# FORMIC ACID/ACETIC ACID/WATER PULPING OF AGRICULTURAL WASTES

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In this paper, mustard branches, mustard stems and lentil stalks were characterized in order to evaluate them as pulping raw materials. These agricultural wastes are characterized by relatively moderate amounts of lignin (20-23%), reasonably low amounts of α-cellulose (35-37%) and relatively high amounts of ash content (4-7%). In this study, pulping of lentil stalks, mustard stems and mustard branches was carried out at atmospheric pressure using a mixture of formic acid, acetic acid, and water (FA/AA/$H_2O$). Increasing formic acid concentration in the acid mixture improved the delignification rate. A higher pulp yield was obtained from lentil stalks with higher residual lignin than those of mustard stems and branches after FA/AA/$H_2O$ treatment. It was found that the delignification of FA/AA/$H_2O$ treated pulp was improved in an efficient and selective manner by using peroxyacid, which facilitated chlorine free bleaching. After prebleaching with peroxyacid, pulp from mustard branches showed the lowest kappa number among the three raw materials. Prebleached pulps were bleached by alkaline peroxide bleaching and final pulp yields reached 47.2%, 45.3% and 41.3% for lentil stalks, mustard stems and mustard branches, respectively. The bleached pulp from mustard stems and branches showed ISO brightness above 80% after alkaline peroxide bleaching, while lentil stalks bleached pulp showed 76% ISO brightness. Acceptable papermaking properties were obtained from these agricultural wastes by organic acid pulping at atmospheric pressure, followed by chlorine free bleaching.

***Keywords***: formic acid/acetic acid pulping, agricultural wastes, delignification, peroxide bleaching, paper strength

## INTRODUCTION

Bangladesh and most of the South Asian countries are densely populated and forest deficient. Therefore, it is critical to find alternative fibrous raw materials for pulping. Papermaking started from non-wood materials in China almost 2,000 years ago, when paper itself was invented. Especially in Asia, cereal straw, reeds, grasses, and sugar cane bagasse have been used in pulping and papermaking ever since. However, the basic raw materials for pulp and paper industries come from the forest. Currently, over 90% of chemical and mechanical pulps are produced from wood. Non-wood pulp capacity has been estimated at 6% of the total paper making capacity.[1]

A growing interest in lignocelluloses biomass has gained impetus to replace petroleum products because of the depletion of world fossil fuels, fluctuating prices and the increasing problem of greenhouse gas emissions. The successful exploitation of biomass to produce value-added chemicals may lead to a stepwise move of the present global economy toward a sustainable bio-based economy with bio-based products, such as biomaterials, biochemicals, and bioenergy. To implement this sustainable bio-based economy, an Integrated Forest Biorefinery concept has been developed. For lignocellulosic materials, pre-extraction of lignocellulosic materials prior to pulping has been considered as an important step for the implementation of integrated forest biorefinery.[2-7] This pre-extracted liquor contains hemicelluloses, lignin and acetic acid, which may be an ideal source for biobased products.[8] But, the pulp produced from the pre-extracted lignocelluloses is inferior in quality.[9] In order to achieve a complete and profitable utilization of lignocellulosic biomass, efforts have been made all over the world to develop processes based on the utilization of organic solvents.[10] Following the general idea of the "biomass fractionation",[11] these processes should improve the weak points of the Kraft pulping technology, including: i) mitigation of the environmental impact, ii) generation of valuable by-products from hemicelluloses, iii) production of soluble, sulphur-free lignin fragments useful for further processing, and iv) reduction of the investment needed for profitable operation.

Non-wood fibrous raw materials are readily available, but are only reluctantly used as raw materials in the pulp and paper industry because of processing problems experienced due to the high silicon content and slow drainage of the resulting pulp. The silicon compounds are largely transformed into soluble silicates, which transfer to the black liquor and cause major problems in the recovery circuit during cooking. Pan and Sano[12] showed interesting results using acetic acid cooking methods, which produced pulp of acceptable mechanical properties, as well as retention of a large part of silica derivatives in the unbleached pulp. Acetic acid cooking needs sulfuric acid as catalyst for delignification. Therefore, the presence of sulfuric acid in the black liquor complicates the recycling of the cooking chemicals and also creates corrosion problems.[13] Several approaches dealing with the fractionation in formic acid media have been reported in aqueous formic acid and formic acid–peroxyformic acid.[14,15] This process effectively fractionates lignin, hemicelluloses and pulp.[14,16] In the spent liquor, a considerable amount of acetic acid is generated from the bound acetyl group in hemicelluloses during FA/PFA delignification process.[13] The separation of acetic acid from the spent liquor makes the recovery system complicated. In this context, an approach has been made to use an acetic acid and formic acid mixture for delignification. Formic acid is used as proton supplier and acetic acid as lignin solvent.[15,17] A large amount of agricultural wastes remain after harvesting crops, which are a potential substitute to wood, such as cotton stalks, corn stalks, rice straw, wheat straw, vegetable wastes, bagasse etc.

In this study, acetic acid/formic acid/water (FA/AA/$H_2O$) delignification of lentil stalks, mustard stems and mustard branches was carried out at atmospheric pressure. The delignified lentil stalks, mustard stems and mustard branches were further bleached by peroxyacid, followed by alkaline peroxide bleaching, and the resulting pulp properties were evaluated.

## EXPERIMENTAL

### Raw materials

Mustard branches, mustard stems and lentil stalks were collected from the Khustia district in Bangladesh after harvesting the crops, which were sun dried in the field, and the leaves were removed. In the laboratory, they were washed with water to remove dirty material, sun dried and cut to 2-3 cm in length. After determination of the moisture content, air dried raw material equivalent to 50 g o.d. (oven dried) was weighed separately in polyethylene bags for subsequent delignification experiments.

### Chemical analysis

The chemical compositions of the raw materials were determined according to Tappi Test Methods (Tappi 2003-4): extractives (T204 om88), water solubility (T207 cm99), Klason lignin (T211 om83). Holocellulose samples were prepared by treating extractive-free raw material meal with $NaClO_2$ solution.[18] The pH of the solution was maintained at 4 by adding $CH_3COOH$-$CH_3COONa$ buffer, and α-cellulose was determined by treating holocellulose with 17.5% NaOH (T203 om 93).

### Formic acid/acetic acid/water

The chopped raw materials (50 g) were placed in an Erlenmeyer flask of 1L capacity and mixed with the required amount of formic acid/acetic acid/water. Then it was refluxed on a hot plate under the following different conditions:

- Formic acid/acetic acid/water (FA/AA/$H_2O$): 30/50/20, 40/40/20 and 50/30/20;
- Reaction time: 1, 2, 3 and 4 h at boiling temperature;
- Liquor to solids ratio of 8:1.

After the desired reaction time, the pulp was filtered in a Buchner funnel and washed with fresh formic acid/acetic acid/water, followed by distilled water. Then the pulp yield was determined gravimetrically and the lignin content in the pulp was determined by Tappi Test Methods (T 222 om-98).

Percentage of lignin in pulp based on o.d. raw material = Percentage of lignin in pulp X Percentage of total pulp yield / 100.

### Peroxyacid treatment

FA/AA/water treated pulp was washed with fresh FA/AA/water (40/40/20), pressed and further delignified with peroxyacid at 80 °C for 120 min. The reaction was carried out in a thermostatic water bath. The peroxyacid was prepared by adding 40/40/20 FA/AA/$H_2O$ acid mixture with 2% $H_2O_2$ with o.d. pulp. Then, the pulp was filtered and washed with FA/AA/$H_2O$ acid mixture, and finally with water. Then, the pulp yield was determined gravimetrically, and Kappa number and viscosity were determined by Tappi Test Methods (T 236 om 99) and (T230 om 99), respectively.

**Bleaching**

Bleaching experiments were carried out with unbleached pulp (50 g) at 10% pulp consistency. The pH was adjusted to 11 by adding NaOH. The hydrogen peroxide charge was 2% on o.d. pulp. The bleaching temperature was 80 $^{o}$C for 1 h. A similar procedure was followed in the 2$^{nd}$ stage of peroxide bleaching.

**Evaluation of formic acid pulp**

FA/AA/$H_2O$ pulp was beaten in a PFI mill for 1500 rev and handsheets were prepared for tensile (T 494 om-96), tear (T 414 om-98) and burst (T 403 om-97) testing.

## RESULTS AND DISCUSSION

### Chemical characterization of agricultural wastes

Table 1 shows the chemical analysis of mustard branches, mustard stems and lentil stalks. The data show that these agricultural wastes are characterized by relatively moderate amounts of lignin (20-23% Klason lignin), reasonably low amounts of α-cellulose (35-40%) and relatively high amounts of ash (4-15%). Klason lignin content in these raw materials varied from 20-23%, which is close to hardwood lignin content.[19] Lentil stalk contains 23.1% Klason lignin and 3.0% acid soluble lignin, while mustard stalk contains 20.0% Klason lignin and 3.4% acid soluble lignin. The lower lignin indicates easier pulping. The structural units of the acid soluble lignin (3.0-3.4%) are mainly represented by syringyl. Higher syringyl units indicate a higher delignification rate.[20] The α-cellulose content of mustard brunches, mustard stems and lentil stalk is lower than that of hardwood[21] and comparable to mangrove species wood.[22] The α-cellulose content in the raw material is based on the pulp yield. The pentosans content is 16-17%, which is lower than the other non-woods and hardwoods in Bangladesh.[23,24] The ash content in these agricultural wastes is much higher (3.5-6.8%) than in wood.[21,25] Mustard stems and brunches have considerably higher ash content. Ash content causes problems in chemical recovery. One percent alkali solubility of mustard branches was the highest (44%) among the raw materials studied. Branches always show higher alkali solubility than the stems.[21] Based on alkali solubility, these raw materials can be expected to provide a medium to low pulp yield. One percent alkali solubility in rice straw was higher than that of the agricultural residues, like cotton stalks, corn stalks, and dhaincha.[2-4]

Table 1
Characteristics of lentil stalks and mustard stems and branches

| | Lentil stalks | Mustard stems | Mustard branches |
|---|---|---|---|
| 1% NaOH solubility | 31.0 | 30.5 | 43.8 |
| Cold water solubility (%) | 10.9 | 16.7 | 19.8 |
| Hot water solubility (%) | 15.4 | 19.7 | 21.0 |
| Lignin (%) | | | |
| Klason lignin | 23.1 | 20.0 | 21.8 |
| Acid soluble lignin | 3.0 | 3.4 | 3.3 |
| Total lignin | 26.1 | 23.4 | 25.1 |
| Holocellulose (%) | 61.6 | 59.5 | 63.0 |
| α-cellulose (%) | 38.0 | 37.0 | 35.4 |
| Pentosans (%) | 15.5 | 16.5 | 16.8 |
| Ash (%) | 3.5 | 6.8 | 5.0 |

### Delignification

Delignification of chopped lentil stalks and mustard stems and branches was carried out by varying cooking time and formic acid ratio in the FA/AA/water mixture. Each factor was studied in relation to pulp yield (%) and residual lignin. The increase of the formic acid proportion in the acid mixture decreased the Klason lignin of both pulps, regardless of cooking time (Tables 2-4). Similar results were observed for jute, dhaincha and kash pulping with FA/AA/water.[15] An earlier study[17] also showed that increasing formic acid concentration in the acid mixture improved delignification and decreased rejects. The lentil stalks, mustard stalks and mustard branches were not delignified sufficiently with any acid mixture.

We kept the water proportion constant (20%) in the acid mixture. A decrease in delignification was observed in a previous study, when the water proportion in the acid mixture was very low.[26] A certain precise amount of water is therefore, necessary for optimal pulping. The reaction below shows hydrolytic dissociation of organic acids in solutions and formation of solvated protons, which facilitate the breakdown of plant matter in an organic acid environment when water is added.

$$RCOOH + H_2O \leftrightarrow RCOO^- + H_3O^+$$

Table 2
Effect of formic acid concentration and cooking time on pulping of mustard stems

| Cooking liquor ($FA:AA:H_2O$) | Cooking time (h) | Cooking yield (%) | Acid insoluble lignin (%) | Acid soluble lignin (%) |
|---|---|---|---|---|
| 50:30:20 | 2 | 70.0 | 18.0 | 2.6 |
| | 3 | 59.1 | 14.7 | 1.9 |
| | 4 | 54.5 | 12.3 | 2.0 |
| 40:40:20 | 2 | 71.73 | 19.0 | 1.9 |
| | 3 | 67.36 | 17.3 | 1.7 |
| | 4 | 61.39 | 15.3 | 1.29 |
| 30:50:20 | 2 | 80.73 | 17.2 | 2.3 |
| | 3 | 77.88 | 16.5 | 1.6 |
| | 4 | 71.66 | 15.5 | 1.8 |

Table 3
Effect of formic acid concentration and cooking time on pulping of mustard branches

| Cooking liquor ($FA:AA:H_2O$) | Cooking time (h) | Cooking yield (%) | Acid insoluble lignin (%) | Acid soluble lignin (%) |
|---|---|---|---|---|
| 50:30:20 | 2 | 52.8 | 16.0 | 1.9 |
| | 3 | 49.0 | 13.1 | 1.7 |
| | 4 | 47.2 | 10.5 | 1.6 |
| 40:40:20 | 2 | 60.1 | 17.8 | 1.1 |
| | 3 | 52.4 | 15.2 | 1.2 |
| | 4 | 52.0 | 13.2 | 0.8 |
| 30:50:20 | 2 | 67.4 | 18.6 | 1.3 |
| | 3 | 61.4 | 17.9 | 1.1 |
| | 4 | 59.1 | 16.6 | 1.2 |

Table 4
Effect of formic acid concentration and cooking time on pulping of lentil stalks

| Cooking liquor ($FA:AA:H_2O$) | Cooking time ( h) | Cooking yield (%) | Acid insoluble lignin (%) | Acid soluble lignin (%) |
|---|---|---|---|---|
| 50:30:20 | 2 | 64.4 | 15.24 | 0.9 |
| | 3 | 63.1 | 12.31 | 0.9 |
| | 4 | 61.9 | 8.45 | 0.8 |
| 40:40:20 | 2 | 67.9 | 18.77 | 1.0 |
| | 3 | 65.3 | 13.19 | 0.9 |
| | 4 | 65.0 | 10.01 | 0.8 |
| 30:50:20 | 2 | 79.1 | 22.64 | 1.0 |
| | 3 | 69.4 | 15.79 | 0.7 |
| | 4 | 66.9 | 13.42 | 0.6 |

In a concentrated organic acid solution, molecules are closely linked to each other by hydrogen bonds; therefore, protons are not readily available. The addition of water is firstly used to break the links between the molecules of organic acid and then to favor the ionization and dissociation of these acids, which then supply the proton.[26]

The mechanism of delignification by acetic acid was studied by Yasuda *et al.*[27] using model lignin. In the first step, carbonium ions are generated by the acid-catalysed rupture of the α-aryl ether bonds of arylglycerol-1,3-aryl ethers, the basic structural units of lignin. Most of the carbonium ions immediately lose three protons to form vinyl ether, which is then hydrolysed, but some undergo intra or intermolecular nucleophilic attack by aromatic rings to produce condensation products.

Figure 1 shows the change of lignin content during organic acid pulping at different FA/AA/water acid ratios. Schematically, we consider the entire period of delignification in a single phase in this experiment. Then, equation (1) becomes:

$$\frac{dL}{dt} = kL_0 \qquad (1)$$

where $L$ is the amount of lignin (Klason lignin and acid soluble lignin) remaining after time, $t$, in a constant composition cook at constant temperature. $L_0$ is the amount of lignin originally present, which reacts accordingly, and $k_i$ is the rate constant of this reaction.

Lignin yield on o.d. raw material is plotted against cooking time (Fig. 1). Lignin yield is defined here as the percentage of residual lignin remaining after delignification based on o.d. raw material. The experimental data fitted well according to equation 1 (Table 5). The correlation coefficient was 0.94-0.99. The delignification rate was increased and residual lignin decreased with increasing formic acid in FA/AA/water. The observed delignification rate was 0.2969 to 0.3433 $min^{-1}$ for lentil stalks, 0.1193-0.3066 for mustard stems and 0.1225-0.2511 for mustard branches. Table 5 indicates that the rate of delignification increased 1.07 to 1.6-fold, depending on raw material for increasing formic acid from 40 to 50 in the FA/AA/water ratio.

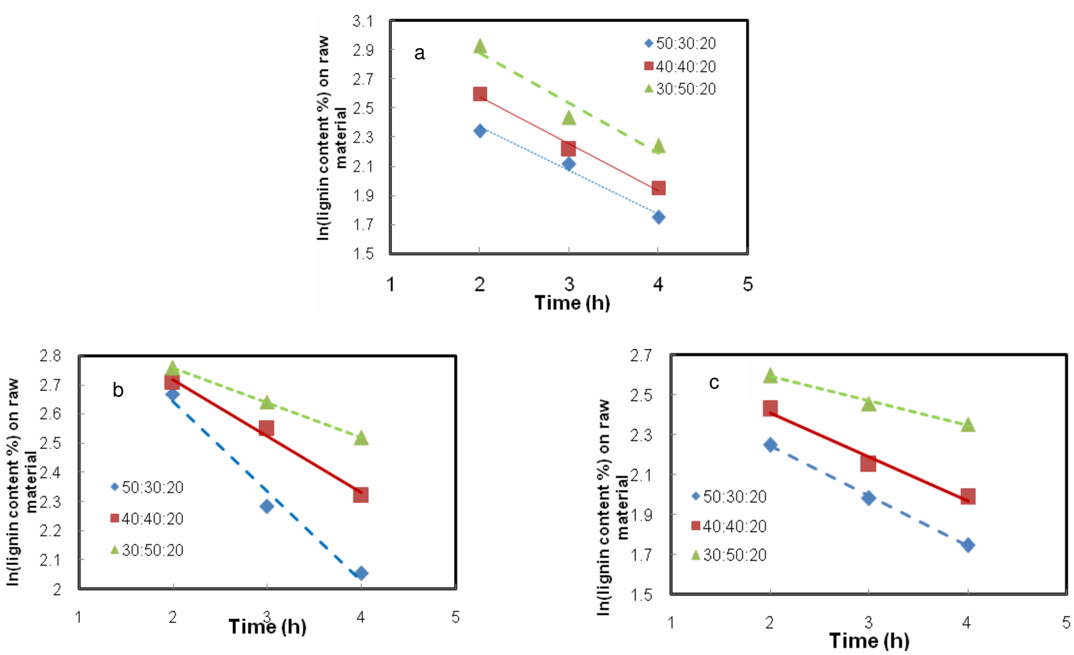


Figure 1: Delignification of (a) lentil stalks, (b) mustard stems and (c) mustard branches by FA/AA/water

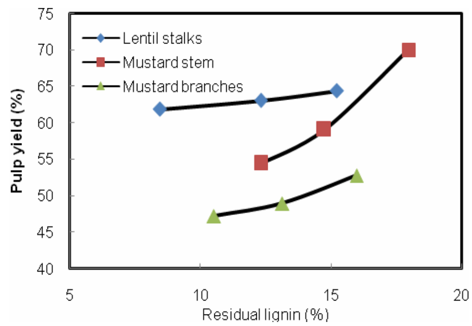


Figure 2: Relationship between pulp yield and residual lignin of pulps from lentil stalks, mustard stems and mustard branches

Table 5
Kinetic data of FA/AA/water delignification of lentil stalks and mustard stems and branches

| $FA:AA:H_2O$ | 50:30:20 | | 40:40:20 | | 30:50:20 | |
|---|---|---|---|---|---|---|
| | Rate constant (k, $h^{-1}$) | $R^2$ | Rate constant (k, $h^{-1}$) | $R^2$ | Rate constant (k, $h^{-1}$) | $R^2$ |
| Lentil stalks | 0.3433 | 0.9816 | 0.3223 | 0.9888 | 0.2969 | 0.9418 |
| Mustard stems | 0.3066 | 0.9788 | 0.1928 | 0.9891 | 0.1193 | 0.9997 |
| Mustard branches | 0.2511 | 0.9987 | 0.2192 | 0.9783 | 0.1225 | 0.992 |

**Pulp yield**

Pulping was not sufficient when the percentage of formic acid was limited to 20% in the acid mixture (data not shown). At the formic acid ratio of 50% in FA/AA/water for 4 h of cooking, the pulp yield was 54.5% for mustard stems, 61.9% for lentil stalks and 47.2% for mustard branches. Figure 2 shows the pulp yield against residual lignin of lentil stalks, mustard stems and mustard branches for the FA/AA/water of 50/30/20. The pulp yield of lentil stalks was higher than the mustard stems and branches in the residual lignin range of 8-15%. The higher pulp yield of lentil stalks can be explained by higher α-cellulose content and lower alkali solubility (Table 1).

**Peroxyformic acid treatment**

Unbleached pulp obtained for the acid mixture of $FA/AA/H_2O$, 40/40/20, in 3 h of cooking was further delignified by peroxyformic acid. Peroxyacid has proved an efficient delignifying agent for the unbleached pulp through the combined action of peroxyacid as an oxidizing agent and formic acid/acetic acid as a solvent for the lignin. The peroxyacid treatment allows obtaining further delignified lentil stalks, mustard stems and mustard brunches by over 50% (Table 6). The Kappa numbers of lentil stalks, mustard stems and mustard branches were 29.5, 22.4 and 25.1, respectively. The brightness of peroxyacid treated pulp was improved to 50.4, 50.3% and 47.5% from 23.2, 20.9 and 18.9% for mustard stems, lentil stalks and mustard branches, respectively. The pulp yield of lentil stalks after peroxyacid treatment was 55.4%, which was 10% higher than that of the mustard branches and 5% more than that of the mustard stems. The pulp yield in $FA/AA/H_2O$ and peroxyacid delignification was much higher than that from other non-woods in a conventional pulping process at an almost similar kappa number.[16,28]

**Bleaching and physical properties**

The bleaching of peroxyformic acid treated pulps from mustard stems, mustard branches and lentil stalks was done by an alkaline peroxide treatment. Mustard branch pulp responded well, compared to mustard stem and lentil stalk pulps, in the same bleaching treatment. The final brightness of mustard stems, mustard branches and lentil stalks reached 81.2, 90.1 and 76.2% ISO, respectively. The bleached pulp yield was the highest for lentil stalks and the lowest for mustard branches, as expected. The prebleached pulp yield was lower by 4-8% on alkaline peroxide bleaching, but it is higher than that for conventional pulping processes. These results show that the bleaching of non-wood formic acid pulp using a TCF sequence is efficient.

Table 6
Effect of peroxyacid delignification of FA/AA/$H_2O$ treated biomass

| Sample | Yield after prebleaching (%) | Kappa no. | Brightness (%) |
|---|---|---|---|
| Lentil stalks | 55.4 | 29.5 | 50.3 |
| Mustard stems | 50.1 | 22.4 | 50.4 |
| Mustard branches | 45.0 | 25.1 | 47.5 |

Table 7
Papermaking properties of bleached pulps obtained from mustard stems, mustard branches and lentil stalks

| Raw material | $^0$SR at 1500 PFI rev | Final yield (%) | Brightness (% ISO) | Tear index ($mN.m^2/g$) | Tensile index (N.m/g) | Burst index ($kPa.m^2/g$) |
|---|---|---|---|---|---|---|
| Lentil stalks | 61 | 47.2 | 76.2 | 4.4 | 33.9 | 1.3 |
| Mustard stems | 62 | 45.2 | 81.2 | 8.5 | 26.3 | 1.3 |
| Mustard branches | 78 | 41.3 | 90.1 | 9.2 | 61.6 | 4.7 |

The papermaking properties of the bleached pulp were determined after beating in a PFI mill for 1500 revolutions, and are shown in Table 7. Only 1500 PFI revolutions increased the beating degree value to above 60 for lentil stalks and mustard stems and 78 for mustard branches. Similar results were reported elsewhere for organic acid pulp.[29,30] It was observed in our earlier study that bleaching of the pulp improved physical properties.[14,30] This can be explained by a better hydration of the pulp during bleaching. Then, fibrillation can take place more easily during beating. In the unbleached organic acid pulp, the hydroxyl groups of cellulose were acetylated or formylated, which reduced pulp hydration. Mustard branch pulp showed higher breaking length and burst index, as compared to those of mustard stem and lentil pulps. All strength properties were comparatively inferior to those of a conventional pulp.[31] The reason may be the damage of fibers during acidic pulping. Similar results were found in acetic acid pulping of wheat straw.[11] It is assumed that organic acid promotes the solvation of lignin fragments but, at the same time, reduces swelling predominantly of the carbohydrate fibers,[32] which may also be the cause of lower strength properties. Ash-rich epidermal cells remaining in formic acid pulp can be considered as another reason of lower strength. These non-fiber cells are short and stiff. They have no contribution to the strength of the pulp, instead, they obstruct bonding between fibers. The two-stage alkaline peroxide bleaching responded very well.

## CONCLUSION

Lentil stalks, mustard stems and mustard branches were characterized by moderate lignin and low α-cellulose contents, which suggest lower pulp yield. The delignification increased with increasing formic acid proportion in the pulping liquor of formic acid/acetic acid and water mixture. Lentil stalks showed a better pulp yield than that of mustard stems and mustard brunches with a residual lignin content of 8-15%. Peroxyacid treatment reduced the residual lignin of these pulps by 50% and improved pulp brightness significantly. The organic acid pulps responded well to alkaline peroxide bleaching. Mustard branch pulp showed the highest brightness (90%). Finally, it can be said that the formic acid/acetic acid/water system pulping can be suitable for small-scale pulping of agricultural wastes.

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