok fiber's oil absorption efficiency as an oil filter. The test revealed that oil absorption efficiency decreased when density of the filter increased. The density of kapok filter at 0.05 g/ml could absorb as much diesel oil as 37.7 g oil/g sorbent, 50.8 g oil/g sorbent for old gasoline and 47.0 g oil/g sorbent for new gasoline.

In 2000, Hori *et al*. [31] studied kapok-fiber-structural model, all physical, chemical and competence in oil absorption. It was clarified that kapok fiber composed of 35% of cellulose, 22% of xylene, and 21.5% of lignin. This indicated that kapok contained 13% of acetyl group , while generally plants contained only 1-2% of acetyl group. It implied that kapok had higher hydrophobicity than other kinds of plants. When it is tested for oil absorption with the oil floating on water, and the oil floating on sea water, it could absorb 40 times more than its dry weight.

In 2007, Lim *et al*. [27] examined the oil sorption capacity and hydrophobic-oleophilic properties of kapok and compared to those of commercial oil sorbent for oil spill cleanup, polypropylene. In this study, different oils such as diesel, hydraulic oil, and engine oil, were used to determine the oil absorbency of kapok. In addition, reusability after application to various oils of kapok also investigated. The results showed that absorbent performance of kapok highly relied on the packing densities. At low density, 0.02 g/cm^3, oil sorption capacities of kapok for diesel, hydraulic oil, and engine oil were 36, 43 and 45 g/g, respectively. The capacity of oil absorbency of kapok was decreased when the density increased, e.g. at 0.09 g/cm^3 the absorbency was 7.9, 8.1 and 8.6 g/g for diesel, hydraulic oil, and engine oil, respectively. Interestingly, it was found that sorption capacities for three oils tested of kapok were higher than those of polypropylene. Furthermore, kapok also showed high oil retention ability and reusability. Kapok exhibited high selectivity for oils on the water and can remove almost all oils spill.

In 2010, Abdullah *et al.* [32] studied the effect of packing density, oil types (diesel and engine oil) and solvent (chloroform and NaOH) treatment on the sorption properties of kapok. In addition, oil sorption capacity, retention capacity, entrapment stability and reusability of kapok were investigated. Results from SEM and FTIR analysis showed that kapok is a lignocellulosic material with hydrophobic waxy coating on the hallow structures. It was found that higher density of kapok at 0.08 g/ml exhibited lower absorbency while giving higher percentage of dynamic oil retention. Even after fifteen cycles of reuse kapok remained stable with only 30% decreased in sorption capacity when 0.04 g/ml of diesel was used. At packing density of 0.08 g/ml, the oil entrapment stability was high with more than 90% of diesel and used engine oil was maintained after shaking. Furthermore, after treatment with chloroform and NaOH for 8 hours, the decrease in sorption capacity of kapok was observed. The results showed that kapok has a great potential for using as oil sorbent due to its high sorption and retention capacity, structural stability and reusability.

In 2007, Lim *et al.* [33] investigated the performance of kapok in oily water filtration. The performance of untreated and solvent-treated kapok in deep-bed filtration of oily water containing 2.5% diesel was examined in which ethanol and chloroform were used as solvent. The filtration performance was determined by measuring the column breakthrough time, filtration rate, filtrate quality and the amount of oil retained by the filter column. As a result, both raw and solvent-treated kapok exhibited great oil/water separation and filtration. Solvent treatment of kapok seemed to have no affect on the filtrate quality in term of turbidity and percent of oil removal. In addition, the oil removal efficiencies were excellent with more than 99% efficiency. However, the column packed with solvent-treated kapok exhibited premature breakthrough of oily influent, generated less filtrate and retained less oil than untreated kapok. This indicated the excellent hydrophobic-oleophilic properties of kapok fiber. The raw kapok fiber was a good filter medium due to its long breakthrough time and large filtrate volume.

In 2012, Wang *et al*. [34] studied the efficiency for oil absorption of kapok. Kapok fiber was treated with different solvents including water, HCl, NaOH, $NaClO_2$ and chloroform. The effect of treatment conditions, temperature and time on oil absorbency 0f kapok was also investigated, using toluene, chloroform, n-hexane and xylene. After treatment, FTIR, SEM, XRD and XPS were used for characterization of the surface morphology, chemical compositions, crystallinity and surface elemental composition. As a result, kapok fiber treated with all solvents, except chloroform, showed increased oil absorbency. When compared with untreated kapok, treating with $NaClO_2$ exhibited the highest oil absorbency. The increased percentage of oil absorbency for toluene, chloroform, n-hexane and xylene was 19.8%, 30%, 21.5% and 24.1 %, respectively. The results indicated that kapok has high oil absorption efficiency, outstanding reusability and good biodegradability, suggesting that kapok could be used as an optional for synthetic oil absorbent.

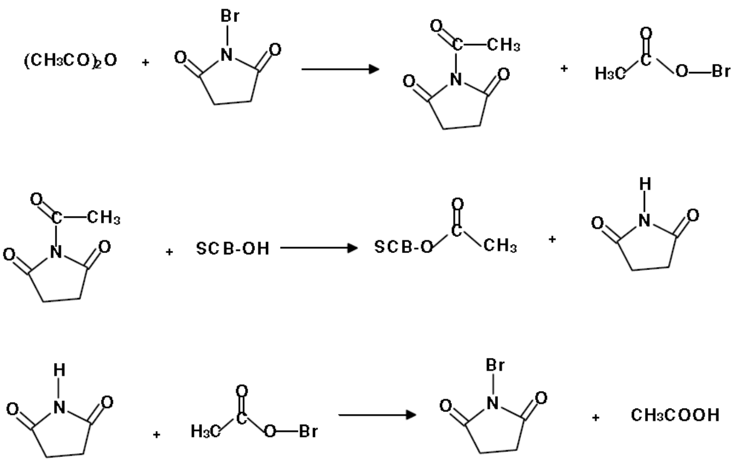
In 2000, Sun *et al*. [35] investigated the alkaline peroxide delignification of rye straw. Rye straw was subjected to different treatment conditions after ground and dried. Lignins were obtained after the treatment of dewaxed and water-extracted rye straw with 2% hydrogen peroxide at pH 11.5 for 12 hours at 20-70 °C. Another alkali lignin was also obtained under similar conditions but in the absence of peroxide. Lignins obtained from these conditions were similar in chemical composition and physico-chemical properties in which they were free of polysaccharide and composed of nearly same amount of noncondensed guaiacyl and syringyl units with less p-hydroxyphenyl units.

In 2002, Sun *et al*. [36] performed experiments by adding acetyl group into rice straw to produce oil absorbent. First, they prepared some rice straw to be reacted by acetic anhydride in the absence and presence of catalysts, namely pyridine, 4-Dimethylamino pyridine (DMAP), *N*-methyl pyrrolidine (MPI) and *N*-methyl pyrrolidinone (MPO). As the result, the optimum condition was at the temperature of 120ºC for 0.5 hour. The most effective catalyst was 4-Dimethylaminopyridine. Acetyl group could be added on the rice straw as much as 15.4% by weight. The results from FR-IR and ^{13}C-NMR indicated that addition reaction of acetyl group really occurred. When the machine oil absorption was tested, it could absorb 24.0 g oil/g acetylated rice straw.

In 2011, Hu *et al*. [17] studied acetylation reaction of bacterial cellulose (BC) with acetic anhydride, used iodine as a catalyst. As the result, degree of substitution (DS) was in the range of 0.23-1.98 and it increased according to the increasing amount of iodine. FT-IR and ^{13}C-NMR results have confirmed that acetylation reaction really occurred. Crystallization and cellulose nanofibers structure were tested by WAXS analysis. Fiber quality was determined using SEM technique, showing that the acquired product, Acetylated BC membrane's surface was hydrophobic.

In 2003, Sun *et al*. [8] studied the addition of acetyl group on sugarcane bagasse (SCB) to produce promising oil absorbent. As for the optimum condition for the treated SCB, it was investigated under a mild condition with various catalysts, *N*-bromosuccinimide (NBS), 4-Dimethylamino pyridine (DMAP), pyridine, *N*-methyl pyrrolidine (MPI), *N*-methyl pyrrolidinone (MPO) in the presence of 0.5% H_2SO_4. The highest result of WPG was 22.3% at 80ºC for 2 hours providing that NBS is the most effective catalyst. The success of acetylated SCB was confirmed by FT-IR and ^{13}C-NMR spectroscopy. The oil absorptivity of acetylated SCB, 18.8 g oil/g, is higher than the commercial polypropylene, 1.9 times, whereas the thermal stability of acetylated SCB is lower than unmodified.

It was reported as the first group to use NBS as catalyst for acetylation. A mechanism of NBS for this work is not clear but it is postulated act as a source for Br^+ that can trigger the carbonyl groups of acetic anhydride to produce the high reactive specie ($CH_3CON(OCCH_2CH_2CO)$), which then further reacts with hydroxyl groups of SCB as described in Scheme 2.4.



Scheme 2.4 Mechanism of acetylation of SCB using NBS as a catalyst.

In 2003, Deschamps *et al.* [37] studied the sorption properties of cotton fiber in dynamic mode. In this study, cellulose was acetylated with octanoic acid under microwave radiations. The degree of substitution and degree of polymerization were 0.15 and 655, respectively. The cotton oil sorption capacity was determined to be 20 g/g in static mode. Sorption and coalescence phenomena of cotton were the recovery of oil from oil in water emulsion during a flow through a bed of cotton. During percolation, column "hold-up" became stable at the equilibrium volume. Therefore, measurement of the cotton sorption capacity could be performed and it was found that sorption capacity of cotton was increased with initial emulsion up to the cotton saturation. The oil-water separation performance increased at low temperature, low flow, deep medium and large oil drops.

In 2011, Diop *et al.* [42] studied the acetylation of corn flour by varyting the ratio of acetic acid and acetic anhydride, using microwave at 100 ºC. The ratio that brought out the most DS at 2.93 was 1:1. FT-IR results showed that the area under the peak of C=O ester (1745 cm^{-1}) increased with the increase DS, while the area under the peak of O-H (3430 cm^{-1}) decreased. This indicated that the hydroxyl group replacement with acetyl group really occurred.

CHAPTER III

EXPERIMENTAL

3.1 Materials chemicals, glassware & equipments and instruments

3.1.1 Materials chemicals

1. Acetic anhydride, Commercial grade: Laboratory reagent
2. *N*-bromosuccinimide (NBS), 99%: Aldrich
3. Ethanol (C_2H_5OH) Commercial grade: Merck kGaA
4. Acetone (CH_3COCH_3), Commercial grade: Merck kGaA
5. Hydrochloric acid (HCl), 37%; CARLO ERBA reagents
6. Sodium hydroxide (NaOH), Commercial grade: Merck kGaA
7. Machine oil; Singer industrial oil
8. Motor oil, SAE 20W-50; PTT (Thailand) Co., Ltd.
9. Bunker C; PTT (Thailand) Co., Ltd.

3.1.2 Glasswares & equipments

1. 100 ml , beaker
2. 250 ml , beaker
3. 600 ml , beaker
4. 100 ml , Round bottom flasks
5. 10 ml , Graduated cylinder.
6. 500 ml, Suction flask
7. Buchner funnel
8. Magnetic stirrer
9. Watch glasses
10. Filter paper
11. Condenser

12. Vacuum pump: model MZZC NT, Vacuubrand
13. Hotplate: model MR 3001, Heidolph
14. Oven: model 7200 WTC, Binder
15. Balance : model ABS, KERN

3.1.3 Instruments

1. Scanning electron microscope (SEM): JEOL, JSM-5410LV
2. Fourier transform infrared spectrometer (FTIR): Perkin-Elmer (Spectrum One) infrared spectrophotometer
3. Solid-state Carbon-13 NMR Nuclear Magnetic Resonance Spectrometer (NMR): Varian, model INOVA
4. Thermalgravimetric analysis : Mettler Toledo, 851e
5. Viscosemeter: Brookfield, Model LVDV III

3.2 Experimental procedure

3.2.1 Sample preparation

3.2.1.1 Jointed grass

Jointed grass was obtained from a local swamp area (Kanchanaburi, Thailand). It were first dried in sunlight and cut as detailed below.

whole stem: peeled off hard skin of jointed grass trunk, washed them with tap water to remove impurities and then dried in an oven at 65°C for day.

dissected parts of whole stem: cut the whole stem in to small pieces, washed them with tap water and then dried in an oven at 65°C for day.

pith: screwed the white part in the middle of fresh jointed glass trunk, washed them with tap water and then dried in an oven at 65°C for day.

3.2.1.2 Kapok fiber

The raw kapok fiber were agricultural product of Thailand (Srisawad, Kanchanaburi). Before use, all dust and lumps in the product had been manually removed and cut into short shape (approximate 2-3 cm) and then dried in an oven at 65˚C for day.

3.2.2 Solvent-treatment [4,38]

Two experiments of the solvent-treated were investigated; with 1% HCl and 1% w/w NaOH. The dried sample (1 g) was placed into 150 mL solvent in a beaker equipped with a mechanical stirrer and refluxed at 50˚C for 1 h. After treatment was completed, sample was filtered and rinsed three times with distilled water to remove any soluble nonstructural constituents and then dried in oven at 65°C overnight to evaporate the residual liquids.

3.2.3 Characterization of treatment cellulose

All of the treatment cellulose were further characterized using scanning electron microscope (SEM) and fourier-transform infrared spectrometer (FT-IR).

3.2.3.1 Scanning electron microscope: SEM

SEM micrographs of treatment cellulose were examined using JEOL JSM-5410LV scanning electron microscope. Before SEM observation, all samples were fixed on aluminum stubs with double-sided conductive adhesive tapes and coated with gold. SEM micrographs were examined using accelerating voltage at 15 kV.

3.2.3.2 Fourier-Transform Infrared Spectrometer: FT-IR

To prepare for FT-IR spectroscopy, the samples were dried and ground into fine particles. For each type of sample, 1 mg of fine particles was mixed with 150 mg of potassium bromide (KBr). The mixture was then compressed into pellet form and then analyzed. To obtain FT-IR spectra, 10 scans were recorded at 2 cm^{-1}, resolution in the region from 400 to 4000 cm^{-1}.

3.2.4 Preparation of acetylated products

The dried sample (1 g) was mixed with acetic anhydride and catalysts in round bottom flask. The reaction was performed in an oil bath with reflux condenser and refluxed at 70-100°C for 1-3 h with mechanical stirring. The volume of acetic anhydride was varied from 20-120 mL and the concentrations of catalysts were 0-3.0% *N*-bromosuccinimide (NBS). When the reaction was completed, the mixture was filtered and washed with ethanol and acetone to remove unreacted acetic anhydride and acetic acid by-product. The acetylated products were dried in an oven at 65 °C for day to constant weight for later use.

3.2.5 Characterization of unmodified and acetylated products

All of the acetylated products were further characterized using scanning electron microscope to analyzed morphology of products, Fourier-Transform Infrared Spectrometer (FT-IR, Perkin-Elmer (Spectrum One) spectrophotometer) was used for determine the degree of substitution (DS), Nuclear Magnetic Resonance (NMR, Varian model INOVA) Spectrometer (Varian INOVA spectrometer) were used to evaluate other characterizations of the received products and Thermalgravimetric analysis were used to measurement thermal stability of unmodified and acetylated products.

3.2.5.1 Scanning electron microscope: SEM

SEM micrographs of unmodified and acetylated products were examined using JEOL JSM-5410LV scanning electron microscope. Before SEM observation, all samples were fixed on aluminum stubs with double-sided conductive adhesive tapes and coated with gold. SEM micrographs were examined using accelerating voltage at 15 kV.

3.2.5.2 Fourier-Transform Infrared Spectrometer: FT-IR

Fourier-Transform Infrared spectra (FT-IR) were performed on a Perkin-Elmer (Spectrum One) infrared spectrophotometer. To prepare for FT-IR spectroscopy, the samples were dried and ground into fine particles. For each type of sample, 1 mg of fine particles was mixed with 150 mg of potassium bromide (KBr). The mixture was then compressed into pellet form and then analyzed. To obtain FT-IR spectra, 10 scans were recorded at 2 cm^{-1}, resolution in the region from 400 to 4000 cm^{-1}. The degree of substitution of the acetylated products was calculated from the absorbance at 1740 cm^{-1} assigned to C=O stretching with an internal standard of absorbance at 897 cm^{-1}assigned to β-glucopyranose rings [26,39].

3.2.5.3 Nuclear Magnetic Resonance (NMR) Spectrometer

The solid-state ^{13}C-NMR spectra were recorded using a Varian, INOVA spectrometer at 500 MHz with magic-angle spinning and cross-polarization (CP-MAS). About 250 mg of sample was packed into zirconia rotors for MAS at approximately 500 rpm. The CP contact time was 3 s, acquisition time 0.02 s, and total time 1.5 h [8].

3.2.5.4 Thermalgravimetric analysis: TGA

Thermal stability of the unmodified and acetylated products was performed using and thermalgravimetric analysis (Mettler Toledo, 851e). The sample weighed between 1 and 3 mg was introduced into a platinum crucible. The scans were run from 25 to 600°C at a rate of 20°C per minute under a dry air atmosphere.

3.2.6 Oil sorption performance of acetylated jointed grass pith and acetylated kapok fiber

These tests involve the use of oils with a range of viscosities and densities as indicated below [40].

Table 3.1 Test oil of ASTM F726-99.

Oil Type	**Viscosity Range (cP)**	**Density Range (g/cm^3)**	**Example**
Light	1 to 10	0.820 to 0.870	Diesel fuel, Machine oil, kerosene, gasoline
Medium	200 to 400	0.860 to 0.970	Crude oil, Canola oil, Motor oil
Heavy	1500 to 2500	0.930 to 1.000	Heavy crude, Cooking oil

3.2.6.1 Sorption capacity in oil suspended in water test

The oil suspended in water test was designed to test for oil uptake in forming an emulate of oil spill. Medium oil (3 ml) was added into a 250 mL beaker that was half-filled with water. Approximately 0.05 g of different sorbents were weighed, and then placed on the oil film for 15 minutes with stirr. After that, using stainless steel wire mesh to remove the sorbent, drained excess unabsorbed liquid for 30 seconds, and then weighed. The oil sorption capacity (g oil/g sample) was calculated from equation 1.

$$\text{Oil sorption capacity (OSC)} = \frac{(S_{ST} - S_0)}{S_0} = \frac{S_S}{S_0} \qquad \text{------ (1)}$$

3.2.6.2 Sorption capacity in oil: Short and Long test

The procedure for determining oil sorption capacity generally base on the ASTM F726-06 method. Each of sorbents was placed into an oil bath until it reached the test time limit as detailed below.

Short test (15 minutes) under dynamic conditions: 100 mL of light oil, medium oil and heavy oil were poured into a beaker. Thereafter, 0.05 g of sorbent were placed on the oil surface. Allowing the sorbent to sorb oil for 15 minutes, the sorbent was removed using a stainless steel wire mesh and drained for 30 seconds and 2 minutes for heavy oil and then weighed. The oil sorption capacity (g oil/g sample) was determined using equation 1.

Long test (24 hours) under dynamic condition: 100 mL of light oil, medium oil and heavy oil were poured into a beaker. Thereafter, 0.05 g of sorbent was placed on the oil surface. Allowing the sorbent to sorbed oil for 24 hours, the sorbent was removed using a stainless steel wire mesh and drained for 30 seconds and 2 minutes for heavy oil and then weighed. The oil sorption capacity (g oil/g sample) was determined using equation 1.

3.2.6.3 Sorption capacity in water test

The dynamic water sorption test was designed to test for water uptake and to determine oleophillic properties of the sorbents under dynamic conditions. Approximately 0.05 g of different sorbents were weighed, and then placed in a 250 mL beaker that was half-filled with water, stirred at the speed of 250 rpm. After that, the condition of the sorbents and water was observed. If 10% or more of the sorbent had sunk, then the sorbent was considered to have failed this test. After 15 minutes, using a stainless steel wire mesh to remove the wet products, drained excess water for 30 seconds and then weighed. The water sorption capacity (g water/g sample) was calculated from equation 2.

$$\text{Water sorption capacity (WSC)} = \frac{(S_{WT} - S_0)}{S_0} = \frac{S_W}{S_0} \qquad \text{------ (2)}$$

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Tested materials for oil sorption capacity from jointed grass and kapok fiber

4.1.1 Jointed grass

Jointed grass samples were prepared as described in Chapter 3. Dried jointed grass sample with different shapes were shown in Figure 4.1, whole stem with 1.0 cm (a) and 1.5-2.5 cm (a’), dissected parts of whole stem with 1.0 cm (b) and 1.5-2.5 cm (b’), and pith with 0.5cm (c) and 1.5-2.5 cm (c’).

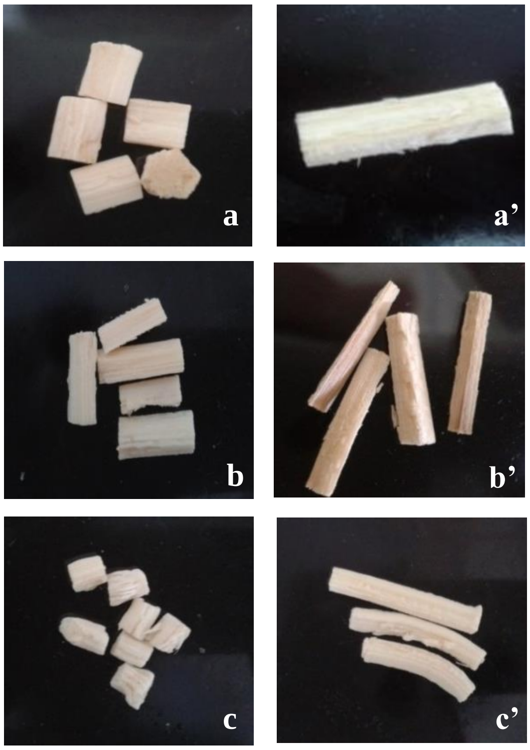


Figure 4.1 Jointed grass sample shapes with difference size.

Sorption capacity of the above samples were short tested using machine oil and the results were display in Table 4.1. As expected, the oil sorption capacity of jointed grass in different physical shape and size should be different. The whole stem was a part of stem after removing the sheath (Figure 4.1 a’), had the least oil sorption capacity (0.06 g oil/g sample) because some parts of sheath still remained and therefore obstructed the sorption of oil. Oil sorption capacity of dissected parts of whole stem (Figure 4.1 b') was 1.21 g oil/g sample which is better than the whole stem part because it had more surface area [41]. The center part of stem was the pith (Figure 4.1 c') which exhibited the highest sorption capacity at 1.84 g oil/g sample. This is because the pith is aerenchyma tissues which were porous as sponge [42], therefore having large intracellular air space to retain oil.

The oil sorption capacity of 3 kinds of jointed grass samples depended on their sizes. Table 4.1 also shows that the sorption capacity increased short size (0.5-1.0 cm) from long size (1.5-2.5 cm) of whole stem, dissected parts of whole stem, and pith were 4.42, 7.00 and 63.57%, respectively. This result showed short size sample had larger surface area.

Among short size samples, jointed grass pith showed promising sorption capacity and more potential being used as one of oil sorbent materials. Previously, Perachula et al [30], reported Ya-Plong pith (jointed grass pith) had high oil sorption capacity at 51.3 g oil/g sample for diesel oil, while this work revealed 3.01 g oil/ g sample for machine oil. The difference may be due to the method of testing, this work followed ASTM F726-99 (1999) while the previous work did not specify.

Table 4.1 Sorption capacity of short size samples increase from long size of jointed grass samples.

Samples	**Long size 1.5-2.5 cm (g oil/g sample)**	**Short size 0.5-1.0 cm (g oil/g sample)**	**Sorption capacity increase (%)**
whole stem	0.06	0.07	4.42
dissected part	1.21	1.30	7.00
pith part	1.84	3.01	63.56

4.1.2 Kapok fiber

Figure 4.2 exhibited kapok fiber as received after removing all dust and lump (Figure 4.2 a) and the fiber was cut in an approximate 2-3 cm (Figure 4.2 b).

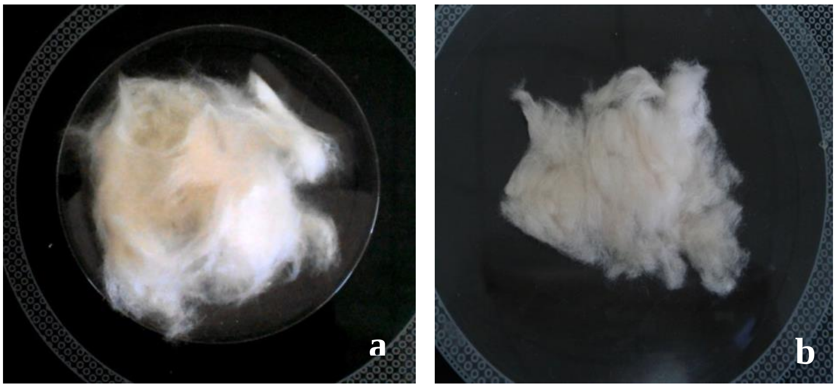


Figure 4.2 Kapok fiber (a) as received, (b) cut into 2-3 cm in length.

The oil sorption capacity of kapok fiber samples with different lengths indicated that lengths of kapok fiber did not significant different levels of sorption capacity. Kapok fiber as received had oil sorption capacity at 42.41 g oil/g sample, while cut kapok fiber sample could absorb 39.10 g oil/g sample. Thus, kapok fiber might be used as received for oil sorbent materials.

Compare between two kinds of sample, jointed grass pith and kapok fiber, the oil sorption capacity of kapok fiber (42.41 g oil/g sample) was higher than jointed grass pith (39.10 g oil/g sample), therefore kapok fiber was more promising for being used as oil sorbent material.

4.2 Solvent-treatment of jointed grass pith and as received kapok fiber

Since natural product surface usually covers with waxy substance, pectin and natural oils [4,7], the pretreatment of natural product before physical or chemical modification is needed. Generally, the most commonly solvent used for pretreatment natural product in this study is HCl and NaOH.

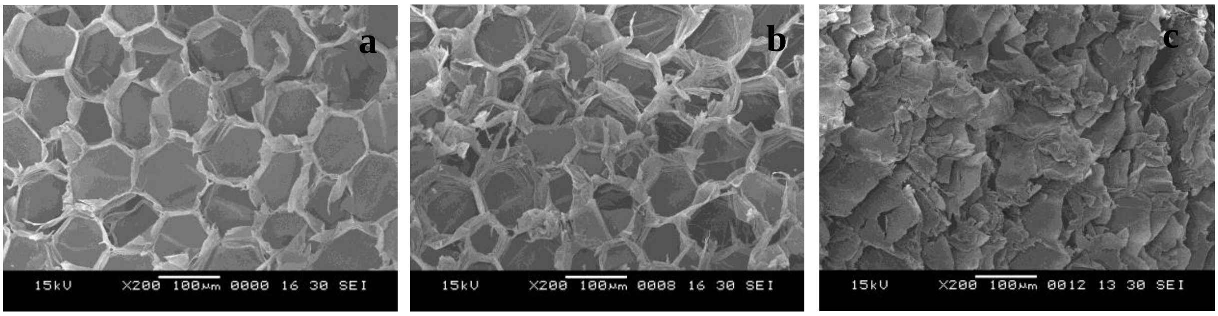


Figure 4.3 SEM images of jointed grass pith samples at magnificent x200, (a) untreated, (b) HCl-treated, and (c) NaOH-treated jointed grass pith.

The surface morphology of untreated and treated jointed grass pith were determined by SEM and the results were shown in Figure 4.3. Figure 4.3 (a) showed that the untreated jointed grass pith exhibited a spongy tissue with large air spaces of aerenchyma tissue with average pore size approximated 94.01 µm. The large pores of the pith enhance the capillary action and the diffusion of oil through the cuticle to the inner pores, thus jointed grass piths can absorb oil as reported in Table 4.1.

When jointed grass pith was treated with HCl, the protrusion on surface was unbound and exposed large pores of jointed grass pith. Moreover, the surface was rougher the before treatment as observed in the previous report by Chand et al [43]. As reported by Wang et al [34], the rough surface resulted is increasing the specific surface area of sample, then the oil storage space of jointed grass pith much increased.

The NaOH-treated jointed grass pith (Figure 4.3 c), morphology of the pith changed drastically, large pores of the pith were destroyed. It may be due to the violent action of the NaOH. The appearance had been explained by Bertoti et al [44] and Bledzki et al. [45], that some lignin and hemicellulose were removed.

The surface morphologies of untreated and treated kapok fiber were analyzed by SEM. The results were shown in Figure 4.4. The untreated kapok fiber exhibits hollow tubular structure (or lumen) with smooth surface, similar observations were made earlier [47-50]. The high oil sorption capacity found in Table 4.1 (42.41 g oil/g sample) postulately caused by the large pore volume in the kapok fiber and void spaces between the fiber assembly (Figure 4.4 a) [18,29,44].

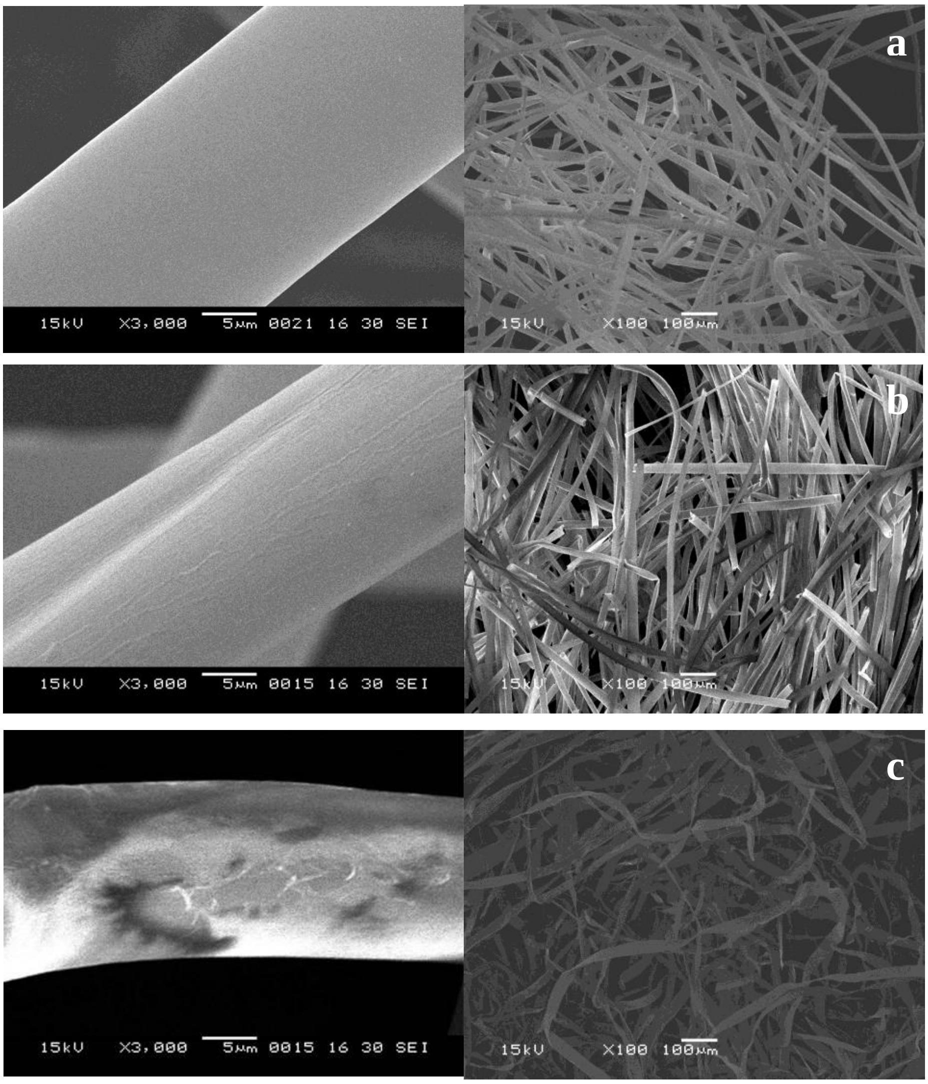


Figure 4.4 SEM images of kapok fiber samples at magnificent x3000 and x100, (a) untreated, (b) HCl-treated, (c) NaOH-treated kapok fiber.

When kapok fiber was treated with HCl (Figure 4.4 b), the surface morphology changed to rough. It may be due to the surface wax of kapok fiber was removed and the hydrophilic surface was exposed. In the previous report [34], the presence of rough surface can increase the specific surface area of kapok fiber and improve the adhesion of fluid to surface, which enables the oil to adhere to the outer surface and penetrate easily into the inner surface of lumen of kapok fiber.

For NaOH-treated kapok fiber (Figure 4.4 c), morphology of the fiber changed drastically, broken hole and shallow pit can be generally observed on the surface. In the report by Wang et al [34], the oil sorption capacity increased when the surface of sample became rough, but these phenomenon did not observer in this work because there was a total disappearance of air entrapment inside kapok fiber and the structure become flattened, alike ribbon structure. It can be revealing that the strong alkali can produce serious damage to the structure of kapok fiber and this result is similar to that was found by Abdullah at el [32].

The SEM results were confirmed by FT-IR. FTIR spectra of untreated and treated jointed grass pith, are depicted in Figure 4.5. For untreated spectra of jointed grass pith (Figure 4.5 a), the strong absorption band at 3419 cm^{-1} originated from O-H stretching vibration can be observed, the peak at 2924 cm^{-1} was assigned to asymmetric and symmetric aliphatic CH_2 and CH_3 stretching. This might be associated with the presence of plant wax, which generally consists of n-alkanes, fatty acids, aldehydes, smaller portion of alcohols, ketones and n-alkyl esters [51]. The prominent peak at 1734 cm^{-1} was attributed to C=O stretching vibration of ketones, aliphatic aldehydes and esters in lignin and acetyl ester groups in xylan [22,52]. The small bands at 1633 and 1514 cm^{-1} were attributed to the aromatic C=C stretch of aromatic ring of lignin. The bands around 1377 and 1250 cm^{-1} were within the range of C-H and C-O bending vibration, respectively. The sharp and strong band at 1048 cm^{-1} is associated with C-O or C-O-C stretching due to the presence of cellulose and hemicellulose in sample [53,31]. The sharp band at 897 cm^{-1} is originated from the β-glucosidic linkages between the sugar units.

By comparing the spectra of untreated (Figure 4.5 a) and treated jointed grass pith (Figure 4.5 b,c), the following observation were obtained. A little increase of absorption bands at 3419 cm^{-1} using the 897 cm^{-1} as an internal standard, can be observed of the treated samples, implying the removal of plant wax from surface and increased number of free hydroxyl groups located in sample walls. In a previous report [21,48], the treatment of wood fibers in acidic medium can bring about the hydrolysis of cellulose and enhance the relative content of lignin resulting in the increase of the band around 1250 cm^{-1}, but it is not found in this work. This is due to relatively mild treatment process.

A remarkable reduction of band intensity at 1734 cm^{-1} and 1250 cm^{-1} occurs for NaOH-treated sample corresponding to lignin characteristics of the backbone structure. This indicates that the lignin in jointed grass pith could be dissolved in alkali solution similarly observed by Liu et al [54] and corresponding to the result by SEM.

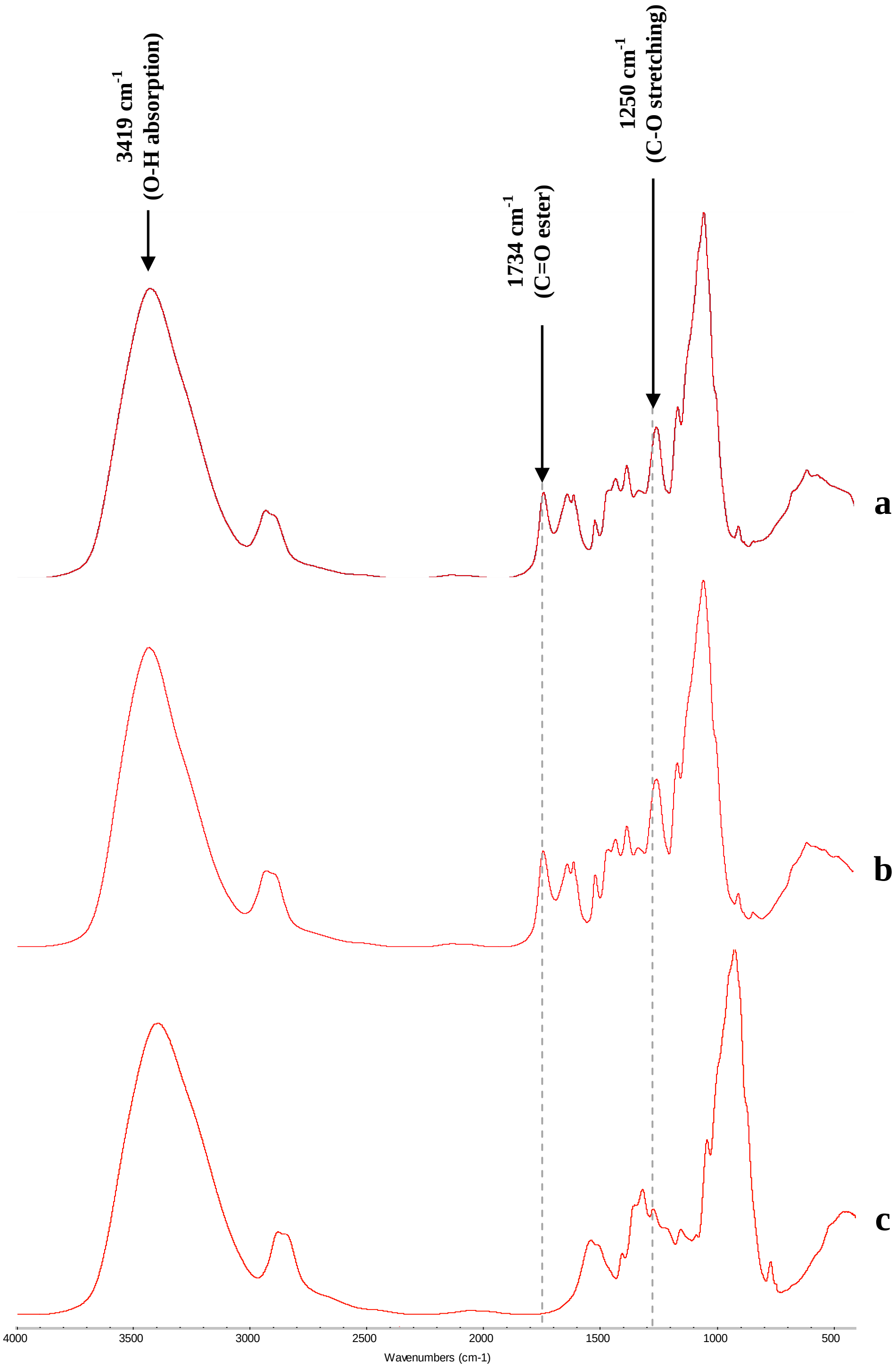


Figure 4.5 FTIR spectra of jointed grass sample (a) untreated, (b) HCl-treated, (c) NaOH-treated jointed grass pith.

FTIR spectra of untreated and treated kapok fiber are depicted in Figure 4.6, confirming similar results with those of jointed grass pith. By comparing the spectra of untreated and treated kapok fiber, the following results were obtained. A little bit increase of absorption bands at 3429 cm^{-1} using the 897 cm^{-1} as an internal standard, can be observed of treated kapok fiber spectra, implying the removal of plant wax from surface and increased number of free hydroxyl groups located in fiber walls.

The evidence of reduction of band intensity at 1740 cm^{-1} and 1243 cm^{-1} in NaOH-treated sample corresponding to lignin characteristics of the backbone structure. This indicates that the lignin in kapok fiber could be dissolved in alkali solution to destroy the hollow tubular structure of kapok fiber, which corresponding to the result by SEM. The destruction of the structure directly affect to the oil sorption capacity.

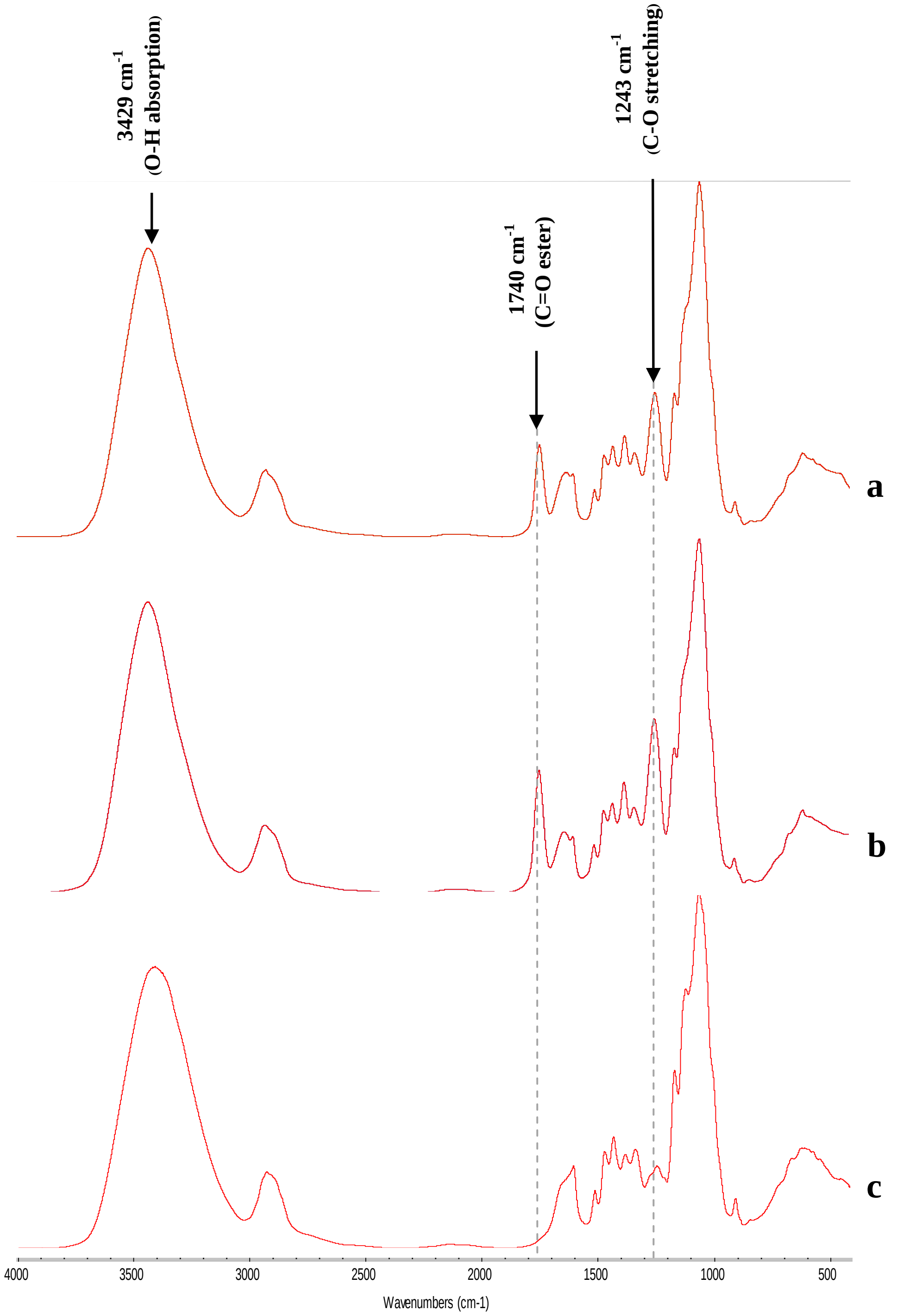


Figure 4.6 FTIR spectra of kapok fiber (a) untreated, (b) HCl-treated, (c) NaOH-treated kapok fiber.

4.3 Acetylation of jointed grass pith and kapok fiber

Due to acetylation, the free hydroxyl groups are replaced by bulkier acetyl groups. Acetyl groups are more hydrophobic than hydroxyl groups, therefore, replacing some of the hydroxyl groups with acetyl groups reduces the hydrophilic property of the cell wall [55].

The jointed grass pith and kapok fiber were acetylated by acetic anhydride in a solvent free system. The extent of the acetylation reaction was determined using degree of substitution (DS), evaluated by FT-IR, of the sample prepared under different conditions. The effects of the reaction conditions such as acetic anhydride content, amounts of NBS catalyst used, reaction temperature and reaction time on the DS were investigated.

4.3.1 Characterization of acetylated kapok fiber

The acetylation of kapok fiber with acetic anhydride and NBS as a catalyst was conducted three times for each experiment and the average values were reported in Table 4.2.

Table 4.2 Effect of reaction conditions on degree of substitution (DS) of acetylated kapok fiber.

Sample no.	Acetylation conditions				DS	OSC
	Volume (mL)	Catalyst (% NBS)	Temperature (°C)	Reaction time (h)		
Effect of acetic anhydride content						
K1	20	1.5	80	2.0	1.52	49.74
K2	40	1.5	80	2.0	2.29	64.78
K3	60	1.5	80	2.0	2.32	69.09
K4	80	1.5	80	2.0	2.59	76.72
K5	100	1.5	80	2.0	2.55	76.69
K6	120	1.5	80	2.0	2.53	73.20
Effect of amount catalyst						
K7	80	0	80	2.0	1.29	48.01
K8	80	1.0	80	2.0	2.23	62.21
K4	80	1.5	80	2.0	2.59	76.72
K9	80	2.0	80	2.0	2.27	62.74
K10	80	3.0	80	2.0	2.26	62.32
Effect of reaction temperature						
K11	80	1.5	70	2.0	1.75	53.50
K4	80	1.5	80	2.0	2.59	76.72
K12	80	1.5	90	2.0	2.00	56.04
K13	80	1.5	100	2.0	1.70	53.01
Effect of reaction time						
K14	80	1.5	80	1.0	2.10	57.09
K4	80	1.5	80	2.0	2.59	76.72
K15	80	1.5	80	2.5	2.16	57.80
K16	80	1.5	80	3.0	1.90	55.02

To determine DS values and confirmed acetylation, the acetylated kapok fiber was evaluated by using FT-IR. FT-IR spectra of unmodified and acetylated kapok fiber with different DS, are depicted in Figure 4.7. The spectra showed the differences between bands before and after acetylation. The main differences of acetylated kapok (Figure 4.7 b-d) in comparison to unmodified spectra (Figure 4.7 a) are the presence of acetyl groups, due to the enchantment of three important ester bands, which are characteristics of the acetyl group at 1740, 1373 and 1243 cm^{-1}, these were attributed to absorption by carbonyl bonds (C=O ester), C-H stretching (-C-CH_3), and C-O stretching in esters (-O-C-CH_3), respectively. In contrast, the intensity of the hydroxyl stretching band (O-H) at 3429 cm^{-1} was decreased. These phenomena occurred because the hydroxyl groups of cell wall of kapok was substituted by acetyl groups. This result is similar to the previous studies [8,7].

The absence of absorption in the region of 1840-1760 cm^{-1} in acetylated spectrum (Figure 4.7 b-d) indicated that the product was free of the unreacted acetic anhydride. The lack of a peak at 1700 cm^{-1} for carboxylic group revealed that the products are also free of acetic acid by-product [36]. These indicated the success of acetylation of kapok fiber.

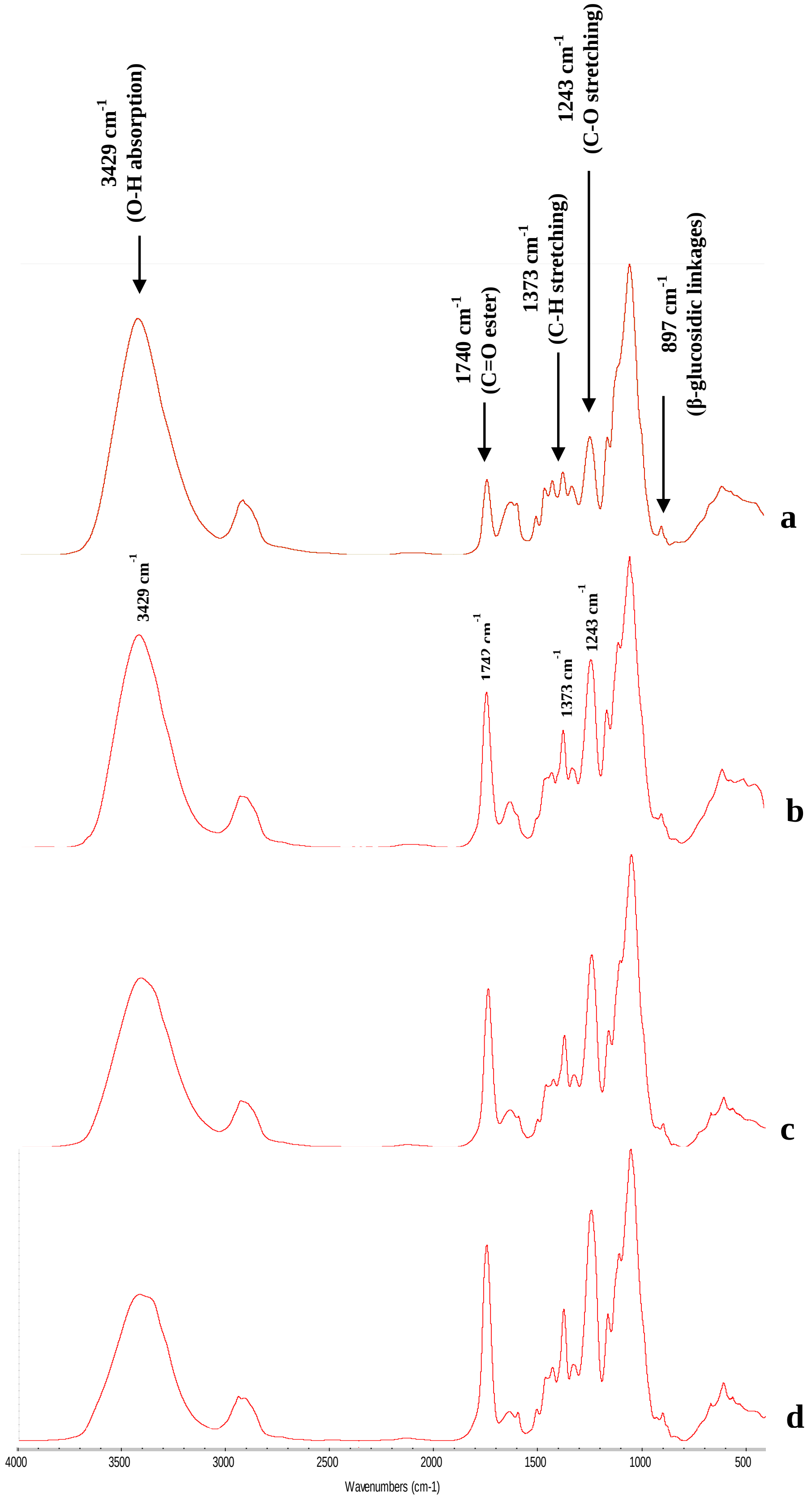


Figure 4.7 FT-IR spectra of unmodified kapok fiber (spectrum a) and acetylated kapok fiber, DS=2.10 (spectrum b), DS=2.32 (spectrum c), DS=2.59 (spectrum d).

The acetylation of kapok fiber were also confirmed by ^{13}C-NMR, because ^{13}C-NMR spectroscopy is an attractive technique for characterization of the natural materials and capable of providing detailed information directly on solid samples [56].

^{13}C-NMR spectra of the unmodified and acetylated kapok fiber, prepared by treatment with 1.5% NBS catalyst at 80˚C for 2.0 h, are displayed in Figure 4.8. The spectrum of acetylated kapok showed methyl band (CH_3) of the acetyl group at 21.1 ppm and the carbonyl (CO) of the acetyl groups at 173.0 ppm, indicating the presence of acetyl groups and apparent of acetylation in products. The result confirms the success of acetylation. A similar observation has been reported in the acetylation of wood [57] and acetylation of sugarcane bagasse [8].

The unmodified and acetylated kapok fiber spectra were very similar in the carbohydrate region between 60 to 110 ppm, although different carbons of sugar unit. The ^{13}C-NMR spectra can be assigned as follows: C-1 (105.0 ppm), C-4 (83.6 ppm), C-2, C-3 and C-5 (73.5 ppm) [p19], and C-6 (63.4 ppm) [9,58].

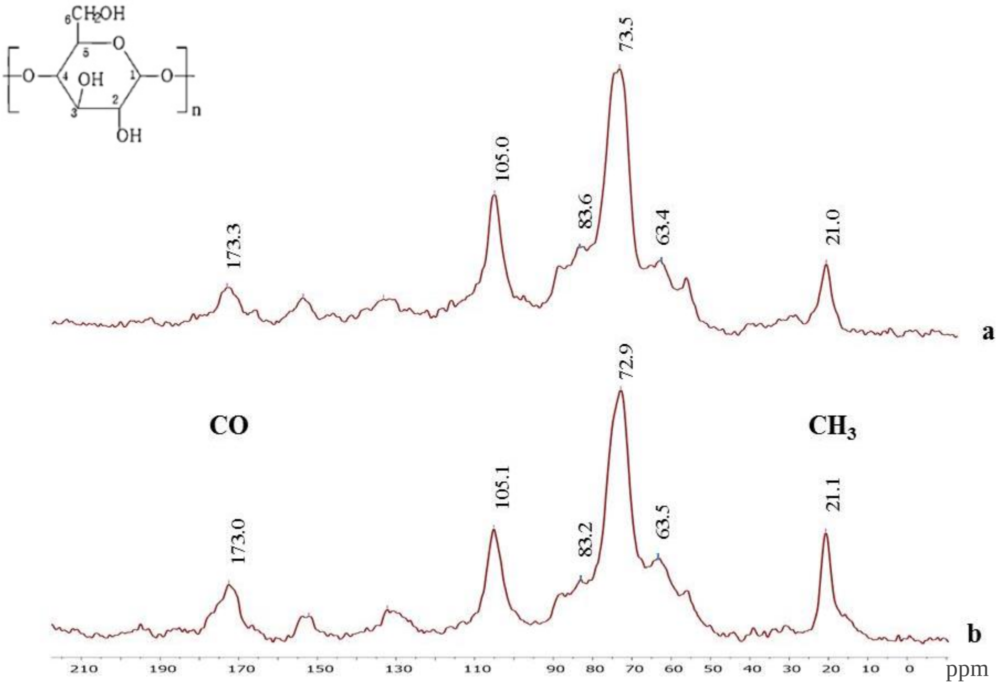


Figure 4.8 ^{13}C-NMR spectra of unmodified (spectrum a) and acetylated kapok (spectrum b) prepared at 80°C for 2.0 h with 1.5%NBS catalyst.

In order to determine the effect of acetylation on the kapok fiber morphology, the acetylated sample was analyzed by SEM. Figure 4.9 shows the SEM images of the kapok fiber before and after acetylation at 80°C for 2 h in 80 mL of acetic anhydride with 1.5% NBS. The surface morphology of unmodified was smooth (as discuses in Chapter 4, 4.2), while the acetylated sample was rougher, indicating that acetylation has affected the structure. These observations are similar to the previous reports [37,44,59]. Because acetyl groups were larger than hydroxyl groups, after the hydroxyl groups were substituted by acetyl groups the surface becomes rougher. These changes are favorable for the oil retention because smooth surface which is not in favor of the adhesion of oil is obviously improved (Table 4.2), while the rough surface being beneficial to the adhesion of oil is generated [34]. In addition, the hollow lumen structure is still intact, which means that the acetylation does not cause severe collapse of the structure.

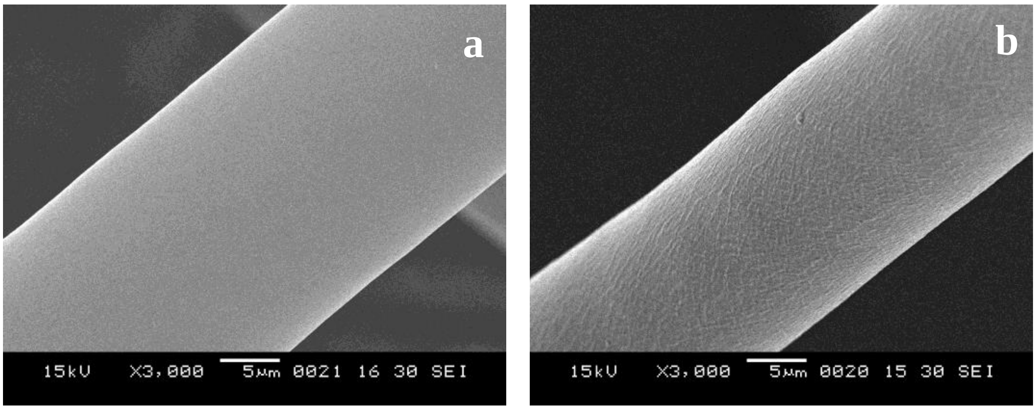


Figure 4.9 SEM images of unmodified kapok fiber at magnificent x3000 (a), and acetylated kapok fiber (b).

4.3.2 Effect of acetic anhydride content on DS of acetylated kapok fiber

The volume of acetic anhydride was varied in the acetylation reaction of kapok fiber from 20 to 120 mL. The effect of acetic anhydride content on DS of acetylated kapok fiber was performed between sample number K1 and K6, as shown in Table 4.2.

Under the condition of 1.5 % NBS, 80°C and reaction time of 2 h, the DS obtained increased with increasing volume of acetic anhydride. The increment is larger at lower volume and reached the maximum DS at 2.59 in sample K4 was obtained at 80 mL of acetic anhydride. When the volume of acetic anhydride is higher than 80 mL, the DS value of acetylated kapok fiber changes little indicating a nearly complete functionalization of all hydroxyl groups, which is similar with previous studies [8,60].

4.3.3 Effect of amount catalyst on DS of acetylated kapok fiber

Based on the study of acetylation of sugarcane bagasse with acetic anhydride, Sun et al. [8], reported that NBS is commercially available reagent, the reaction is clean (no detectable by-products), therefore, this is a novel and highly effective catalyst for acetylation. In this study, the effect of NBS on DS of acetylated kapok fiber was performed between samples number K4, K7 and K10.

In comparison of DS values amount of NBS catalysts used (Table 4.2), it is apparent that NBS is suitable for acetylation reaction of kapok fiber. The DS increased as the amount of NBS catalyst increased. At 80 °C for 2 h, 1.5% of NBS in the reaction system resulted in an increase DS values from 1.29 in sample K7 to 2.59 in sample K4, which was approximately two times higher than obtained under the same conditions without catalyst. When the amounts of NBS catalyst were higher than 1.5%, the DS decreased to 2.27 at 2.0% NBS and 2.26 at 3.0% NBS between sample K9 and K10, which is similar with previous reported by Sun et al [8]. Sun et al [8], reported the actual role of NBS is not clear but conceivably turn activates the carbonyl groups of acetic anhydride to react with hydroxyl groups of cellulose. Thus, the decrease of DS when the amounts of NBS higher than 1.5% in this work, is probably appearnce of deacetylation. After acetic anhydride was used up, excess NBS which in turn activates the carbonyl groups of acetylated product, thus, DS was reduced.

4.3.4 Effect of reaction temperature on DS of acetylated kapok fiber

The reaction temperature was varied in the acetylation reaction of kapok fiber from 70 to 100°C. The effect of reaction temperature on DS of acetylated kapok fiber was between studied samples number K4, K11 and K13.

The influence of reaction temperature was presented in Table 4.2. At 2 h, the increasing in reaction temperature from 70 to 80°C shows an increase of the DS value from 1.75 in sample K11 to 2.59 in sample K4. However, when the reaction temperature was increased from 80 to 100°C, the DS value was decreased with the increment of reaction temperature, from 2.59 to 2.00 at 90°C and 1.70 at 100°C, indicating that cellulose molecular structure was destroyed at high temperature and it may occur evaporation of some acetic anhydride. The boiling point of acetic anhydride is 139 °C [62]. The result was similar the previous reported [1,37].

4.3.5 Effect of reaction time on DS of acetylated kapok fiber

The reaction temperature was varied in the acetylation reaction of kapok fiber from 1.0 to 3.0 h. The effect of reaction temperature on DS of acetylated kapok fiber was performed between sample number K4, K14 and K16.

The increase in reaction time from 1 to 2 h at 80 °C, the DS increased further from 2.10 in sample K14 to 2.59 in sample K4. However, when increase the reaction time higher than 2 h, the DS value was not increased. The decreasing after 2 h was probably due to reduced the concentration of acetic anhydride and appearance of acetic acid by-product. The appearance of acetic acid conducted to a partial solubilization of some acetylated product on the cellulose surface which is similar with previous studies [37,63,64]. Therefore, the optimum condition for the preparation of a new oil sorbent material form kapok was 80 mL of acetic anhydride with 1.5% NBS, 80 °C at 2 h.

4.3.6 Characterization of acetylated jointed grass pith

The acetylation of jointed grass pith with acetic anhydride and NBS as a catalyst was conducted three times for each experiment and the average values were reported in Table 4.3.

Table 4.3 Effect of reaction conditions on degree of substitution (DS) of acetylated jointed grass pith**.**

Sample no.	**Acetylation conditions**				**DS**	**OSC**
	Volume (mL)	**Catalyst (% NBS)**	**Temperature (°C)**	**Reaction time (h)**		
Effect of acetic anhydride content						
J1	20	1.5	80	2.0	2.14	6.23
J2	40	1.5	80	2.0	2.79	7.46
J3	80	1.5	80	2.0	2.85	7.52
J4	100	1.5	80	2.0	2.90	7.62
Effect of amount catalyst						
J5	40	0	80	2.0	1.20	4.48
J6	40	1.0	80	2.0	2.25	6.45
J2	40	1.5	80	2.0	2.79	7.46
J7	40	2.0	80	2.0	1.90	5.95
J8	40	3.0	80	2.0	1.77	5.40
Effect of reaction temperature						
J9	40	1.5	70	2.0	1.42	4.53
J2	40	1.5	80	2.0	2.79	7.46
J10	40	1.5	90	2.0	1.52	4.81
J11	40	1.5	100	2.0	1.53	5.10
Effect of reaction time						
J12	40	1.5	80	1.0	1.59	5.32
J2	40	1.5	80	2.0	2.79	7.46
J13	40	1.5	80	2.5	1.82	5.70
J14	40	1.5	80	3.0	1.45	4.65

To determine DS values and confirmed acetylation, the acetylated jointed grass pith was evaluated by using FT-IR. FT-IR spectra of unmodified and acetylated jointed grass pith with different DS, are depicted in Figure 4.10. The spectra showing similar results with spectra of unmodified and acetylated kapok fiber. The main differences of acetylated jointed grass pith (Figure 4.10 b-d) in comparison to unmodified spectra (Figure 4.10 a) are the presence of acetyl groups, due to the enhanced of three important ester bands, which are characteristics of the acetyl group at 1740, 1375 and 1245 cm^{-1}. These were attributed to absorption by carbonyl bonds (C=O ester), C-H stretching ($-C-CH_3$), and C-O stretching in esters ($-O-C-CH_3$), respectively. In contrast, the intensity of the hydroxyl stretching band (O-H) at 3423 cm^{-1} was decreased. These phenomena occurred because the hydroxyl group was substituted by acetyl groups. This result is similar to the previous reported by Sun et al [8].

The absence of absorption in the region of 1840-1760 cm^{-1} in acetylated spectrum (Figure 4.10 b-d) indicated that the product was free of the unreacted acetic anhydride. The lack of a peak at 1700 cm^{-1} for carboxylic group revealed that the products are also free of acetic acid by-product. These indicated that acetylation of jointed grass pith was certain progresses.

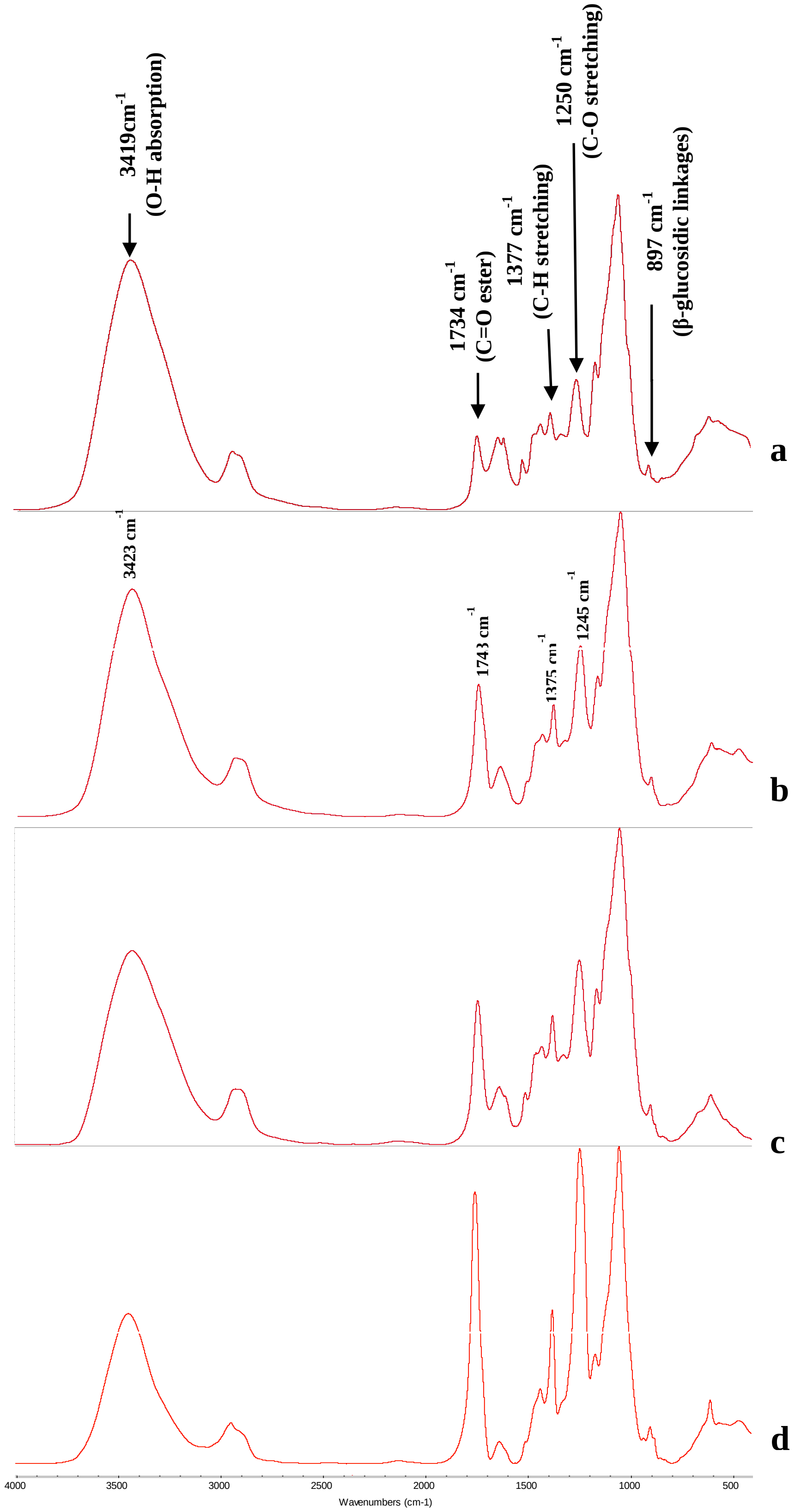


Figure 4.10 FT-IR spectra of unmodified jointed grass pith (spectrum a) and acetylated jointed grass pith, DS=1.77 (spectrum b), DS=1.90 (spectrum c), DS=2.90 (spectrum d).

The acetylation of jointed grass pith was also confirmed by ^{13}C-NMR.

^{13}C-NMR spectra of unmodified and acetylated jointed grass pith, prepared by treatment with 1.5% NBS catalyst at 80 °C for 2.0 h, were in Figure 4.11. The spectra of acetylated jointed grass pith showed methyl band (CH_3) of the acetyl group at 21.2 ppm and the carbonyl (CO) of the acetyl groups at 172.7 ppm, indicating the presence of acetyl groups and apparent of acetylation in products. The result confirms the success of acetylation.

The unmodified and acetylated kapok fiber spectra were very similar in the carbohydrate region between 60 to 110 ppm, which is similar with previous studies by Sun et al [8] and Adebajo et al [58].

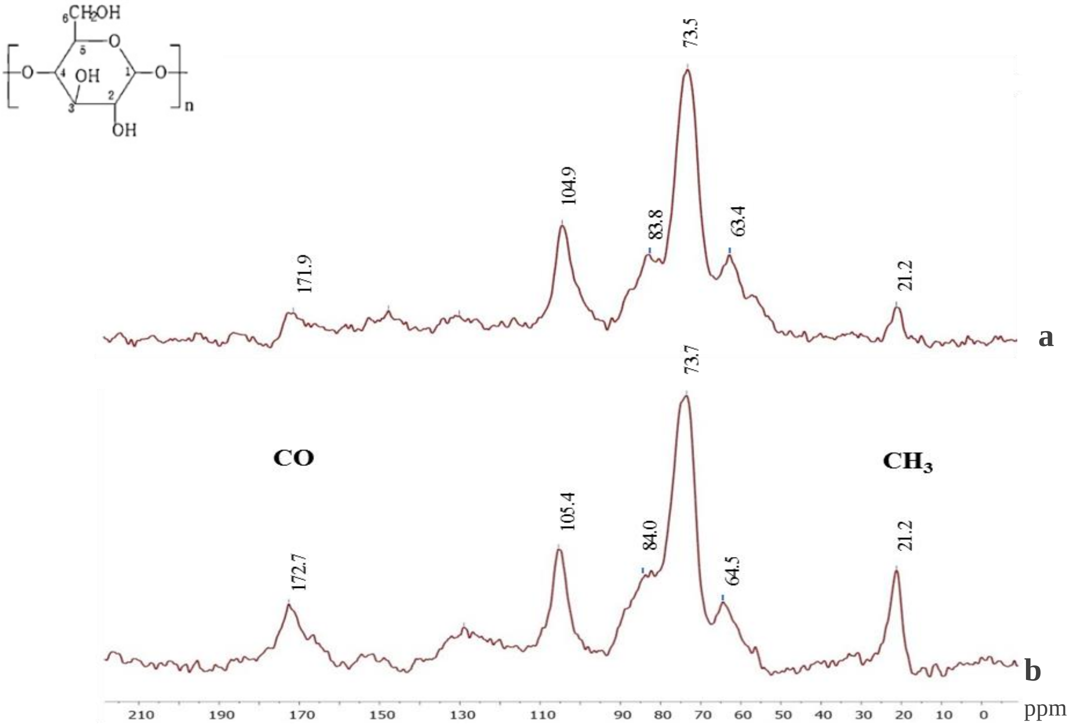


Figure 4.11 ^{13}C-NMR spectra of unmodified (spectrum a) and acetylated jointed grass pith (spectrum b) prepared at 80°C for 2.0 h with 1.5%NBS catalyst.

In order to determine the effect of acetylation on the jointed grass pith morphology, the acetylated sample was analyzed by SEM. Figure 4.12 shows the SEM images of the jointed grass pith before and after acetylation at 80°C for 2 h in

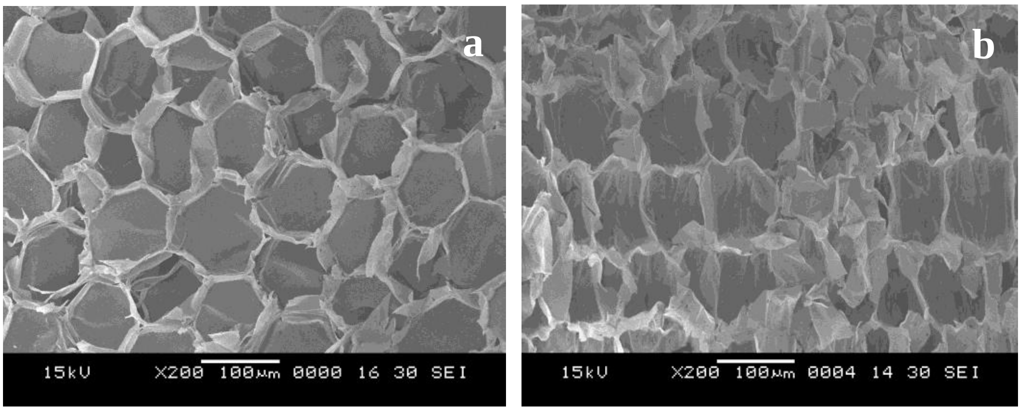


Figure 4.12 SEM images of unmodified jointed grass pith at magnificent x200 (a), and acetylated jointed grass pith (b).

40 mL of acetic anhydride with 1.5% NBS. The surface morphology of unmodified was smooth pore (as discuses in Chapter 4, 4.2), while the acetylated sample was rough and rib, indicating that acetylation has affected the structure. These observations are similar to the previous reports [37,44,59]. Because acetyl groups were larger than hydroxyl groups, after the hydroxyl groups were substituted by acetyl groups the surface becomes rougher. These changes are favorable for the retention oil because smooth surface which is not in favor of the adhesion of oil is obviously improved (Table 4.3). In the previous reported [34], the rough surface being beneficial to the adhesion of oil is generated. In addition, the pore structures like sponge are still intact, which means that the acetylation does not cause severe collapse of the structure.

4.3.7 Effect of acetic anhydride content on DS of acetylated jointed grass pith

The content of acetic anhydride was varied in the acetylation reaction of jointed grass pith from 20 to 100 ml. The effect of acetic anhydride content on DS of acetylated jointed grass pith was performed between sample number J1 and J4, as show in Table 4.3.

Under the condition of 1.5 % NBS, 80 °C and reaction time of 2 h, the DS obtained increases with increasing content of acetic anhydride. The increment is larger at lower content and reached the maximum DS 2.90 in sample J4 was obtained at 100 mL of acetic anhydride.

However, acetylation reaction of jointed grass pith at 40 ml of acetic anhydride obtained DS was 2.79, was not much different from the maximum value. Thus, 40 mL of acetic anhydride could be considered sufficient for acetylation reaction of jointed grass pith and high DS could be obtained.

4.3.8 Effect of amount catalyst on DS of acetylated jointed grass pith

The effect of among of NBS on DS of acetylated jointed grass pith was performed between sample number J2, J5 and J8.

In comparison of DS values among of NBS catalysts used (Table 4.3), it is apparent that NBS is a suitable for acetylation reaction of jointed grass pith. The DS increased as the amount of NBS catalyst increased. At 80 °C for 2 h, 1.5% of NBS in the reaction system resulted in an increase DS values from 1.20 in sample J5 to 2.79 in sample J2, which was approximately two times higher than obtained under the same conditions without catalyst. When the amount of NBS catalyst was higher than 1.5%, the DS decreased to 1.90 at 2.0% NBS and 1.77 at 3.0% NBS between sample J7 and J8. This is probably appears the problem of deacetylation for using amounts of catalyst higher than 1.5%.

4.3.9 Effect of reaction temperature on DS of acetylated jointed grass pith

The reaction temperature was varied in the acetylation reaction of jointed grass pith from 70 to 100°C. The effect of reaction temperature on DS of acetylated jointed grass pith was performed between sample number J2, J9 and J11.

The influences of reaction temperature are presented in Table 4.3. At 2 h, an increase in reaction temperature from 70 to 80°C resulted shown an increase of the DS value from 1.42 in sample J9 to 2.79 in sample J2. However, when the reaction temperature was increase from 80 to 100°C, the DS value was decrease with the increment of reaction temperature, from 2.79 to 1.52 at 90°C and 1.53 at 100°C.

4.3.10 Effect of reaction time on DS of acetylated jointed grass pith

The reaction temperature was varied in the acetylation reaction of jointed grass pith from 1.0 to 3.0 h. The effect of reaction temperature on DS of acetylated jointed grass pith was performed between sample number J2, J12 and J14.

The increase in reaction time from 1 to 2 h at 80 °C, the DS increased with increase reaction time from 1.59 in sample J12 to 2.79 in sample J2. However, when increase the reaction time higher than 2 h, the DS value was not increased anymore.

According to the effect of reaction conditions on the DS value, the optimum condition for the preparation of a new oil sorbent material for jointed grass pith was 40 mL of acetic anhydride with 1.5% NBS, 80 °C at 2 h.

4.4 Comparison of sorption performance of acetylated jointed grass pith and acetylated kapok fiber

Three types of oils were tested for the application of sorbents to represent a wide variety of oil. Besides, machine oil represents low-viscosity oils, such as gasoline and kerosene, then motor oil represents medium-viscosity oils, such as canola oil and crude oil, and Bunker C oil represents heavy-viscosity oils, such as heavy crude and cooking oil [48]. The viscosity and density of oils are investigated and summarized in Table 4.4.

Table 4.4 Physical properties of the investigated oils at 25±3°C.

Type of Oil	**Viscosity (cP)**	**Density (g/cm^3)**
Machine oil	32.2	0.820 [a]
Motor oil	352	0.884 [b]
Bunker C	2265	0.960 [b]

[a] Obtained from the product specifications provided by Singer.

[b] Obtained from the product specifications provided by PTT.

4.4.1 Sorption capacity in oil suspended in water test

The sorption capacity of oil suspended in water was examined using motor oil as experimental oil in this study and the data are given in Figure 4.13. The oil was suspended in water and removed with acetylated product. It was found that the acetylated products floated on the surface and then immediately absorbed oil. The acetylated samples showed the satisfied result of agglomeration performance, better than unmodified samples. The acetylated kapok gave the highest oil sorption capacity among others. In addition, clear water was observed after draining-off the amount of oil with the remaining of oil odor.

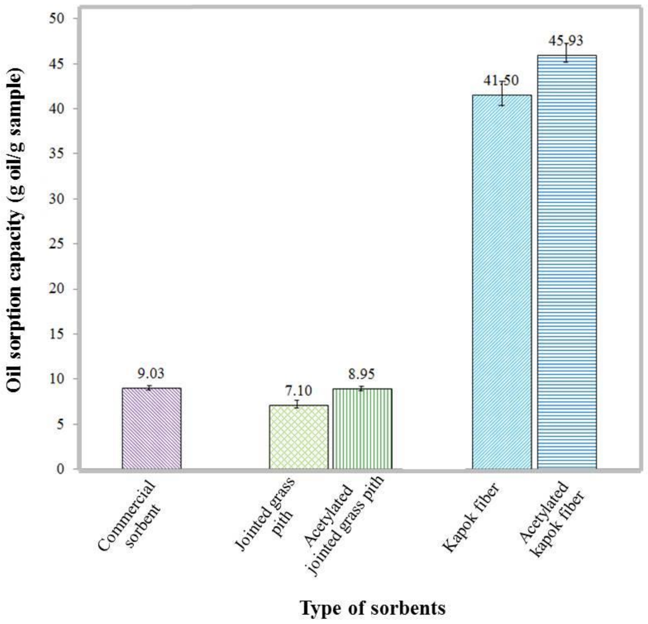


Figure 4.13 Oil sorption capacity of different sorbents.

As expected, acetylation of jointed grass pith and kapok fiber led to an increment in oil sorption capacity from 7.10 to 8.95 g oil/g sample for acetylated jointed grass pith and from 41.50 to 45.93 g oil/g sample for acetylated kapok fiber. It can be indicated that acetylation was successful to improve oil sorption capacity.

The PP based sorbent used as representative of commercial sorbent, which was oil sorption capacity at 9.03 g oil/g sample. The result from Figure 4.13 shows that oil sorption capacity of acetylated jointed grass pith is not significantly different to the commercial sample. Interestingly, the acetylated kapok showed the highest oil sorption capacity, which in the result is better than the commercial sorbent. From the result, the acetylated products are potentially as promising candidate to use for the oil spill cleanup.

4.4.2 Sorption capacity in oil: Short and Long Test

Sorption capacity in oil without water was investigated. Sorption capacity may be vary under difference environment. The experiments were performed using three types of pure oil and the data are given in Figure 4.14 (Short and Long test).

Figure 4.14 showed that oil sorption capacity by the sorbent in the oil was slightly higher than the oil sorption in oil suspended in water. Therefore, it can be concluded that these acetylated natural sorbent material should be suitable to remove oil not only from the surface of water, but also from places in which no water is involved [15].

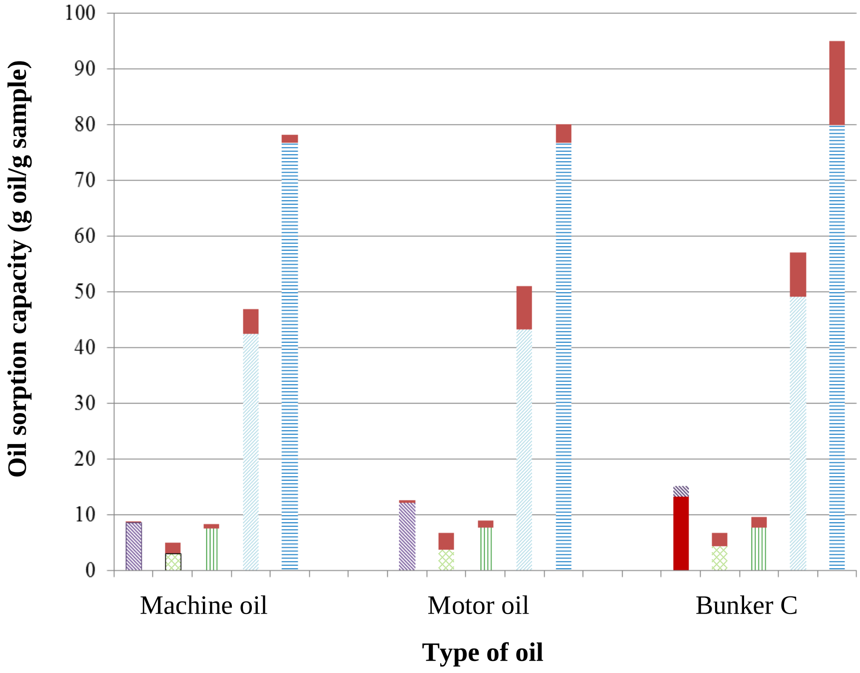


Figure 4.14 Oil sorption capacity: Short test of ▨ the commercial sorbent, ▨ jointed grass pith, ◫ acetylated jointed grass pith, □ kapok fiber, ☰ acetylated kapok fiber and Long test ■ .

Oil viscosity is one of the factors to control the capable of oil sorption capacity of sorbents. In Figure 4.14, oil owning high viscosity tends to have a great initial sorption capacity, which is in the agreement with the previous reports [50,66]. As predicted therefore, Bunker C, which has the highest viscosity among the test oils, showed much greater sorption for all types of sorbent. It is explained that high viscous oil is difficult to drain out from the pores and lumen [47].

After 15 min of immersion, the result of oil sorption capacity of the acetylated products shows the good sorption capacity for all oil-types. The high oil sorption capacity for all categories used acetylated kapok fiber was observed as 76.72, 76.74 and 79.89 g oil/g sample in pure machine oil, motor oil and Bunker C, respectively. The result was agreed to the long sorption test given that the high oil sorption of treated kapok fiber was 78.19, 80.00 and 95.04 g oil/g sample in pure machine oil, motor oil and Bunker C, respectively. This result can be affirmed that it is possible to use the acetylated kapok fiber as a promising sorbent for oil spill treatment due to its capability of high oil intake rate.

4.4.3 Sorption capacity in water test

The result shows unmodified jointed grass pith gave the highest sorption capacity in water as 12.74 g water/g sample, among other materials, including the commercial sorbent, provided that 0.30 g water/g sample of sorption capacity. In addition, all acetylated samples exhibited the lower water sorption capacity compared with all unmodified samples. The reason is that the acetylated samples were enhanced with an increase of partial hydrophobic acetyl group on the surface of materials providing a lower water capacity of acetylated samples was obtained.

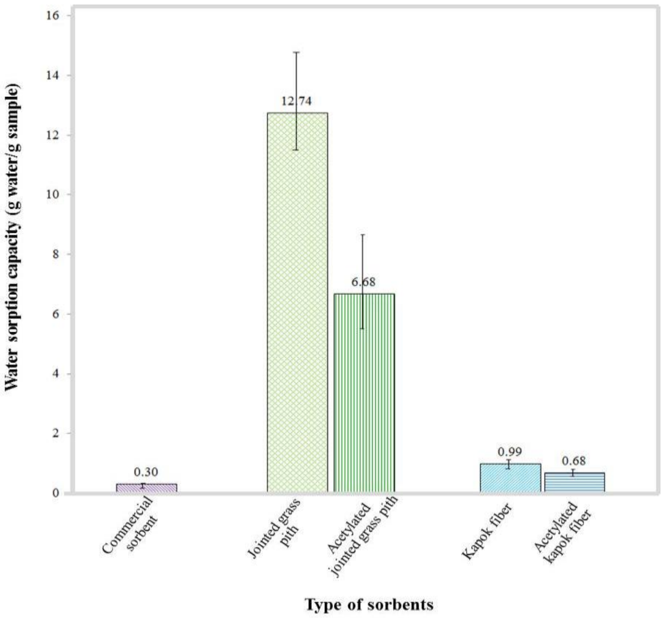


Figure 4.15 Water sorption capacity of difference sorbents.

4.5 Thermal analysis

The thermogravimetry analysis is a technique of evaluating the thermal decomposition kinetics of materials by monitoring the weight loss of the unmodified and acetylated products in a dry air as a function of temperature [67].

The thermogravimetric curve of unmodified and acetylated products are very similar. The initial decrease stage form room temperature to 65°C during to the other residue solvent vaporized [68].

The thermogravimetric curve of unmodified kapok is shown in Figure 4.16, mass was decreased from about 93.965% (at 70°C) to 17.411 % (at 317°C) . Mass of the acetylated kapok decreased from about 92.415% (at 65°C) to 20.300 % (at 305 °C). The limits of their work demonstrated by completely decomposed, the decomposition temperature occurs at 317°C for unmodified and 305°C for acetylated kapok. This decreasing trend of decomposition temperature implies that the thermal stability of the acetylated kapok is lower than that of the unmodified kapok. Different regions can be associated with the hemicellulose degradation in the 200-260 °C regions, cellulose degradation at 240-350 °C, and lignin degradation at 280-500°C [67].

The thermogravimetric curve of jointed grass pith is shown in Figure 4.17, mass was decreased from about 91.577% (at 70°C) to 89.542 % (at 190°C) and to 16.387% (at 311°C). Mass of the acetylated jointed grass pith decreased from about 91.381% (at 67°C) to 7.558 % (at 306°C). The complete decomposition temperature occurs at 311◦C for unmodified and 306°C for acetylated jointed grass pith. This decreasing trend of decomposition temperature implies that the thermal stability of the acetylated jointed grass pith is lower than that of the unmodified jointed grass pith, that is similar result from acetylated kapok fiber.

The thermogravimetry analysis results indicate the thermal stability of jointed grass pith and kapok fiber is slightly decreased due to the acetylation , which similar with previous studies [8,48,69]. Though acetylating results in the decrease of thermal stability it has little or almost no effect on the functional properties of acetylated products.

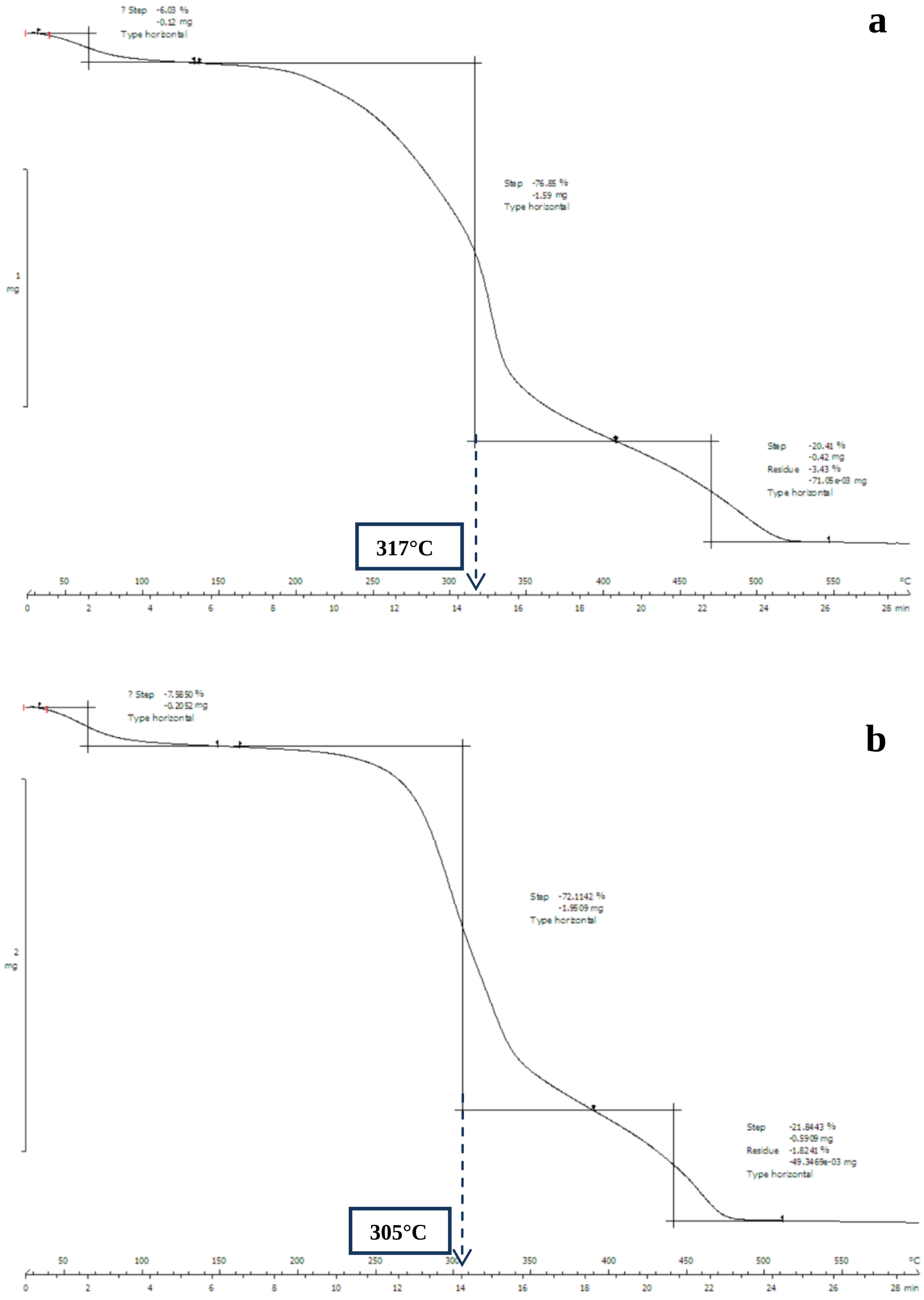


Figure 4.16 Thermo gravimetric curves of unmodified (a) and acetylated kapok fiber (b).

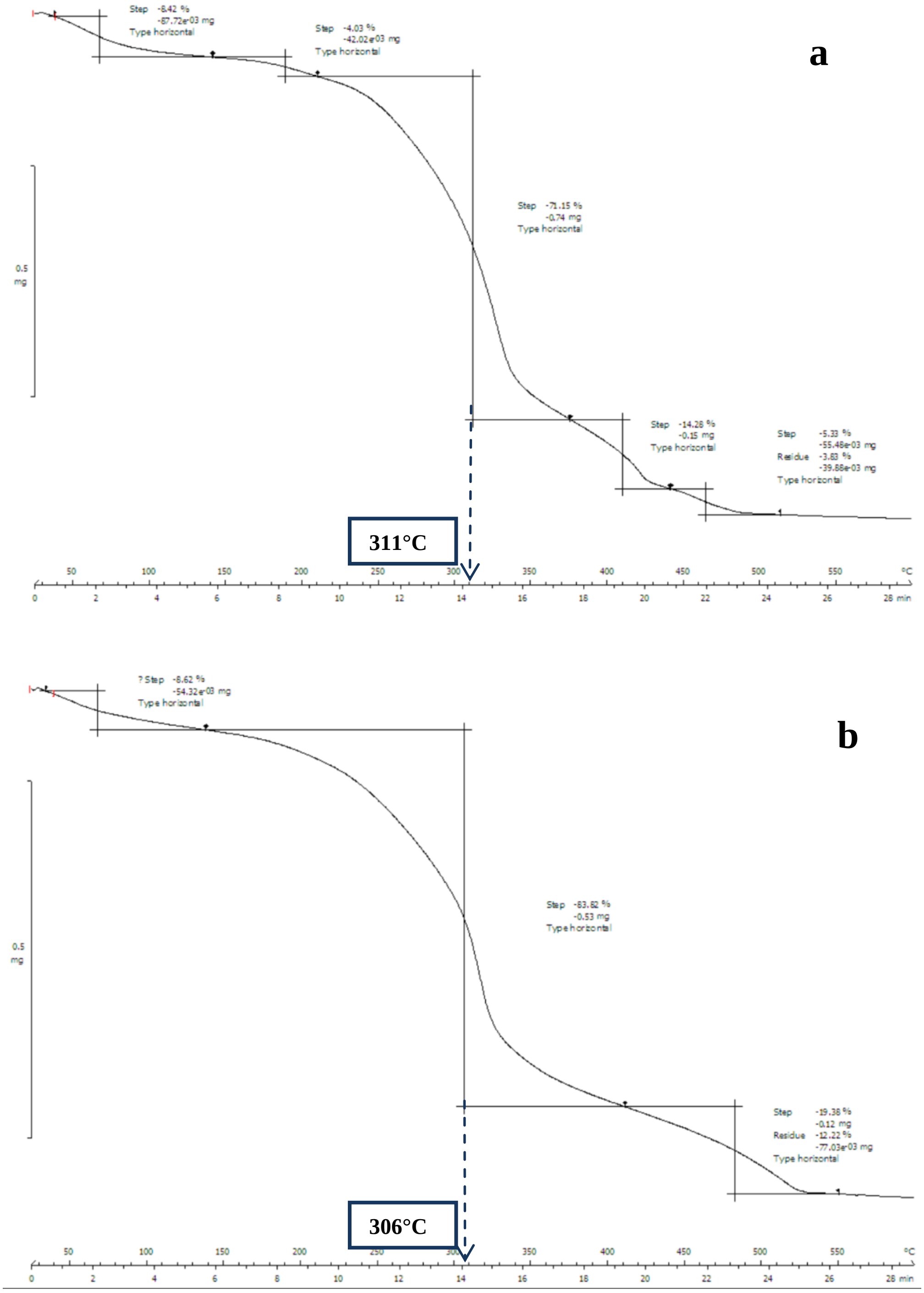


Figure 4.17 Thermo gravimetric curves of unmodified (a) and acetylated jointed grass pith **(**b**)**.

4.6 Various sorbent and their oil sorption capacities

Many natural resources had been used as sorbent for various oils as indicated in Table 4.5. The aim of this research is to compare these performance different kinds of material for oil sorbent.

Table 4.5 List of sorbents and their oil sorption capacity.

Materials	Type of oil	Oil sorption capacity (g/g)	Reference
Natural materials			
Walnut shell	Canola oil	0.51	[70]
Cotton fiber	Vegetable oil	30	[37]
Milkweed fiber	Diesel	38.12	[36]
Kenaf fiber	Diesel	6.25	[36]
Kapok fiber	Machine oil	40	[31]
Leaves residues	Crude oil	4	[41]
Sponge gourd	Crude oil	7	[41]
Coir fiber	Crude oil	7.8	[41]
Sawdust	Crude oil	6	[41]
Sisal	Crude oil	7.6	[41]
Silk-floss	Crude oil	85.8	[41]
Sugi bark	Bunker A	13.4	[29]
Acetylated natural materials			
Acetylated corn straw	Crude oil	67.54	[12]
Acetylated sugarcane bagasse	Machine oil	21.5	[8]
Acetylated rice straw	Machine oil	24	[11]
Acetylated wheat straw	Machine oil	28.8	[9]
Acetylated banana fiber	Machine oil	18.12	[10]
Acetylated jointed grass pith	Machine oil	7.46	This work
	Motor oil	7.61	This work
	Bunker C	7.70	This work
Acetylated kapok fiber	Machine oil	76.72	This work
	Motor oil	76.74	This work
	Bunker C	79.89	This work

The results showed that oil sorption capacities were varied with type of sorbents. As can be seen in Table 4.5, silk-floss had high oil sorption capacity at 85.8 g oil/g sample (for 24 h), whereas walnut shell had lower oil sorption capacity. Annunciado et al [41] reported, that specific gravity of silk-floss (<0.62 g/cm^3) is lighter than water. It may influence their performance on the sorption, especially wet system.

In part of acetylated natural materials, it is shown that acetylated corn straw [12] and acetylated kapok fiber from this work reveal high potential to be used a general oil sorbent even though it is not as good as silk floss. Despite the fact that during the same time and type of oil, acetylated kapok could absorb better (95.04 g oil/g sample for 24 h) but the good performance of unmodified silk-floss was also interesting in the future.

CHAPTER V

CONCLUSION AND SUGGESTION

Jointed grass pith and kapok fiber can be used as oil sorbents. The jointed grass pith sample which was prepared with in the shorter length exhibited the higher oil sorption capacity and the highest oil absorption was obtained at the 0.5 cm. Kapok fiber is not significantly different on oil sorption capacity in the comparison with in the length of the prepared samples.

Either kapok fiber or jointed grass pith, the acid treatment removed the exterior wax out of the surface of the both provided that a more free hydroxyl functional groups to react with the acetylating agent and also giving a rougher surface which was good for surface modification to enhance the oil sorption capacity, whereas pore and lumen structure of both sorbents were destroyed by the base treatment, which could reduce the composition of cellulose and also decreased the oil sorption capacity.

Jointed grass pith and kapok fiber has been successfully acetylated by reacting with acetic anhydride in the presence of NBS catalyst. The reaction can proceed at mild condition in a solvent free system. The DS and oil sorption capacity vary with reaction conditions and the optimum condition of this reaction was found at 40 mL of acetic anhydride with 1.5% NBS at 80^oC under 2.0 hour for acetylated joined grass pith and 80 mL of acetic anhydride with 1.5% NBS at 80^oC under 2.0 hour for acetylated kapok fiber, respectively. The thermal stability of acetylated product was a little lower than that of the unmodified. More importantly, it was found that the oil sorption capacity of the acetylated kapok fiber was much higher than commercial sorbent while that of acetylated jointed grass pith about the same as the commercial. Oil with higher viscosity tends to have a higher oil sorption capacity. Acetylated jointed grass pith and acetylated kapok fiber are derived from natural products therefore biodegradability, quick oil uptake and easy to desorb, thus, they could be partially or totally substituted the commercial sorbent because they are more friendly to the environment.

5.1 Further works

- To synthesize and investigate the sorption capacity of the acetylated cellulose of silk-floss, which showed the high sorption capacity of untreated (85 g oil/g sample for 24 hours) [41].

- To increase the mechanical strength and reduce the cost, blending acetylated product with PP, rayon or other synthetic fibers.

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APPENDICES

APPENDIX A

Calculations

Oil sorption capacity

The initial dry acetylated kapok fiber is 0.05 g, weight of after oil absorb is 4.22 g. We obtain the oil sorption capacity for 80.05 g oil/g sample.

Example:

$$\text{Oil sorption capacity} \quad = \frac{4.22 - 0.05}{0.05} = 80.05 \text{ g oil/g sample}$$

Sorption increase

Oil sorption capacity of jointed grass pith is 1.84 g oil/g sample, when cut into short size, oil sorption capacity increase to 3.01 g oil/g sample. We obtain the sorption capacity increase for 63.56%.

Example:

$$\%\text{Sorption increase} \quad = \left(\frac{3.01-1.84}{1.84}\right) \times 100 = 63.56\%$$

Degree of substitution

Absorbance value of acetylated jointed grass pith at 1750 cm^{-1} is 0.61, at 897 cm^{-1} is 0.21.We obtain degree of substitution for 2.59.

Example:

$$\text{Degree of substitution} \quad = \frac{0.61}{0.21} = 2.90$$

APPENDIX B

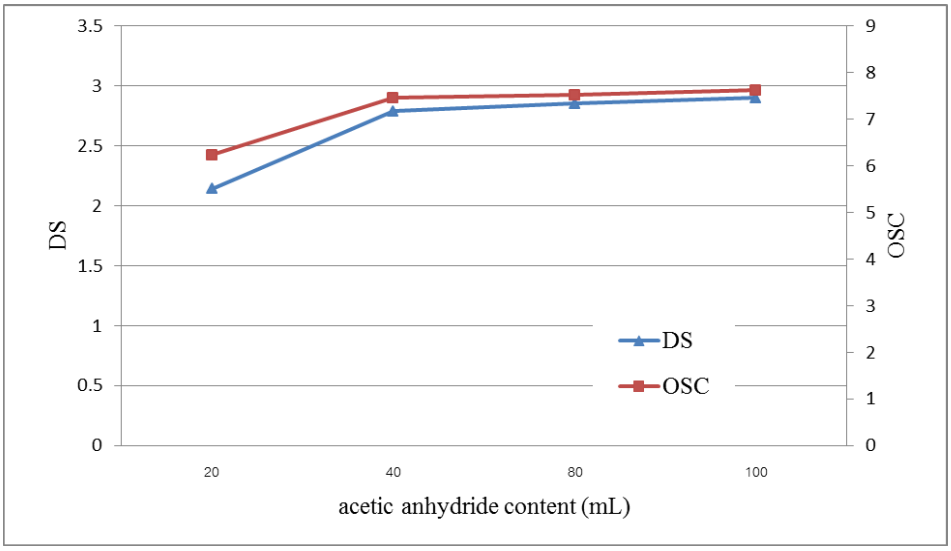

Figure B-1 Effect of acetic anhydride content of acetylated jointed grass piths on DS and OSC using 1.5%NBS at 80°C 2 h.

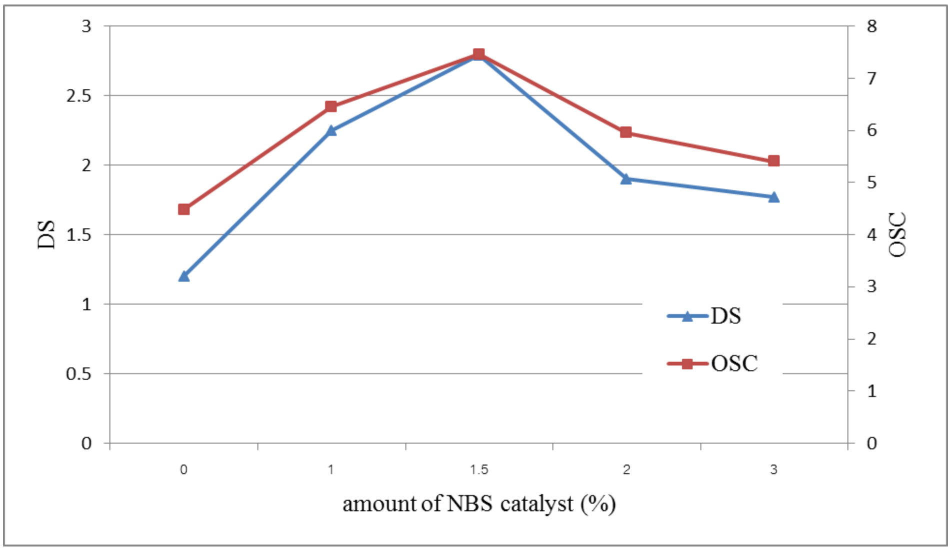

Figure B-2 Effect of amount catalyst of acetylated jointed grass piths on DS and OSC with 40 mL acetic anhydride at 80°C 2 h.

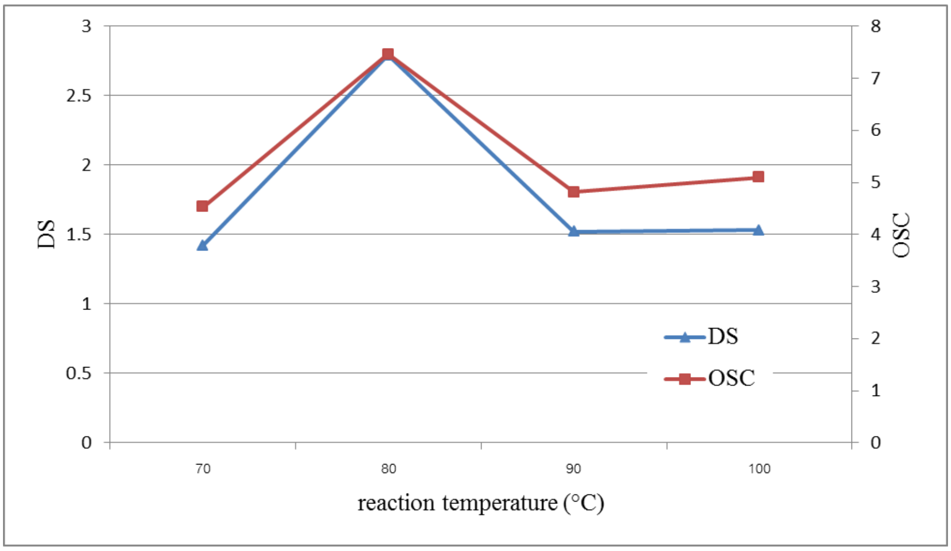

Figure B-3 Effect of reaction temperature of acetylated jointed grass piths on DS and OSC with 40 mL acetic anhydride 1.5%NBS for 2 h.

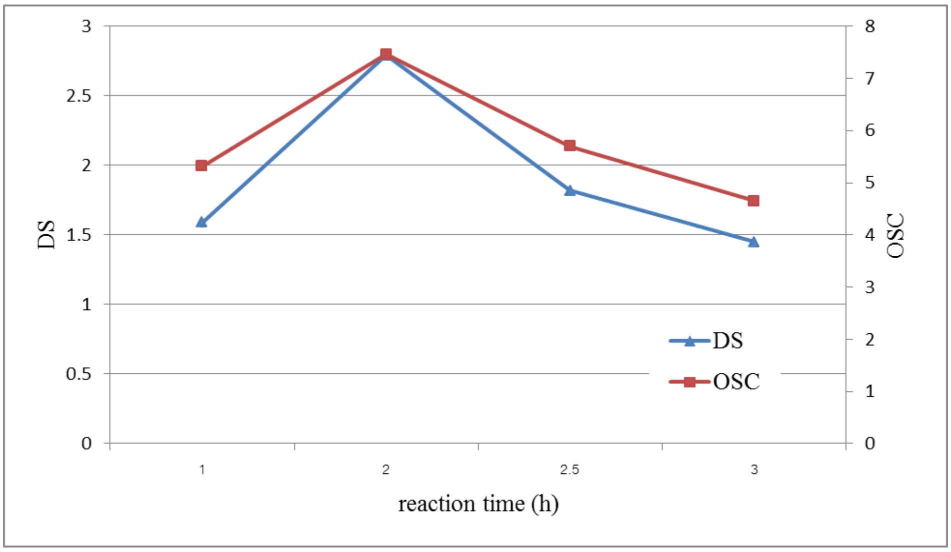

Figure B-4 Effect of reaction time of acetylated jointed grass piths on DS and OSC with 40 mL acetic anhydride 1.5%NBS at 80^{o}C.

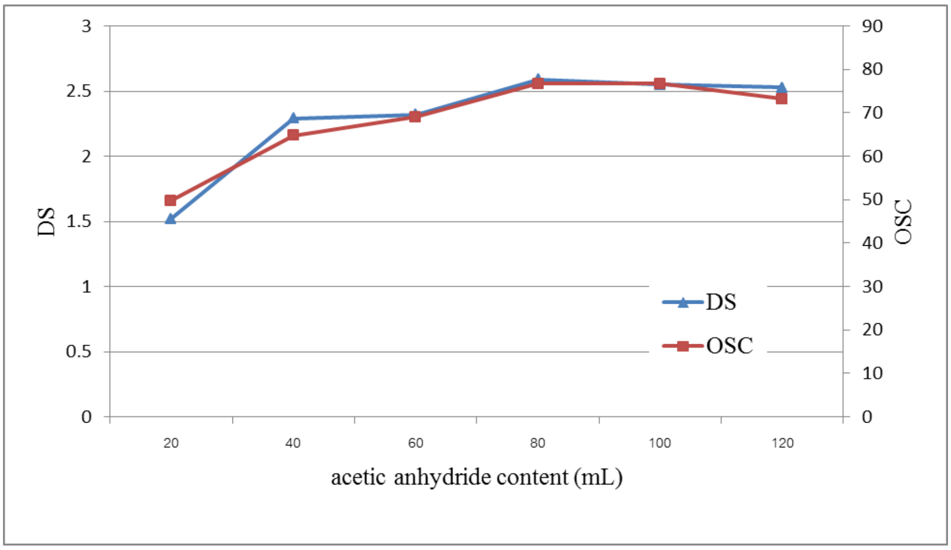

Figure B-5 Effect of acetic anhydride content of acetylated kapok fiber on DS and OSC using 1.5%NBS at 80°C 2 h.

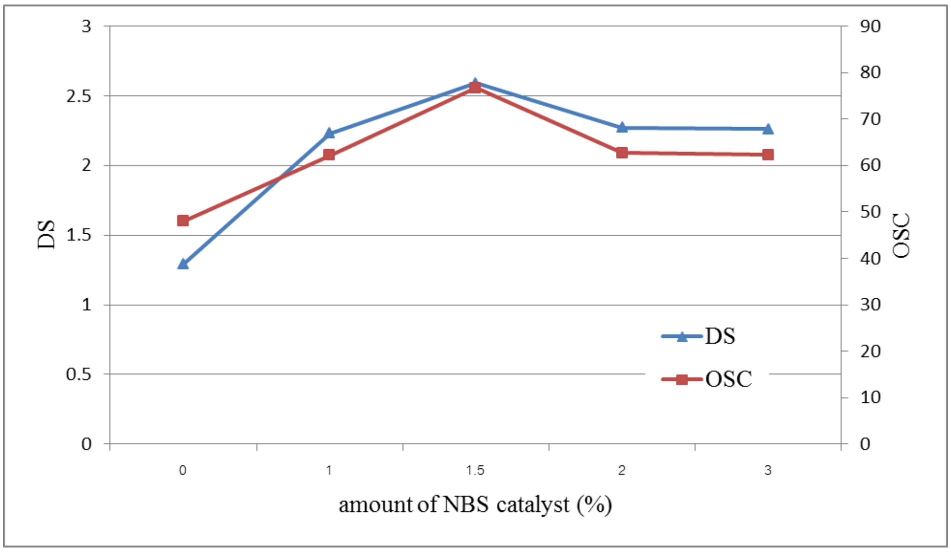

Figure B-6 Effect of amount catalyst of acetylated kapok fiber on DS and OSC with 80 mL acetic anhydride at 80°C 2 h.

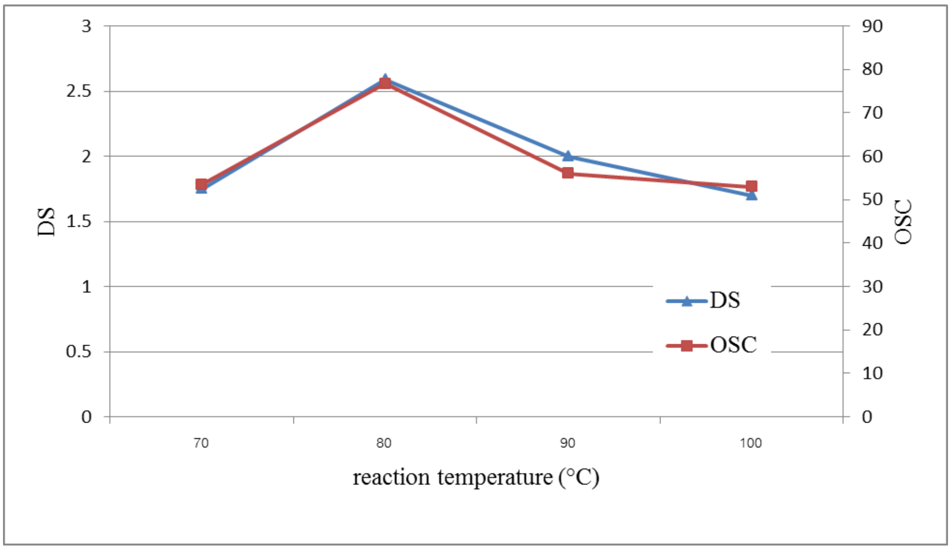

Figure B-7 Effect of reaction temperature of acetylated kapok fiber on DS and OSC with 80 mL acetic anhydride 1.5%NBS for 2 h.

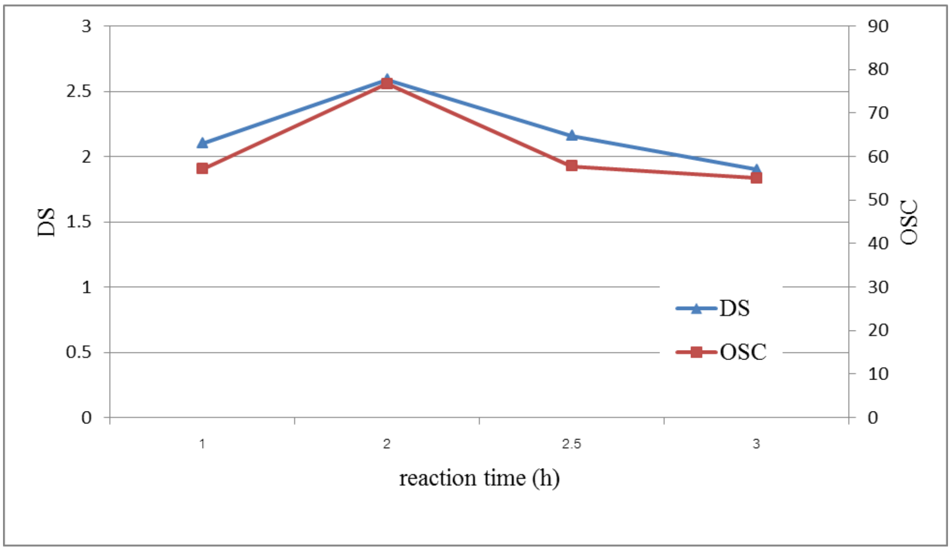

Figure B-8 Effect of reaction time of acetylated kapok fiber on DS and OSC with 40 mL acetic anhydride 1.5%NBS at 80^{o}C.

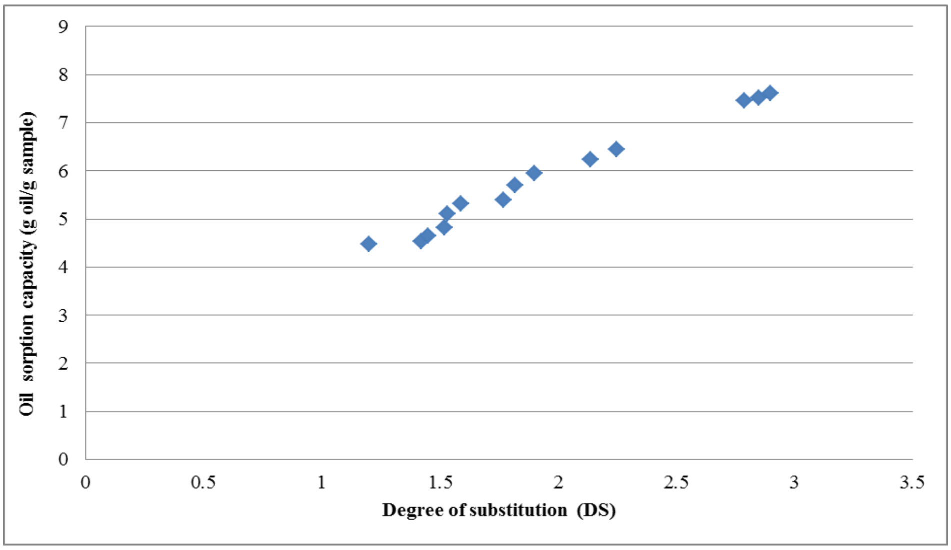

Figure B-9 Relationship between oil sorption capacity (machine oil-short test) and degree of substation of acetylated jointed grass pith.

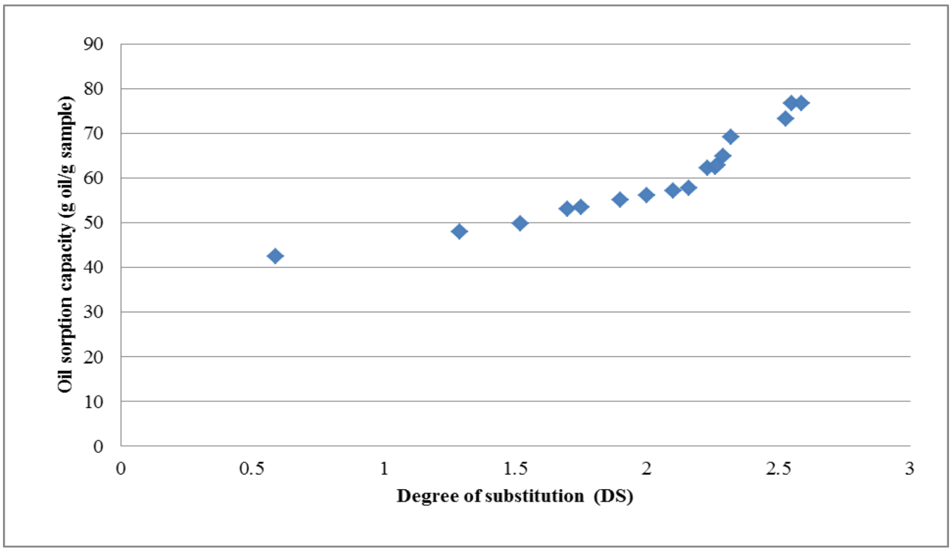

Figure B-10 Relationship between oil sorption capacity (machine oil-short test) and degree of substation of acetylated kapok fiber.

VITAE

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