PREDICTION OF METHOXYL GROUPS CONTENT IN LIGNIN
BASED ON ULTIMATE ANALYSIS

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Different lignins (44 samples) were used in this study for predicting the correlation between the content of methoxyl groups in lignin and the hydrogen and oxygen contents. A significant linear correlation was found between the content of methoxyl groups of the lignin and its H and O contents. The contents of O and H were determined by ultimate analysis in previous studies reported in literature. The content of methoxyl groups (wt%) of lignin was calculated using the following equation: $OCH_3 = -18.5769 + 4.0658(H) + 0.34543(O)$, where the correlation coefficient was 0.766. The average absolute error of this correlation is 13.9%.

Keywords: lignin, prediction, methoxyl groups

INTRODUCTION

Lignin is the second most abundant natural polymer after cellulose. It is generally known that lignin is a phenolic polymer derived primarily from three hydroxycinnamyl alcohols or monolignols.[1] Lignins are polymers consisting of C9 units in which the aromatic rings are substituted with one methoxyl group (guaiacylpropane units), with two methoxyl groups (syringylpropane units) or are lacking the methoxyl substituent (p-hydroxyphenylpropane units).[2] There are quite a few options regarding the linkages between these units.[2,3] Typical C-O links between the monomeric units of lignins are β-O-4, α-O-4, 4-O-5 and C-C links are β-5, 5-5, β-1 and β-β linkages.[4] The heterogeneity of lignin is caused by the variation in its composition, size, cross-linking and functional groups.[5] The structure analysis of lignin is an important issue in wood chemistry, pulping,[6] green chemistry[7] and the chemistry of lignin-based materials.[8] Lignin contains functional groups, such as methoxyl, phenolic hydroxyl, aliphatic hydroxyl and other carbonyl groups.[8]

Analytical methods of lignin characterization are classified into two groups: destructive and non-destructive methods.[1-29] The methoxyl content of the residual lignin could be measured using a modification of the suggested TAPPI method T 209 su-72 "Methoxyl Content of Pulp and Wood". The principle of this method is based on the reaction of the methoxyl groups with hydroiodic acid to generate methyl iodide.[9] The classical method of Zeisel for methoxyl determination of lignin uses hydriodic acids to promote demethylation. Another method is Vebock and Schwappach determination,[23] which is based on the quantitative cleavage of the methoxyl groups and the creation of methyliodide. The created methyliodide can be determined by titration or by the chromatographic method. Other modified methods are the micromethod[24] and the analysis by the capillary gas chromatography.[25] Another method is based on the hydrolytic cleavage of the methoxyl groups, which uses concentrated sulphuric acid. The next step is oxidation to formaldehyde and after the reaction with chromotropic acid, it is determined by the colorimetric method. The method used for the direct determination of methanol was modified by gas

chromatography.[26,27] Methoxyl determination by infrared spectroscopy can be also applied. Although the method depends on about 17 signals of the spectra,[28] it can be used as a non-destructive method, which from this point of view, has an advantage over the rest of the methods. Lignin could also be characterized by other methods, such as nuclear magnetic resonance (NMR) spectroscopy[1,10] and ^{1}H NMR.[11,29] ^{1}H NMR can readily determine methoxyl groups, aromatic hydrogens and structural components. ^{1}H NMR characterization of lignin depends on the internal standard selected, such as the aromatic units and methoxyl groups,[29] and it can be a good alternative to the time-consuming and expensive traditional methods of methoxyl determination. In this study, a new empirical correlation based on the ultimate analysis of different lignins is used to predict the content of methoxyl groups.

EXPERIMENTAL
Methodology

A database of ultimate analysis data, as well as the experimental content of methoxyl groups in lignin, was obtained from the literature and is presented in Table 1.[10,13-22]

Table 1
Contents of OCH_3, C, H and O (wt%) in different lignins[10,13-22]

No.	OCH_3 (wt%)	C (wt%)	H (wt%)	O (wt%)	Reference
1	21.4	60.36	6.16	33.54	(13)
2	9.5	48.78	5.1	29.8	(13)
3	16.25	54.13	6.47	38.61	(14)
4	10.9	63.7	5.7	22.9	(15)
5	12.5	47.1	4.9	25.7	(10)
6	15.1	62.1	6.2	29	(10)
7	20.47	58.01	6.35	35.64	(16)
8	21.6	57.13	5.67	37.2	(16)
9	21.6	56.73	5.81	37.46	(16)
10	13.7	60.9	6.2	32.9	(17)
11	21.8	58.5	6.2	35.3	(17)
18	24.1	61.4	6.3	32.3	(17)
13	12.2	57.8	5.77	35.5	(18)
14	17.8	58	6.59	34.6	(18)
15	14.76	62.04	5.69	32.27	(19)
16	15.33	64.34	4.98	30.68	(19)
17	10.57	63.22	3.58	33.2	(19)
18	3.02	62.01	2.91	35.08	(19)
19	2.17	62.45	2.46	35.09	(19)
20	1.25	62.43	2.51	35.06	(19)
21	11.06	56.84	5.7	33.3	(19)
22	12.31	61.12	5.22	29.83	(19)
23	12.11	63.8	4.51	28.45	(19)
24	3.65	65.34	3.88	27.32	(19)
25	2.6	66.77	3.33	26.15	(19)
26	1.34	66.66	3.05	26.41	(19)
27	1.24	68.86	2.66	23.99	(19)
28	15.63	54.34	5.98	39.68	(19)
29	16.94	56.56	5.54	37.9	(19)
30	15.95	60.7	4.59	34.71	(19)
31	15.38	61.51	3.9	34.59	(19)
32	8.37	61.43	3.34	35.23	(19)
33	2.71	62.16	2.71	35.13	(19)
34	11.47	55.87	5.36	34.32	(19)
35	15.01	58.03	4.79	34.26	(19)
36	11.42	57.81	3.97	35.27	(19)
37	6.67	57.77	4.02	34.05	(19)

38	14.03	58.23	5.22	35.62	(20)
39	17.9	59.12	4.77	35.26	(20)
40	16.6	61.8	6	32.2	(21)
41	14.4	63.8	5.7	26.24	(21)
42	15.7	58.6	5.5	35.5	(22)
43	14.5	61	5.2	33.4	(22)
44	16.9	64.9	6	28.4	(22)

Evaluation of correlation

The multiple regression model with forward selection was used (Statgraphics Plus). To evaluate the correlations accuracy, the average absolute error (AAE) was used. The defined AAE is described elsewhere.[12]

$$AAE = \frac{1}{n} \sum_{i=1}^{n} \left| \frac{\text{Value}_P - \text{Value}_M}{\text{Value}_M} \right| \times 100\% \quad (1)$$

In Eq. 1, subscripts P and M denote the predicted and measured values, respectively, and n is the number of data points. AAE indicates the average absolute error of the correlation. The lower the AAE value, the smaller the error of the correlation.

RESULTS AND DISCUSSION

It is well-known that ash, volatile matter, moisture, fixed carbon, content of carbon, hydrogen, nitrogen and oxygen can be used to predict the heating value of different renewable and nonrenewable raw materials, comprising all types of agricultural and silviculture vegetation.[30,31] To utilize lignin as a raw material for green chemistry in different applications requires to know the content of methoxyl groups. Several studies investigated the content of methoxyl groups of isolated lignins from different biomass species.[1,2,4,10-22] The weight percentages of C, H, O elements and the content of methoxyl groups of different lignins, including commercial ones, are listed in Table 1. In this study, the content of methoxyl groups was found to range between 1.24 and 24.1 wt%. New correlations were formulated by means of multiple regression analyses. The regression of the content of methoxyl groups of different lignins with hydrogen and oxygen contents resulted in a square of the correlation coefficient (r^2) value of 0.766 (Fig. 1). Since the p-value is less than 0.01, there is a statistically significant relationship between the variables at a confidence level of 99%. The content of methoxyl groups of a lignin is a function of its H and O contents. The following formula was used for the model:

$$OCH_3 = -18.5769 + 4.0658(H) + 0.34543(O) \quad (2)$$

where OCH_3 is the content of methoxyl groups in lignin (wt%), H is the hydrogen content (wt%) and O is the oxygen content (wt%) determined by ultimate analysis.
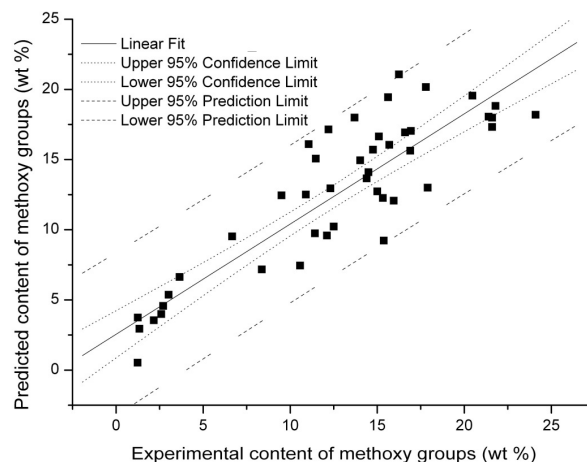

Figure 1: Dependence between predicted and experimental content of methoxyl groups

The created model was used to calculate the content of methoxyl groups, allowing to compare the results obtained with those reported in the literature. Fig. 1 shows the comparison between predicted and experimental content of methoxyl groups for the developed correlation (Eq. 2). It

can be seen that most of the plotted values remain close to the curve of $OCH_{3predicted} = OCH_{3experimental}$, indicating good accuracy of the correlations. The calculated AAE is 13.9%. AAE reached a relatively high value. However, if we compared the AAE of different models for prediction of a higher heating value, the AAE would range very widely. Fassionu *et al.*[32] analyzed different models for prediction of a higher heating value and the AAE values found were in the range from 0.07 to 28.3%. Therefore, we could conclude that the model used for prediction of the content of methoxyl groups can be used as a new empirical relationship to calculate the methoxyl groups in lignin.

CONCLUSION

A simple empirical correlation based on ultimate analysis has been developed via the multiple regression method for predicting the content of methoxyl groups in lignin. This correlation is easy to apply by simple manual calculation and requires to know only hydrogen and oxygen contents (wt% dry material basis).

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