KRAFT PULPING OF EUCALYPTUS WITH ANTHRAQUINONE, POLYSULFIDE AND SURFACTANT

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ABSTRACT

In this research the effect of three chemical additives used in the kraft pulping process of chips of hybrid *Eucalyptus grandis* x *Eucalyptus urophylla*: anthraquinone, surfactant and polysulfide and their possible interactions are evaluated. The results point to the fact that the efficiency of the surfactant may be related to the wood characteristics and chip dimensions. The efficiency of the polysulfide is related to the significant modifications of the pulping parameters that can lead to modifications of mill installations. The anthraquinone proved its efficiency on the kraft process independently to the wood characteristics and pulping process parameters and can be effectively classified as a kraft pulping additive.

INTRODUCTION

The pulp and paper industry is facing social pressure related to its environmental and sustainable efficiency which is leading to technological evolutions. Nowadays ECF and TCF bleaching sequences are commercial available but its implementation requires significant changes at the pulping process in order to reduce the residual delignification levels and also increase the pulping yield. The need to increase the delignification efficiency of the pulping process lead to the concept of the modified pulping process.

Besides engineering pulping process modifications, the use of chemical additives at the pulping process represents an interesting possibility to reduce the kappa number and increase the pulp yield. Among those chemical products are anthraquinone, polysulfide and surfactants. In Brazil and in other countries, some of those additives are used individually by some pulp mills. The conjunct use of the mentioned pulping additives is an aspect that should be carefully evaluated in terms of technical and economical feasibility once they have different functions at the pulping process; their conjunct use can show synergistic and beneficial aspects for the pulping process in global terms.

The objective of this research was the evaluation of the effect of anthraquinone, polysulfide and surfactant and different charges on the kraft pulping of the hybrid of *E. grandis* x *E. urophylla*.

The effects of anthraquinone and polysulfide on the kraft pulping are well established but for surfactant there is a need for specific research. Some research shows that the efficiency of the surfactant is related to the wood characteristics, chip dimensions and impregnation step parameters.

In this research industrial chips of hybrid of *E. grandis* x *E. urophylla* seven-year-old trees planted in the state of São Paulo – Brazil were used. In terms of additive, powder anthraquinone and a non-ionic commercial surfactant were used; the polysulfide was generated by the addition of sulfur to the hot white liquor (80^{o}C) under agitation until its complete dissolution.

The wood chips were evaluated in terms of dimensions, basic density and chemical composition (holocellulose, lignin and extractives).

The experimental design considered the following factors and levels:

Factor 1: anthraquinone charge: 0, 0,025 and 0, 05% based on o.d. wood chips

Factor 2: surfactant charge: 0, 0,025 and 0,05% based on o.d. wood chips

Factor 3: polysulfide charge: 0, 1,5 and 3% based on o.d. wood chips

The experimental design had 27 treatments (3x3x3) and 2 replications.

For the pulping process, M/K digester with 2 vessels with 10 liters each was used to pulp 1000o.d. g of wood chips considering the conditions mentioned on Table 1.

Table 1. Pulping conditions	
Parameter	
Alkali charge (% as Na_2O)	14
Sulfidity (%)	25
Anthraquinone charge (% on od wood chips)	0 – 0,025 – 0,05
Surfactant charge (% on o.d. wood chips)	0 – 0,025 – 0,05
Polysulfide charge (% on o.d. wood chips)	0 – 1,5 – 3,0
Maximum temperature (^oC)	166
Heating time (min)	60
Cooking time (min)	120
Wood/liquor ratio	4/1

After each cook the pulp obtained was washed, centrifuged, disaggregated, stored in polyethylene bags and refrigerated at 5 $^oC \pm 2^oC$. For each cook the total yield, the screened yield, and the rejects content (0.2 mm gap) were determined. The pulp was analyzed according to the parameters described in Table 2.

Table 2. Kappa number, viscosity and black liquor analysis.

Analysis	Norms
Kappa number	TAPPPI T236
Viscosity	TAPPI T230
Black liquor solids	TAPPI T650
Residual alkali	TAPPI T625

RESULTS

The concept of the kraft pulping process is relatively simple but when considered in detail it is affect by different variables in a large range of manners. Among the variables related to the raw materials, basic density, chemical composition and chip dimensions are the most important ones. On Table 3 are shown the characteristics of the wood chips used to perform this research.

Table 3. Wood chip characteristics	
Parameters	
Basic density, g/cm^3	0,607
Chip length, mm	25,40
Chip width, mm	23,20
Chip thickness, mm	4,39
Holocellulose content, %	70,09
Lignin content, %	24,90
Total extractives, %	5,01

The results on Table 3 point to the fact that wood chip characteristics are very similar to the wood of *E. urophylla* what is an indication of the genetically predominance of this specie on the hybrid considered for this research.

The pulping results are summarized on Table 4.

Table 4. Pulping results

Treat	AQ (%)	Surfac (%)	PS (%)	TY (%)	SY(%)	Rejects (%)	# kappa	Viscosity(cP)
1	0	0	0	49.51	49.25	0.26	18.65	47.00
2	0	0	1.5	54.09	48.25	5.84	36.30	65.25
3	0	0	3.0	58.98	42.14	16.83	71.95	39.88
4	0	0.025	0	49.31	49.00	0.31	19.20	51.80
5	0	0.025	1.5	52.60	51.04	1.56	24.45	63.00
6	0	0.025	3.0	57.55	47.03	10.53	54.85	47.65
7	0	0.05	0	50.08	49.65	0.43	19.85	48.45
8	0	0.05	1.5	51.98	50.76	1.23	23.80	59.95
9	0	0.05	3.0	57.09	45.93	11.16	54.45	45.75
10	0.025	0	0	50.52	50.34	0.18	16.90	44.45
11	0.025	0	1.5	52.50	50.47	2.03	25.55	62.65
12	0.025	0	3.0	57.35	46.81	10.54	47.60	42.25
13	0.025	0.025	0	51.30	51.11	0.19	17.75	44.45
14	0.025	0.025	1.5	52.54	50.76	1.78	23.85	57.20
15	0.025	0.025	3.0	55.61	48.17	7.44	46.90	47.50
16	0.025	0.05	0	50.04	49.69	0.35	17.55	46.10
17	0.025	0.05	1.5	52.68	50.94	1.74	22.75	55.55
18	0.025	0.05	3.0	56.34	46.16	10.18	46.65	52.60
19	0.05	0	0	49.40	48.89	0.51	17.60	42.90
20	0.05	0	1.5	52.31	50.60	1.71	22.10	56.40
21	0.05	0	3.0	56.63	47.23	9.41	43.10	53.00
22	0.05	0.025	0	49.99	49.49	0.50	17.40	46.60
23	0.05	0.025	1.5	51.75	50.30	1.45	20.60	57.90
24	0.05	0.025	3.0	57.44	43.64	13.80	48.80	52.55
25	0.05	0.05	0	49.55	49.14	0.41	17.40	42.00
26	0.05	0.05	1.5	52.44	50.97	1.48	22.85	50.40
27	0.05	0.05	3.0	57.42	48.73	8.69	45.95	50.15

AQ = anthraquinone charge; SURFAC = surfactant charge; PS = polysulfide charge; TY = total yield ; SY = screened yield.

Considering the experimental design, the results were statistically analyzed in order to detect the effect of the additives over the main pulping process variables.

The pulping yield is one of the pulping process parameters of great importance due to its economical importance, once the wood is the main factor on the eucalyptus pulp costs. On Table 5 are the result of the analysis of variance for screened pulp yield.

Table 5. Analysis of variance for screened yield.

Variation Causes	D.F.	S.S.	M.S.	F value	Pr>F
AQ	2	144,340,259	72,170,130	9,03	0,0010
Surfac	2	80,465,037	40,232,519	5,04	0,0139
PS	2	1,823,445,481	911,722,741	114,10	0,0001
AQ x Surfac	4	278,652,296	69,663,074	8,72	0,0001
AQ x PS	4	56,983,519	14,245,880	1,78	0,1614
Surfac x PS	4	39,935,407	0.9983852	1,25	0,3139
AQ x Surfac x PS	8	306,633,259	38,329,157	4,80	0,0009

The results on Table 5 show that there is an impact of anthraquinone, surfactant and polysulfide over the screened yield and there is also an interaction between anthraquinone and surfactant.

Based on the results obtained the use of 0,05% of anthraquinone, 0,05% of surfactant and 1,5% of polysulfide lead to the best results in terms of screened yield for *E. grandis* x *E urophylla* kraft pulping.

For the evaluation of a pulping process modification the analysis of screened yield is not enough once it is related to the extent of the delignification, measured as kappa number. On Table 6 are the results of the analysis of variance for kappa number.

Table 6. Analysis of variance for kappa number

Variation Causes	D.F.	S.S.	M.S.	F value	Pr>F
AQ	2	59,565.778	29,782.889	132.24	0.0001
Surfac	2	11,053.000	5,526.500	24.54	0.0001
PS	2	1,103,794.111	551,897.056	2,450.46	0.0001
AQ x Surfac	4	26,246.889	6,561.722	29.13	0.0001
AQ x PS	4	31,971.111	7,992.778	35.49	0.0001
Surfac x PS	4	7,721.222	1,930.306	8.57	0.0001
AQ x Surfac x PS	8	19,602.222	2,450.278	10.88	0.0001

The results on Table 6 show that the kappa number is greatly influenced by the use of pulping additives and its interactions.

The analysis of the interactions shows that the kappa number has 3 distinct patterns due to the polysulfide charge. The use of polysulfide in a single stage pulping process lead to a consumption of active alkali due to the reactions of degradation the polysulfide specially at temperatures above 100^oC. The reduction of alkali availability for the pulping reactions due to reactions of degradation of polysulfide leads to increase in kappa number. Based on those considerations for an effective use of polysulfide it is necessary to implement a specific system at the pulping process for the use of polysulfide, basically on the impregnation step.

For the surfactant, the effect on the kappa number is not very expressive once the function of such kind of products is to increase the impregnation rate of the chips by the pulping liquor.

The addition of 0,05% of anthraquinone leads to a significant reduction in the kappa number.

The pulp viscosity provides information about the impact of the pulping process parameters on the carbohydrates wood fraction. On Table 7 are the results of the analysis of variance for pulp viscosity.

Table 7. Analysis of variance for pulp viscosity

Variation Causes	D.F.	S.S.	M.S.	F value	Pr>F
AQ	2	39,926.204	19,963.102	7.69	0.0023
Surfac	2	40,187.870	20,093.935	7.74	0.0022
PS	2	1,691,461.759	845,730.880	325.88	0.0001
AQ x Surfac	4	83,707.963	20,926.991	8.06	0.0002
AQ x PS	4	405,499.074	101,374.769	39.06	0.0001
Surfac x PS	4	177,652.407	44,413.102	17.11	0.0001
AQ x Surfac x PS	8	78,862.593	9,875.824	3.80	0.0042

Considering the difference in kappa number observed on the different pulps obtained on this research and the influence of the kappa number on the pulp viscosity, a careful analysis should be considered for pulp viscosity. The results on table 7 show that all the additives have a significant impact on the pulp viscosity.

CONCLUSIONS

Anthraquinone, surfactant and polysulfide have an effect on the kraft pulping process of hybrid of *E. grandis* x *E. urophylla*.

Polysulfide lead to an increase in pulp yield and also to a very high increase in the kappa number; the increase in kappa number in some treatments reach levels of unbleachable grades pulps.

That effect of the surfactant was positive but seems related to the wood characteristics specially the basic density.

Anthraquinone showed a beneficial effect on the pulping process despite the cooking conditions and wood characteristics.

The use of anthraquinone, surfactant and polysulfide present different interactions patterns for the parameters considered on this research.

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Jacksonville – October - 2007

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KRAFT PULPING developments

- reduction of the kappa number
- increase yield
- improve pulp quality

KRAFT PULPING MODIFICATIONS

- improve pulp quality
- increase yield
  - reduction of wood consumption
    - silvicultural activities
  - lower solids production
    - higher industrial production
  - lower production costs

KRAFT PULPING ADDITIVES

- quinonic compounds
  - anthraquinone
  - DDA
- polysulfide
- sodium borohidrate
- surfactants

KRAFT PULPING ADDITIVES

- **advantages**
  - low installation cost
  - do not require a mill shutdown for installation
- **difficulties**
  - development of stable compounds under pulping conditions

BENEFITS OF THE USE OF ANTHRAQUINONE

- reduction in alkali consumption
- reduction in steam consumption
- reduction or elimination of sulfidity
- increase of pulp production
- increase in refining development

DISADVANTAGES OF THE USE OF ANTHRAQUINONE

- lower solubility in cooking liquor
  - difficulty in industrial use
- high cost
- potential scaling problems during black liquor evaporation

BENEFITS OF THE USE OF SURFACTANTS

- better impregnation of the chips
- reduction in the reject content
- increase in the screened yield
- better pulping uniformity

DISADVANTAGES OF THE USE OF SURFACTANTS

- high cost
- resistance/efficiency on the pulping environment
  - high pH
  - high temperature
- difference in chemical composition
  - depend on the supplier

WOOD

- complex anatomic structure
- complex capillary systems
  - differences between hardwoods and softwoods
  - differences between sapwood and heartwood
  - differences among trees of the same specie
  - differences among trees of the same clone
  - difference among positions in same tree

COOKING LIQUOR PENETRATION
FLUID MECHANICS

Poiseulle Equation

$$h = \sqrt{\frac{r \,.\, \sigma .\, \cos\theta \,.\, t}{2 \,.\, \eta}}$$

Lucas-Washburn Equation

$$V = k.\frac{n.r^4.\Delta p}{l.\eta}$$

BENEFITS OF THE USE OF POLYSULFIDE

- increase in the delignification rate
- reduction in alkali charge
- better pulp quality

DISADVANTAGE OF THE USE OF POLYSULFIDE

- increase in the production of mercaptans
- potential corrosion problems

OBJECTIVES

- evaluate the effect of additives on eucalyptus kraft pulping
- evaluate the effect of different charges of additives on eucalyptus pulping
- evaluate the interaction among additives and charges.

EXPERIMENTAL

MATERIAL

- industrial chips of hybrid of *Eucalyptus grandis* x *Eucalyptus urophylla* (E. urogandis)
  - from 7-year-old trees
- powder anthraquinone
- polysulfide
  - orange liquor produced at lab scale using sulfur
- surfactant
  - commercial product

EXPERIMENTAL DESIGN

- factor 1 – alkali charge
  - 12, 13 and 14% as Na_2O
- factor 2 – anthraquinone charge
  - 0, 0.025 and 0.05% on o.d. chips
- factor 3 – surfactant charge
  - 0, 0.025% and 0,05% on o.d. chips
- factor 4 – polysulfide charge
  - 0, 1.5 and 3% on o.d. chips
- 3x3x3x3 = 81 conditions
  - 2 replications/conditions = 162 cookings

PULPING CONDITIONS

- sulfidity: 25%
- maximum temperature: 166ºC
- time to maximum temperature: 60 minutes
- time at maximum temperature: 120 minutes
- wood/liquor ratio: 4/1
- lab digester
  - 10L 2 vessels M/K digester

PARAMETERS CONSIDERED FOR STATISTICAL ANALYSIS

- kappa number
  - TAPPI T236
- pulp viscosity
  - TAPPI T230
- residual alkali
  - TAPPI T625
- black liquor solids
  - TAPPI 650

RESULTS

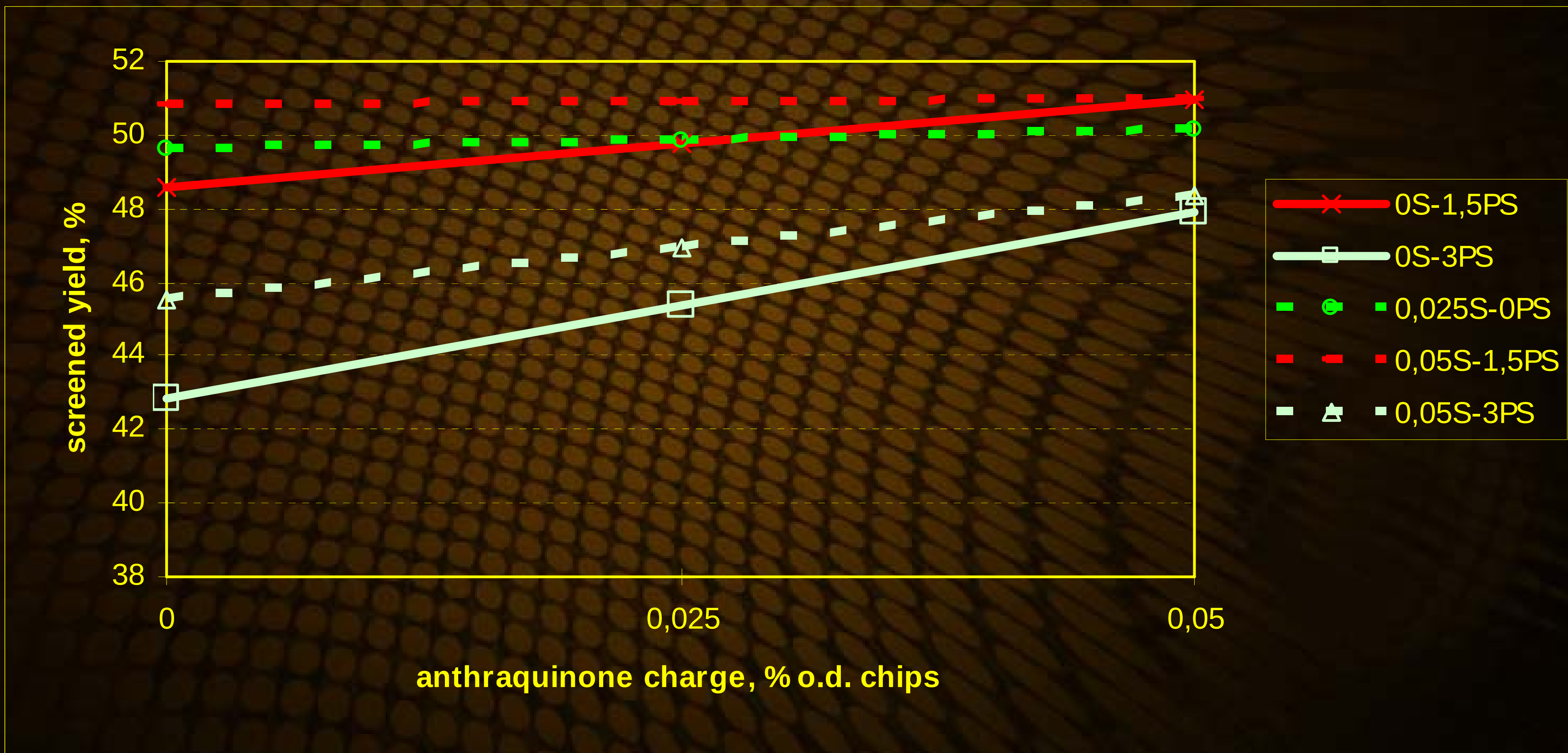
WOOD CHARACTERISTICS

PARAMETERS	
Basic density, g/cm^3	0,607
Chip length, mm	25,40
Chip width, mm	23,20
Chip thickness, mm	4,39
Holocellulose content, %	70,09
Lignin content, %	24,90
Total extractives, %	5,01

ANOVA – Screened yield

Variation Causes	D.F.	S.S.	M.S.	F value	Pr>F
AQ	2	144,340,259	72,170,130	9,03	**0,0010**
Surfac	2	80,465,037	40,232,519	5,04	**0,0139**
PS	2	1,823,445,481	911,722,741	114,10	**0,0001**
AQ x Surfac	4	278,652,296	69,663,074	8,72	**0,0001**
AQ x PS	4	56,983,519	14,245,880	1,78	0,1614
Surfac x PS	4	39,935,407	0.9983852	1,25	0,3139
AQ x Surfac x PS	8	306,633,259	38,329,157	4,80	0,0009

SCREENED YIELD



ANOVA – Kappa number

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AQ	2	59,565.778	29,782.889	132.24	**0.0001**
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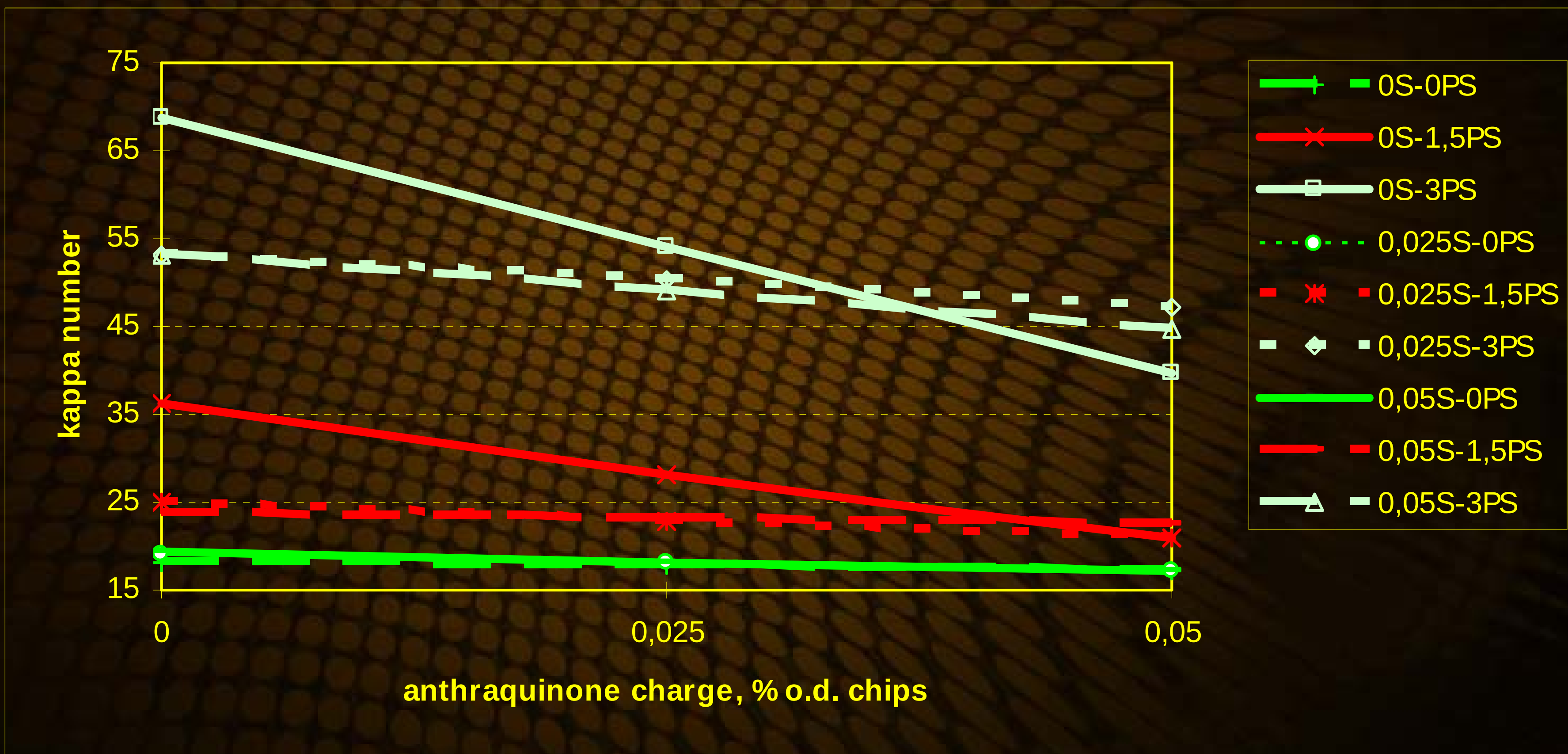
AQ x Surfac	4	26,246.889	6,561.722	29.13	**0.0001**
AQ x PS	4	31,971.111	7,992.778	35.49	**0.0001**
Surfac x PS	4	7,721.222	1,930.306	8.57	**0.0001**
AQ x Surfac x PS	8	19,602.222	2,450.278	10.88	**0.0001**

KAPPA NUMBER



ANOVA – Pulp viscosity

Variation Causes	D.F.	S.S.	M.S.	F value	Pr>F
AQ	2	39,926.204	19,963.102	7.69	**0.0023**
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AQ x Surfac x PS	8	78,862.593	9,875.824	3.80	**0.0042**

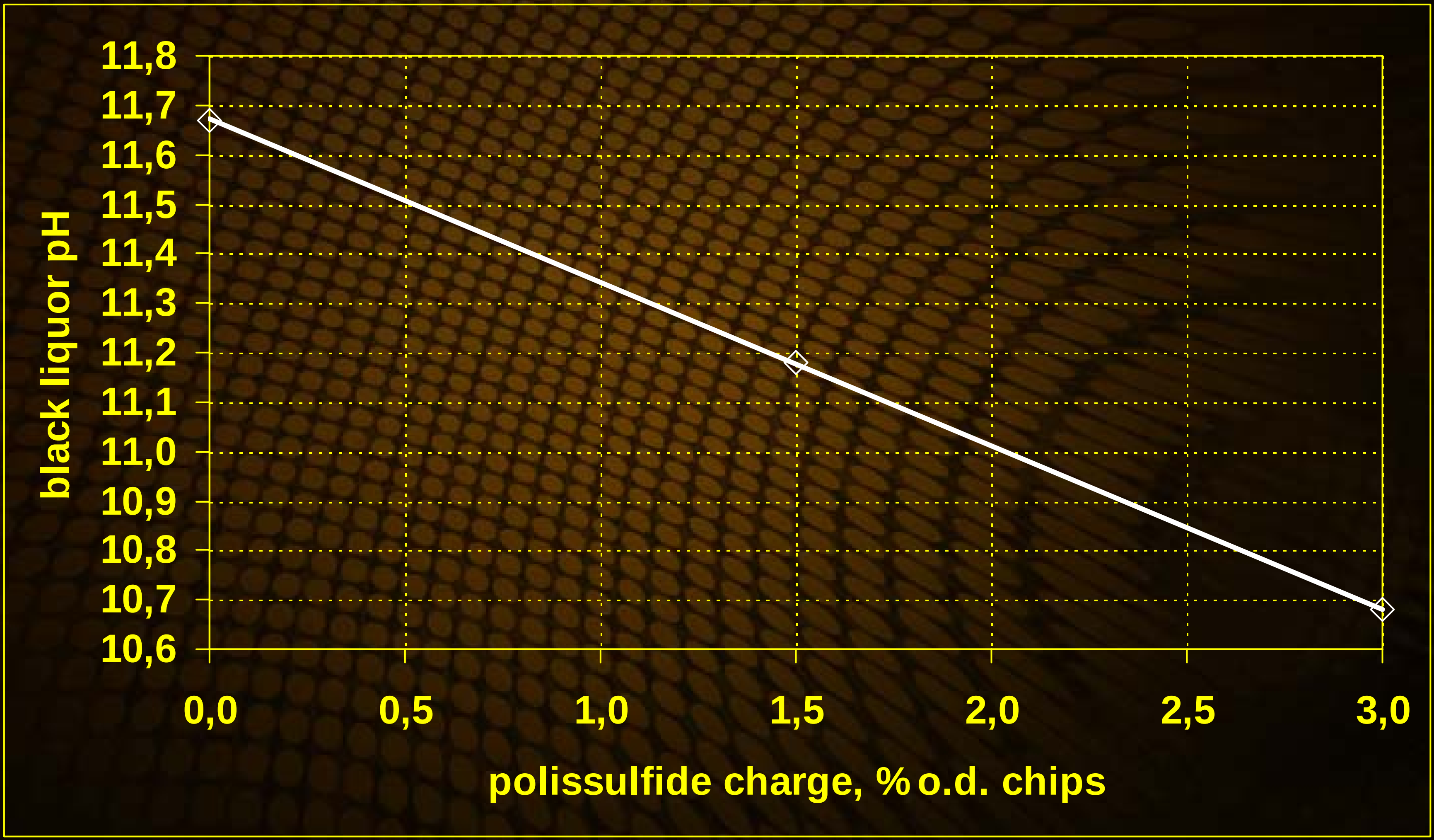
PULP VISCOSITY

- wide range of kappa number
  - method restriction
- its importance on unbleached eucalyptus kraft pulp is questionable

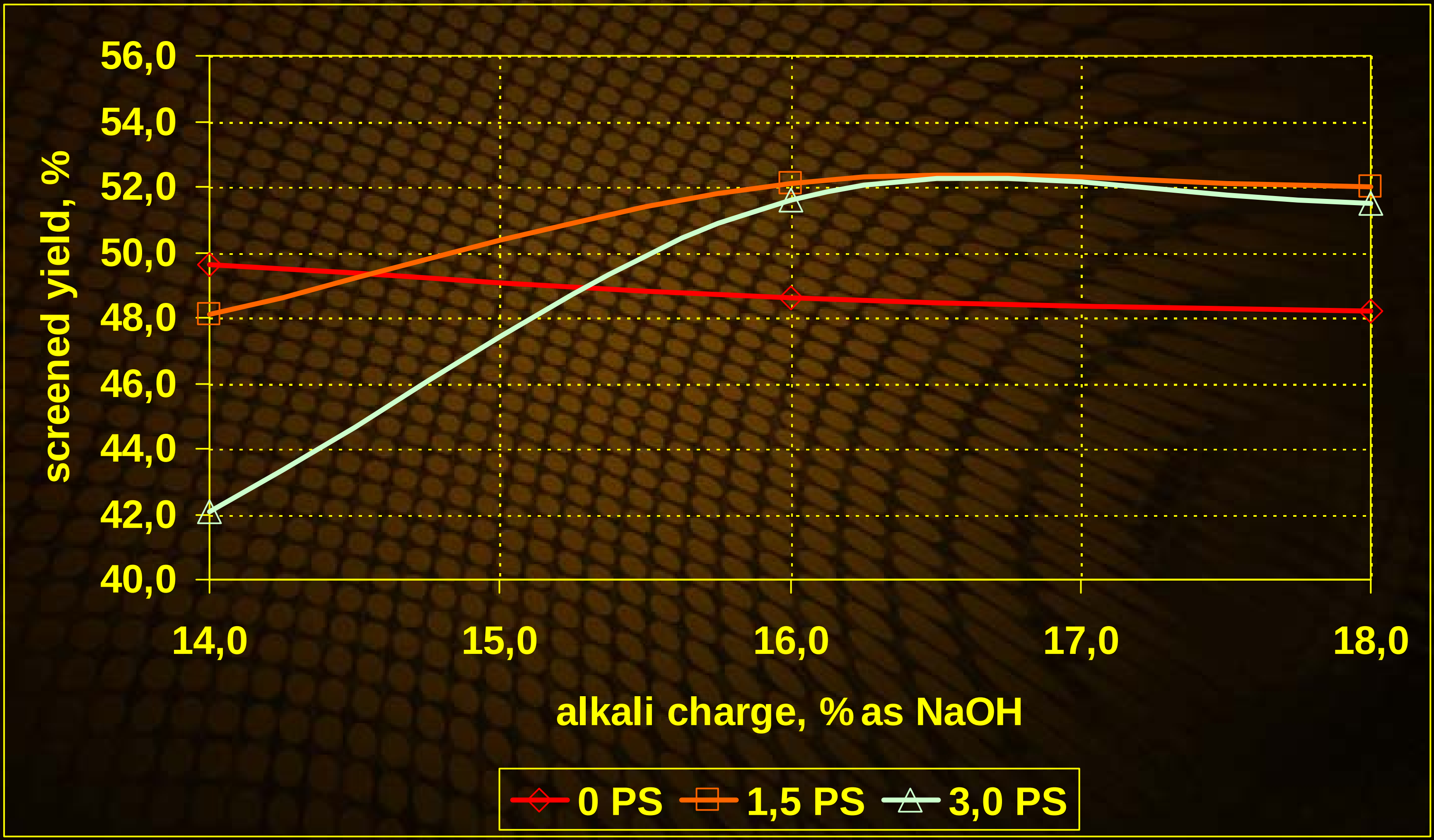
PRELIMINARY CONCLUSIONS

- polysulfide is a clustering parameter on this experiment
  - kappa number
- detailed analysis
  - statistics
  - and back to the lab

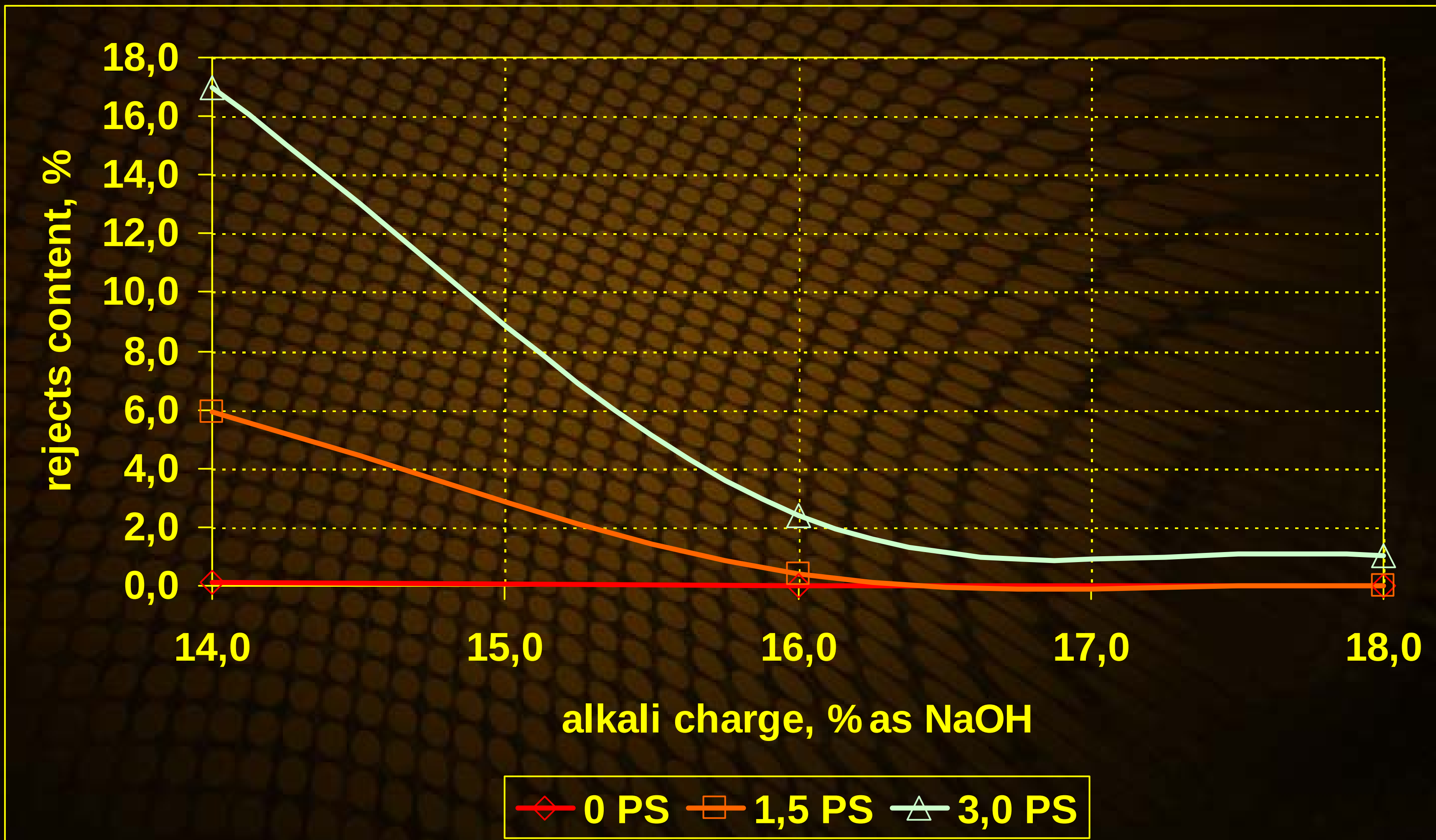
POLYSULFIDE – black liquor pH



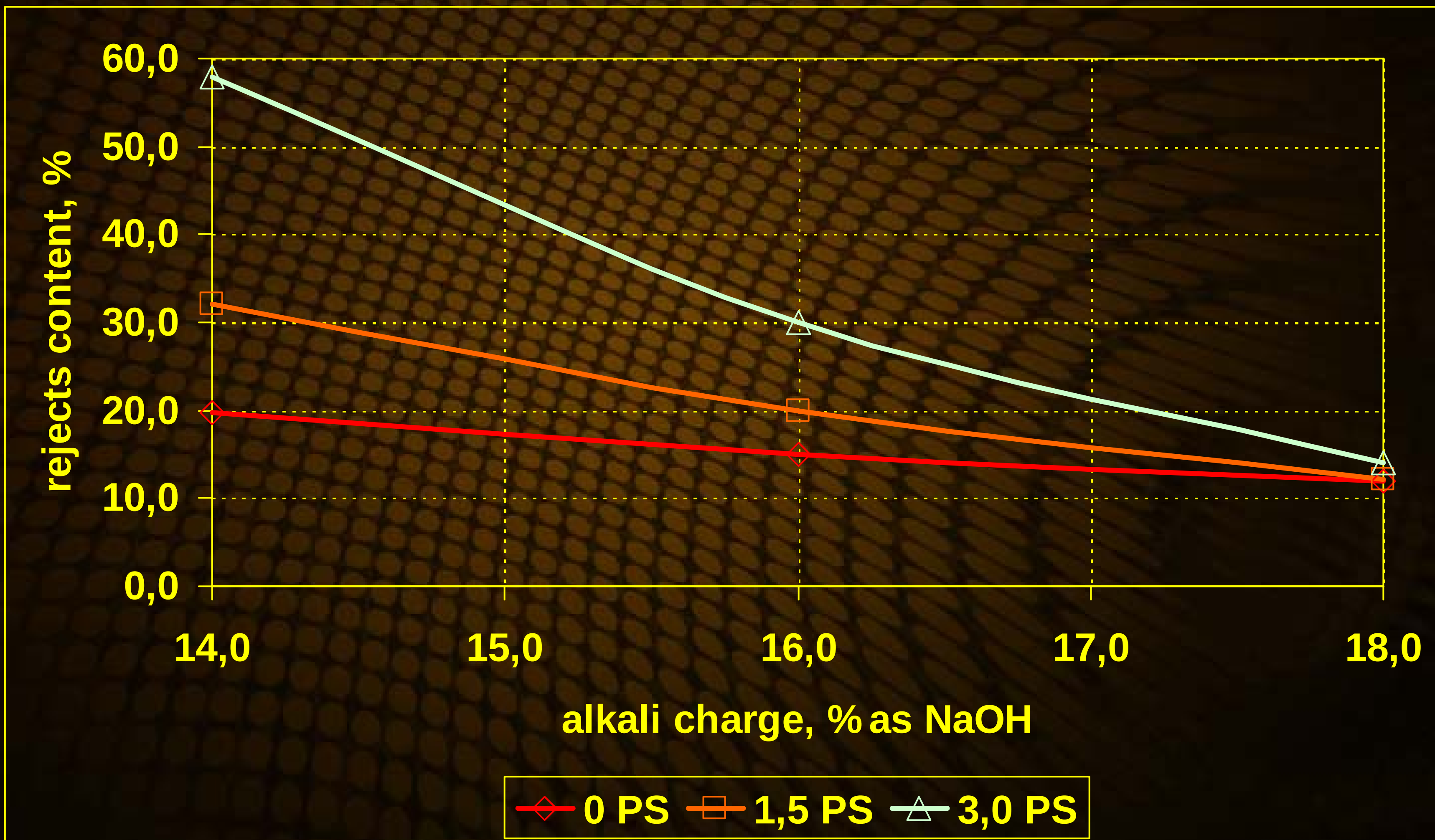
POLYSULFIDE – alkali charge



POLYSULFIDE – rejects



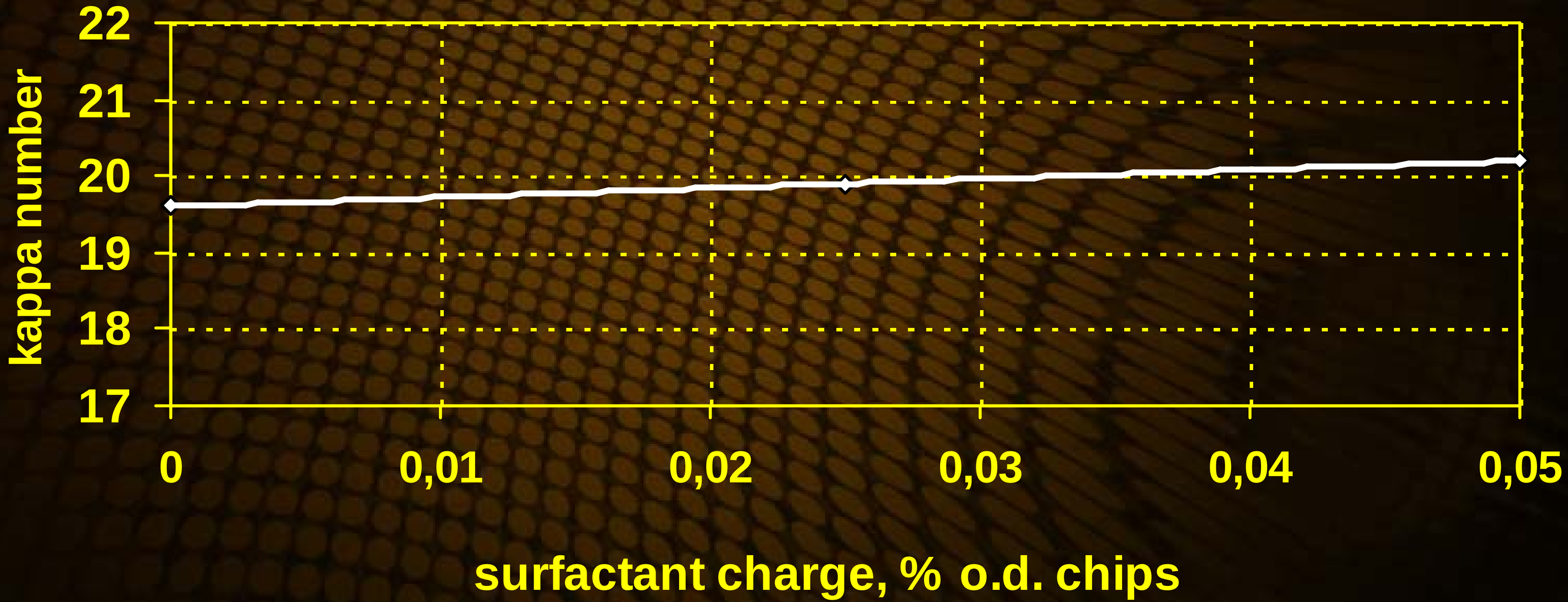
POLYSULFIDE – kappa number



POLYSULFIDE

- 1,5% showed the best results in terms of yield
- requires an increase in the alkali charge
  - degradation consumes active alkali
  - increase the dead load in liquor
    - increase solids
      - reduce pulp production
- alternative for pulping systems with distinct liquor lines/vessels

SURFACTANT – kappa number



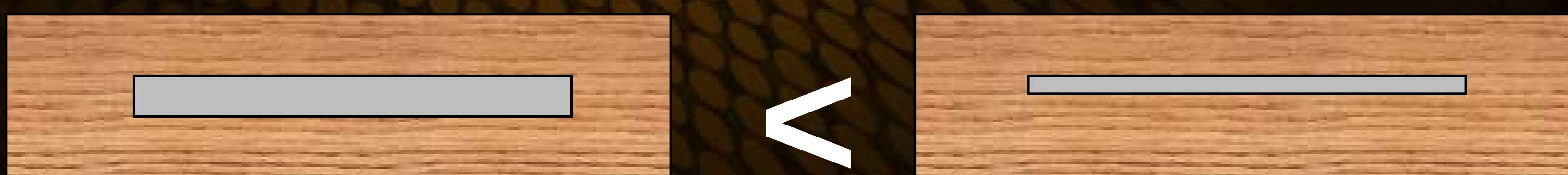
SURFACTANT

- small increase in kappa number
  - –no “delignification” effect
- related to the impregnation

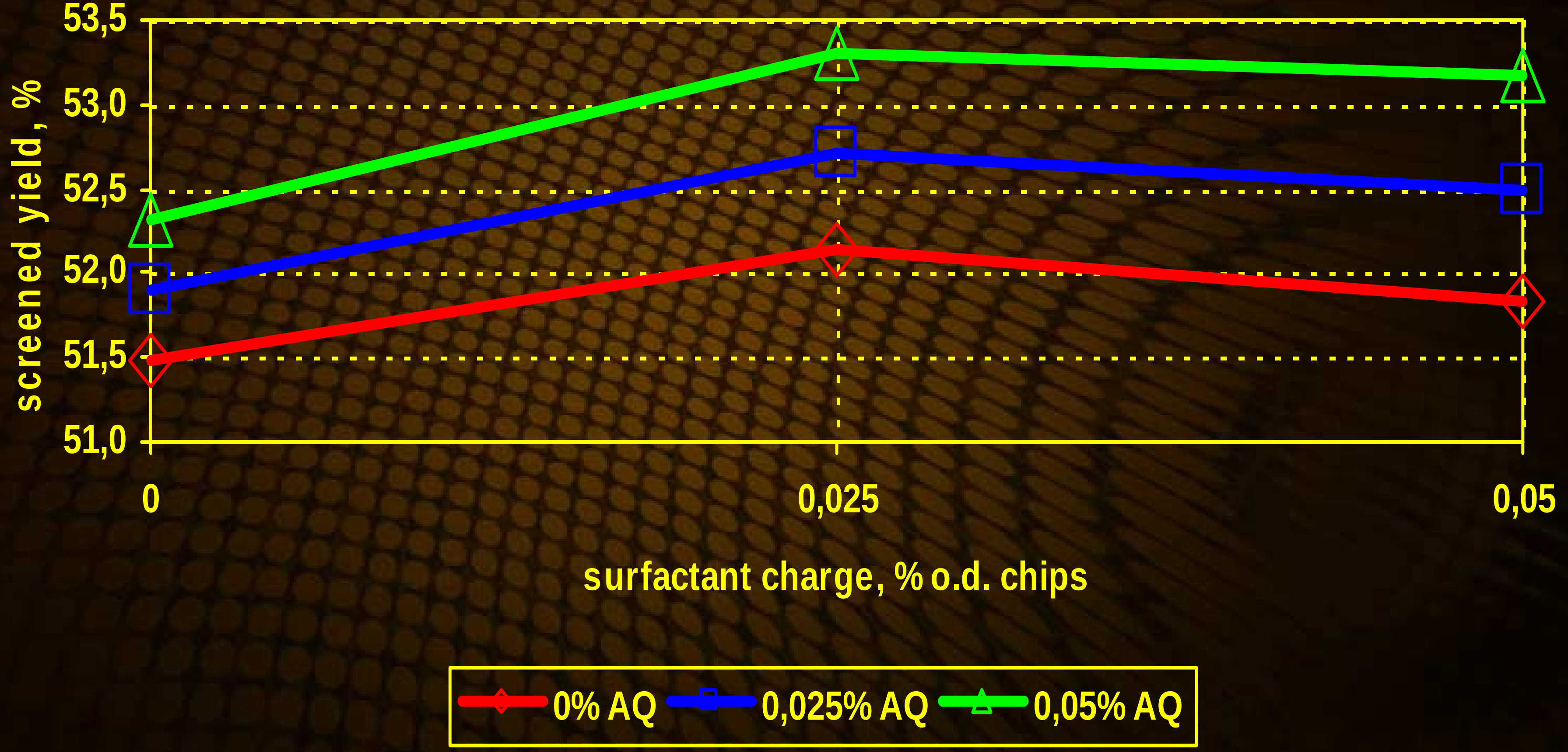
EFFECT OF THE SURFACTANT ON PULPING - mass balance

without surfactant **with surfactant**

wood mass considered for alkali charge balance



EFFECT OF ANTHRAQUINONE AND SURFACTANT



CONCLUSIONS

- anthraquinone, surfactant and polysulfide have an effect on the kraft pulping process of hybrid of *E. grandis* x *E. urophylla*;
- polysulfide leads to an increase in pulp yield and also to a very high increase in the kappa number; the increase in kappa number in some treatments reach levels of unbleachable grades pulps
- that effect of the surfactant was positive in terms of yield;
- anthraquinone showed a beneficial effect on the pulping process;
- the use of anthraquinone, surfactant and polysulfide present different interaction patterns for the parameters considered on this research.