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Chemical Evaluation of Some Lignocellulosic Residues for Pulp and Paper Production

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Abstract: Lignocellulosic residues cause many environmental problems, so conversion of these residues to pulp and paper production will reduce these problems in Saudi Arabia. Residues from *Phoenix dactylifera*, *Triticum aestivum*, *Conocarpus erectus*, in addition to *Tamarix aphylla* (hardwood) and *Juniperus procera* (softwood) were evaluated using chemical characteristics to investigate the suitability of these residues for pulp and paper industry. Evaluation was carried out at Laboratory of Wood Technology, College of Food and Agricultural Sciences, King Saud University, Saudi Arabia. Results revealed that, significant differences among raw materials in chemical composition were obtained. Date palm gave the highest average values of extractive content followed by *T. aestivum* and the least average value was of *J. procera*. Generally, extractive content was high in lignocellulosic residues compared to woody materials which imply that the quantity cooking and bleaching chemicals will be increased with lignocellulosic residues and consequently this will raise the cost of paper production. Cellulose content in the lignocellulosic residues under study was in the range between softwood (*J. procera*) and hardwood (*T. aphylla*), so it can be used as alternative substance for pulp and paper production. Regarding lignin content, *T. aphylla* gave the highest average values, while the lowest one was obtained from *T. aestivum*. Lignin in lignocellulosic residues was low compared to woody materials except *C. erectus*, so we believe that the color of pulp yield from lignocellulosic residues will be light brown compared to others materials.

Key words: Hardwood · Softwood · Extraction · Cellulose content · Lignocellulosic residues

INTRODUCTION

The availability of writing material has always gone hand in hand with the development of society. The earliest media for writing was the stone tablet. Pulp and paper have been important in the development of mankind from prehistoric to present time. The development of written communication has been increasing rapidly, a day without paper is unthinkable, but now the use of paper has been expanded to encompass not only communication but also to the packaging and hygiene sectors. The major consumption of wood and lignocellulosic materials in Asia and Africa is still for fuel purposes whereas in Europe and North America, they are dominant for the production of paper and board. Saudi Arabia, like many countries in arid and semi-arid zones, is poor in natural forests [1]. Increasing demand of forest resources for wood fuel and wood industries leads to continuous efforts in finding an alternative raw material to forest wood. Researches to find this alternative material have been conducted by both industry and research institutions. Agricultural residues are renewable resources that can be utilized as raw materials for wood industry [2, 3]. A wide variety of agricultural residues and non-woody materials, such as midribs of date palm, wheat straw [1], rattan [3] and coconut shell of babacu [2] have been studied. Fortunately, Saudi Arabia has relatively large quantities of lignocellulosic materials, including *Conocarpus* prunings and date palm residues. Enormous quantities of *Conocarpus erectus*, yield huge quality of biomass annually through seasonal pruning as regular agricultural practice to achieve the purposes of these plantations in the public garden and streets in different engineering forms. No data were available in this field

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about the amount of *Conocarpus* tree residues. In the Kingdom of Saudi Arabia, the number of date palm trees exceeds 28 million. A large quantity of this date palm population sheds huge quantity of plant biomass annually from seasonal pruning as an essential agricultural practice. Average of palm residues is obtained per tree annually about 35kg, about one million metric tons of date palm biomass are wasted annually from seasonal trimming of the palm tree population in Saudi Arabia. *Tamarix aphylla* is forest tree, fast growing, drought resistant and salt-tolerant species, planted throughout the Kingdom. This wood species constitutes a renewable resource that could be used as a source of woody raw material required for several local uses, instead of depending totally on imported woods [4].

In many countries wood is not available in sufficient quantities to meet the rising demand for pulp and paper. In recent years, active researches have been undertaken in Europe and North America to find a new, non-wood raw material for paper production [5]. The driving force for searching for new pulp sources was twofold: the shortage of short-fiber raw material (hardwood) in Nordic countries, which export pulp and paper and, parallel overproduction of agricultural crops. At the same time, the consumption of paper, especially fine paper, continued to grow, increasing the demand for short fiber pulp [6]. Commercial non-wood pulp production has been estimated to be 6.5% of the global pulp production and is expected to increase [7]. China produces 77% of the world's non-wood pulp [7]. In China and India over 70 % of raw material used by the pulp industry comes from non-woody plants. The main sources of non-wood raw materials are agricultural residues from monocotyledons, including cereal straw and bagasse, a fibrous residue from processed sugar cane (*Saccharum officinarum* L.). Bamboo, reeds and some grass plants are also grown or collected for the pulp industry. Thus, available lignocellulosic residues (*Conocarpus erectus* pruning, *Phoenix dactylifera* residues and *Triticum aestivum* straw) were used in the current study. Hardwood *(Tamarix aphylla)* and softwood (*Juniperus procera*) were used for comparing purposes. Chemical composition is important technology properties for lignocellulosic residues uses. Therefore, before suggesting proper utilization of these residues, it is essential to evaluate their basic technological properties. Thus the objective of the study was to evaluate the suitability of some lignocellulosic residues for pulp and paper production by determining their chemical composition including extractives, cellulose, hemicelluloses, lignin and ash contents. This work was carried out in the Plant Production Department, Food and Agricultural Sciences Collage, Saudi Arabia during January 2012 to January 2013.

MATERIALS AND METHODS

Raw Materials: Residues such as date midrib fronds (*Phoenix dactylifera*), wheat straw (*Triticum aestivum*) as well as trees pruning of *Conocarpus erectus* were collected from different locations in the Kingdom for pulp and paper production. The woody materials also such as *Tamarix aphylla* as hardwood and *Juniperus procera* as softwood were collected from Al-Kharj and Al-Qassim. After collection they were fragmented separately into small pieces using band and disk saw. The fragmented materials were then fed through a lab type Hammer mill using different sizes of screen. Thereafter, a lab type sieve shaker and separator were used to separate the wood meal into -0.4/+0.2 mm to be used for chemical analysis and -12/+4 mm for pulping process.

Extractives Content Determination: Samples of air-dried lignocellulosic residues and woody materials were ground to pass through 0.42 mm screen and retained on a 0.25 mm screen. The procedure is based on National Renewable Energy Laboratory (NREL) [8]. Air-dried samples were extracted by ethanol (95%) in a Soxhlet extractor apparatus for 24 hours and the heating rate was adjusted to give four to five solvent exchanges per hour in the Soxhlet thimble. Approximately 100-120 siphons are required during the 24 hour period. The percentage of extractives was calculated based on the oven-dry weight of the samples samples.

Wood Chemical Analysis: Extractive-free meal samples were used to determine the contents of cellulose, hemicellulose and lignin according to the method described by Nikitin [9], Rozmarin and Simionescu [10] and ASTM, D1106-84 [11], respectively. In addition, ash content of wood was determined according to the NREL [12].

Statistical Analysis: The analysis of variance was carried out using complete randomized design (CRD), according to Snedecor and Cochran [13], in order to examine the variability in extractives, cellulose, hemicelluloses, lignin and ash contents among the five materials used. Also, the least significant difference method at 95% level of probability ($L.S.D_{0.05}$) was used to test the differences among the means of each parameter if the differences are significant. The data were exported to a PC-SAS data set for statistical analysis using the GLM procedure.

RESULTS AND DISCUSSION

Chemical Analysis of the Lignocellulosic Residues and Woody Materials: The statistical analysis of the results indicated that the differences among species were highly significant for all chemical components of woody and lignocellulosic residues including extractives, cellulose, hemicelluloses, lignin and ash.

Extractives Content: Table 1 shows the mean values, standard deviation and range of extractives content of the five raw materials used in pulp and paper. Generally, it can be seen that *P. datylifera* gave the highest average values of extractive content (20.31%) with standard deviation 0.03 and range from 20.28 to 20.34% followed by *Triticum aestivum* (17.50%) with standard deviation 0.22 and range from 17.26 to 17.71% and the least average value was *Juniperus procera* (6.38%) with standard deviation 0.17 and range from 6.21 to 6.56%. Because of the high extractive content of date palm, a decrease in pulp yield was expected and an increase in chemicals needed in cooking and bleaching, since the more extractive content results in the less pulp yield. Generally, extractive content was high in lignocellulosic residues compared to woody materials, so the cooking and bleaching chemicals will be increased with lignocellulosic residues and this increase in chemicals will raise the cost of paper. Some researchers could control extractives by different silvcultural treatments such as fertilization, where they found that the fertilization by sewage sludge or dried sludge had increased extractives [14, 15]. The differences among species in extractive content were in agreement with those obtained by Abdel-Aal and Kayad [16] who found that the differences among species were highly significant and these species were *Citharexylem quadrangulare, Cordia myxa and Eugenia cumini.* Taylor *et al.* [17] also found that the heartwood extractives were chemically complex and varied significantly within and between trees and tree species.

Cellulose Content: Cellulose plays the most important role in fiber strength and subsequently paper strength as well as pulp yield. About 90% of pulp and paper in the world is produced from softwood and hardwood. Cellulose content in the lignocellulosic residues under study was in the range between softwood (*J. procera*) and hardwood (*T. aphylla*), where *P. datelifera, T. aestivum* and *C. erectus* had cellulose content of 45.04, 47.14, 42.10%, respectively, whereas softwood and hardwood were 49.91% and 39.47%, respectively. So it may be concluded that these residues can be used for pulp and paper production to reduce the negative effects of such substances to the environment (Fig. 1).

Table 1: Extractives content, standard deviation and the range of raw materials used in pulp and paper

Raw materials	Species	Mean (%)	SD	Range (%)
Lignocellulosic residues	*Phoenix datylifera*	20.31[a]	0.03	20.28-20.34
	Triticum aestivum	17.50[b]	0.22	17.26-17.71
	Conocarpus erectus	10.86[d]	0.09	10.78-10.97
Woody materials	*Tamarix aphylla* (hardwood)	15.68[c]	0.34	15.40-16.07
	Juniperus procera (softwood)	6.38[e]	0.17	6.21-6.56

Each value of mean and standard deviation is an average of three samples per species.
Mean values sharing the same letter in column are not significantly different according to LSD test at 0.05% level.
SD is Standard Deviation

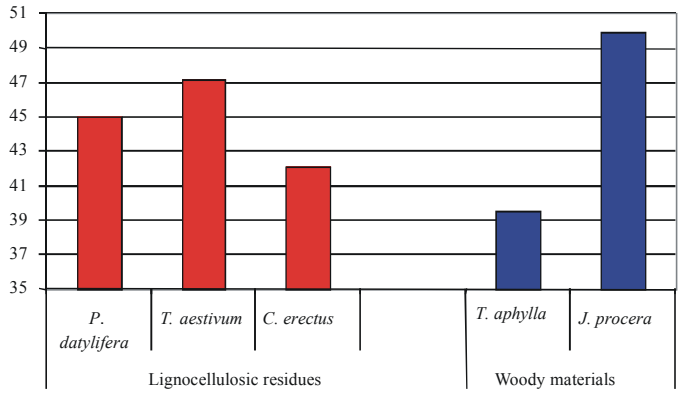

Fig. 1: Cellulose content of lignocellulosic and woody materials

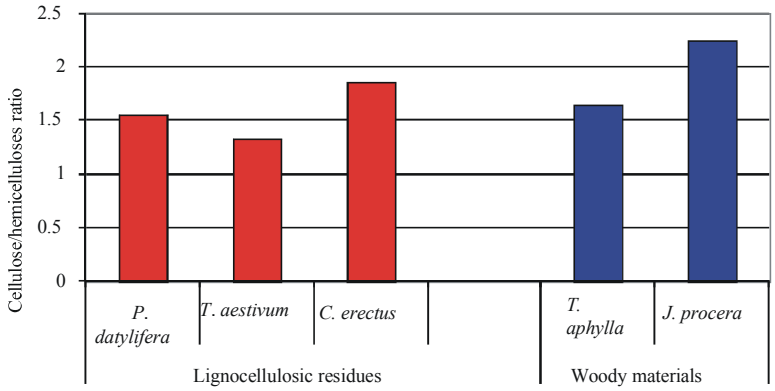

Fig. 2: Cellulose/hemicelluloses ratio of lignocellulosic and woody materials

Table 2: Hemicelluloses content, standard deviation and the range of raw materials used in pulp and paper

Raw materials	Species	Mean (%)	SD	Range (%)
Lignocellulosic residues	*Phoenix datylifera*	29.13[b]	0.03	28.62-29.78
	Triticum aestivum	35.37[a]	0.22	34.43-35.97
	Conocarpus erectus	22.73[d]	0.09	22.31-23.05
Woody materials	*Tamarix aphylla* (hardwood)	24.20[c]	0.34	23.83-24.84
	Juniperus procera (softwood)	22.11[d]	0.17	21.75-22.71

Each value of mean and standard deviation is an average of three samples per species.
Mean values sharing the same letter in column are not significantly different according to LSD test at 0.05% level.
SD is Standard Deviation

Some important properties of cellulosic fibers are high tensile strength, water insoluble, hydrophilic, wide range of dimensions, ability to absorb modifying additives and chemically stable. So it is expected that the pulp yield and strength will be high in papermaking from species that has high cellulose content like *J. procera* and *T. sativum*. These results are in agreement with those obtained by Page *et al.* [18] who found that, fiber strength commonly increases with increasing cellulose content and Molin [19] who found that, increasing of the cellulose content would also increase the strength of the paper. Some researchers found that, cellulose content in the raw materials can be controlled by thinning treatments, where heavy thinning gave higher cellulose values. The wide spacing gave the highest yield of cellulose while, the narrow spacing gave the lowest [16, 20, 21]. Others found that, irrigation can affect cellulose content. The sewage irrigated Eucalypt plantation resulted in a significant increase in alpha cellulose content [14,15]. The differences among species are in agreement with those reported Abdel-Aal and Kayad [16] who found that, the differences among species were highly significant in cellulose content.

Hemicelluloses Content: Data presented in Table 2 indicated that, *Triticum aestivum* gave the highest average values of hemicelluloses content (35.37%) with standard deviation 0.22 and range from 34.43 to 35.97% followed by *Phoenix datylifera* fronds (29.13%) with standard deviation 0.03 and range from 28.62 to 29.78%, while the least average value was *Juniperus procera* (22.11%) with standard deviation 0.17 and range from 21.75 to 22.71%. Several authors [22, 23] observed that increased hemicellulose content gave a lower tear index and a higher tensile index. Hemicelluloses content affect mechanical properties of paper although it is soluble in 18.5% NaOH and has low-molecular-weight which it becomes soluble in diluted alkali at elevated temperatures, such as in kraft and soda cooking. Hemicelluloses increase the strength of paper, especially tensile, burst and fold and the pulp yield [24, 25]. So it is expected that the pulp yield, tensile and burst strength will be high in paper from species had high hemicelluloses content like *T. aestivum* and *P. datylifera.* Some industries need raw materials with high hemicelluloses while others need low hemicelluloses and fortunately hemicelluloses content in the raw materials can be controlled by silvicultural treatments as stated before [14, 15, 16, 21].

Cellulose to Hemicelluloses Ratio: From Fig. 2, it can be noticed that, *J. procera* gave the highest average values of cellulose/hemicelluloses ratio (2.25) followed by *C. erectus* (1.85), while the lowest average value was

Table 3: Lignin content, standard deviation and the range of raw materials used in pulp and paper

Raw materials	Species	Mean (%)	SD	Range (%)
Lignocellulosic residues	*Phoenix datylifera*	25.82[d]	0.38	25.38-26.08
	Triticum aestivum	17.48[e]	0.63	16.89-18.15
	Conocarpus erectus	35.16[b]	0.22	35.03-35.43
Woody materials	*Tamarix aphylla* (hardwood)	36.32[a]	0.18	36.12-36.47
	Juniperus procera (softwood)	27.97[c]	0.80	27.06-28.59

Each value of mean and standard deviation is an average of three samples per species.

Mean values sharing the same letter in column are not significantly different according to LSD test at 0.05% level.

SD is Standard Deviation

Table 4: Ash content, standard deviation and the range of raw materials used in pulp and paper

Raw materials	Species	Mean (%)	SD	Range (%)
Lignocellulosic residues	*Phoenix datylifera*	1.33[d]	0.04	1.29-1.38
	Triticum aestivum	6.81[a]	0.13	6.69-6.95
	Conocarpus erectus	2.21[c]	0.10	2.12-2.32
Woody materials	*Tamarix aphylla* (hardwood)	6.06[b]	0.17	5.91-6.25
	Juniperus procera (softwood)	0.87[e]	0.05	0.82-0.93

Each value of mean and standard deviation is an average of three samples per species.

Mean values sharing the same letter in column are not significantly different according to LSD test at 0.05% level.

SD is Standard Deviation

T. aestivum (1.33). Generally, cellulose/hemicellulose ratio of lignocellulosic residues was between softwood and hardwood ratios, except *T. aestivum* which is low because it had high hemicellulose content. This ratio affects mechanical properties of paper, where Molin [19] found that the increased cellulose/hemicellulose ratio increased the tear index, toughness and folding endurance, while the tensile index decreased. It is expected that handsheet formed from *J. procera* pulps will be high in tear index and folding but it will be low in tensile index.

Lignin Content: Data presented in Table 3. indicated that, *T. aphylla* had the highest average values of lignin content (36.32%) with standard deviation 0.18 and range from 36.12 to 36.47% followed by *C. erectus* 35.16 % with standard deviation 0.22 and range from 35.03 to 35.43%, while the lowest average value was *T. aestivum* (17.48%) with standard deviation 0.63 and range from 16.89 to 18.15%. Generally, it can be seen that lignin content in lignocellulosic residues was low compared to woody materials except *C. erectus* which had lignin content 35.16%, so we believe that pulp yield from lignocellulosic residues will be light brown compared to others materials. Also, it is expected that pulp yield decreases with *T. aphylla* because the more lignin the less pulp yield, also the color of pulp yield will be dark brown, this expected is in agreement with Akadiri [26] who found that lignin content contributes to the brown color of the pulp and decrease the pulp yield. Thinning and fertilization treatments can affect lignin content, the thinning treatments increased lignin content. [16, 21]. Also, the fertilization by dried sludge increases lignin content [14].

Ash Content: Ash is the residue that remains after complete combustion of the wood material at 575±25°C. It is composed primarily of inorganic substances such as calcium oxide (CaO) and silica (SiO_2) and small percentages of alumina (Al_2O_3), iron oxide (Fe_2O_3) and magnesium oxide (MgO). Ash is another secondary wood component and is considered an undesirable material in most industrial situations. The increase of wood utilization as a fuel may cause an ash disposal problem because it will accumulate in furnaces, this problem may be eliminated since ash is useful as a soil conditioner and fertilizer when supplemented with nitrogen to produce the compost from wood wastes as a peat moss like substance [27-30]. *T. aestivum* had the highest average values of ash content (6.81%), then *T. aphylla* (6.06%), but the lowest average value was *J. procera* (0.87%) with standard deviation 0.05 and range from 0.82 to 0.93% (Table 4). It is known that there is relationship between strength and ash content, the paper strength decrease is mainly due to ash increase. So it is expected that the strength of paper will be low in papermaking from lignocellulosic residues that has high ash content such as *T. aestivum*. The results obtained were in agreement with Abdel-Aal and Kayad [16] who found that, the differences among species were highly significant in ash content.

CONCLUSIONS

Based on the findings of the current study, it may be concluded that, extractives content was high in lignocellulosic residues compared to woody materials, so the quantity of cooking and bleaching chemicals will increase with lignocellulosic residues and this will raise the cost of paper production. Cellulose content in the lignocellulosic residues obtained in the present study was in the range between softwood (*J. procera*) and hardwood (*T. aphylla*), so these residues can be utilized in pulp and paper production to reduce the negative effects of such substances to the environment. The ratio of cellulose to hemicellulose affects mechanical properties of paper; this ratio of lignocellulosic residues was between softwood and hardwood ratios, except *T. aestivum* which is low because it had high hemicellulose content. Also, it can be seen that lignin content in lignocellulosic residues was low compared to woody materials except *C. erectus*, so we believe that pulp yield from lignocellulosic residues will be light brown compared to others materials

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