



ChemTech

International Journal of ChemTech Research

CODEN(USA): IJCRGG, ISSN: 0974-4290, ISSN(Online):2455-9555

Vol.10 No.2, pp 424-448, 2017

Agricultural Residues (Wastes) for Manufacture of Paper, Board, and Miscellaneous Products: Background Overview and Future Prospects

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Abstract: An extensive background overview on the use of agricultural residues (wastes) for production of paper, board, binderless board, energy, different types of fuels by pyrolysis (solid, liquid and gaseous fuel), many petrochemicals substitutes, charcoal (active carbon), dissolving pulps and rayon. It includes both scientific and industrial data, case studies, current status, sustainability of paper and sugar industries, green nanotechnology, and future prospects.

Keywords: Agricultural Residues (Wastes); Paper and Board manufacture; Sustainability of Paper and Sugar Industries; Green Nanotechnology; Future Prospects.

Introduction

In 1954, the first author of this overview (Prof. Dr. Yehia Fahmy) founded the Cellulose and Paper Department, National Research Center, Cairo, Egypt. Since then, extensive research work was conducted -for the first time- on agricultural residues (wastes) in this department. The mentioned work encompassed the use of agricultural residues (wastes) for manufacture of paper, board, and miscellaneous products. Several research works of the first author were transferred into successful industrial factories eg. Rakta Paper Factory in Alexandria in Egypt, Edfo Paper Factory which is affiliated to the Egyptian Sugar Company, Faraskor Board Factory in Egypt etc^{1-81, 90-110}.

Agricultural residues are residues accumulated after the harvest of annual plants, i.e. seasonal crops available during summer or autumn. Only about 8 % of global paper and board production is based on agricultural wastes. 92 % of world production depends upon wood whether softwood or hardwood.

Many countries, which lack forests, are obliged to utilize agricultural residues as raw materials for paper and board manufacture. However, in countries rich in forests, there is a trend to use agricultural residues – if available – in order to reduce deforestation. It is expected that the percentage of utilization of agricultural residues for paper and board manufacture will gradually increase. A percentage of at least 10 % is anticipated for the near future.

The estimated global availability of the most common agricultural residues is given in Table 1.

The following Table shows the estimated global availability of agricultural residues

| Raw Material | Bone Dry Metric Tons (bdmt) |
|-----------------------|-----------------------------|
| Cotton Linters | 2,700,000 |
| Cotton Staple | 18,300,000 |
| Cotton Stalks | 68,000,000 |
| Sugarcane Bagasse | 102,000,000 |
| Sorghum Stalks | 252,000,000 |
| Corn Stalks | 750,000,000 |
| Straws | |
| Flax (oil seed) | 2,000,000 |
| Grass Seed | 3,000,000 |
| Rye | 40,000,000 |
| Oat | 55,000,000 |
| Barley | 195,000,000 |
| Rice | 360,000,000 |
| Wheat | 600,000,000 |
| Total Residues | 2,448,200,000 |

The estimated planted areas of the most important crops in Egypt are given in Table 2. The residues remaining after harvesting the crops i.e. agricultural wastes can be estimated as about 2-3.5 ton/Feddan (except sugarcane).

Table 2 The estimated planted areas of the most important crops in Egypt

| Item | Year of Production | Planted Area (Feddan) |
|----------------|--------------------|-----------------------|
| Wheat | 2002 | 2,450,428 |
| Cotton | 1998 | 788,812 |
| Rice | 2001 | 1,340,270 |
| Corn (maize) | 2000 | 1,228,248 |
| Corn (sorghum) | 2000 | 386,980 |
| Barley | 2001 | 73,554 |
| Sugarcane | 2001 | 311,986 |
| Banana | 2001 | 54,447 |

It is evident that wood is the dominant raw material for manufacturing pulp, paper and board industry. For this reason, agricultural residues are termed non-woods. Both wood and non-woods are fibrous plants i.e. plants rich in fibers.

Paper and board are composed mainly of fibers. Theoretically speaking any plant containing a reasonable amount of fibers can be used as a raw material for pulp and paper production. In practice, this is not the case. Besides the abundance of the plant, a steady supply and many other requirements are necessary. The fiber content of the plant is important. The plant contains in addition to fibers, many non-fibrous cells e.g. parenchyma cells. Fibers themselves vary much in different plants regarding their length, width, fine or microstructures, as well as their chemical composition. In one and the same plant there are different types of fibers. The same fiber type is not equal in dimension but contains a spectrum of different dimensions. For this reason, one speaks of "average fiber length". The length of the fiber is one of the most important parameters affecting paper strength.

Apart from cotton rags and cotton linters, softwood is the most homogeneous raw material used in pulp and papermaking, as far as anatomical structure is concerned. About 90 % of the softwood structure is made of trachieds. Paper maker designate all elongated cells, whether bast fibers, wood vessel segments, or trachieds as "fibers". Therefore, we say 90% of softwood structure is constituted of fibers. These fibers could be as long as 5 mm.

Hardwoods are less homogeneous in anatomical structure than softwoods, and contain fewer fibers. The average fiber length of hardwood is shorter than those of softwoods and is about 1.5-2 mm.

Agricultural residues –except the specific case of cotton linters or flax– are much more heterogeneous than softwoods. They are even less homogeneous than hardwoods – regarding anatomical structure. The average fiber length of most agricultural residues is nearly equal to the average fiber length of hardwoods¹⁻⁸⁹.

2. Types, Properties, and Characteristics of Agricultural Residues (Wastes): -

Agricultural wastes vary much in morphological structure, anatomical structure, as well as chemical composition. In the following, the most common and most important agricultural residues are discussed¹⁻⁸⁹.

2.1. Cotton linters: -

After ginning i.e. removing the cotton staple fibers from the cotton seeds, some short fibers remain on the seed. These fibers are called cotton linters. They cause troubles while pressing the seeds for oil extraction. They absorb some oil and anyhow should be removed from the oil. Therefore, it is preferable to remove cotton linters from the seeds before sending them to oil refineries. This is done by delinting machines. The obtained linters are much shorter than staple fibers and cannot be used for producing textiles. The average fiber length of cotton linters is about 6.0 to 7.0 mm for first cut linters, 2.0 mm for second cut linters, and 3.5-5.0 mm for mill run linters. Usually the cellulose of linters is about 90 %, the rest being resins, mineral, etc. It becomes evident that fiber length of linters is as long as fiber length of softwoods or even longer. In paper industry, all elongated cells are called fibers whether tracheids or wood vessels. Linter as a raw material is superior to softwood. This is due to its higher cellulose content. Cellulose with its abundant hydrophilic hydroxyl groups is the main strength maker of paper. The adjacent fibers in the paper web become held together by hydrogen bonds formed between hydroxyl groups located on the surface of adjacent fibers. However, in order to fulfill this phenomenon, the fibers must be flexible and must be capable of swelling in water. One has to remember that paper is produced from a water suspension of fibers, called slurry. Not all fibers swell in water to the same extent. The swellability depends upon the structure of the fiber wall i.e. cell wall of the fiber. Fibers used in papermaking are dead mature elongated cells whose protoplasm has died and decayed. In other word we are dealing with cylinders of cell walls with a lumen, which the protoplasm had earlier occupied.

The cell wall is a composite made of different layers and elements. These are fine thread like microscopic elements called fibrils, which in turn are made of microfibrils. These elements are arranged in different patterns in the secondary cell wall.

Besides the microstructure or fine structure of the cell wall, the ratio of cell wall thickness to cell lumen plays a role in papermaking. A narrow lumen decreases flexibility of the fibers and minimizes their conformation during paper sheet formation on the sheet former. This reduces hydrogen bonding and hence paper strength. Again, the molecular weight of cellulose i.e. degree of polymerization of glucose units in cellulose, called DP is of importance. High DP promotes paper strength. Cotton linters cellulose possesses a very high DP.

Taking the before mentioned factors into consideration it becomes evident that cotton linters rate as no. 1 as a raw material for papermaking and even surpasses softwood. Thus among the agricultural residues, cotton linters is a distinguished raw material for papermaking. However most other agricultural residues except ramie and flax are inferior to softwood and even to some hardwoods.

Cotton linters - compared to woods and nonwoods - are loose fibers. Therefore, they can be easily transformed into pulp. Cotton linters represent a small morphological part of the cotton plant i.e. merely the seed hairs. If you take the rest of the plant i.e. the cotton stalks, you have then a whole plant consisting of stems, branches, leaves and cotton bolls.

Egyptian cotton species are characterized by low content of cotton linters. Cotton linters represent a costly agricultural waste. It possesses long fibers and is made mainly of cellulose characterized by high DP. It is used only for production of specialty paper, where permanence and durability are required. These are security paper, document paper, filter paper etc.

2.2. Cotton stalks: -

Cotton stalks represent an important agricultural waste in Egypt. Here, the fibers i.e. the cells are held strongly together within the stem of the plant and are not loose as cotton linters. Hence to obtain paper from them one has at first to loosen and destroy a part of the cell wall in order to disintegrate the cells i.e. fibers from each other. In other words, one has to eliminate or liberate the individual fibers of the plant. This process is called pulping and can be done either mechanically or chemically, or by both processes leading to a mass of loose fibers easily suspended in water. This product is called pulp and it is the intermediate raw material in papermaking. Technically this process depends almost upon dissolving the lignin that holds the cells together in the plants as in the tree trunk. Therefore, the process is also called delignification. Different plants contain different amounts of lignin. Lignin in plant acts as the cement which holds the bricks together in building. Lignin has different chemical structure in different plants and it varies in the ease in which it can be removed according to plant type. The chemical composition of the fibers defines and affects pulpability i.e. the ease of pulping of the plant raw material. The ease of lignin removal is an important factor affecting pulpability.

2.2.1. Morphological structure

Cotton stalks are branched and carry leaves and unopened cotton bolls. They still retain the roots. The stalks consist of the bark and woody core. The bark constitutes about 25 % and the woody core about 75 % by weight of the whole stalk.

2.2.2. Anatomical structure

The average length of bast fibers in the bark amounts to 2.0 mm. The average length of woody fibers is about one half that of bark fibers (range 0.4 mm – 2.4 mm)

2.2.3. Chemical composition

The chemical analysis of cotton stalks varies from season to season and depends on species. The woody core contains about 42 % of alpha cellulose, 21% of lignin, 21 % of pentosans and 2 % of ash. The bark contains less lignin but more ash.

2.3. Wheat straw: -

2.3.1. Morphological structure

The whole straw, as purchased, is constituted of stems and leaves. The stem is made up of internodes and nodes, and carries rachies. The leaf is made of leaf sheath and leaf blade. Compared to wood, which is the most popular raw material for pulp production, straw is more heterogeneous. Wood arrives to the factory in form of logs. After debarking one gets a homogeneous material namely trunk or stem. In the case of straw one gets stems, leaves, rachies, dirt and dust adherent to straw. This is due to straw morphological nature, and mode of collection and baling.

2.3.2. Anatomical structure

Anatomically straw is made up of vascular bundles, bast fibers, parenchyma cells (pith cells), and epidermis cells. The percentage of these constituents is different in different morphological parts of straw. The leaves contain more epidermis cells than the stem. Straw fibers, which are principally derived from the bast cells in the internodes, are fairly long (about 1.5 mm) slender with sharply pointed ends. The short non-fibrous cells (called O-fibers) consisting of epidermal cells, platelets, serrated cells and spirals are more or less undesirable for papermaking. Each group of these cells has different cell wall structure i.e. different pore sizes and different surface area. Also these cells vary much in chemical composition.

It becomes evident that we are dealing with highly heterogeneous system compared to softwoods, which are constituted of one main group, namely 90 % tracheids. The high percentage of non-fibrous cells in straw reduces the strength of paper obtained from straw. Also, considerable portions of these non-fibrous cells, also called fines, are lost during washing of straw pulp. This state of affairs reduces the yield of the pulp, but at the same time improves the paper strength.

2.3.3. Chemical composition

Different morphological parts of wheat straw possess different chemical composition. Best fibers are highest in cellulose content. Epidermis cells are highest in mineral and silica content. This high ash content is a disadvantage for paper properties. Therefore, it is sometimes preferable to remove a large portion of leaves especially blades from straw before pulping. The chemical analysis of wheat straw varies from season to season and depends on species. The chemical analysis of one species of Egyptian wheat straw is as follows: Alpha cellulose 47.7 %, Pentosans 17.1 %, Lignin 18.2 %, Ash 8.34 %, Silica 3.42 % .

2.4. Rice straw: -

2.4.1. Morphological structure

This is similar to the morphological structure of wheat straw except that the percentage of leaves in rice straw is much higher than in wheat straw and could amount to more than 35 % of the whole straw. Accordingly, the amount of silica in rice straw is much higher than in the case of wheat straw, and could be as high as 18 % of the whole straw.

2.4.2. Anatomical structure

This is similar to wheat straw except the presence of higher percentage of epidermis cells in rice straw.

2.4.3. Chemical composition

The chemical analysis of rice straw varies from season to season and depends on species. In the following the chemical analysis of an Egyptian rice straw sample is given: Alpha cellulose 41.8 %, Pentosans 21.6 %, Lignin 13.6 %, Ash 18.4 % and Silica 16.7 %.

2.5. Sugarcane bagasse: -

2.5.1. Morphological structure

Bagasse is the fibrous mass or residues left after the crushing and extraction of sugar from sugar cane.

2.5.2. Anatomical structure

Bagasse contains fibers of 1.7 mm average length and 20 microns in diameter. These are mainly bast fibers. In addition, bagasse contains shorter fibers namely vessel segments and a large amount of parenchyma cells arising from the pith, as well as epidermis cells arising from the outer sheath of the cane. The average fiber length of whole bagasse according to number amounted to 0.85 mm., while according to length it was 1.46 mm.

2.5.3. Chemical composition

The chemical analysis of bagasse varies from season to season and depends on species. In the following the chemical analysis of partially depithed Egyptian bagasse (co. 413) was: Alpha cellulose 43.2 %, Pentosans 21.2 %, Lignin 18.2 %, Ash 1.98 % and methanol-benzene extractives 8.3 %.

2.6. Corn stalks: -

2.6.1. Morphological structure

It is made up of the stems and leaves.

2.6.2. Anatomical structure

It is more or less similar to sugar cane but has more pith. The pith cells i.e. the parenchyma cells are somewhat smaller than in bagasse. A high percentage of these cells are undesirable for papermaking, as the same in the case of bagasse.

2.6.3. Chemical composition

The chemical analysis of corn stalks varies from season to season and depends on species. In the following the chemical analysis of an Egyptian corn stalks sample is given: Holocellulose 77 %, Alpha cellulose 53.6 %, Hemicellulose 16.2 %, Lignin 22.2 % and Ash 3 %.

3. Utilization of Agricultural Wastes for Paper and Board Production: -

3.1. Prerequisites for the use of agricultural wastes for paper and board production: -

For using a certain agricultural waste for paper and board production, the waste must be found in abundant amount. A steady and continuous supply should be secured over the years. The agricultural waste should be easily collectable. Ease of baling and ease of transportation to the factory site is necessary. Before all the agricultural wastes should be cheap and of no more valuable or profitable use than if utilized for papermaking. The agricultural wastes should be capable of being stored for at least one year without deterioration. Storage and protection means for storage should be not costly.

If these parameters are applied to the agricultural residues listed before, it becomes evident that all of them, more or less, meet these requirements. Wheat straw may be the most expensive raw material because it is used as feed or fodder for farm animals, and could be sometimes unavailable, but its superiority for pulp and paper production could make wheat straw an attractive raw material. Again, cotton stalks due to its bushy and voluminous character might not be easily baled and pressed. However, this difficulty could be overcome by taking some measures¹⁻⁸⁹.

3.2. Suitability of Agricultural Wastes for Pulp, Paper, and Board Production:

The raw material must undergo several operations in order to produce paper. These operations are:- preparation of the raw material, pulping, bleaching, screening, washing, refining or beating, blending, and finally paper machine operations¹⁻⁸⁹.

3.2.1. Preparation of the Raw Material (Agricultural Wastes):

3.2.1.1. Preparation of woody raw materials such as cotton stalks: -

Cotton stalks is an agricultural residue but it is not a real non-wood as other agricultural residues. Nevertheless, some literature describes cotton stalks as non-wood since it is an agricultural waste and is harvested annually. It is obvious that for paper industry wood means logs of grown trees of more than 5 or 10 years old. These logs are of substantial strength and stiffness. As known the outer layer of trees is bark. Bark contains some best fibers but more cork cells. Bark is generally undesirable for papermaking. This is mainly due to the dark color, bark implements on the pulp, if not removed before pulping. For coarse grade pulp used for production of cheap packaging paper, the whole tree can be used for pulping. For finer pulp, debarking is necessary before pulping. There are several debarking methods using abrasive, hydraulic or mechanical debarkers. In some cases the wood can be backed by hand by stripping off the bark with a spade or by shaving with a draw knife. Usually bark represents about 7-10 % of the wood weight.

In the case of cotton stalks bark can be easily removed by hand after certain pretreatment. A debarking machine for cotton stalks had been designed in the National Research Center, Cairo, Egypt (N. R. C.) and applied to Egyptian cotton stalks. The purpose was to gain bast fibers, which were found to be equivalent to jute fibers. These fibers were used for making sacs. The debarked cotton stalks is then used for pulping.

Cleaning is necessary after debarking as well as in the case of using the whole undebarked cotton stalks. Water sprays are used to clean the wood and wash away the dirt from the bark. After cleaning it is necessary to cut the raw material in small pieces otherwise it would be difficult to pulp it. This is affected by chippers. Cutting wood into small pieces improves the penetration of the cooking chemicals. The chipper consists of a large disk fitted with sharp knives. The disk rotates at high speeds.

3.2.1.2. Preparation of straws: -

The straw bales have at first to be opened by removing the wrapping wires. The straw is then cut to pieces about 6 cm in length. After coming out from the cutter, the chopped straw is sucked into a cyclone separator where the loose fines and dust are drawn out through a screen at the top. Such cleaning is sufficient for wheat straw. On the other hand rice straw requires a further cleaning step. After cutting straw, the leaves of rice straw, especially the blades are broken into fine brittle parts which are undesirable for papermaking. Leaf blades contain less fiber and more fines than rice straw stem, and contains high percentage of silica. The second step of cleaning rice straw is affected by charging the chopped straw in hydra pulpers with false bottom. Through agitation in water, the dirt and leaf particles can be easily removed.

3.2.1.3. Preparation of bagasse: -

Bagasse comes out from the sugar mill in a more or less clean state after extracting the juice from it. Bagasse contains a considerable amount of pith cells which are undesirable for papermaking. Therefore, it is necessary to remove them as much as possible. A few amount of pith cells, however, can act as binder for the fibers, and thus improve paper properties. There are several types of depithing processes which depend on mechanical treatment of bagasse to separate the pith cells from the rest of the fibers. Depithing of bagasse can be affected in wet state or in dry state or even in water suspension. Usually disc refiners are used for this purpose. There is also a biological method proposed for depithing based on dissolving the pith cells.

3.2.2. Pulping, Pulpability and Technology: -

The pulping process aims at liberation of the plant fibers from the plant raw material. In other words pulping separates plant fibers from each other. There are several pulping processes. The choice of the pulping process depends upon the type of pulp and paper which is to be produced.

3.2.2.1. The simplest process of pulping is the mechanical process:

This method implies mechanical destruction of lignin which glue the fibers and hold them together. The most widely used mechanical method is the stone ground wood method. This method involves the wet grinding of wood into a fibrous mass by means of a large revolving grinding stone. Logs of wood are hold with pressure against the surface of the stone. A stream of water is sprayed on the stone to carry the pulp away. Ground wood pulp contains practically all the lignin of the original wood. The yield is about 95 % of the original wood. The ground wood pulp contains individual fibers, broken fibers, fines and coarse fiber bundles. The disadvantage of ground wood pulping is that grinding weakens the fiber and that lignin is not removed. Ground wood pulp fibers are not as strong as their chemically lignin free counterparts. But the great advantage is the high yield and low cost.

This pulp is used mainly for newsprint where cheapness is necessary. A disadvantage is the presence of the whole lignin in the pulp. This causes yellowing of the paper after short time. Yellowing is however allowed in newsprint since the newspaper is dispensed with, after a short time. Unfortunately grinding cannot be applied to agricultural residues even to cotton stalks, which are woody in nature. In grinders, logs are cut to about one meter pieces and the logs are strong and resist the pressure of grinding so that they only defibrize after grinding. Mechanical treatment of some agricultural residues using other mechanical devices, rather than grinding stones, practically destroys the fibers to a more or less powdery state. However, in the case of cotton stalks we were able to produce a mechanical pulp with reasonable properties.

3.2.2.2. Thermomechanical process: -

This process is a variation of mechanical process where heat is used. Wood chips or pieces of agricultural wastes are softened by steam. While the wood has been softened and is still heated, it is pumped into the refiners where fibrization takes place.

3.2.2.3. Whole wood fiber manufacturing process: -

Here the wood is reduced to a fibrous state without chemical action on the wood and without appreciable delignification so that the final product has essentially the same composition of the original raw

material. Ground wood pulp, described earlier, is essentially a whole fibers pulp. In these processes the yield varies between 90 % and 98 %. In other processes, the raw material is treated with steam or hot water. This weakens the bonds between fibers and the produced pulp contains fewer broken fibers than in pure mechanical pulping at room temperature. Steaming also reduces the power consumption required for defibring. Pulp produced by the whole wood processes are suitable only for coarse wallboards, insulating materials saturating felt and corrugating paper.

They can also be formed into fiber board or hard board. Agricultural residues can be used for this process by using different mechanical means after steaming. The produced pulp is run on a Fourdrinier or cylinder paper machine till wet web is formed. After pressing, the web it is taken out and cut into pieces then fed automatically into multiple – deck driers where the board is dried by means of steam coils under pressure. To produce hardboard which is a type of fiber board, fibers are welded together by pressing the board at high temperature (e.g. 195 °C) and high pressure. It is desirable to add heat – setting resins e.g. phenol formaldehyde to the stock before hot pressing. We have successfully prepared hardboards at Cellulose and Paper Department (N. R. C.) from several Egyptian raw materials.

Another process for production of fiber board is the Masonite process. It is a unique process. The raw material chips about 2 cm long are fed into a battery of digesters or “guns” where they are steamed at high pressure and then exploded. Steaming is applied in two steps, both for 30 seconds till a pressure of 1,200 p.s.i.. Then the digester is blown by means of a quick opening valve to release the contents into a cyclone. The explosive effect of this rapid release breaks up the chips into a fibrous mass. The high temperature causes acid hydrolysis, which dissolves a part of the hemicellulose and softens the lignin. Thus, the lignin in the pulp fibers contains sugars and organic acids, which must be washed out of the pulp in order to obtain a satisfactory product. These useful by-products can be recovered from the wash liquor. After refining, the fibers can be formed into a light weight, low density board used for insulating purposes. Because of the reactive nature of the lignin in the Masonite process, the fibers can be pressed into a product of extreme durability and hardness. This board has a specific gravity of about 1.00 and is a good building material.

3.2.2.4. Semichemical pulping process: -

All processes of semichemical pulping deliver (high yield pulp). In semichemical pulping a mild or reduced chemical treatment is applied to the raw material. This treatment is just capable of dissolving lignin partially, and leads to incomplete release of individual fibers. We get rather fiber aggregates. However the remaining lignin in the treated raw material become sufficiently soft to be destroyed by a further mechanical treatment. Semichemical pulping is economical because of the high yield it delivers, and the low chemical consumption. In semichemical pulping only 30 – 50 % of the lignin and 35 – 40 % of the hemicellulose is removed. On the other hand, in ordinary chemical pulping 90 – 95 % of the lignin is removed and 60 – 68 % of the hemicellulose is removed. The yield of semichemical pulp varies between 65 % and 85 % compared to less than 50 % or 40 % in the case of chemical pulping. The properties of semichemical pulp are intermediate between whole wood fibers (e.g. mechanical pulp) and full chemical pulp. Any of the pulping reagents used in chemical pulping can be applied for semichemical pulping but under much reduced conditions of concentration, temperature, pressure and pulping time. However, there are some chemical reagents used specifically for semichemical pulping, namely sodium sulfite alone or in mixture with sodium hydroxide and/or sodium sulfide. The neutral sulfite method uses sodium sulfite and some sodium hydroxide which acts as a buffer to neutralize the organic acids which are formed when the raw material is heated at 120 °C and more. When making a bleachable pulp, the yield should not exceed 70 % by semichemical pulping. This assures that a sufficient amount of lignin is dissolved out. Thus, the bleaching process can be effective and a degree of brightness of 70 % could be achieved. The conditions of semichemical pulping are adjusted according to the type of pulp which has to be produced, the coarse–grade pulp or high–grade pulp. After chemical treatment, the cooked mass is then refined without washing in a disc refiner. For semichemical pulping, batch cooking in rotary digesters can be used. Continuous cooking equipment is preferable. This has the advantage of continuous operations and the great advantage of delivering the cooked raw material quickly to the refiner at high temperature. An example of such equipment is the defibratorchemipulper. A reaction chamber is used which consists of a series of closed, horizontal stainless steel screws. This equipment embodies a combination of continuous digestion and continuous mechanical refining under pressure. In the case of coarse pulps, the most desirable combination of high yield and acceptable strength is obtained in the yield range 70 to 80 %. The obtained coarse pulp is suitable for making corrugating medium, coarse wrapping paper, liner board, hardboard, insulating board etc.

Pulps for the finer grade of paper (e.g. book, bond, glassine waxing and tissue paper) have to be produced in lower yields. Bleachable grades are made by adjusting cooking conditions to a lignin of about 10 % content. This pulp can be bleached in a single hypochlorite stage to give a brightness of 70 – 75 % without appreciable loss in strength. It is worth mentioning that experiments on Egyptian raw materials in the department of cellulose and paper at National Research Center in Cairo have shown that semichemical pulps can be produced at considerably low temperature and pressure than those reported. Even it was possible to obtain pulps at atmospheric pressure, low temperature and low chemicals concentration. Semichemical pulp when used alone in the paper furnish, it produces paper with high bursting strength but with low tear strength, and the paper tend to be too stiff and rattly. When blended with chemical pulp in small ratio, paper acquires good properties.

From our work, it could be concluded that semichemical pulp in high yield can be easily produced from wheat straw, rice straw, corn stalks, cotton stalks etc. Either coarse grade pulp or fine grade pulp can be obtained by semichemical pulping. As shown earlier, the lignin content of these residues is low and much lower than lignin of wood, this facilitates delignification i.e. pulping. Moreover, the open structures of agricultural residues make them more accessible to the chemical reagents used in cooking. The reagent molecules diffuse and penetrate quickly and deeply in the cell wall fine structure. Thus, this makes agricultural residues more pulpable than wood.

3.2.2.5. Chemical pulping: -

In mechanical pulping, the lignin cementing the fibers is destroyed but not removed. The fibers are separated from each other but they still retain the lignin. Almost all the lignin of wood is still present in the obtained pulp and the pulp yield could be as high as 98 % of the original wood. In semichemical pulping mild, reduced pulping conditions are used. About 70 % of the lignin is dissolved out and the separation of the fibers is not enough. Therefore, the pulp is mechanically treated in refiners in order to liberate more and more fiber. The obtained pulp still contains around 7 % lignin based on pulp.

In chemical pulping, more severe pulping conditions are applied. These conditions result in removal of over 95 % of the lignin. In the case of easy bleachable pulps, the lignin left in the pulp amounts to not more than 2 % based on pulp. Consequently, chemical pulping can be safely termed “Delignification”. These pulps are classified as “soft” pulps when well cooked and are of high purity and have good tearing strength. When pulps are not well cooked, they are classified as “hard” and are of lower purity and have high bursting strength and high bleach consumption.

Chemical pulps do not need further mechanical treatment in fibrators or refiners to complete the liberation of the individual fibers. Sometimes such treatment might be necessary, but only for a short period.

For chemical pulping there are two major processes in use. Both processes depolymerize and solublize the lignin.

The sulfite process makes use of a buffered acid solution of calcium bisulfite or magnesium bisulfite. The sulfur dioxide and bisulfite convert the lignin into soluble lignosulfonic acid and consequently lignosulfonate.

The other process is the alkaline process namely the soda process and it makes use of NaOH solution which reacts with the free –OH groups in the lignin molecules and converts it into sodium ligninate (alcoholate). This is soluble in the cooking liquor i.e. NaOH solution.

However a part of NaOH is replaced by Na₂S in order to lower the degradation effect of NaOH on cellulose. Usually Na₂S enhances the delignification due to its reaction with lignin. Accordingly the duration or temperature of pulping can be reduced. This results in stronger pulp and paper and hence the process is called the “Kraft” process referring to the German word “Kraft” means strength. It is called also the sulfate process because sodium sulfate is added in the chemical recovery system where it is reduced to Na₂S.

The degree of cooking is generally measured by methods which are related to the lignin content of pulp. These are bleachability tests such as permanganate number.

Complete purification is not necessary to be achieved in the cooking process, since final purification can be obtained in the bleaching process under milder conditions which are not so degrading on the fiber as pulping.

The acid sulfite process is not suitable for pulping agricultural wastes since these wastes contain a substantial amount of minerals especially silica. These substances cannot be dissolved out in acid medium. On the other hand silica is easily dissolved in alkaline medium. Therefore, for agricultural wastes the alkaline process is recommended. It is also worth mentioning that the Kraft process, which is an alkaline process, accounts for greater than 90 % delignification of wood into bleachable grade pulp.

3.2.2.5.1. Variables in alkaline pulping: -

The variables in alkaline pulping are: Composition of cooking liquor i.e. sulfidity etc., concentration of cooking liquor, chemical-to-raw material ratio, temperature and time of cooking.

It is important that the liquor penetrates the raw material easily in order to reach the innermost layers of the raw material. The reagent molecules must reach the middle lamella where lignin is located. Thus, the reagent could dissolve the lignin cementing the fibers together, and defibrize the raw material. Fortunately, due to the open supermolecular structure of the cell wall of straws, bagasse and other agricultural wastes, there is no problem facing the penetration of the reagent molecules.

The concentration of the cooking liquor is of prime importance for the rate and extent of delignification. The maximum temperature of cooking (also termed digestion) plays also a great role together with the chemical concentration. These are followed by the time duration of the cooking process. In all cases the alkali is consumed in the early stages of cooking. The mechanism of cooking is not only restricted to delignification a great part of the carbohydrates fraction especially the hemicellulose is dissolved out. The cellulose also becomes partially degraded as seen by the drop in the molecular weight i.e. degree of polymerization (D.P.) of cellulose. Therefore, the time of pulping or cooking should be adjusted to prohibit substantial cellulose degradation. The cellulose degradation leads to yield loss and decrease in pulp and paper strength. It is well known that D.P. of cellulose is one of the main factors affecting paper strength.

In contradistinction to wood, agricultural wastes are easily penetratable by cooking chemicals and are easily delignifiable. Summing up they are easily pulpable. It is the duty of the chemist in charge of the cooking operation to stop the reaction and blow the digesters at the proper time. The rest of lignin not removed during cooking is removed safely during bleaching. Bleaching –which is an extension of delignification- is carried out under more mild conditions than pulping. Thus there is no fear to degrade cellulose during bleaching if certain precautions are taken especially pH.

The alkali respectively the sulfate or Kraft process are old processes but they are still being used all over the world, sometimes with minor modifications.

The cellulose and paper department in N. R. C., Cairo has done an extensive research work regarding the suitability of agricultural wastes for production of all types of pulps and papers, and board. This research work has started in 1954 when this department has been founded by the first author of this overview. The work is still going on by a large number of researchers.

Hundreds of scientific and technical papers have been published since that time in leading international and scientific and technical journals. The research in this laboratory is keeping pace with scientific progress abroad. Thus, modification and innovation has been taken up recently to improve the pulping of raw materials.

Several chemical additives have been suggested to accelerate delignification and to decrease degradation of the carbohydrate fraction, hemicellulose and cellulose itself. Anthraquinone and polysulfide have been successively used. Polysulfide also reduces the amount of toxic sulfur compound and reduces odor emission. The addition of surfactant-based additives reduces surface tension and improves wetting of the raw material resulting in a quick penetration or diffusion of the chemical reagent used in cooking. Under certain precautions oxygen can be used for partial delignification. Peroxyacids have been used for pulping. Preparation of peroxy carboxylic acids, its use in pulping and properties of obtained paper have been reviewed. Peroxy mineral acids were also successfully used for pulping.

Another group of pulping processes is organosolv pulping. The advantages of organosolv pulping over conventional methods have been reported by many authors including ourselves. Organosolv pulping by different alcohols have been extensively studied in the cellulose and paper department in N. R. C., Cairo, to delignify bagasse, cotton stalks and wheat straw. Uncatalyzed ethanol and methanol pulping of bagasse resulted in a suitable pulp provided that a proper washing procedure is applied to the pulp. Alkali addition to ethanol pulping leads to an easily bleachable pulp. Bagasse pulping by butanol gave comparable results. We have studied Organosolv pulping of wheat straw using aqueous ethanol and alkali ethanol. Best results obtained in the alkaline ethanol process gave a pulp yield of 56.5 % and chlorine number 3 by using 8.4% NaOH on raw material, 0.05 % anthraquinone and ethanol concentration 50 % at 150 °C for 90 minutes. Cotton stalks can be partially pulped by aqueous ethanol process while the alkali process constitutes possibilities for chemical pulp quality. Screened yield was 41 %, rejects 1.5 %.

Another innovative process, also applied in our laboratory is biopulping process. Enzymes from wood destroying fungi are used to degrade lignin selectively. This biochemical process operates at low temperature and at atmospheric pressure but requires very long time. It can, then, be used as first step as partial pulping that must be then followed by mechanical or chemical pulping, but using reduced conditions.

3.2.2.6. Technology of pulp manufacture: -

Pulp can be produced by a batch process or by a continuous process. Alkaline pulping is carried out in welded steel digesters, usually without lining. The digesters can be heated with either direct or indirect steam. In some cases outside liquor circulating system is used. Continuous digestion is more efficient. This process permits an uninterrupted flow of wood chips or chopped straw to pass through the cooking cycle without the delays encountered in loading and discharging the batch digester. The chips are metered and then transferred to a steaming vessel by a rotary lock. The chips and liquor are mixed and pumped to the top of the digester. The chips pass through impregnating zone of the digester (reactor) in a time period reaching till 45 minutes according to the type of raw material, when it reaches the heating zone where hot liquor is circulated through the chips. The pulp is continuously blown from the digester to the diffusion washer. In alkaline pulping, spent liquor is often used as part of the cooking liquor in order to save chemicals and to utilize the heat of the waste liquor.

3.2.2.7. Washing: -

Depending upon the applied conditions about 50 % of the raw material is dissolved out during pulping and is found in the spent liquor. Due to the many reactions taking place during pulping the spent liquor of alkaline pulping is black in color and therefore called black liquor. The black Liquor contains practically all alkali originally added, together with over about half of the original raw material. During washing or after washing the pulp has to be screened in order to remove undigested parts or rejects and to remove dirt and dust.

The technology of washing and screening is so specific and specialized so that we are not going to discuss it here in detail. It should be, however, stated that washing is correlated with the recovery of chemicals from the spent liquor. In most mills the chemicals used in pulping, e.g. NaOH, which at last is found in the black liquor is regained or recovered from this liquor. Therefore washing should be done with little amount of water as possible in order to reduce the costs of evaporating the black liquor, which is the first step in chemicals recovery.

In the case of agricultural wastes, in general, washing of the obtained pulp is more difficult than washing wood pulp. This arises from the presence of a higher fine content i.e. parenchyma cells, epidermis cells and cell debris in agricultural wastes pulps. Cell debris is formed due to over cooking of some cells. This difficulty can be eliminated by increasing the number of vacuum filters and washing drums etc.

3.2.2.8. Recovery of pulping chemicals: -

The first step in recovery is to concentrate the dilute black liquor in order to increase its solid content. This is done by evaporation. There are several types of evaporators. Usually the liquor passes upward in vertical tubes countercurrent to the flow of steam. Vacuum also could be applied in one step or more. The concentration of the black liquor rises to about 50 % solid content. The liquor is further concentrated in direct contact

evaporators to a solid content more than 55 % and could reach 70 %. At this concentration, the liquor can be burned easily with stable combustion in the recovery furnaces.

The presence of much silica in rice straw black liquor causes severe difficulties during this process. Silica precipitates at the surface of the evaporating tubes and in the nozzles leading to low heat exchange and even clogging.

Therefore, desilication of the black liquor is necessary before sending the liquor to the evaporators. Several experiments and designs have been proposed for desilication. A pilot plant had been built 10 years ago in Raktapapercompany through a UNIDO project by a German factory in collaboration with Egyptian experts. The results were promising but the project was not completed. It should be noted that rice straw due to its open structure is easily pulpable and does not require high sodium hydroxide liquor concentration. Moreover, the price of rice straw is much cheaper than other agricultural residues. Even without recovery of chemicals, production of chemical pulp from rice straw was economically feasible. For instance rice straw cost represents one sixth of the total production cost of pulp while wood cost represents up to third of the cost of production. However, production of pulp consumes about 500 tones water based on the weight of raw material. The disposal of this great water amount directly into water stream causes environmental pollution. Other alternatives were proposed. The spent liquor instead of being discharged in a body of water can be used, as it is, for different purposes. One of the uses is the direct application of the lignin in the liquor as adhesive in brick industry.

The black liquor can also be treated easily in special installations to lower its B.O.D. demand. Then it can be safely discharged in water stream without causing pollution.

On the other hand, other agricultural wastes such as wheat straw, corn stalks, cotton stalks do not cause a problem in recovery. They are more or less suited for chemicals recovery as in the case of bagasse black liquor.

3.2.2.9. Recovery furnace operations: -

As seen before we have discussed each industrial operation during pulp manufacture in order to assess the suitability of agricultural wastes for full industrial manufacture of pulp. Now in the following a brief account of recovery furnace operations is given.

At first, the remaining water in the heavy liquor, coming out from the evaporators is further evaporated. The organic part of the solid matter is ignited and burnt in the recovery furnace. This part includes lignin, and its degradation products, as well as hemicellulose and its degradation products. The sodium in the liquor is converted into sodium carbonate because of the excess carbon dioxide evolving during burning. It should be mentioned that in factories using sugar cane bagasse as pulping raw material, the concentration of the black liquor charged in the furnace is usually less than average values of black liquor concentration of wood pulp. This, however, does not much affect the profitability of the production.

Many burner types are used in the furnace. The recovered chemical is discharged from the furnace bottom as a melt or smelt consisting of sodium carbonate in the case of soda process, or a mixture of sodium carbonate and sodium sulfate in the case of sulfate process. This smelt, after partial dissolution in weak dissolving liquor, is sent to the recaustizing department.

The heat generated from burning black liquor is recovered by passing hot gases into a boiler to generate steam. The amount of recovered heat is usually sufficient for all the heat requirements of the pulp factory and there could be still some heat for other uses.

The recovered chemicals from the furnace are dissolved in water. The resulting liquor is known as green liquor. This color is imparted by iron compounds.

3.2.2.10. Causticization of green liquor:-

This operation consists of reacting lime with green liquor after clarification. Lime reacts with sodium carbonate to produce sodium hydroxide and calcium carbonate. The causticizing reaction proceeds to about 85

to 90 % completion. In continuous causticizing systems the causticized liquor containing the suspension of calcium carbonate is pumped to decanters, and the clean liquor called white liquor is sent to storage tanks. From there it is pumped to the digesters for further pulping.

3.2.2.11. Land filling: -

This involves the discharge of the black liquor in the earth and then covers the waste with earth. Designating an area for land fill is an engineering project. The geological features of the area are considered, since there will be a certain amount of settling. Minimum pulp washing is necessary. Also partial evaporation to reduce water content should be considered.

3.2.2.12. Treatment of liquor to reduce Biological Oxygen Demand (B.O.D.): -

Before discharging the black liquor into the sewer or water stream, the B.O.D. has to be reduced. In a primary treatment the liquor can be partially neutralized, then clarified. This takes place in big basins. The liquid is then pumped to large lagoons. The natural self cleaning process is enhanced by aeration or by pumping oxygen in the liquid.

3.2.3. Bleaching, Bleachability, and Technology: -

Pure cellulose is white in color. This is illustrated by the natural white color of cotton staple fibers. The dark color of the pulp obtained from wood and other raw materials is due to the non-cellulosic components, and to their degradation products, and other impurities still found in the pulp.

The object of bleaching is to remove the non-cellulosic impurities –especially the lignin- in order to brighten the color of the pulp. The cost of removing lignin is less in the pulping process than in the bleaching process. It is more economic to cook an "easy bleaching" pulp than to bleach an under cooked pulp. Bleaching can be considered as continuation of the cooking or digestion process. In fact bleaching is more or less a delignification process.

Lignin is the principal colored matter in the pulp. It is either removed in bleaching process or decolorized. Excessive bleaching causes chemical degradation of cellulose which reduces the strength of the pulp. Therefore conditions of bleaching have to be carefully chosen in order minimize degradation. Different pulps show different bleachability and may require different bleaching agents.

Mechanical pulp which contains almost the whole amount of lignin as in the original raw material, is bleached with peroxide. Chemical and semichemical pulps are usually bleached with chlorine compounds either directly with chlorine or by hypochlorites in one or more steps. Chemical pulps are usually bleached by a multistage process. Usually chlorine is applied in the first step followed by alkali wash then hypochlorite in the third step. This is the most conventional sequence. The hypochlorite can be divided into two steps. Before bleaching, it is necessary to determine or measure the bleachability of the pulp. Bleachability can be measured by several methods e.g. chlorine number, permanganate number and hypochlorite test. According to the result we can estimate the amount of chlorine or hypochlorite necessary for bleaching to attain a certain degree of brightness. Usually degree of brightness from 70 – 80 % is required for average and high-grade paper. 85 % degree of brightness or more could be also necessary in some paper types. In newsprint on the other hand even 60 % brightness is sufficient.

Generally speaking, pulps from agricultural wastes, even semichemical pulps are easily bleachable. This is due to the lower lignin content in these pulps compared to wood pulps and to their open fibrous structure. Such pulps require less chlorine than wood pulps. Bleaching with chlorine and hypochlorite takes place at normal pressure and at temperatures varying from 20 to 40 °C.

Environmental legislation has forced the pulp and paper industry to reduce or eliminate chlorinated organic compounds in water effluents. To satisfy this governmental demand, elemental chlorine is substituted by chlorine dioxide. This is called elemental chlorine free process or (ECF) process. Some factories have completely dispensed with chlorine and chlorine compounds bleaching and shifted to the total chlorine free process. This is abbreviated as (TCF) bleaching process. Several studies have shown that the effluents are

similar in ECF and TCF especially in toxicity tests. The ECF bleaching process is preferred because of its lower capital cost compared to TCF process.

Another method for bleaching is oxygen bleaching. In fact oxygen has been used since long time for partial delignification of wood and other raw materials as a stage in the pulping process. It cannot achieve more or less complete delignification because the pulp will be excessively degraded.

3.2.3.1. Hydrogen peroxide bleaching: -

Hydrogen peroxide is a mild oxidant, which has been applied since long time in the industry especially for bleaching of mechanical pulps. It is now applied to bleach chemical pulp in order to reduce the use of chlorine in bleaching. Additives, temperature etc. play a big role in peroxide bleaching. Details cannot be given in this overview but it is worth mentioning that bleaching of Egyptian agricultural residues pulps have been successfully bleached by hydrogen peroxide at the Cellulose and Paper Department (N.R.C.).

3.2.3.2. Ozone bleaching: -

Ozone is another oxygen-based agent producing no chlorinated organic materials in the bleaching effluent. However cellulose is susceptible to oxidation and can be easily degraded during oxygen bleaching or ozone bleaching. Several measures have to be taken to prohibit or reduce this degradation.

3.2.3.4. Other bleaching processes: -

These include peracids bleaching, bleaching with activated oxygen, and catalytic oxidative bleaching.

3.2.3.5. Biobleaching: -

This process represents a new biotechnological approach to reduce toxic effects of conventional chlorine bleaching processes. Biobleaching can be classified in two categories.

- Microbial bleaching in which growing cells are used (bacteria, yeast, fungi or algae).
- Enzymatic bleaching in which preformed enzymes are employed.

However, biobleaching has not been solely used for pulp bleaching. It should be fortified by a previous or a following chemical bleaching step.

3.2.3.6. Bleaching equipment: -

Bleaching as in digestion can be carried out as batch process or as continuous process. Bleaching towers are used. If the consistency of the bleached pulp is high say 10 – 25 %, the stock no larger acts as a fluid. Therefore, agitators are needed.

3.2.3.7. Washing of bleached pulps: -

As in the case of unbleached pulps, bleached pulp has to be washed to eliminate the solubilized lignin, colored matter, and degradation products. Washing equipment is more or less similar to those used in unbleached pulp.

3.2.4. Fiber Preparation Before Papermaking: -

The bleached pulp cannot be directly delivered to the paper machine. If untreated bleached pulp is used straight away for paper formation, it yields weak and highly porous paper. Only in filter paper, blotting paper, and newsprint, the pulp can be sent directly to the papers machine. For other paper types, the pulp has to be mechanically treated before sheet formation. The pulp slurry i.e. the pulp suspension in water is directed to certain equipments called beaters or refiners. Here the fibers are squeezed between a roll with knives on its surface and a bedplate. The consistency of the slurry is of importance and must be adjusted. Thus fibers undergo bruising and fibrillation, whereby the fibrils and micro fibrils constituting the fiber become loose and protrude on the surface of cell wall. In other words, the external surface area of the fibers increases. Thus, more

points of contact and more entanglement of the fibers with each other during sheet formation, takes place. Consequently, the numbers of inter fiber bonds increase. This in turn, leads to an increase in paper strength.

There are several types of refiners e.g. conical refiners, disc refiners etc. The type of refiner and slurry consistency affect the beating degree, also the time of beating. During beating or refining, some fibers are cut and not fibrillated. Pulps from agricultural wastes are very sensitive to refining if compared to wood pulp. Much care has to be taken during agricultural wastes pulp beating.

The degree of beating is called "freeness" and should be accurately measured. After reaching the desired freeness the pulp becomes ready to be sent to the paper machine.

However, pulp is not sent to the paper machine right away from the beater. Different chemicals have to be added to the pulp in the beater or in an extra chest. These are called additives.

3.2.5. Additives in Papermaking: -

These are the non-fibrous part in the paper furnish. In ancient days of paper making, mineral matter was added to pulp prior to sheet formation in order to increase the weight of paper. This process has been considered as adulteration. Later on it was realized that the addition of certain minerals to paper is highly beneficial. These added minerals are termed fillers.

The process itself is called filling or loading. Fillers, when added in certain amounts, improve the opacity of paper and increase the smoothness of paper surface. Thus it improves the suitability of paper for printing. The most popular filler is kaolin or clay. Another important group of additives are the sizing agents. Sizing makes the paper resistant to liquid penetration, e.g. writing inks. Unsized paper could not be suitable for writing. The oldest sizing agent used is rosin size. There is a lot of other additive such as dry strength and wet strength additives. Attention must be paid, that pulp alone does not make paper. Other components are needed.

Due to the high ash content in rice straw, one can more or less dispense with fillers. Due to the closed surface of paper sheets produced from this raw material, only slight sizing is needed to improve the writability.

Besides using additives in paper making, the agricultural wastes pulps have to be blended with other pulp sorts, preferably soft wood pulp to ensure reasonable speed of the paper machine, and to compensate some defects in paper.

3.2.6. Blending: -

Mixing of different pulps together is termed blending. Addition of minerals is termed filling as already mentioned. All these processes i.e. blending, and filling as well as sizing and applying other types of additives are carried out in the beater or in an extra chest. The produced mixture is called "paper furnish". This can be charged directly to paper machine.

3.2.7. Papermaking: -

The conditions of paper former have a significant effect on paper properties.

Sheets made in the laboratory are handmade. They are stronger than those made from the stock on the paper machine. Thus it is clear that laboratory results, although reliable, yet, do not predict exactly the properties of the manufactured paper.

The paper machine consists basically of three parts. The first part is the wire department or the sheet formation department. The second part is the press part and the third is the drier part. Then follow the calender and/or supercalender. Also surface sizing equipment or surface coating machine can be attached directly to the paper machine.

The most common paper machine is the Fourdrinier machine. On the wire (which is a moving continuous belt) the suspension of fibers i.e. the stock (with about 98 %water) flows from the head box through the slice. Due to the effect of shaking and suction boxes, a wet paper sheet is formed. This is transferred to the

wet pressing part and the paper sheet enters this part with about 20 % moisture content. The sheet is passed through several press rolls. Then it goes to the drier part.

The paper machine is highly sophisticated. The speed of paper production can be as fast as 2000 meters per minute on modern paper machine at a machine width of 6 meters and more.

Now, what is the behavior of agricultural wastes pulp on the paper machine ? These pulps as reported before contain much fines and are highly hydrophilic due to their high hemicellulose content.

This means that they do not part easily from water when compared to wood pulp. Consequently, the paper machine cannot be run at high speeds. The runability of these pulps on the paper machine is low. The paper sheets can also pick at the process. These problems can be solved by taking considerable measures. It should be noted that not all paper types could be produced at high machine speed. Newsprint is a paper type that is produced at high speeds.

3.2.8. Paper Coating: -

Many types of paper need to be surface sized or coated in order to modify some of paper properties or to implement new properties.

Pigment coating is one of the most important coating processes. It is used mainly for the production of printing papers for magazine, catalogues etc.

Usually an aqueous mixture of pigments (e.g. clay) and an adhesive (e.g. starch) is applied to the surface of paper. When this coat is applied to a cheap dark rough-surfaced paper, one can get a paper of high brightness. In other words, the paper defects are overcome by an economic process, and the paper become suitable for fine printing.

Other types of coating make paper resistant to water vapor and air as required for packaging of food and beverages etc.

3.2.9. Paper Types and Properties of Paper:

These are divided into physical, optical, chemical, electrical and microscopical properties. Physical properties include thickness, basis weight, tensile strength, tear strength, etc. Agricultural wastes pulps can possess high tensile strength but usually low tear strength. Optical properties include brightness and opacity. These can be tailored by bleaching ...etc. Agricultural wastes paper can be made equal in this respect to paper produced from hard woods.

Agricultural wastes are suitable for producing almost all types of packaging and wrapping paper except the Kraft liner in corrugated board as well as cement bags.

Agricultural wastes are more or less suitable for producing many types of fine paper as middle grade printing or writing paper. There are some limitations for producing newsprint from agricultural residues. Cotton linter is suitable for producing security paper such as currency and bond paper.

3.2.9.1. Paper Types: -

There are enormously many types of paper including the examples given before. The most common paper types are:

Newsprint, stationery papers (printing and writing), lightweight coated paper for magazine, currency paper, hygienic tissue paper (sanitary and household), paper card, solid board for boxes, wrapping and packaging paper, corrugated board. In the following some paper types are discussed in details.

3.2.9.1.1. Newsprint:

All daily newspapers use this type because it is the most economical. All newsprint is almost made of mechanical softwood pulp. Up till now only one factory in the whole world is producing newsprint from

agricultural residues. This kind of paper is lower in quality and cannot be accepted by some consumers. As mentioned before, in the Cellulose & Paper Department (N.R.C.), experiments were done on preparation of newsprint from agricultural wastes. The results were promising.

3.2.9.1.2. Offset paper:

This is the printing paper and uncoated. This paper type is about three times expensive than newsprint. The reason is that this paper should be chemical free. It requires extensive washing during the manufacturing process as well as extensive bleaching. Filling, sizing, and other additives are required.

3.2.9.1.3. Opaque paper:

This is used for high quality printed paper as annual reports.

3.2.9.1.4. Tablet paper:

For school purposes, cheap paper with a partial ground wood content is produced for maximum economy.

3.2.9.1.5. Bond paper:

This paper should be durable and resistant to aging. It is usually made of rags or cotton linters.

3.2.9.1.6. Manifold:

It is a light-weight paper used for snap-out forms.

3.2.9.1.7. Coated paper:

Mentioned before.

3.2.9.1.8. Glassine paper:

Highly beaten paper and almost non-porous and transparent. This is called (in Arabic) butter paper and is used for packaging fatty and greasy food materials.

4. Case Study: -

Research done in the fifties abroad and at the Cellulose & Paper Department (N.R.C.) had shown that wheat straw was one of the most suitable agricultural residues for producing pulp and paper.

In Egypt wheat straw is used as animal fodder. It was decided at that time to erect an integrated pulp and paper mill for manufacturing writing and printing paper. Rice straw was chosen as raw material despite its less suitability than wheat straw.

Rice straw is available in large quantities and it is of no use for the farmers. There are several difficulties encountering the use of rice straw for pulp and paper production. Some of these difficulties have already been stated in this present overview. Due to research done in the Cellulose & Paper Department (N.R.C.) supervised by the first author, solutions had been found. However, research in the laboratory is indicative but cannot give conclusive or comprehensive results. It does not represent an accurate basis for feasibility study.

Paper sheet formation in the laboratory involves simple operations. On the other hand, in the industry, the situation is completely different. In fact, the paper machine used in the industry represents one of the most complicated and sophisticated continuous machinery. As being reported, it consists of different parts applying different techniques for removal of water from stock. The stock flows from the headbox to the wire in a consistency of about 1-2 % fibers, i.e. about 98 % water, and paper leaves the end of the machine at only 6 % water or moisture content. As paper machine runs at speed of up to 2000 meter / minute and at a machine width up to 6 meters or more, it becomes evident that production under such conditions necessitates highly

technological devices to synchronize sheet transfer from each part of the machine to the next part. Any slight misfit causes the paper sheet to tear either on the wet or on the dry state.

Before going up from the laboratory scale to full industrial scale, it is advisable to carry out pilot plant scale experiments.

After call for tenders in the late fifties different pulping processes were proposed by different participants. Comparison was made between the different processes on full industrial scale regarding easier production, less technical difficulties and economic feasibility. On basis of all these steps of the study the most suitable process and most suitable conditions were chosen.

As before mentioned the presence of high amount of silica in rice straw, and consequently in black liquor, prohibits the recovery of chemicals from black liquor. Therefore, no recovery unit was established. Despite the disposal of black liquor containing the pulping chemicals in water stream yet the process was used, and is still economic. Due to its open microporous structure and low lignin content, rice straw is easily pulpable and bleachable. In other words, the consumption of sodium hydroxide is less than half as in the case of other raw materials.

In order to find a solution for water stream pollution several experiments were undertaken. One is the desilication of black liquor before pumping to the evaporators. Pilot plant equipment has been designed and tried experimentally. Another trial was based on new design for recovery furnace. Till now neither was realized industrially.

According to stricter environmental legislation nowadays, factories utilizing rice straw for pulp manufacture are reducing their dependence on this raw material and shift to other cellulose materials, so far that the problem of silica is not solved.

At the same time –in the fifties- the Cellulose & Paper Department (N.R.C.) investigated the suitability of Egyptian sugar cane bagasse for pulp and paper manufacture. The obtained results were successful and had been already published in 1959.

Sugar cane bagasse was chosen because it accumulates in sugar companies. On basis of research done at the Cellulose & Paper Department (N.R.C.) and experience gathered at that time by colleagues from the industry in Egypt and U.S.A., the first pulping mill in Egypt based on bagasse was erected in the early sixties. With this raw material, only minor problems in recovery are encountered when compared to wood [1-89].

5. The Present Status of Production of Paper and Board from Agricultural Wastes in Egypt: -

Rice straw was the first agricultural waste used for production of paper and board in Egypt. In the thirties, cheap packaging and wrapping paper was produced from rice straw. Production of stationary paper from rice straw has begun in the early sixties. The amount of rice straw used in this industry increased steadily since that time till it reached more than 60000tons of pulp and more annually. However due to more and more strict environmental legislation, the utilization of rice straw has decreased.

Experimental work on laboratory scale and pilot scale has shown that difficulties, encountering chemicals recovery from black liquor could be overcome, to a great extent. Nevertheless, realization on industrial scale has not yet taken place. Apart from chemicals recovery, treatment of black liquor to decrease the B. O. D. before disposal in water stream has not been seriously considered up till now.

Sugar cane bagasse is historically the second raw material used in Egypt for pulp and paper production. In the middle sixties, the first pulp mill on basis of bagasse was erected in Upper Egypt. Difficulties regarding chemicals recovery from black liquor were minor since the problem of silica is trivial in bagasse. The production of writing and printing paper from bagasse has raised steadily and reached now about 160000 tons annually.

6. Future prospects: -

The present annual consumption of different paper and board types in Egypt is till now much higher than the amount produced locally and has surpassed 500000 tons annually.

Growth of pulp and paper production from bagasse could be expected. This is however correlated to the situation of sugar manufacture in Egypt and is dependent upon the decision of the sugar company. Another decisive factor is the price of oil compared to bagasse as fuel.

Since the middle sixties, the sugar company has been interested in manufacturing newsprint from bagasse. This has not been realized till now. The reasons are given earlier in this overview. Nevertheless, this idea should not be abandoned, and might be revived in the near future.

The utilization of more rice straw in future depends upon finding a suitable solution for the disposal problem of black liquor. It is possible to fulfill the environmental requirements by one or more methods. Lowering the B. O. D. before disposal of the black liquor in water stream might be reasonable. However, desilication of the black liquor before combustion in chemicals recovery furnace may be the best method. This needs further research.

Other Egyptian agricultural residues which could be proposed for future use are wheat straw, corn stalks and cotton stalks. Extensive laboratory research has been carried out on these raw materials as sources for pulp and paper making. It has been shown that almost all types of pulp and paper can be produced from these raw materials. These experiments were carried out in Cellulose and Paper Department (N. R. C.). For probable industrial use, pilot scale and full industrial experiments are recommended as before mentioned.

Nevertheless, Egyptian agricultural wastes could be used successfully for producing other valuable products than pulp and paper. In the Cellulose and Paper Department (N. R. C.) many experiments have been done over the last 62 years regarding production of hardboard, particleboard from these raw materials.

Binderless board composites were prepared from Egyptian agricultural residues with great success. Moreover, eliminating the need to use binders in board making has environmental privileges^{90,91}.

Another research program regarding production of several silvi chemicals of important industrial uses has been successfully executed in our laboratory.

Production of energy, different types of fuels (solid, liquid and gaseous fuel), many petrochemicals substitutes, and charcoal (active carbon), from Egyptian agricultural wastes, have been also experimented in the same laboratory in Cairo and abroad under supervision of the first author. This involved advanced rapid continuous pyrolysis processes⁹²⁻⁹⁵.

Pioneering innovations introduced green nanotechnology of natural fibers, and its Manipulations in the Cellulose and Paper Discipline⁹⁶⁻¹⁰⁵.

Also, pioneering innovations succeeded to enhance the sustainability of both the paper and sugar industries via molasses⁹⁸⁻¹⁰².

Examples of the above-mentioned pioneering achievements include:

For the first time, introducing an advanced nanocomposite involving two additives –nanoadditive and a conventional additive– within a matrix of natural cellulose fibers. The first additive (the nanoadditive) is sucrose, which incorporates the nanoporous structure of the cell walls of cellulose fibers. The second additive (the conventional additive) is kaolin, the famous paper filler. Kaolin is enmeshed between the adjacent cellulose fibers. This advanced paper nanocomposite was prepared by simple techniques. The work shows, for the first time, that sucrose can overcome the ultimate fate of deterioration in strength of paper, due to addition of inorganic fillers such as kaolin. This deterioration was counteracted by incorporating cellulose fibers with sucrose. We assume that regions of the cell wall lamellae, on both sides of the sucrose spacers, are stressed during drying because the sucrose spacers hinder them to relax. This leads to a strain, which makes some microfibrils partially released and protrude out of the fiber. Thus, a sort of fiber beating takes place. We called this phenomenon incorporation beating or encapsulation beating to differentiate it from chemical and

mechanical beatings, and it explains the great increase in breaking length of the paper nanocomposites prepared. Moreover, sucrose was proven – for the first time – to act as retention aid for inorganic fillers such as kaolin. We called this phenomenon incorporation retention to differentiate it from the conventional types of retention of inorganic fillers⁹⁶⁻¹⁰⁵.

Introducing molasses, for the first time worldwide, as a new additive in papermaking. The resulting paper composites exhibit greater breaking length and remarkably higher water uptake (WRV) in comparison to paper, which did not involve molasses as an additive. Incorporating the cell wall microstructure of cellulose fibers with sucrose greatly enhance the breaking length and water uptake of paper. Also, it is well established in the literature that using gums (including starch) as additives in papermaking enhances the strength of paper. Molasses contains both sucrose and gums (including starch).

Molasses is a byproduct of sugar industry, which is cheaper than sucrose; and a major part of sucrose lost in sugar industry resides in molasses. Therefore, molasses was chosen as a new additive in papermaking.

This work leads to sustainability (responsible management of resources consumption) of both paper and sugar industries. It, simultaneously, upgrades agricultural residues or recycled waste paper and creates a new use for molasses (an important byproduct of the sugar industry)⁹⁸⁻¹⁰².

Introducing electrical purposes paper from agricultural residues and recycled old newsprint^{106,107}.

Green denatured plant proteins as additives to upgrade pulps of different origins^{108,109}.

Mild potassium permanganate treatment as a new approach for upgrading pulp and paper quality¹¹⁰.

Acknowledgments

The authors wish to record their sincere thanks to UNDP / GEF / EEAA Bioenergy Project.

References

1. Fahmy Y, Fadl M H (1958) Digestion of wheat straw for the economical preparation of cellulose, low in silica. *Textil-Rundschau* 13:709-19
2. Fahmy Y, El-Ashmawy A E (1958) A new method for production of viscose rayon pulp from bagasse. *Tappi* 41:439-42
3. Fahmy Y, Fadl M H (1958) The Production of low silica viscose pulps from rice straw. *Egyptian Journal of Chemistry* 1(2):377-84
4. Fahmy Y, Fadl M H (1959) Digestion of rice straw for the economical preparation of cellulose, low in silica. *Textil-Rundschau* 14:259-60
5. Fahmy Y, Fadl M H (1959) Solubility of ash and silicic acid in alkaline pulping of cereal straw. *Papier* 13:311-14
6. Fahmy Y, Fadl M H (1959) Comparison of methods used in the pulping of rice straw. *Papier* 13:15-17
7. Fahmy Y, El-Ashmawy A E (1959) Suitability of *Eucalyptus camuldulensis* Dehn; for the production of viscose pulps. *APPITA* 12:210-15
8. Fahmy Y, Abou-state M A (1959) Suitability of *Phragmites communis* for viscose rayon manufacture. *Tappi* 42:492-5
9. Fahmy Y, El-Ashmawy A E (1959) Pulp and paper from sugar cane bagasse. *Indian pulp and paper* XIV(5):1-7
10. Mustafa A, Dawoud A, Fahmy Y (1960) Nitratibility of differently treated cotton linters. *Tappi* 43:725-9
11. Fahmy Y, Abou-state M A (1961) Evaluation of rayon grade dissolving pulps. I. The influence of morphological, chemical, and certain physical properties of the pulps on the filterability of their viscose solutions. *Papier* 15:44-51
12. Fahmy Y, Abou-state M A (1961) Evaluation of rayon grade dissolving pulps. II. The influence of the average degree of polymerization and the zero-fiber fraction on the filterability of viscose. *Papier* 15:188-90

13. Fahmy Y, Abou-state M A, Roffael E (1961) Evaluation of rayon grade dissolving pulps. III. Pulps produced from reeds by various bisulfite and prehydrolysis sulfate procedures. *Papier* 15:666-71
14. Fahmy Y, Fadl M H, Mansour O (1961) Strength properties of straw pulps. *Wochenblatt für Papierfabrikation* 89:187-90
15. Fahmy Y, Fadl M H (1964) On Emulsion xanthation of cellulose. I. Xanthation in the presence of sodium hydroxide and potassium hydroxide solutions. *Svensk Papperstidning* 67(3):101-9
16. Fahmy Y, Fadl M H (1964) On Emulsion xanthation of cellulose. II. Aspects of the reaction mechanism and acceleration of cellulose emulsion xanthation by inclusion or occlusion with CS₂ in fibers. *Svensk Papperstidning* 67(7):279-85
17. Fahmy Y, Mustafa A, Fadl M H (1964) On Emulsion xanthation of cellulose. III. Rate curves of included and nonincluded cellulose. *Svensk Papperstidning* 67(15):573-8
18. Fahmy Y, Fadl M H (1964) On Emulsion xanthation of cellulose. IV. Correlation between dissolution rate curves and technical viscose filterability 67(16):622-5
19. Fahmy Y, Roffael E (1964) Evaluation of rayon grade dissolving pulps. IV. The influence of hydrolytic and oxidative degradation of cotton linters and wood pulps and their effects on the properties and filterability of viscose solutions. *Papier* 18(4):159-63
20. Fahmy Y, Nagati A (1965) Evaluation of rayon grade dissolving pulps. V. The classification of rayon grade pulps. *Papier* 19:570-72
21. Fahmy Y, Fadl M H, Roffael E (1965) On emulsion xanthation of cellulose. V. Influence of some chemical and mechanical treatments on pulp reactivity and properties of viscose from included cellulose fibers. *Svensk Papperstidning* 68(16):549-52
22. Fahmy Y, Mansour O (1965) Properties of writing and printing papers containing rice straw pulp. *Industria Della Carta* 3(6):207-11
23. Fahmy Y, Mansour O (1966) On Carboxymethylation of cellulose. I. Dissolving carboxymethylation and analysis of the all-over dissolution rate. *Indian Pulp and Paper* 20(9):535-40, 551
24. Fahmy Y, Mansour O (1966) On Carboxymethylation of cellulose. II. Influence of the manner of addition of carboxymethylating chemicals, inert and non-inert solvents on the reaction rate in dissolving and non-dissolving carboxymethylation. *Indian Pulp and Paper* 21(2):143-5, 148-51
25. Fahmy Y, Mansour O (1967) On Carboxymethylation of cellulose. III. Influence of type of alkali cellulose, average degree of polymerization and temperature on the reaction rate. *Indian Pulp and Paper* 21(7):449, 451-3, 455
26. Fahmy Y, Mansour O (1967) On Carboxymethylation of cellulose. IV. Rheological and filtering properties of CMC solutions. *Indian Pulp and Paper* 21(10):627-31, 634-5, 639
27. Fahmy Y, Koura A (1967) On Fibrous acetylation of cellulose. I. Acetylation of cotton fibers. *Cellulose Chemistry and Technology* 1(3):301-12
28. Fahmy Y, Koura A (1969) On Fibrous acetylation of cellulose. II. Acetylation of viscose rayon. *Cellulose Chemistry and Technology* 3(2):179-87
29. Fahmy Y, Fadl M H (1968) On Emulsion xanthation of cellulose. *Journal of Chemistry of the United Arab Republic* 11(3):397-399
30. Fahmy Y, Mobarak F (1968) Black liquor silica as added filler, filler in situ, and coating pigment in paper making. *Cellulose Chemistry and Technology* 2(2):185-93
31. Fahmy Y, Fadl M H, Fadl N A (1969) Studies of pulping methods of bagasse for newsprint making. *Journal of Chemistry of The United Arab Republic* 12(2):219-27
32. Fahmy Y, Ibrahim H (1970) Rice straw for paper making. *Cellulose Chemistry and Technology* 4(3):339-348
33. Fahmy Y, El-Kalyoubi S (1970) Fibrous acetylation of cellulose. III. Acetylation of paper pulps. *Cellulose Chemistry and Technology* 4(6):613-19
34. Fadl M H, El Shinnawy N A, Fahmy Y (1971) Preparation of furfural from rice hulls. *Research and Industry* 16(4):263-264
35. Fahmy Y, Mobarak F (1971) On fine structure of cellulose fibers. *Svensk Papperstidning* 74(1):2-9
36. Fahmy Y, Mobarak F (1971) Fine structure and reactivity of cellulose. *Journal of Polymer Science Part B Polymer Letters* 9(10):767-769
37. Fahmy Y, Mobarak F (1972) Fine structure of acetylated cellulose fibres. *Svensk Papperstidning* 75(21):853-8
38. Fahmy Y, Mobarak F (1972) Reactivity of biological cellulose and properties of some of its derivatives. *Cellulose Chemistry and Technology* 6(1):61-65

39. Fahmy Y, Saleh T M, Hafez O M A (1972) On the Deleignification of rice straw and sugar cane bagasse. *Egyptian Journal of Chemistry* 15(6):591-599
40. Fahmy Y, Mobarak F, Augustin H (1972) Influence of starch addition on filler retention and paper properties of straw and wood pulps. *Cellulose Chemistry and Technology* 6(1):67-70
41. Fahmy Y, Mansour O, Nagaty A (1973) Physical and optical properties of paper made from chemically modified kraft pulp. *Indian Pulp and Paper* 26(11):161-74, 8
42. Nagaty A, Mansour O, Fahmy Y (1972) Carboxymethylation of Cellulose Acetate. *Holzforchung* 27(2):68-70
43. El-Ashmawy A E, Mobarak F, Fahmy Y, (1973) Hemicelluloses as additive in papermaking. I. Isolation and characterization of hemicelluloses from straw and wood pulps. *Cellulose Chemistry and Technology* 7(3):315-23
44. Mobarak F, El-Ashmawy A E, Fahmy Y (1973) Hemicelluloses as additive in papermaking. II. The role of added hemicellulose, and hemicellulose in situ on paper properties. *Cellulose Chemistry and Technology* 7(3):325-35
45. Fahmy Y, Mansour O Y, El-Dien M S (1973) Structure of alkali hemilignins isolated by short and long cooking cycles from rice straw and its leaves. *Indian Pulp and Paper* 27(10):11-15
46. Fahmy Y, El-Saied H (1974) Chemical Modification of Pulp and Physically Added Chemicals in Paper Making. Pt. I. Fiber Modification by Classical Cellulose Hydrophilizing and Hydrophobizing Reactions in Comparison to Physically Added Cellulose Derivatives. *Holzforchung* 28(1):29-34
47. Fahmy Y, El-Saied H (1974) Chemical Modification of Pulp and Physically Added Chemicals in Paper Making. Pt. II. Grafting Copolymerization with Hydrophilic and Hydrophobic Monomers and Their Binary Mixtures in Comparison to Physically Added Homopolymers and to Classical Chemical Modification. *Holzforchung* 28(2):61-66
48. El Shorbani S, Tawfik I, El Sadani M, Fahmy Y (1974) Preparation of viscose rayon pulp from sugar-cane bagasse. *Egyptian Journal of Chemistry* 17:255-65
49. Fahmy Y, Fadl N A (1974) A study of the production of hardboard from some indigenous agricultural residues. *Egyptian Journal of Chemistry* 17(3):293-301
50. Mobarak F, Nada A M, Fahmy Y (1975) Fibreboard from exotic raw materials. I. Hardboard from rice straw pulps. *Journal of Applied Chemistry and Biotechnology* 25(9):653 - 658
51. El-Ashmawy A E, El-Kalyoubi S, Fahmy Y (1975) Hemicelluloses of bagasse and rice straw. *Egyptian Journal of Chemistry* 18:149-156
52. Fahmy Y, Fadl M H, El-Shinnawy N A (1975) Saccharification of cotton stalks. *Research and Industry* 20(1):7-10
53. Fahmy Y, Mobarak F (1976) On the properties of never-dried and nature-dried cotton. *Cellulose Chemistry and Technology* 10(3):261-4
54. Mobarak F, Fahmy Y, Augustin H (1976) Cationic starch in papers with high content of bagasse pulp. 1. Influence on strength properties of kraft papers. *Papier* 30(1):16-19
55. Fahmy Y, Ibrahim H (1976) Cotton stalks as a fibrous source for fine paper and rayon. I. Bleached pulp for fine paper. *Cellulose Chemistry and Technology* 10(6):723-35
56. Mobarak F, Fahmy Y (1977) Newsprint from cotton stalks. *Indian Pulp and Paper* 35(5):15
57. Fadl M H, Hiekel S, Fahmy Y (1977) Bleachability of rice straw and bagasse paper pulps and their mixture. *Indian Pulp and Paper* 32(2):7-9
58. Fahmy Y, Ibrahim H (1979) Cotton stalks as a fibrous source for fine paper and rayon. II. Dissolving pulp for viscose rayon. *Cellulose Chemistry and Technology* 13(1):385-90
59. El-Ashmawy A E, El-Kalyoubi S, Fahmy Y (1979) Hemicelluloses as additive in papermaking. V. Effect of oxidation of hemicelluloses on their binding properties. *Cellulose Chemistry and Technology* 13(1):77-82
60. Fahmy Y, El-Ashmawy A E, El-Kalyoubi S (1979) Hemicelluloses as additive in papermaking. VI. Effect of hemicelluloses isolated from steeping lye of alkali cellulose on paper properties. *Cellulose Chemistry and Technology* 13(5):673-5
61. Fahmy Y, Fadl N A (1979) Acetylation in particle board making. *Egyptian Journal of Chemistry* 20(4):397-403
62. Ibrahim H, El-Ashmawy A E, Fahmy Y (1978) IR spectra of cotton stalks lignin before and after pulping. *Egyptian Journal of Chemistry* 21(6):443-9
63. Fahmy Y, Mobarak F, Nada A M (1982) On the activation of cellulose through xanthation. II. Viscose and rayon from activated cellulose. *Cellulose Chemistry and Technology* 16(4):415-20

64. El-Shinnawy N A, Heikal S, Fahmy Y (1983) Saccharification of cotton bolls by concentrated sulphuric acid. *Research and Industry* 28(2):123-6
65. Mobarak F, Nada A M, Fahmy Y (1985) Mixed partial xanthation and carboxymethylation of cotton linters and wood pulp for paper making. *Cellulose Chemistry and Technology* 19(1):97-102
66. Fahmy Y, Haikal S, Elsamahy M (1992) Corn stalks as a source for fine paper pulp. 1. influence of sulfidity and oxygen in alkali pulping on pulp properties. *Research and Industry* 37(4):218-222
67. Fahmy Y, Ibrahim A, El-Sakhawy M (1994) Acetylation and carboxymethylation of wood, bagasse and rice straw pulps. *Research and Industry* 39(1):29-34
68. Nada A M, Fahmy Y, Elbaiuomy H (1994) Spectroscopic studies of bagasse butanol lignin. *Polymer Degradation and Stability* 46(3):295-302
69. El-Sakhawy M, Fahmy Y, Ibrahim A, Lönnberg B (1995) Organosolv pulping. I. Alcohol pulping of Bagasse. *Cellulose Chemistry and Technology* 29(5):615-629
70. Nada A M, Ibrahim A, Fahmy Y, Abou-Yousef H E (1995) Bagasse pulping with butanol-water system. *Research and Industry* 40(3):224-30
71. El-Sakhawy M, Lönnberg B, Ibrahim A, Fahmy Y (1995) Organosolv Pulping. 2. Ethanol Pulping of Cotton Stalks. *Cellulose Chemistry and Technology* 29(3):315-329
72. El-Sakhawy M, Lönnberg B, Fahmy Y, Ibrahim A (1996) Organosolv pulping. 3. Ethanol pulping of wheat straw. *Cellulose Chemistry and Technology* 30(1-2):161-174
73. El-Sakhawy M, Lönnberg B, Ibrahim A, Fahmy Y (1996) Organosolv pulping. 4. kinetics of alkaline ethanol pulping of wheat straw. *Cellulose Chemistry and Technology* 30(3):281-296
74. Nada A M, Fahmy Y, El-Bayoumi H (1996) Bleaching of Egyptian bagasse pulps with CEH and CEOH sequences. *Journal of scientific and industrial research* 55(7):516-522
75. El-Sakhawy M, Lönnberg B, Fahmy Y, Ibrahim A (1996) Organosolv pulping. 5. Bleachability and paper properties. *Cellulose Chemistry and Technology* 30(5-6):483-495
76. Nada A M, Fahmy Y, Abo-Yousef H E (1998) Kinetic study of delignification of bagasse with butanol - Water organosolv pulping process. *Journal of scientific and industrial research* 57(8):471-476
77. Nada A M, Ibrahim A, Fahmy Y, Abo-Yousef H E (1999) Peroxyacetic acid pulping of bagasse and characterization of the lignin and pulp. *Journal of scientific and industrial research* 58(8):620-628
78. Nada A M, Ibrahim A, Fahmy Y, Abo-Yousef H E (2002) Peroxyacetic acid pulping of bagasse. I. Two-stage pulping. *Cellulose Chemistry and Technology* 36(1):123-136
79. El-Wakil N A, Abou-zeid R, Fahmy Y, Mohamed A Y (2007) Modified wheat gluten as a binder in particleboard made from reed. *Journal of Applied Polymer Science* 106(6):3592 - 3599
80. Abou-zeid R, El-Wakil N A, Fahmy Y, Dufresne A, El-Sherbiny S (2010) Liquid Crystalline Behavior of Hydroxypropyl Cellulose Esterified With 4-Alkoxy Benzoic Acid. *Bioresources* 5(3):1834-1845
81. Abou-zeid R, El-Wakil N A, Fahmy Y (2015) Thermoplastic Composites from Natural Reed Fibers. *Egyptian Journal of Chemistry* 58(3):287-298
82. Casey JP (1962) "Pulp and Paper", Interscience Publishers Inc., New York
83. J. C. Roberts, "Paper Chemistry", an imprint of Chapman and Hall, (1996).
84. Roger M. Rowell, Raymond A. Young, and Judith K. Rowell, "Paper and Composites from Agro-Based Resources", CRC Press, Inc., Lewis Publishers, (1997).
85. Sittig M., "Pulp and Paper Manufacture", Noyes Data Corporation, New Jersey (1977).
86. Saltman D., "Paper Basics", Van Nostrand Reinhold Company, New York (1978).
87. Paavilainen L, "Non-Wood Fibers in Paper and Board Grades - European Perspective", *TAPPI Non-Wood Fibers Short Course Notes*, (1997).
88. Rowel, R. M. and Cook, C., "Types and Amounts of Non-Wood Fibers Available in the U.S.", *TAPPI North American Non-Wood Fiber Symposium*, (1998).
89. Lathrop E C and Fouad Y, Northern Regional Laboratory, USA, Cleaning of Rice Straw, *Private Communication*.
90. Mobarak F, Fahmy Y, Augustin H (1982) Binderless lignocellulose composite from bagasse and mechanism of self-bonding. *Holzforschung* 36(3): 131-136.
91. Fahmy TYA, Mobarak F (2013) Advanced binderless board-like green nanocomposites from debarked cotton stalks and mechanism of self-bonding. *Cellulose* 20(3): 1453
92. Fahmy Y (1982) Pyrolysis of agricultural residues. I. Prospects of lignocellulose pyrolysis for producing chemicals and energy sources. *Cellulose chemistry and technology*16(3): 347-55

93. Fahmy Y, Mobarak F, Schweers W (1982) Pyrolysis of agricultural residues. II. Yield and chemical composition of tars and oils produced from cotton stalks, and assessment of lignin structure. *Cellulose chemistry and technology* 16(4):453-9
94. Mobarak F, Fahmy Y, Schweers W (1982) Production of phenols and charcoal from bagasse by a rapid continuous pyrolysis process. *Wood Science and Technology* 16(1): 59-66.
95. Mobarak F (1983) Rapid continuous pyrolysis of cotton stalks for charcoal production. *Holzforchung* 37(5): 251-254
96. Fahmy TYA, Mobarak F, Fahmy Y, Fadl MH, El-Sakhawy M (2006) Nanocomposites from natural cellulose fibers incorporated with sucrose. *Wood Science and Technology* 40(1): 77-86
97. Fahmy TYA, Mobarak F (2008) Nanocomposites From Natural Cellulose Fibers Filled with Kaolin in Presence of Sucrose. *Carbohydrate Polymers* 72(4): 751
98. Fahmy TYA (2007) Introducing molasses as a new additive in papermaking. *Tappi Journal* 6(8): 23
99. Fahmy TYA (2007) Molasses as a new Additive in papermaking: for high alpha-cellulose wood pulp. *Professional Papermaking* 4(1): 42
100. Fahmy TYA, Mobarak F (2009) Advanced nano-based manipulations of molasses in the cellulose and paper discipline: Introducing a master cheap environmentally safe retention aid and strength promoter in papermaking. *Carbohydrate Polymers* 77(2): 316
101. Fahmy TYA, Mobarak F (2014) Sustainability of Paper & Sugar Industries via Molasses: Novel Green Nanocomposites from Upgraded Recycled Cellulose Fibers. *Journal of American Science* 10(9):1
102. Fahmy TYA (2017) Molasses as A New Additive in Papermaking: for Bagasse and Kaolin Filled Bagasse pulps. *Professional Papermaking* 14(1): 26
103. Fahmy TYA, Mobarak F (2008) Vaccination of biological cellulose fibers with glucose: A gateway to novel nanocomposites. *International Journal of Biological Macromolecules* 42(1): 52
104. Fahmy TYA, Mobarak F (2011) Green Nanotechnology: A Short Cut to Beneficiation of Natural Fibers. *International Journal of biological macromolecules* 48(1): 134
105. Fahmy TYA, Mobarak F, Fahmy Y (2016) Incorporation of Never-Dried Cotton fibers with Methylmethacrylate: A Gateway to Unique Transparent Board-Like Nanocomposites. *International Journal of ChemTech Research* 9(12): 191-200
106. Fahmy TYA, Mobarak F, El-Meligy MG (2008) Introducing Undeinked Old Newsprint As A New Resource Of Electrical Purposes Paper. *Wood Science and Technology* 42(8):691
107. Fahmy TYA, El-Meligy MG, Mobarak F (2008) Introducing Deinked Old Newsprint As A New Resource Of Electrical Purposes Paper. *Carbohydrate Polymers* 74(3): 442
108. Fahmy TYA, Abou-Zeid RE, Fahmy Y (2014) Response of pulps of different origins to the upgrading effect of bulk added green denatured soy protein, in correlation to morphological structure & chemical composition of cellulose fibers. *Nature and Science* 12(4): 79-83
109. Fahmy Y, El-Wakil N A, El-Gendy A A, Abou-Zeid R E, Youssef M A (2010). Plant proteins as binders in cellulosic paper composites. *International journal of biological macromolecules* 47(1): 82-85
110. Fahmy T Y A, Mobarak F, Kassem N, Abdel-Kader A H (2008) New approach for upgrading pulp & paper quality: Mild potassium permanganate treatment of already bleached pulps. *Carbohydrate polymers* 74(4): 892-894.
