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Applicability of Some Models to Pinus nigra Kraft Pulping

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Abstract: Kraft pulping is very complex operation of chemical and physical process. There are a lot factors which effect and determine the process of delignification. Besides initial variables are the main technological parameters of the process which have crucial influence on the output variables of the produced pulps. In modern plants, checking and controlling of the pulping process has been achieved by the application of computers. Controlling and optimization of a pulping process with computers require mathematical models. In the last three decade a lot of empirical and semi theoretical equations have been developed for defining the properties of the pulp and paper. In this study, some mathematical equations in literature were tested whether usable for this raw material and pulping method or not using kappa number and total yield values obtained from kraft pulping of Anatolian Black Pine chips. Consequently, this paper presents that, *Model B* [7] is not suitable for prediction of Anatolian Black Pine kraft pulps' yield. However Hotton's[8] total yield model *(Model G)* and Tasman's[12] kappa number models *(ModelF)* gave the excellent fit between experimental and calculated parameter values.

Key words: Empirical models, Kraft pulping, H-factor, Pinus nigra

INTRODUCTION

It is known that; there are a lot of plants using kraft pulping method in the world. Viewed a fundamental level, kraft pulping of wood is a very complex process with several stages in heterogeneous phase. It is very difficult to develop a rigorous mathematical model of delignification. For this reason, in the course of developing the mathematical model of kraft process, kinetic was mostly expressed by reactions of the first or pseudo first order [1,2,3].

Controlling and optimization of a pulping process require a mathematical model. Such a model is generally based on a time-temperature study, resulting in an equation that gives the lignin dissolution as a function of the time-temperature variable known, according to Vroom[4], as the H-factor. The results of pulping depend on a great number of variables among which the most important is the time-temperature variable (H-factor) and the alkali charge in cooking liquor[5] .

Great numbers of researchers have developed empirical or semi theorical equations for prediction of pulping yield and lignin content in pulp depending on different input parameters of kraft pulping[6,7,8,9,10,11,12,13,14,15,16]. All these models are applicable within a limited range of some variables of kraft process and can be used only for specific raw material under strictly defined conditions.

Controlling and checking the pulping process with a computer depends mainly on the accuracy of the pulping model. The purpose of the present work was to test the validity of the some mathematical equations in literature probably most well known of all for our output variables

MATERIAL AND METHODS

Anatolian Black Pine (*Pinus nigra* sbsp. *pallassiana*) wood specimens obtained from four different geographic zone of West Blacksea Region of Turkey. In the previous study, the chemical composition of the wood was determined as to be Holocellulose; 72.34%, cellulose; 51.89%, " - cellulose; 43.55%, lignin; 26.4%, ash; 0.18%, solubility in alcohol-benzene; 3.45%, solubility in cold water; 2.02%, solubility in hot water; 3.17%, solubility in 1% NaOH; 13.0% [17].

Pulping trials were carried out in a 15 l. batch cylindrical reactor which was heated electrically. Temperature was controlled by Omron E5CK type digital

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controller unit in the range of ±0.2 °C, cooked material was disintegrated by a laboratory type 2 l. pulp mixer for 10 min. at 2% consistency. Then, the pulp screened on a Noram laboratory type pulp screen with 0.15 mm slots. Reject ratios, screened pulp yields and total yields were calculated on oven dry wood chips. For all pulping trials wood to liquor ratio was selected as 1: 4.

Pulp yields were determined gravimetrically drying at 100 °C for 24 hours and kappa number was obtained according to TAPPI test methods.
Following relationships were used for this study:

Model A [7] : $KN = a - b. [Log10 (H).E^n]$
Model B [7] : $TY = a - b. [Log10 (H).E^n]$
Model C [12]: $TY=10**[[a-b.(E.Log10(S))/Log10(E)]/H]+[[c+d.Log10(S))]/Log10(E)]$
Model D [11]: $KN = [a. (WL^{0,136})] / [(A^{1,171}). (H^{0,175})]$
Model E [11]: $KN = [a.(WL^x)] / [(A^y).(H^z)]$
Model F [12]: $KN = [a-(x.Log10 (H))]*[E.Log10(S)]^y$
Where
KN: Kappa number, *TY*: Total yield, *H*: H-factor, *E*: Effective alkali charge, *A*: Active alkali charge, *WL*: Wood to liquor ratio, *S*: Sulphidity rate and a, b, c, d, x, y, z and n are constants depending on wood species.

For each model equation, these constant values were determined with non-linear regression analyses in SPSS Statistical Package Program. Obtained these new models were run for prediction new kappa number and total yield values. So calculated values and experimental values were analyzed with statistically paired-t test.

RESULTS AND DISCUSSION

Three different independent variables were considered in pulping trials, viz. the active alkali charge, sulphidity and H-factor based on the experimental design (3^3 Factorial experimental design) used, the number of experiments required was 27 and all trials were done double in order to obtain standard error values. Table 1 shows the values of the independent pulping variables and dependent output variables viz. kappa number and total yield values can be seen from Table 3 for 54 trials.

R^2 values and coefficients to be exist on each model equation, were calculated with non-linear regression analyse techniques using experimental results (Table 2). Derived new equations were run for obtaining calculated dependent variables (kappa number and total yield values).

In Table 3 experimental values of kappa number and total yield are given. Besides, calculated dependent variable values with developed new equations are shown in Table 3 too. To compare experimental results and

Table 1: Plan of pulping trials.

PT	S	H	AA	EA
1	15	800	14	12,95
2	15	800	18	16,65
3	15	800	22	20,35
4	15	1600	14	12,95
5	15	1600	18	16,65
6	15	1600	22	20,35
7	15	2400	14	12,95
8	15	2400	18	16,65
9	15	2400	22	20,35
10	30	800	14	11,9
11	30	800	18	15,3
12	30	800	22	18,7
13	30	1600	14	11,9
14	30	1600	18	15,3
15	30	1600	22	18,7
16	30	2400	14	11,9
17	30	2400	18	15,3
18	30	2400	22	18,7
19	45	800	14	10,85
20	45	800	18	13,95
21	45	800	22	17,05
22	45	1600	14	10,85
23	45	1600	18	13,95
24	45	1600	22	17,05
25	45	2400	14	10,85
26	45	2400	18	13,95
27	45	2400	22	17,05

PT: pulping trials, S: Sulphidity rate (%), H: H-factor, AA: Active alkali charge (%), EA: Effective alkali charge (%)

calculated parameter values obtained from new equations in Table 3 statistical paired t-test was applied. So obtained mean values, standard deviation, standard error, correlation coefficient, t-value and significant level (2-tailed) values were shown in Table 4.

On the basis of the data from Table 4, it can be seen clearly that Model A, Model C, Model D, Model E, and Model F are suitable for experimental data because of the significant level (2-tailed) values are higher than 0,05 (P>0,05) and R^2 values are 0.84, 0.97, 0.95, 0.95 and 0.97 respectively. Between experimental values and calculated parameters obtained from Model B (t-value = -10,43, sig.= 0,000, R^2 = 0,88) are not significantly relationship (P>0,05). So this equation did not provide very good fit with experimental data. In other words, Model B, Hotton's[7] total yield equation are not suitable for prediction of Pinus nigra kraft pulping yield.

Tasman's[12] total yield equation (*Model C*) is the most suitable for practice for kraft pulping of *Pinus nigra* in the other *TY* models as shown in Table 4 (*sig. 0,889, t-value: -0,14, R^2=0,97, P>0,05*). This appears to be confirmed in Figure 1, where values of total yields TY_{exp} and TY_C are presented in a form of histogram. Between these parameters an excellent fit of the results is obtained for *Model C*.

In all kappa number equations, Tasman's[12] kappa number model (*Model F*) gave the most suitable results using experimental data (sig.*=0,976, t-value* =

Tablo 2: Coefficient values for calculating kappa number (*KN*) and total yield (*TY*)

Coefficients	Models					
	Model A	Model B	Model C	Model D	Model E	Model F
a	244	91,98	2129,59	6921,3	38,3	93888,5
b	15	2,45	-82,04			
c			52,58			
d			-0.49			
n	0,51	0,6				
x					-6,95	23114,9
y					2,24	-1,97
z					0,41	
R^2	0,71	0,86	0,95	0,69	0,91	0,92

R^2 values and coefficients to be exist on each model equation, were calculated with non-linear regression analyze techniques using experimental results (Table 2). Derived new equations were run for obtaining calculated dependent variables (kappa number and total yield values).

Table 3: Experimental and calculated dependent variable values from each model equation

S	H	AA	EA	KN_{exp}	TY_{exp}	A	B	C	D	E	F
15	800	14	12,95	118,35	65,75	83,23	58,91	64,86	80,94	102,31	125,29
15	800	18	16,65	76,00	50,67	61,24	53,53	53,00	60,30	58,27	76,37
15	800	22	20,35	50,70	45,50	41,55	48,61	45,86	47,67	37,17	51,43
15	1600	14	12,95	95,40	54,95	66,56	55,48	51,01	71,69	77,00	92,74
15	1600	18	16,65	44,10	45,31	42,29	49,55	45,80	53,41	43,85	56,53
15	1600	22	20,35	27,85	41,58	20,56	44,12	42,21	42,23	27,98	38,07
15	2400	14	12,95	80,10	49,86	56,81	53,48	49,38	66,78	65,21	73,70
15	2400	18	16,65	35,00	44,39	31,21	47,21	44,76	49,76	37,14	44,92
15	2400	22	20,35	22,60	39,74	8,28	41,48	41,57	39,34	23,69	30,25
30	800	14	11,9	100,95	60,84	90,01	60,55	57,90	80,94	102,31	94,47
30	800	18	15,3	61,05	47,86	68,96	55,43	48,85	60,30	58,27	57,58
30	800	22	18,7	43,05	44,60	50,09	50,76	43,49	47,67	37,17	38,78
30	1600	14	11,9	73,50	52,58	74,05	57,29	51,33	71,69	77,00	69,93
30	1600	18	15,3	38,10	46,08	50,81	51,64	46,03	53,41	43,85	42,62
30	1600	22	18,7	29,55	43,40	29,99	46,48	42,42	42,23	27,98	28,70
30	2400	14	11,9	79,65	50,67	64,71	55,38	50,35	66,78	65,21	55,57
30	2400	18	15,3	29,30	42,96	40,19	49,43	45,49	49,76	37,14	33,87
30	2400	22	18,7	20,30	40,84	18,23	43,98	42,17	39,34	23,69	22,81
45	800	14	10,85	92,70	58,26	97,10	62,24	57,68	80,94	102,31	90,78
45	800	18	13,95	57,55	48,13	77,01	57,40	49,17	60,30	58,27	55,33
45	800	22	17,05	39,10	45,20	59,02	52,98	44,10	47,67	37,17	37,26
45	1600	14	10,85	76,60	54,28	81,87	59,16	52,77	71,69	77,00	67,19

Table 3: Continued.

45	1600	18	13,95	39,35	46,58	59,70	53,82	47,22	53,41	43,85	40,96
45	1600	22	17,05	27,00	42,76	39,84	48,94	43,47	42,23	27,98	27,58
45	2400	14	10,85	71,90	52,27	72,96	57,36	51,97	66,78	65,21	53,40
45	2400	18	13,95	33,35	45,85	49,57	51,72	46,81	49,76	37,14	32,55
45	2400	22	17,05	21,35	42,42	28,62	46,57	43,30	39,34	23,69	21,92
15	800	14	12,95	113,50	63,61	83,23	58,91	64,86	80,94	102,31	125,29
15	800	18	16,65	78,35	50,80	61,24	53,53	53,00	60,30	58,27	76,37
15	800	22	20,35	52,80	45,34	41,55	48,61	45,86	47,67	37,17	51,43
15	1600	14	12,95	93,60	54,96	66,56	55,48	51,01	71,69	77,00	92,74
15	1600	18	16,65	46,10	46,31	42,29	49,55	45,80	53,41	43,85	56,53
15	1600	22	20,35	28,00	42,73	20,56	44,12	42,21	42,23	27,98	38,07
15	2400	14	12,95	82,45	49,74	56,81	53,48	49,38	66,78	65,21	73,70
15	2400	18	16,65	35,20	43,88	31,21	47,21	44,76	49,76	37,14	44,92
15	2400	22	20,35	20,90	40,23	8,28	41,48	41,57	39,34	23,69	30,25
30	800	14	11,9	95,00	58,14	90,01	60,55	57,90	80,94	102,31	94,47
30	800	18	15,3	59,20	48,16	68,96	55,43	48,85	60,30	58,27	57,58
30	800	22	18,7	40,60	45,45	50,09	50,76	43,49	47,67	37,17	38,78
30	1600	14	11,9	71,40	51,07	74,05	57,29	51,33	71,69	77,00	69,93
30	1600	18	15,3	38,50	45,97	50,81	51,64	46,03	53,41	43,85	42,62
30	1600	22	18,7	25,10	43,19	29,99	46,48	42,42	42,23	27,98	28,70
30	2400	14	11,9	61,10	49,15	64,71	55,38	50,35	66,78	65,21	55,57
30	2400	18	15,3	31,30	44,72	40,19	49,43	45,49	49,76	37,14	33,87
30	2400	22	18,7	20,20	41,85	18,23	43,98	42,17	39,34	23,69	22,81
45	800	14	10,85	88,60	59,25	97,10	62,24	57,68	80,94	102,31	90,78
45	800	18	13,95	55,70	48,51	77,01	57,40	49,17	60,30	58,27	55,33
45	800	22	17,05	39,30	45,68	59,02	52,98	44,10	47,67	37,17	37,26
45	1600	14	10,85	73,40	54,46	81,87	59,16	52,77	71,69	77,00	67,19
45	1600	18	13,95	37,70	46,70	59,70	53,82	47,22	53,41	43,85	40,96
45	1600	22	17,05	25,20	43,28	39,84	48,94	43,47	42,23	27,98	27,58
45	2400	14	10,85	67,60	51,46	72,96	57,36	51,97	66,78	65,21	53,40
45	2400	18	13,95	34,30	45,20	49,57	51,72	46,81	49,76	37,14	32,55
45	2400	22	17,05	20,10	41,30	28,62	46,57	43,30	39,34	23,69	21,92

S: Sulphidity rate (%), H: H-factor, AA: Active alkali charge (%), EA: Effective alkali charge (%), KN_{exp}: Experimental kappa number values, TY_{exp}: Experimental total yield values, A, B, C, D, E, F : Calculated dependent variables from Model A, Model B, Medel C, Model D, Model E, Model F, respectively.

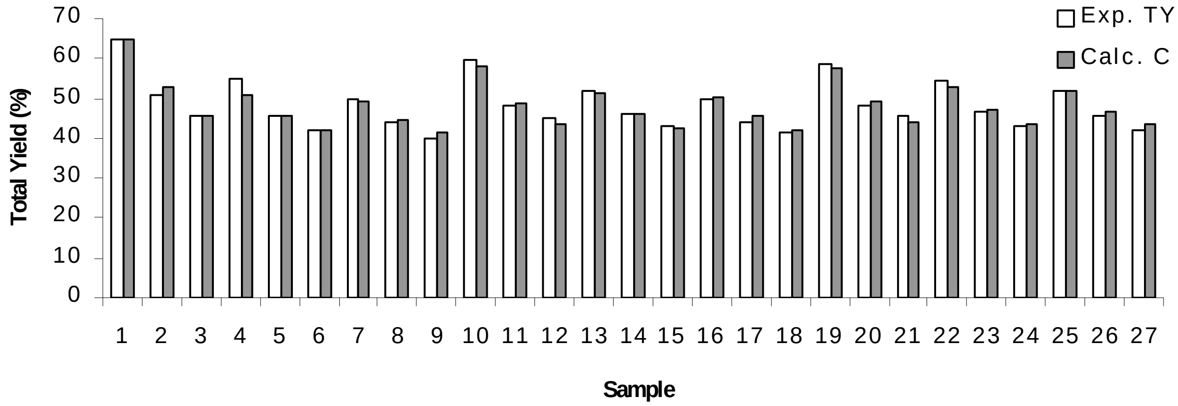

Fig. 1: Experimental (TY_{exp}) and calculated (TY_{calc}) values of total yield on the basis of the *Model C* applied

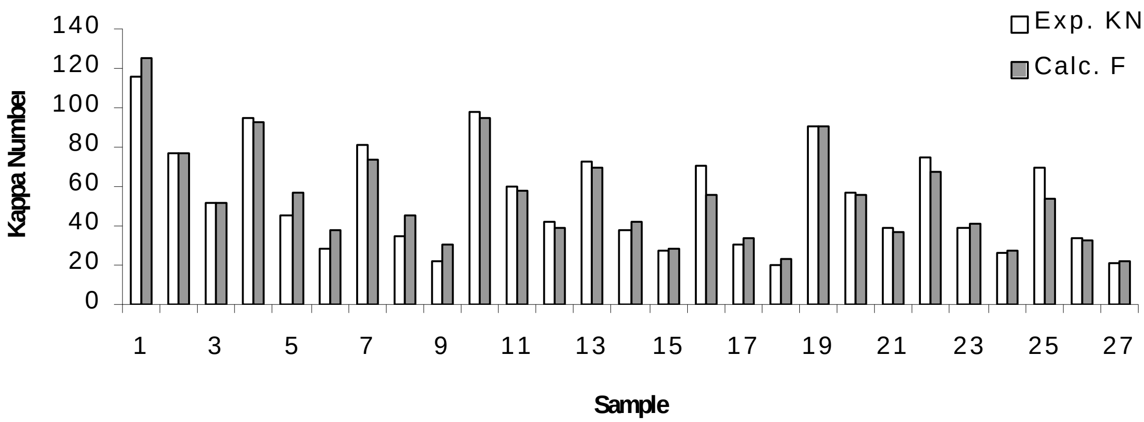

Fig. 2: Experimental (KN_{exp}) and calculated (KN_{calc}) values of kappa number on the basis of the *Model F* applied.

Tablo 4: Versus the kappa number and total yield values obtained from experimental results and calculated from different equations

Equation	Pairs	Mean	N	Std. deviation	Std. Error mean	Correlation	t-value	Sig.(2-tailed)
A	KN_{exp}	54,1	54	26,9	3,7	0,94	1,69	0,097
	KN_B	52,0	54	25,8	3,5			
B	KN_{exp}	54,1	54	26,9	3,7	0,84	-0,09	0,932
	TY_D	54,2	54	22,7	3,1			
C	TY_{exp}	48,2	54	6,0	0,8	0,97	-0,14	0,889
	TY_E	48,3	54	5,6	0,8			
D	TY_{exp}	48,2	54	6,0	0,8	0,88	-10,43	0,000
	TY_D	52,4	54	5,4	0,7			
E	KN_{exp}	54,1	54	26,9	3,7	0.95	1,39	0,171
	KN_G	52,2	54	24,4	3,3			
F	KN_{exp}	54,1	54	26,9	3,7	0,95	-1,41	0,164
	KN_F	56,9	54	13,4	1,8			
H	KN_{exp}	54,1	54	26,9	3,7	0,97	-0,03	0,976
	KN_H	54,1	54	25,2	3,4			

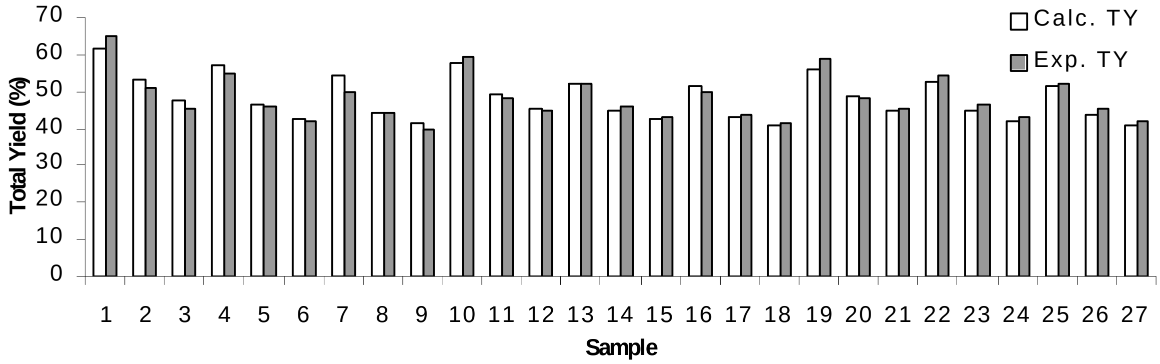

Fig. 3: Experimental (TY_{exp}) and calculated (TY_{calc}) values of total yield on the basis of the *Model G* applied

Tablo 5: Versus the experimental and calculated pulp yields on the basis of *Model G*

PN	Total yield TY_{exp} (%)	Total yield TY_{calc} (%)	$\frac{TY_{exp} - TY_{calc}}{Ty_{exp}} \cdot 100$	Paired t-test results
1	64,68	61,47	4,96	Sig. (2 tailed): 1,000
2	50,74	53,18	-4,81	R^2: 0,957
3	45,42	47,73	-5,09	t-value: 0,000
4	54,96	56,89	-3,51	Mean exp: 48,23
5	45,81	46,31	-1,09	Mean calc: 48,23
6	42,16	42,63	-1,11	Std.error mean: 0,24
7	49,80	54,05	-8,53	
8	44,14	44,17	-0,07	
9	39,99	41,31	-3,30	
10	59,49	57,63	3,13	
11	48,01	49,53	-3,17	
12	45,03	45,61	-1,29	
13	51,83	52,17	-0,66	
14	46,03	44,86	2,54	
15	43,30	42,51	1,82	
16	49,91	51,72	-3,63	
17	43,84	43,14	1,60	
18	41,35	40,99	0,87	
19	58,76	56,06	4,59	
20	48,32	48,78	-0,95	
21	45,44	45,05	0,86	
22	54,37	52,71	3,05	
23	46,64	44,90	3,73	
24	43,02	42,24	1,81	
25	51,87	51,59	0,54	
26	45,53	43,90	3,58	
27	41,86	41,09	1,84	

PN: Pulping number

-0,03, R^2=0,97). At first sight it can be seen that mutual variations KN_{exp} and KN_F within formed groups of are very low (Figure 2) and that differences between mean values are even smaller (Table 3). Applied *Model F* also provided very good fit in calculating kappa number of the produced pulp. Variations between KN_{exp} and KN_{calc} are more acceptable level than the other kappa number models, *Model A*, *Model D* and *Model E.*

We tried to explain the relationship and dependence of pulp yield (*TY*) on kappa number (*KN*) on the basis of equation which was also suggestd by Hotton [8]. The linear form of equation is;

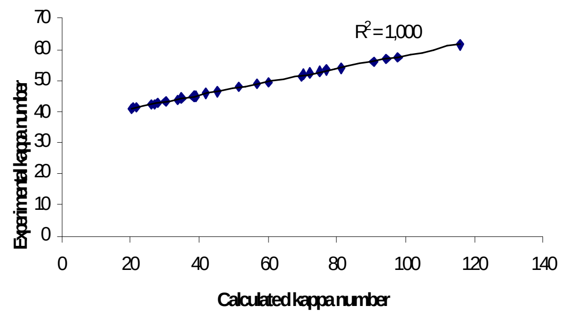

Fig. 4: Experimental (TY_{exp}) and calculated (TY_{calc}) values of total yield on the basis of the *Model G* applied

Model G [8]: $TY = a + b\,(KN)$

Where,
TY: total yield, *KN*: kappa number, *a, b* coefficients depending on wood species.

On the basis of our results for pulping of Anatolian Black Pine wood *a* = 36,7 and *b* = 0,21 (R^2= 0, 92) were obtained

The experimental total yield values and the calculated results from *Model G* and their variations are given in Table 5 for mean values of each two trials. Also, paired t-test results between *Tyexp* and Ty_{calc} are shown in Table 5.

On the basis of the obtained results in Table 5 insignificant variations can be seen between experimental and calculated values of yield, which maximum variation is %5 (except 7 th pulping trial). Variations between individual results are also very low. According to paired-t test results, significance level (2-tailed): 1,000 and t-value: 0,000 were found and there isn't any difference between experimental and calculated mean values. It can be easily stated that Hotton's yield equation is suitable for *Pinus nigra* kraft pulping data. This can be seen in Figure 3, where values of *TYexp* and *TYcalc* for samples of pulp obtained kraft pulping of *Pinus nigra* are presented in a form of histogram. And also seen in Fig. 4 in a form of x-y-distribution graphic.

Conclusions: We tested the validity of the some equations exist on the literature. Coefficients of these models that related with wood species were determined on the basis of the experimental kappa number and total yield values. So new equations were derived in the following form for kraft pulping of *Pinus nigra*;

Model A: $KN = 244 - 15. [Log10 (H).E^{0,51}]$

Model B: $TY = 91,98 – 2,45. [Log10 (H).A^{0,6}]$

Model C: $TY=10**[[2129,59-(-82,04).(E.Log10(S))/Log10(E)]/H]+[[52,58+(-0,49).Log10(S))]/Log10(E)]$

Model D: $KN = [6921,3. (WL^{0,136})] / [(A^{1,171}).(H^{0,175})]$

Model E: $KN = [38,3.(WL^{-6,95})]/[(A^{2,24}).(H^{0,41})]$

Model F: $KN = [93888,5-(23114,9.Log10 (H))]*[E.Log10(S)].^{-1,97}$

Model G: $TY = 36,7 + 0,21 (KN)$

Obtained results from paired t-tests confirmed excellent fit of calculated and experimental data and so because of the 2-tailed significance level values are higher than accepted (except *Model D*). Unfortunately relationship between experimental and calculated dependent output variables obtained from *Model D* is not strong according this test results (P>0,95). Thus, it can be clearly stated that *Model D* isn't suitable to predict output variables for kraft pulping of *Pinus nigra*.

Evaluated with total yield, differences between experimental ($TY_{exp.}$) and calculated (TY_{calc}) values on the basis of *Model G* are the lowest value. So *Model G* is the most suitable model for our data.

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