Oxygen delignification (OD) process chemistry for *Acacia*

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  - Background
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  - Pulp strength & OD selectivity (1)
  - Extractive removal & OD selectivity (2)
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Introduction

- Economic and environmental benefits of OD have been recognized since 1960s (Fapet 2000)
  - Lower effluent treatment cost
  - Heat recovery
  - Lower refining energy
  - Lower oxygen cost

Introduction

- OD is today well established in industry (Fapet 2000)
- As environmental issues have now been addressed, research has returned to the performance of this OD technology (Chakar 2000)
- This study evaluates the response of *A. mangium* kraft pulp on OD process with respect to pulp strength, basic chemistry, fiber structures and extractives

Background

- 21-25% DZSTS loss of *A. mangium* kraft pulp after OD compared to 8-14% of other kraft pulps (IPST)
- *A. mangium* contains extractives twice as much to those of *Eucalyptus* wood (Neto, 2004), and eight times as much to those of MHW (pulp)

Introduction - 1

- Background
  - 21-25% DZSTS loss of *A. mangium* kraft pulp after OD compared to 8-14% of other kraft pulps (IPST)
- Objective
  - Determine key OD process parameter to obtain better selectivity and pulp strength

Literature review

Lignin and extractives content of five hardwoods

	Lignin[a], %	Extractives[b], %
A. mangium	27.6	4.46
B. pendula	21.5	2.24
E. globulus	22.1	1.72
E. urograndis	27.9	1.91
E. grandis	26.7	2.10

[a]Klason [b]ethanol/toluene Neto et al, NPPRJ, 2004

Literature review

Comparison: Hardwoods kraft pulping and bleaching (DEDED)

	active alkali	unbleached	ClO_2	bleached
	$\%Na_2O$/wood	Kappa#	%/pulp	Brightness
A. mangium	24	15.9	7.4	90.7
B. pendula	18	16.4	7.2	90.4
E. globulus	16	15.0	4.4	90.5
E. urograndis	20	15.7	5.3	90.3
E. grandis	19	16.1	5.4	90.5

Neto et al, NPPRJ, 2004

Literature review

Mill oxygen delignification conditions

	Acacia	MHW
Temperature, °C	87-90	87-90
O_2 charge, kg/ADT	14-17	14-17
NaOH charge, kg/ADT	14-16	16-18
pH	10.8-11.0	10.8-11.0
Consistency, %	12	12
Reaction time, minutes	120	120
Starting Kappa number	12 – 13	13 - 14

Literature review

Effect of alkali charge in OD of sweet gum kraft pulp

BS Kappa#	13.6		14.4	
BS Viscosity, cP	24.8		23.3	
	1% NaOH	4% NaOH	1% NaOH	4% NaOH
Kappa#	8.3	7.0	9.3	8.1
Viscosity, cP	16.8	12.1	15.6	11.5
Bleachability	5.3 →	1.6	5.1 →	1.6
Selectivity	0.66 →	0.52	0.66 →	0.53

Yang et al, IECR, 2002

Objectives

1. Determine key OD process parameter to obtain better selectivity and pulp strength
2. Determine the best pretreatment methods prior to OD on extractives removal and selectivity improvement

Experiment

- Material
  - *Acacia mangium* kraft pulp from Indonesia
  - All chemicals were purchased commercially
  - De-ionized water used

Experiment

- Methods
  - OD process: time, temperature, alkali charge, mechanical pretreatment
  - Pulp properties: strength, fiber morphology, cellulose, HexA, charge, extractive, Kappa, viscosity
  - Yates' algorithm
  - Four pretreatment methods

Experiment

Oxygen delignification experimental conditions

	a			b			c			d		
Sample code	1	2	3	4	5	6	7	8	9	10	11	12
Reaction time, min	60	90	120	90	90	90	90	90	90	90	90	90
Temperature, °C	90	90	90	90	90	90	85	90	95	90	90	90
NaOH charge, g/kg OD pulp	16.67	16.67	16.67	16.67	20.00	23.33	16.67	16.67	16.67	20.00	20.00	20.00
O_2 pressure, kPa	1,034	1,034	1,034	1,.034	1,034	1,034	1,034	1,034	1,034	1,034	1,034	1,034
Consistency, %	12	12	12	12	12	12	12	12	12	12	12	12
Quantum mixer time, sec	0	0	0	0	0	0	0	0	0	5	10	15

Experiment

Oxygen delignification experimental condition for Yates' algorithm

Experiment number	y1	y2	y3	y4	y5	y6	y7	y8
Reaction time, min	60	120	60	120	60	120	60	120
Temperature, °C	70	70	100	100	70	70	100	100
NaOH charge, g/kg OD pulp	10.0	10.0	10.0	10.0	30.0	30.0	30.0	30.0
O_2 pressure, kPa	1,034	1,034	1,034	1,034	1,034	1,034	1,034	1,034
Consistency, %	12	12	12	12	12	12	12	12
Quantum mixer time, sec	15	15	15	15	15	15	15	15

Experiment

- Four pretreatment methods
  - ultrasound for 2 hours at 1 % consistency, temperature of 25 °C, amplitude 40 %, energy 1.0 MJ, then filtered and washed
  - heat up to 70 °C for 2 hours at 12.8 % consistency, 0.5% $MgSO_4$
  - heat up to 70 °C for 2 hours at 12.8 % consistency, 0.5% $MgSO_4$, 2% NaOH
  - mix in Quantum mixer at speed 2200 rpm, 12.8 % consistency for 5 seconds, 0.5% $MgSO_4$

Experimental

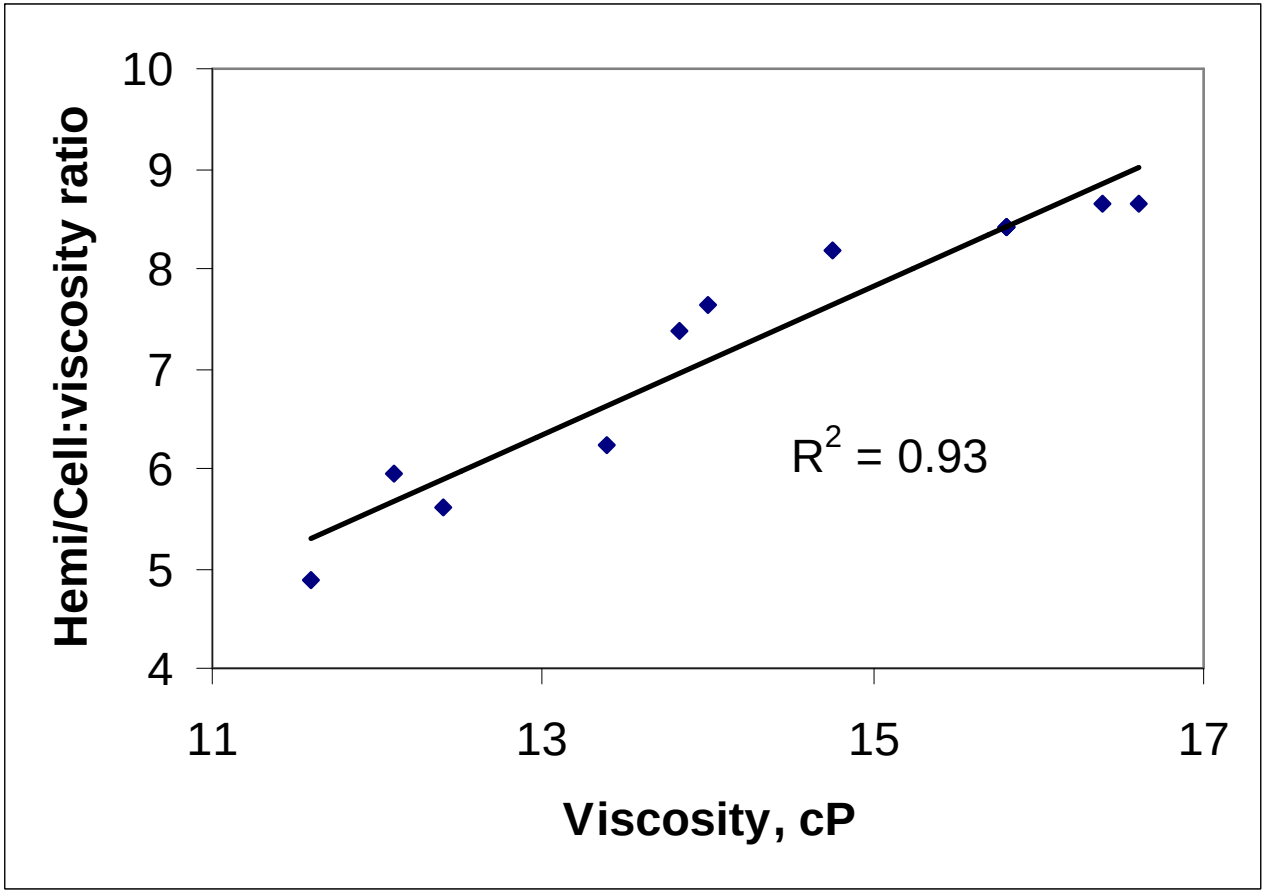
Experimental std dev errors

	Properties	% error, avg
1	DZSTS (Dry Zero Span Tensile Strength)	2.8
2	WZSTS (Wet Zero Span Tensile Strength)	3.5
3	Tensile index	4.0
4	Tear index	8.3
5	Burst index	7.4
6	Brightness	0.5
7	Fines	5.3
8	Fiber length	2.3
9	Fiber curl	1.5
10	Fiber kink	2.8
11	Kappa number	1.5
12	Viscosity	0.9
13	Hexenuronic acid	0.8
14	DCM extractive	2.4
15	Total charge	1.4
16	Cellulose/hemicelluloses	2.4

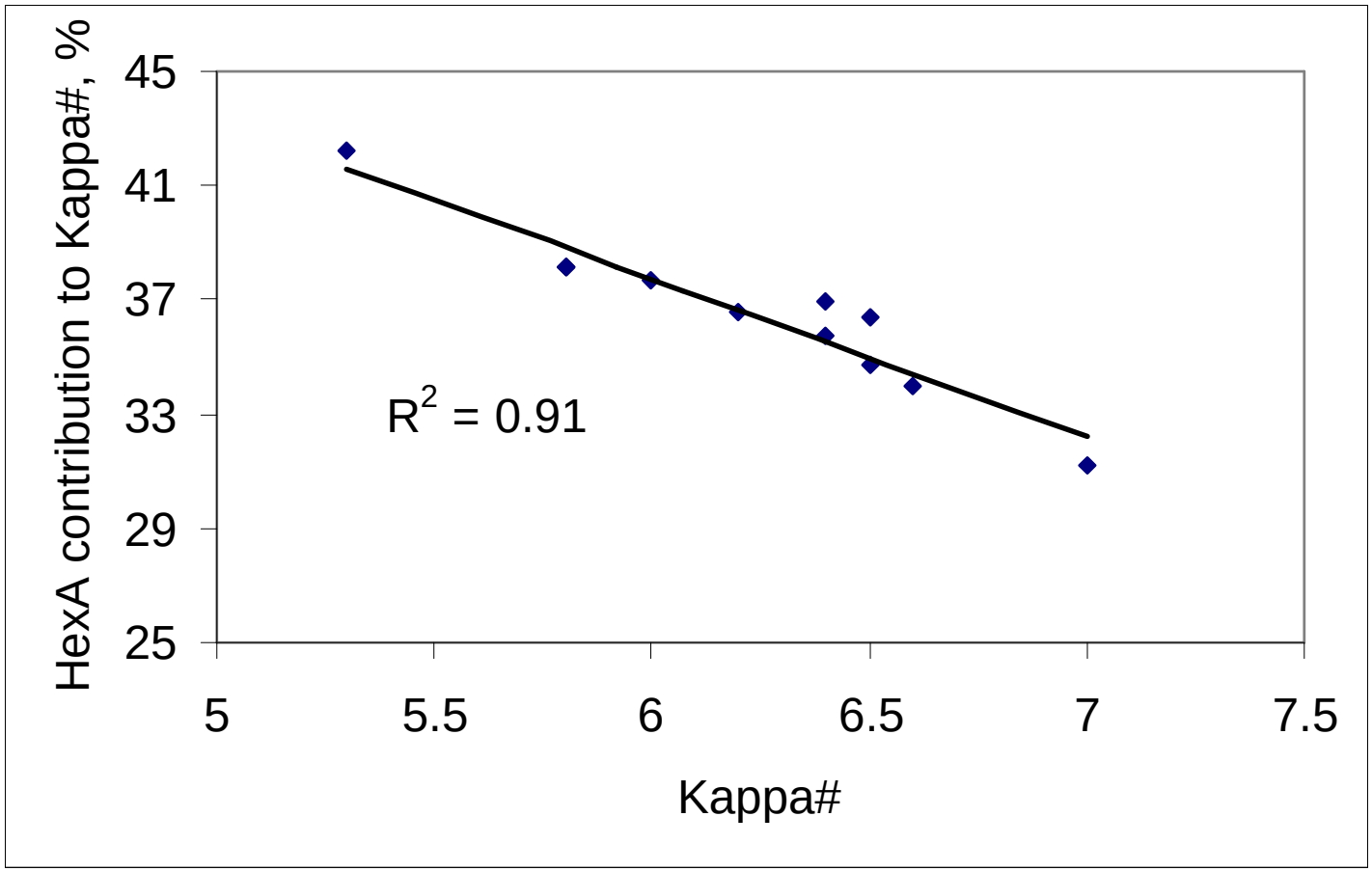
Results-detail

					reaction time, min			NaOH charge, g/kg pulp			reaction temperature, °C			mixing time, sec		
	Parameter	Unit	Pre O_2	Post O_2	60	90	120	16.67	20.00	23.33	85	90	95	5	10	15
1	Kappa number		9.6	4.9	6.2	5.8	5.3	5.8	6.4	6.5	7.0	5.8	6.0	6.6	6.5	6.4
2	Viscosity	cP	23.5	12.4	16.6	15.8	14.0	15.8	14.8	13.8	16.4	15.8	13.4	12.1	12.4	11.6
3	HexA	µMol/g	29.6	23.4	28.0	27.3	27.6	27.3	28.2	27.9	27.0	27.3	27.9	27.7	29.2	29.2
4	Total charge	µeq/g	77.1	64.3	73.6	74.2	70.0	74.2	72.9	74.2	77.0	74.2	69.6	72.7	70.7	70.3
5	DCM extractive	%	1.08	0.49	0.41	0.43	0.41	0.43	0.42	0.55	0.61	0.43	0.37	0.26	0.27	0.27
6	Alpha-cellulose	%	35.2	34.4	34.2	34.8	35.3	34.8	35.7	34.8	34.6	34.8	31.8	33.0	31.1	29.6
7	Gamma-cellulose	%	8.3	8.2	6.4	6.3	8.3	6.3	6.4	6.1	7.4	6.3	4.5	5.8	7.7	4.8
8	Beta-cellulose	%	56.4	57.5	59.4	59.0	56.4	59.0	57.9	59.1	58.0	59.0	63.7	61.2	61.2	65.6
9	DZSTS	kPa	307	290	272	270	266	270	264	264	278	270	260	275	279	264
10	WZSTS	kPa	269	248	237	234	233	234	230	226	217	234	224	215	221	199
11	Tear Index	$mN.m^2/g$	6.46	6.95	4.79	5.59	4.91	5.59	4.80	4.88	4.42	5.59	3.95	5.96	6.22	5.91
12	Burst Index	$kPa.m^2/g$	1.96	2.31	1.22	1.17	1.16	1.17	1.23	1.14	1.19	1.17	0.97	1.47	1.51	1.26
13	Tensile Index	Nm/g	43.7	43.0	26.9	24.5	26.0	24.5	27.1	25.4	26.6	24.5	21.9	30.6	30.9	27.4
14	Brightness	%	41.7	57.9	51.0	52.2	55.0	52.2	53.6	54.9	51.9	52.2	56.5	52.8	52.8	53.9
15	Fines	%	0.66	0.79	0.78	0.63	0.62	0.63	0.70	0.66	0.73	0.63	0.91	0.79	0.89	0.88
16	Fiber length	mm	0.69	0.66	0.68	0.67	0.67	0.67	0.67	0.66	0.70	0.67	0.67	0.66	0.66	0.67
17	Fiber Curl		0.072	0.076	0.078	0.085	0.088	0.085	0.091	0.090	0.082	0.085	0.095	0.071	0.081	0.084
18	Fiber Kink index	1/mm	1.23	1.37	1.34	1.45	1.54	1.45	1.53	1.53	1.48	1.45	1.64	1.31	1.45	1.44

Results – part 1



Results – part 1



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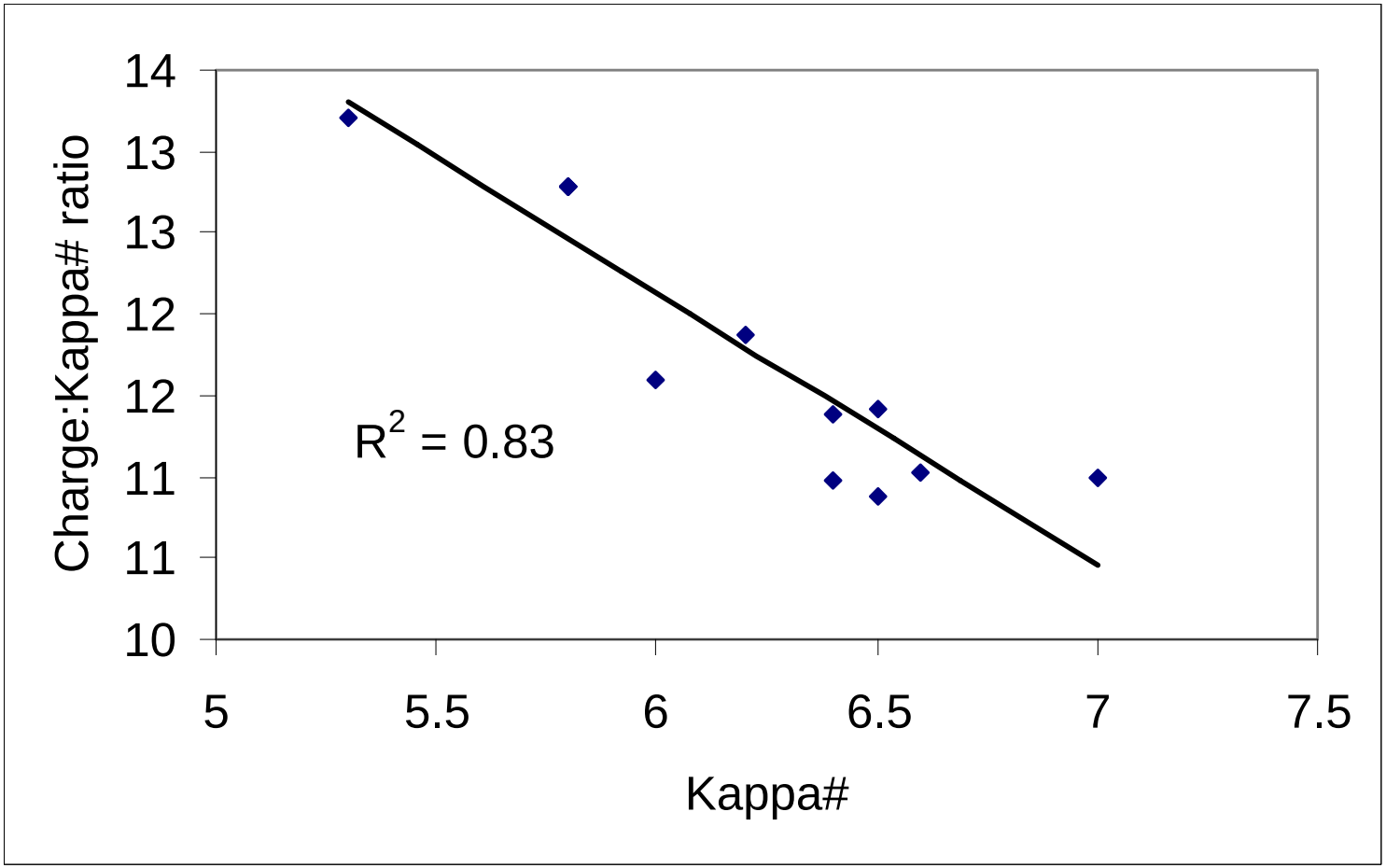


Results – part 1

Metal profile of *Acacia mangium* pulp

Element	Concentration
	mg/kg
K	1,268
Na	14,300
Ca	494
Mg	71.4
Mn	3.5
Cu	1.1
Fe	7.9
Ni	0.5

Molar Mg/Mn=46

Results – part 1

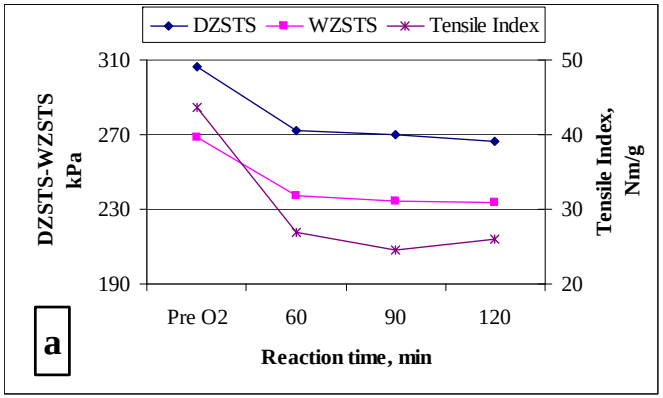
Mill pulp properties (1), *A. mangium*

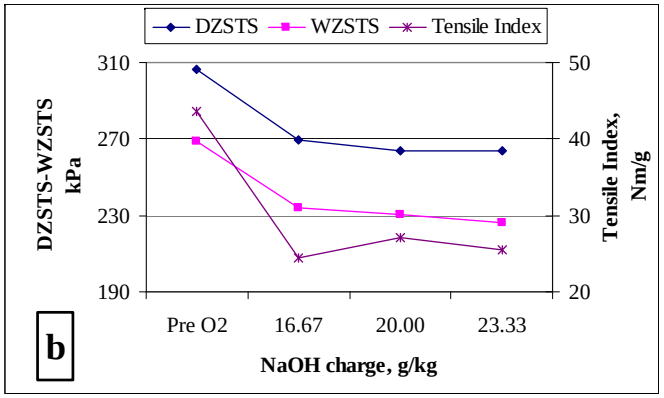
	Properties	Unit	Pre O_2	Post O_2
1	Kappa number		9.6	4.9
2	Viscosity	cP	23.5	12.4
3	DZSTS	kPa	307 →	290
4	WZSTS	kPa	269	248
5	Tensile index	Nm/g	6.46	6.95

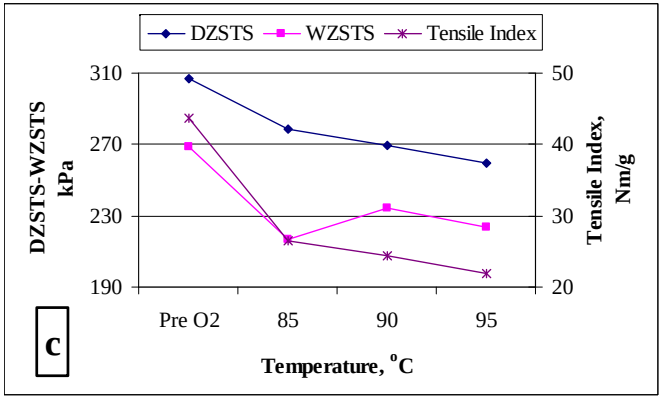
5% loss

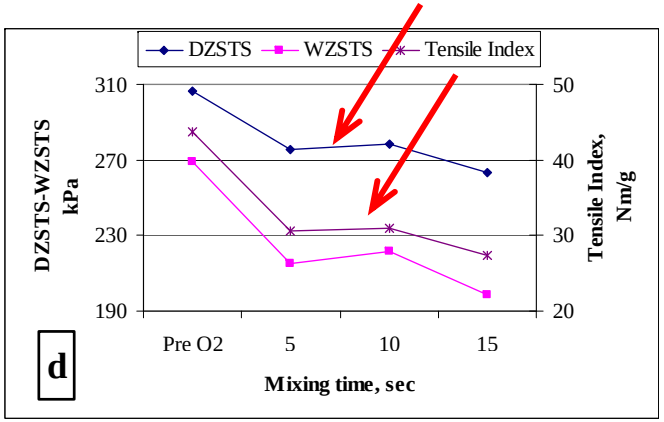
Results – part 1

Effect of OD process on DZSTS, WZSTS, & tensile index

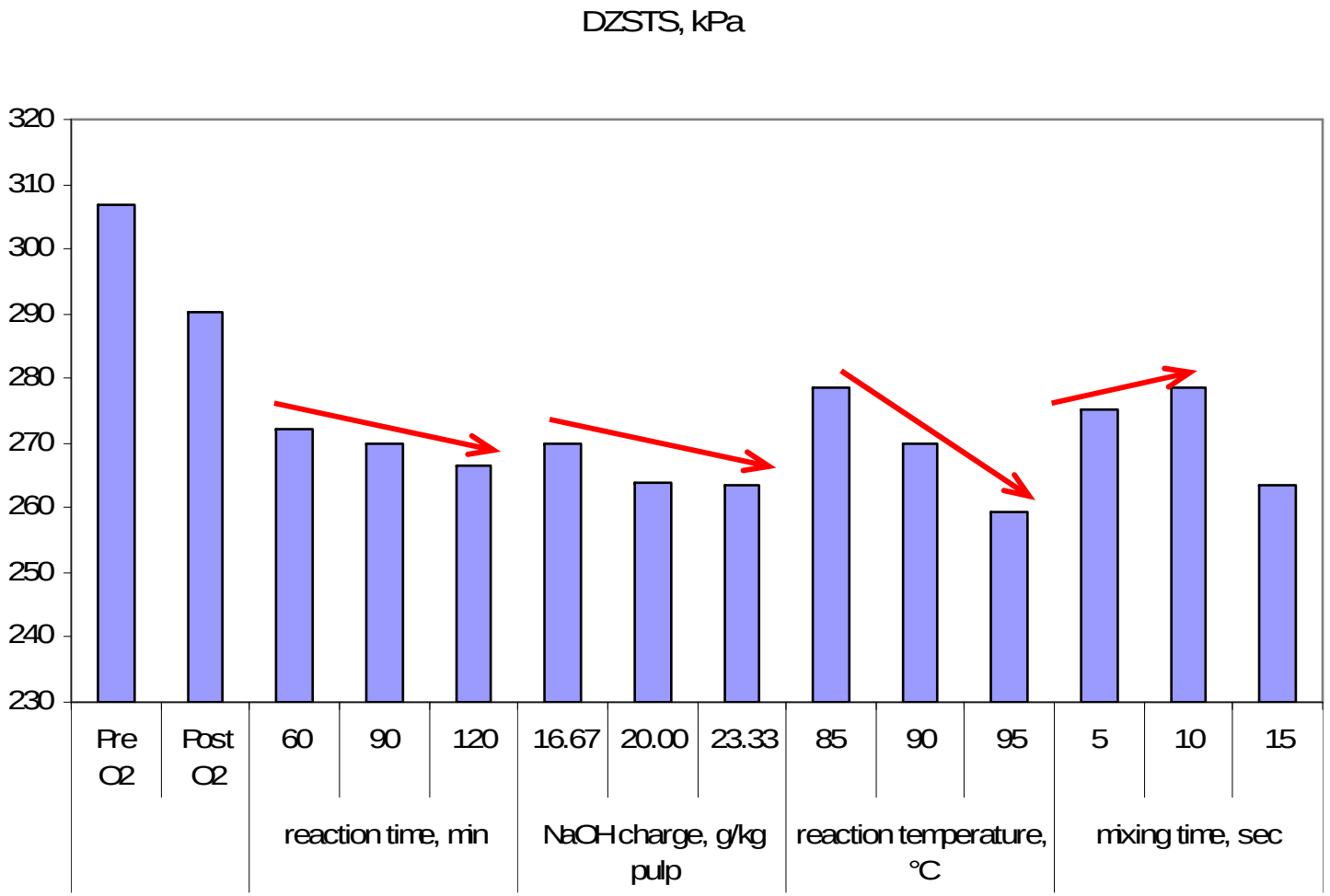








Results – part 1



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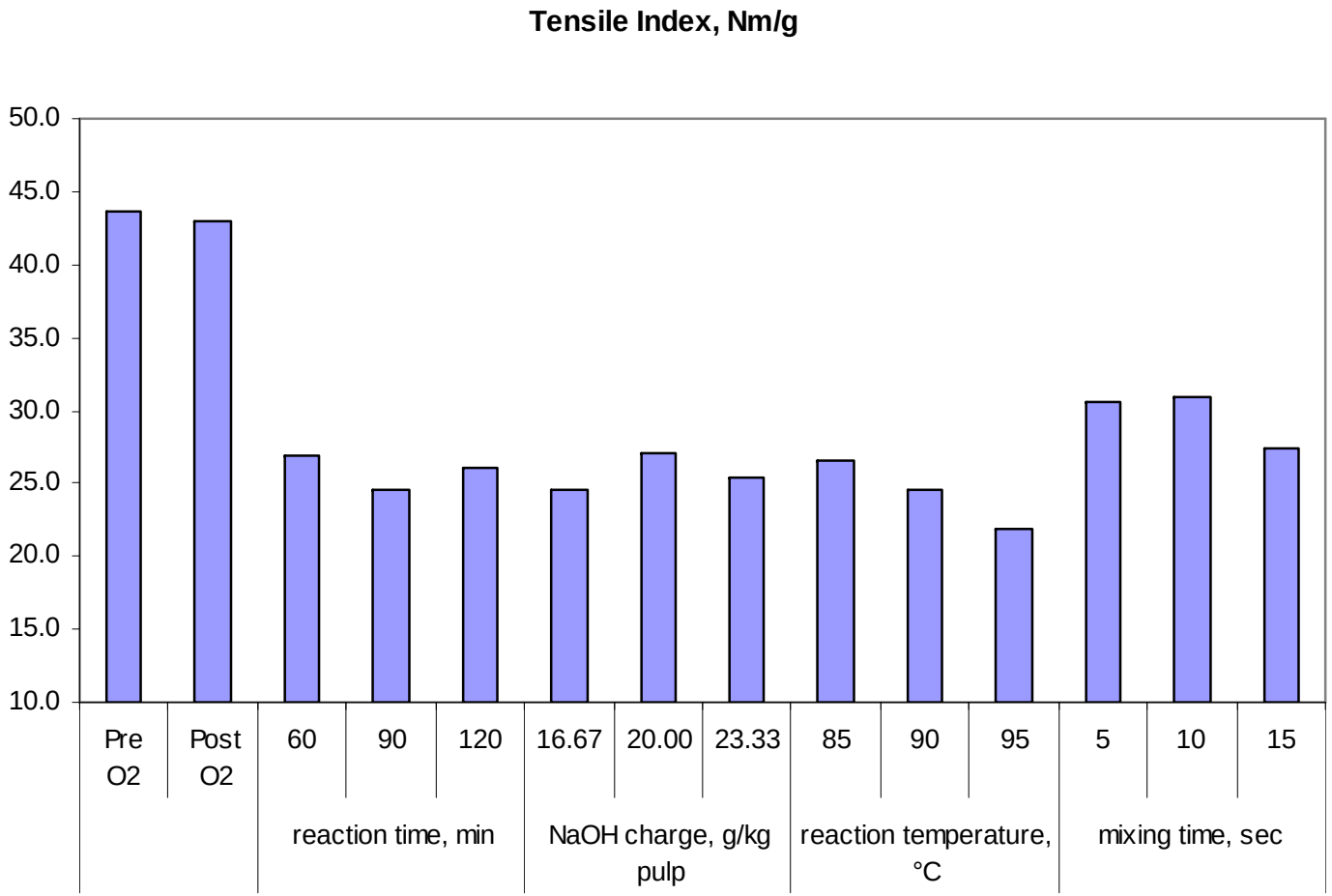
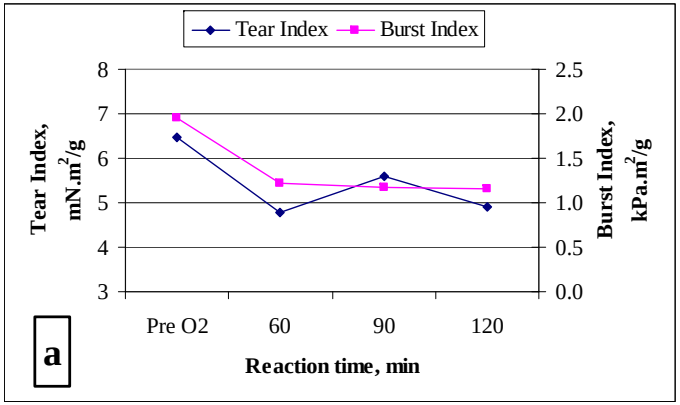
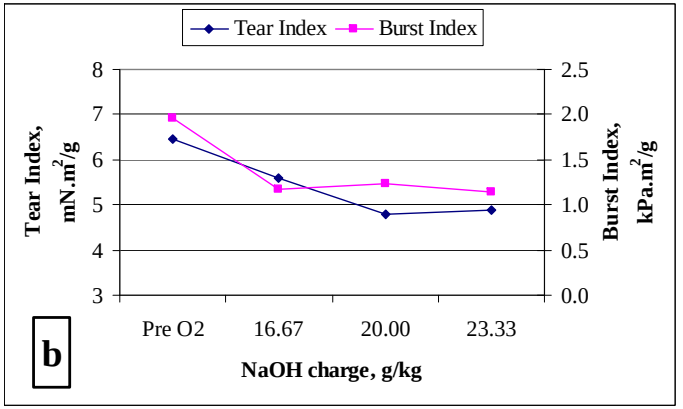
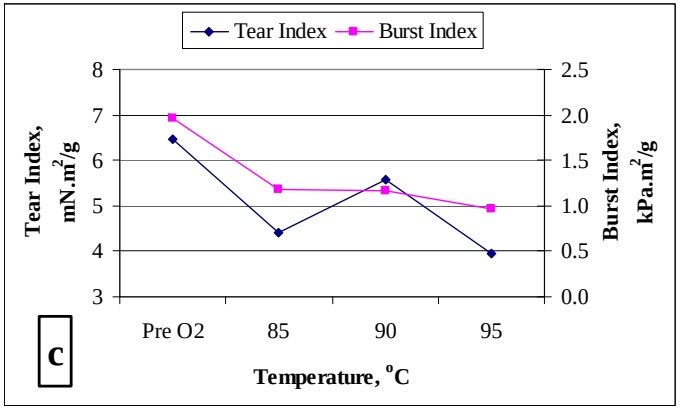


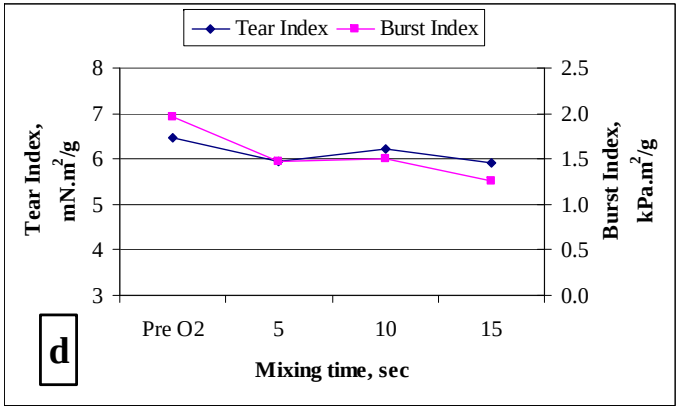
Results – part 1

Effect of OD process on tear & burst index



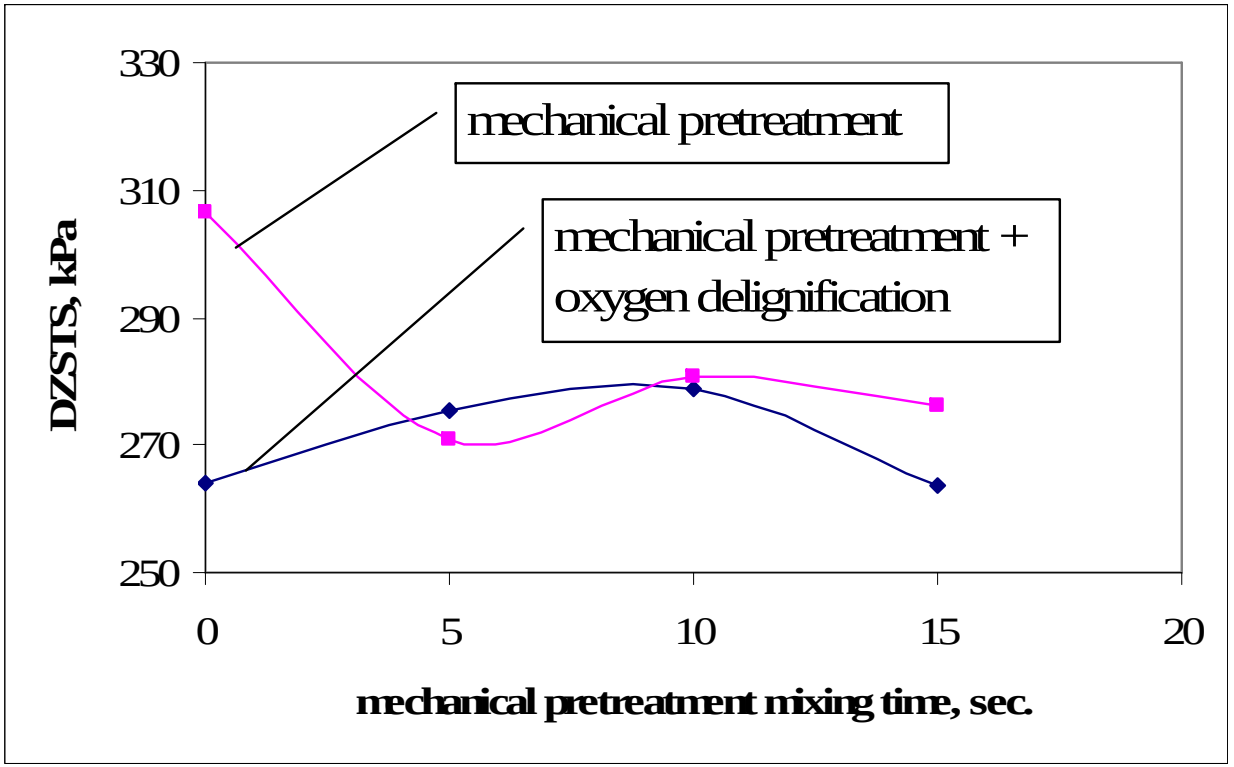






Results – part 1

DZSTS at different pretreatment time

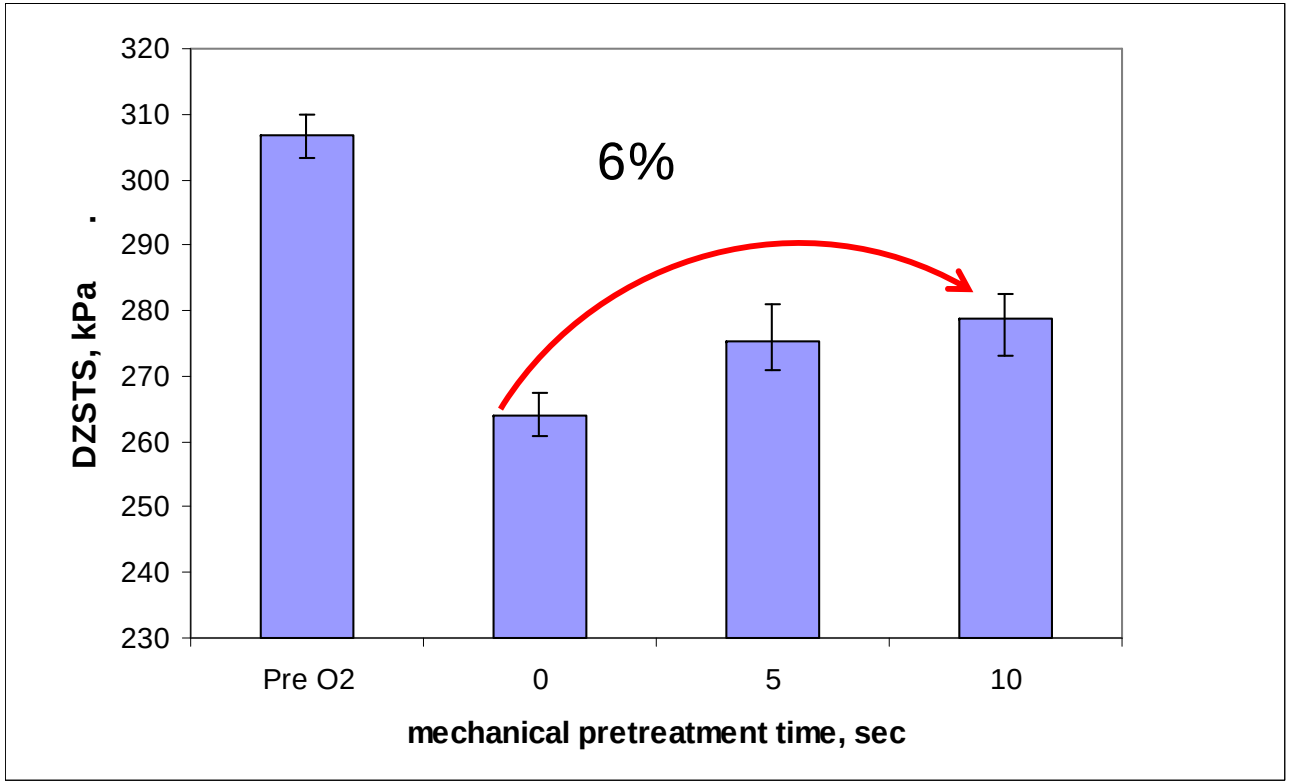


OD conditions:

- t=90 min
- T=90 °C
- NaOH=20 g/kg
- Cons=12 %
- O_2 press=1034 kPa

Results – part 1

DZSTS at different pretreatment time

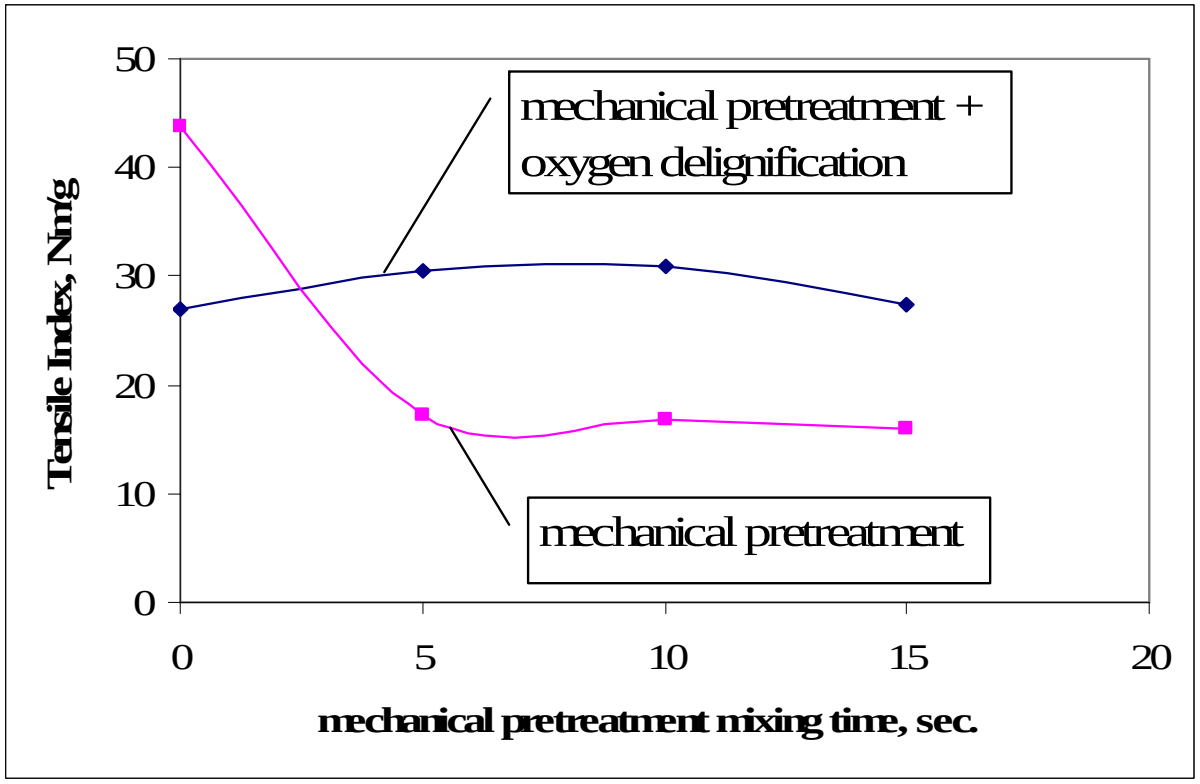


OD conditions:

- t=90 min
- T=90 °C
- NaOH=20 g/kg
- Cons=12 %
- O_2 press=1034 kPa

Results – part 1

Tensile index at different pretreatment time



OD conditions:

- t=90 min
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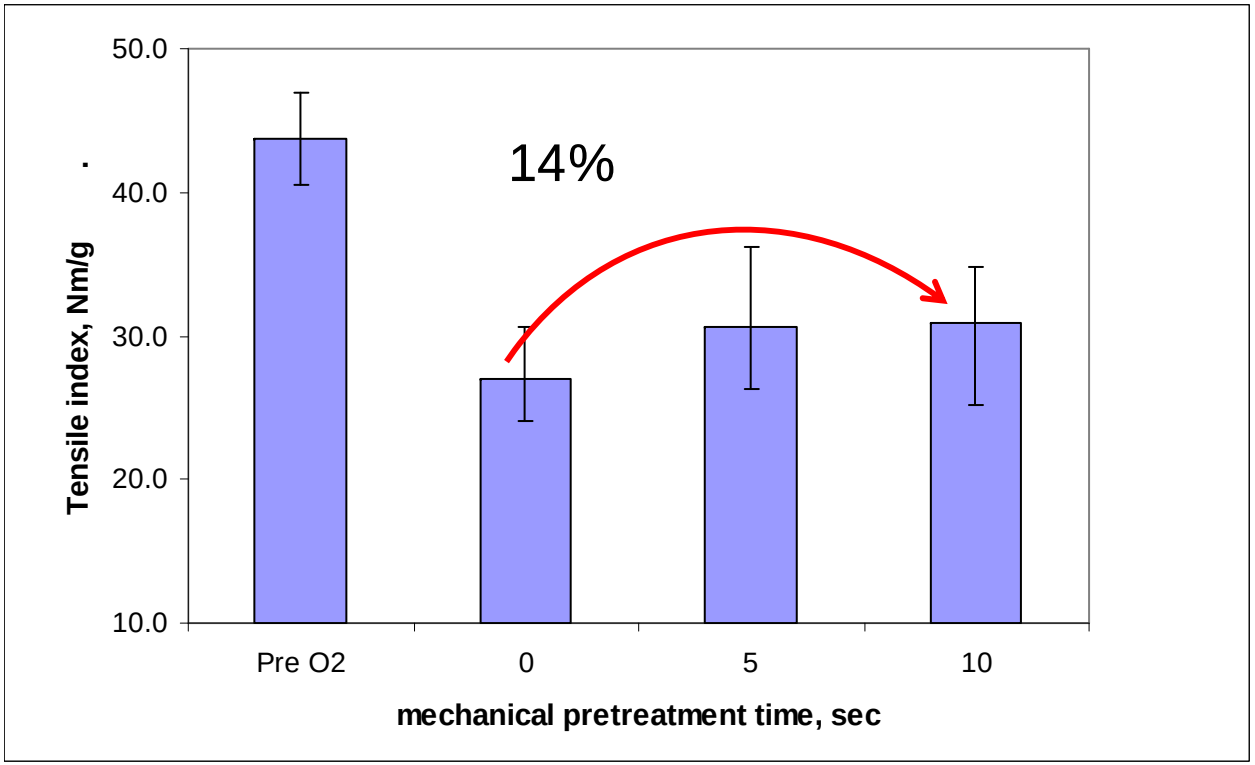
- NaOH=20 g/kg
- Cons=12 %
- O_2 press=1034 kPa

Results – part 1

Tensile index at different pretreatment time

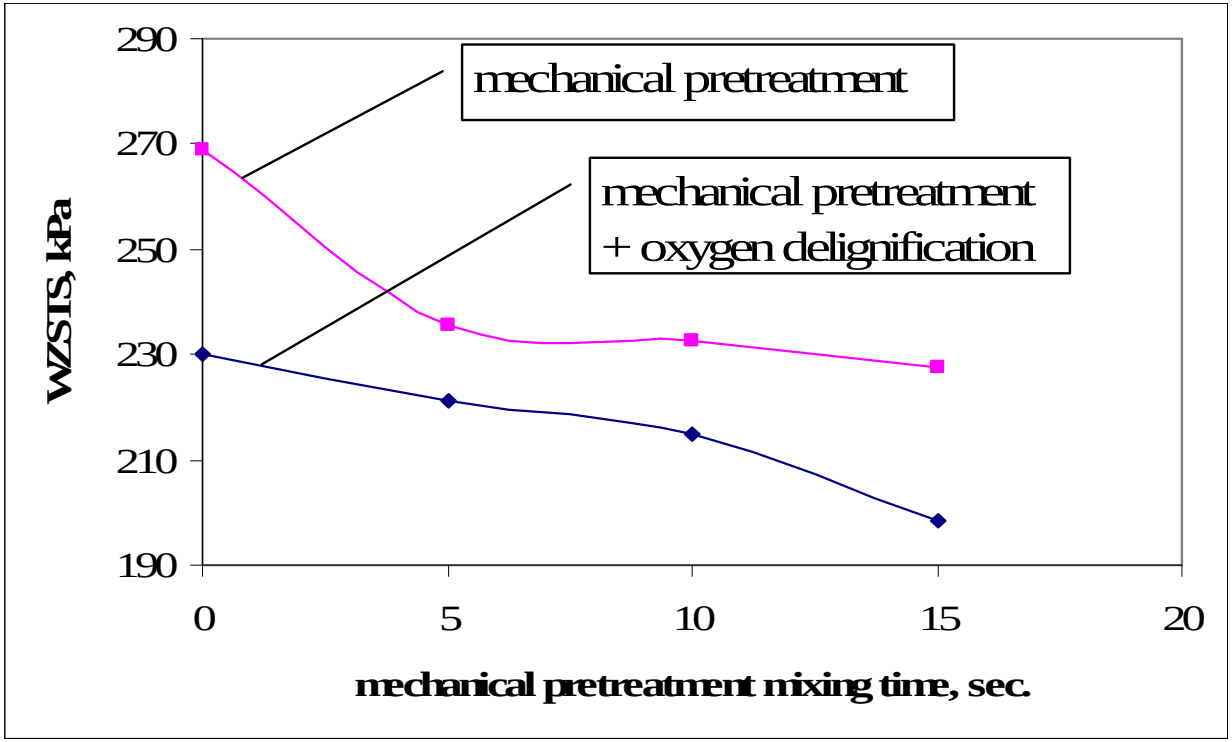


OD conditions:

- t=90 min
- T=90 °C
- NaOH=20 g/kg
- Cons=12 %
- O_2 press=1034 kPa

Results – part 1

WZSTS at different pretreatment time

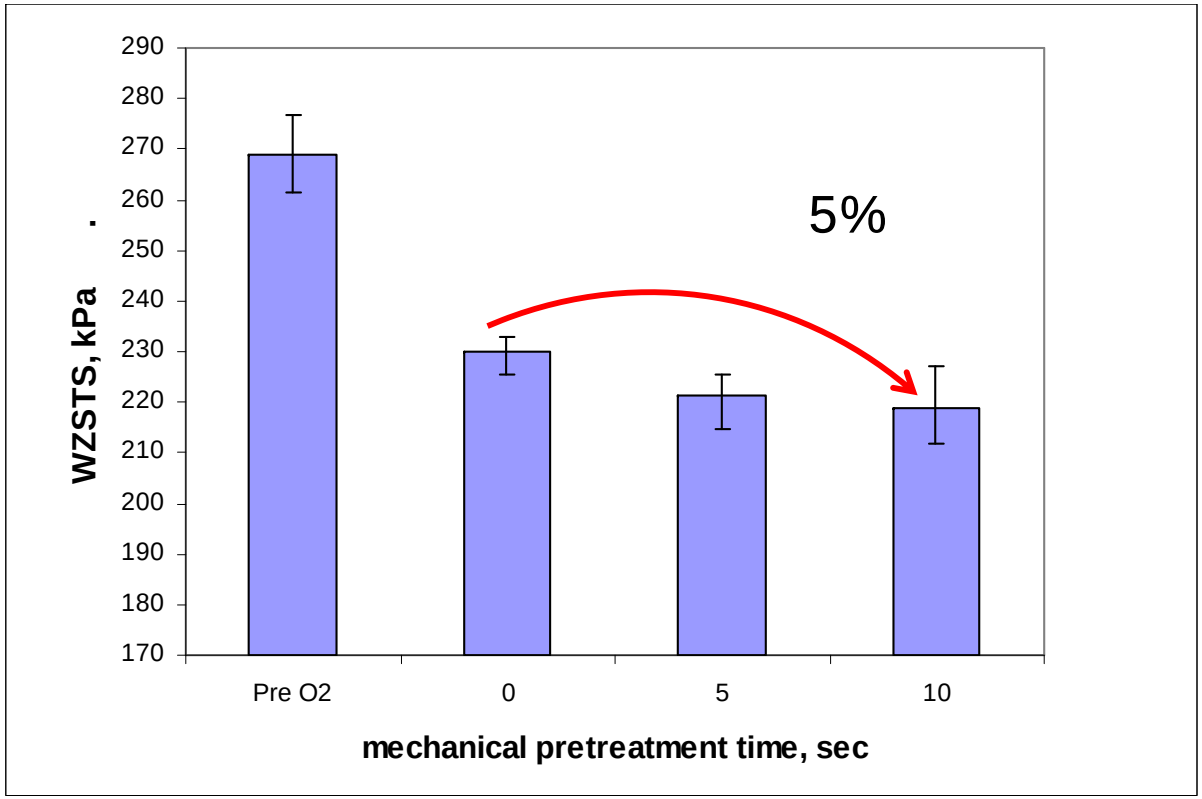


OD conditions:

- t=90 min
- T=90 °C
- NaOH=20 g/kg
- Cons=12 %
- O_2 press=1034 kPa

Results – part 1

WZSTS at different pretreatment time

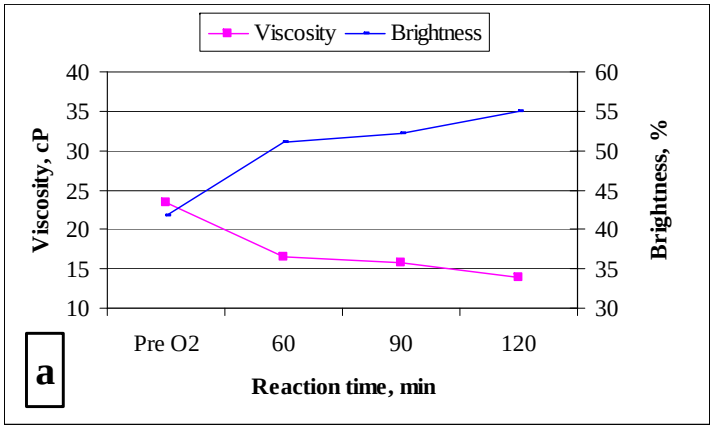


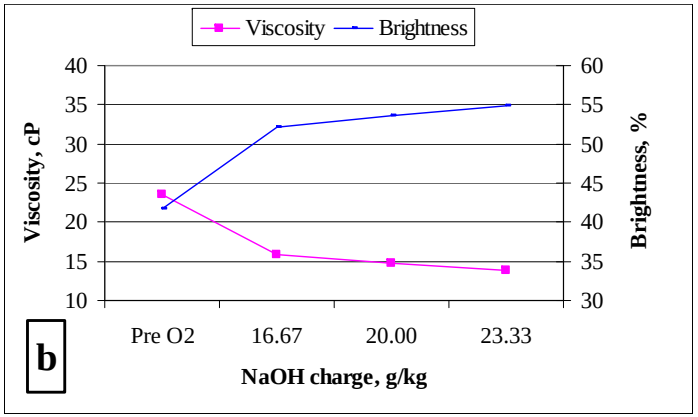
OD conditions:

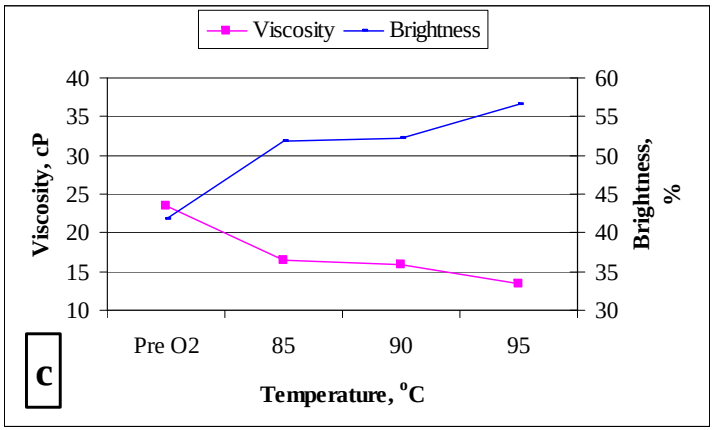
- t=90 min
- T=90 °C
- NaOH=20 g/kg
- Cons=12 %
- O_2 press=1034 kPa

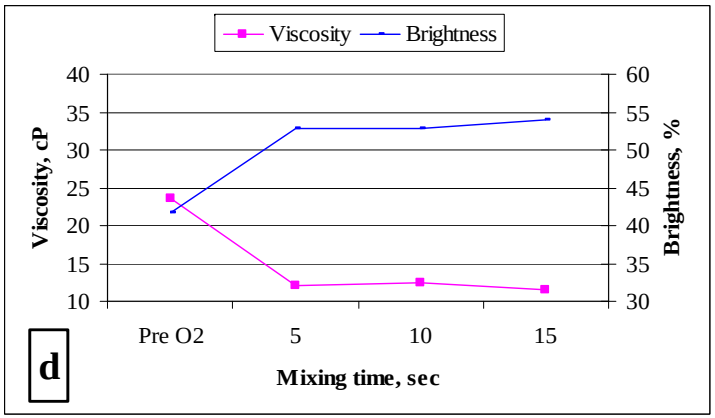
Results – part 1

Effect of OD process on viscosity & brightness



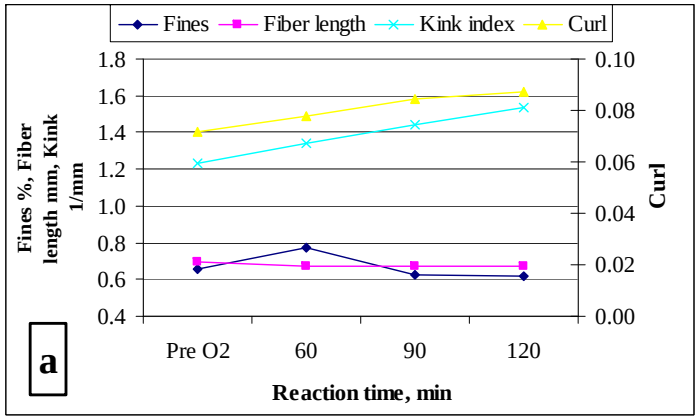


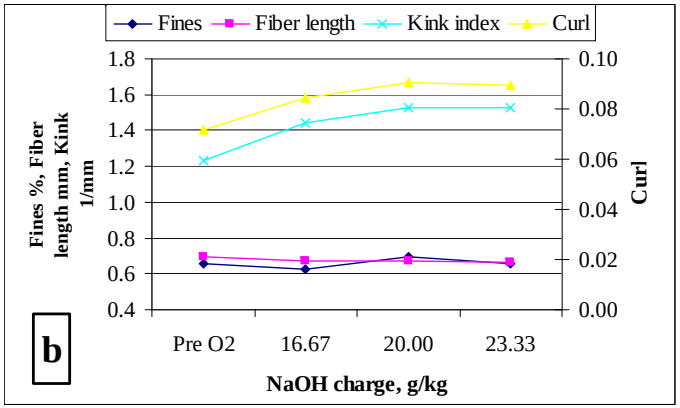


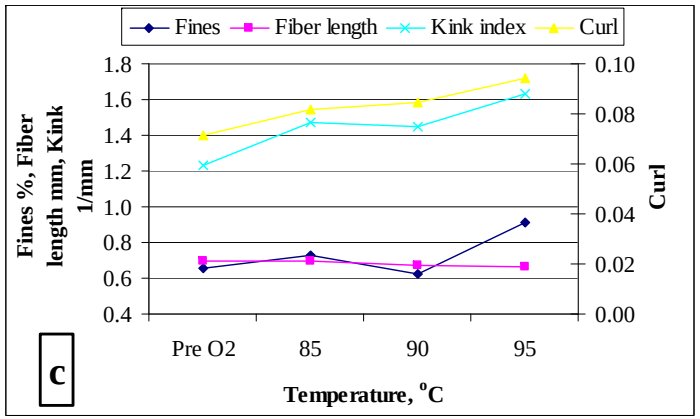


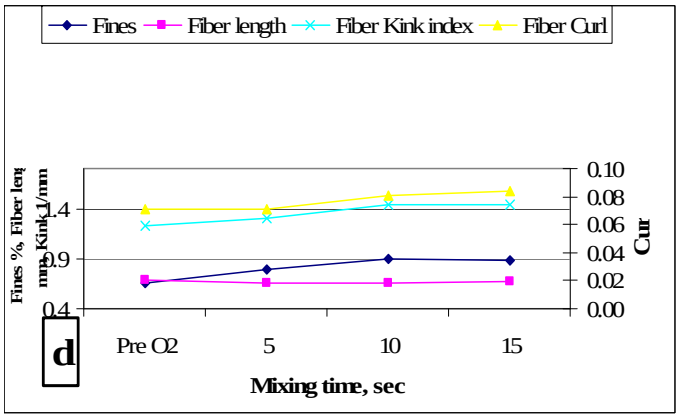
Results – part 1

Effect of OD process on fines, fiber length, curl, & kink

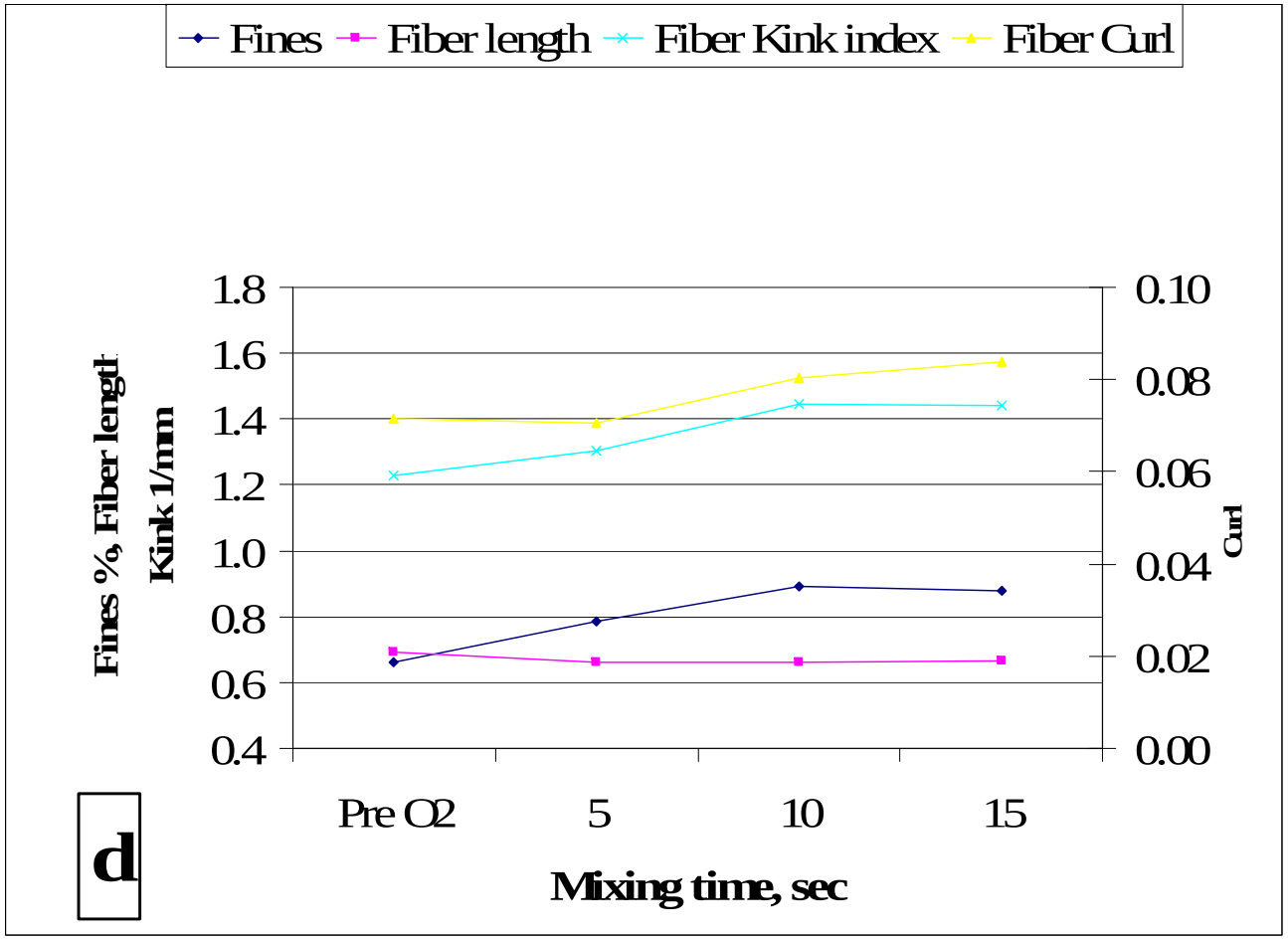






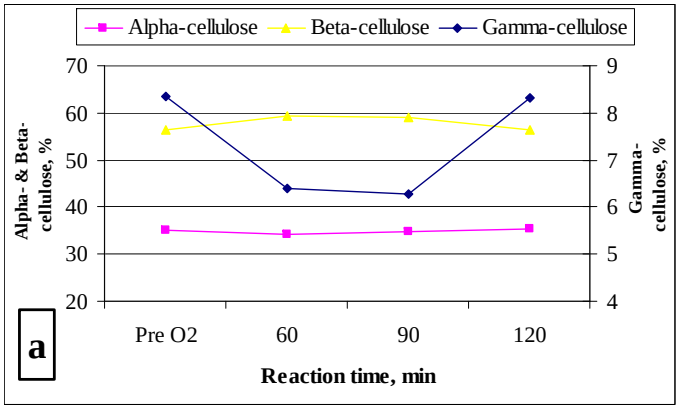


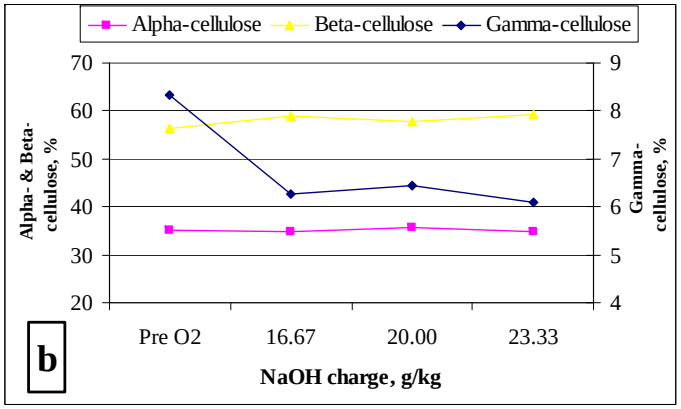
Results – part 1

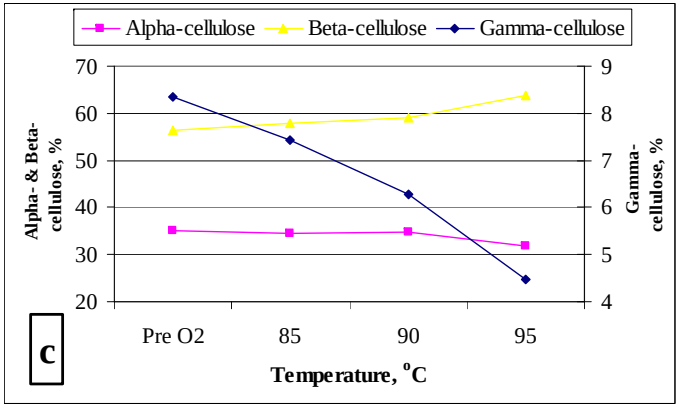


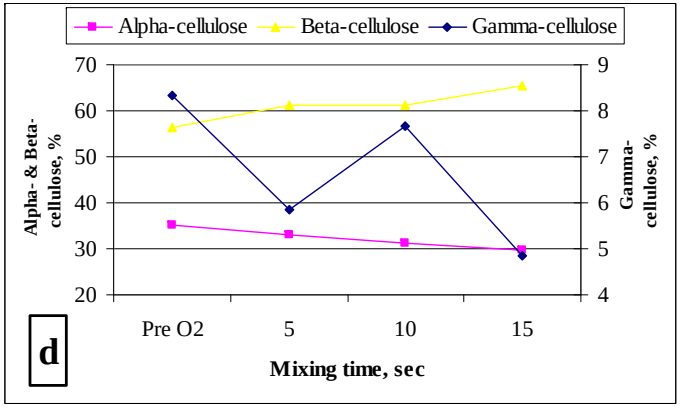
Results – part 1

Effect of OD process on alpha-, beta-, & gamma-cellulose



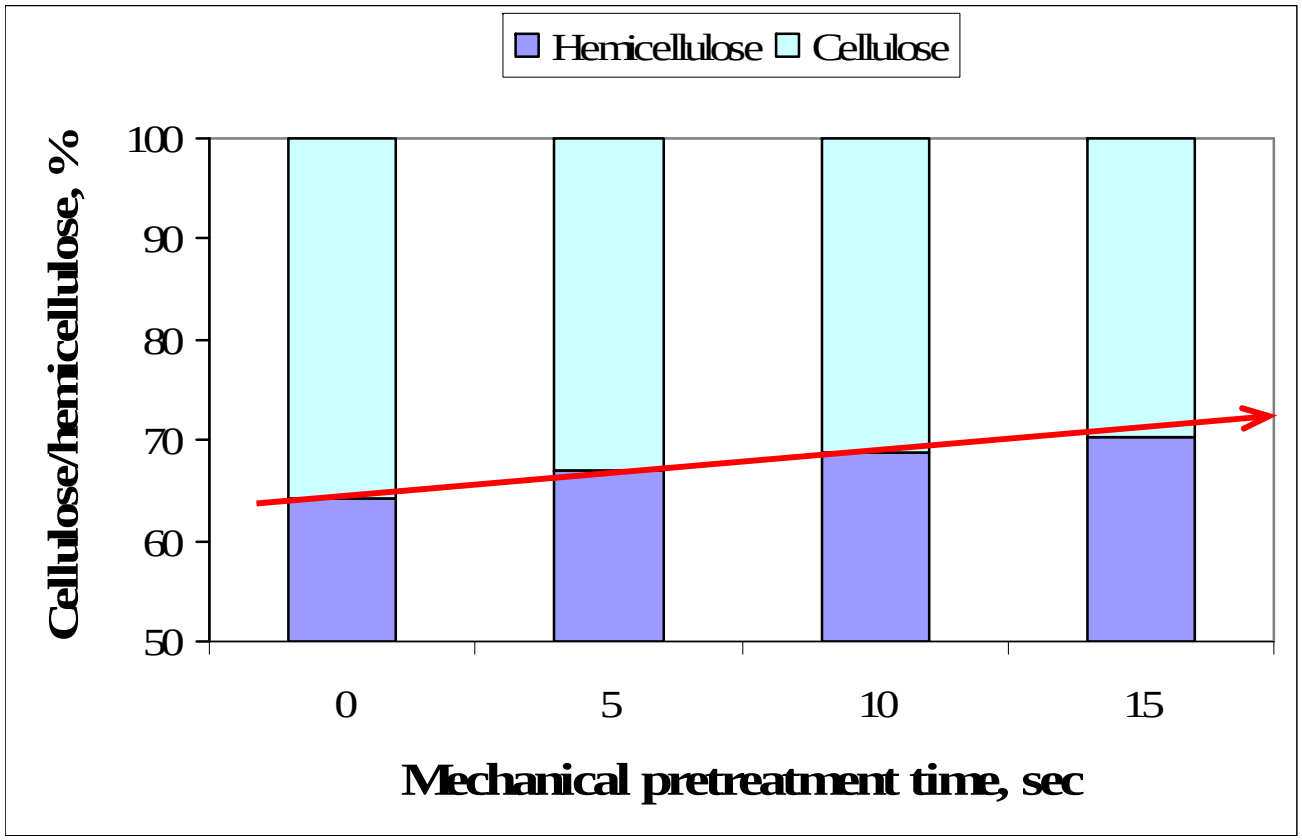






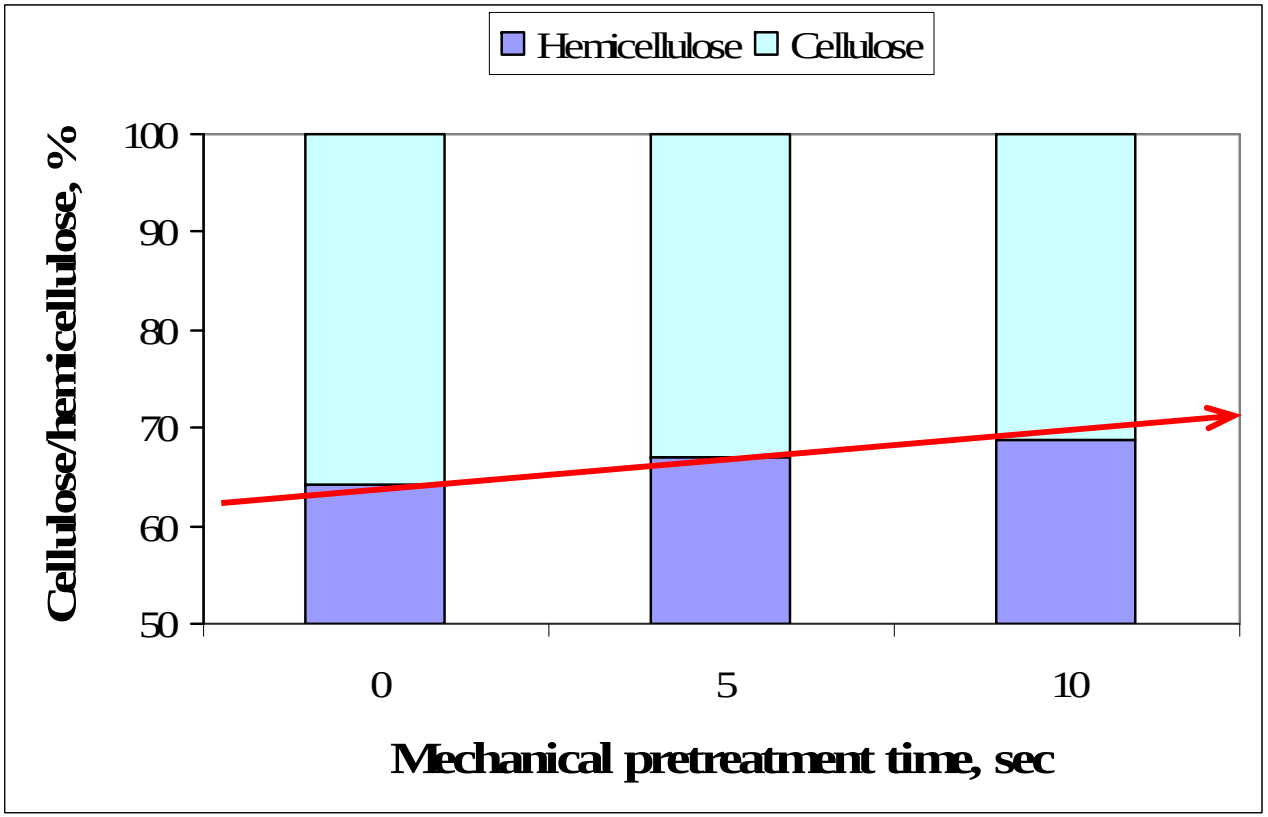
Results – part 1

Cellulose/hemicelluloses at different pretreatment time



Results – part 1

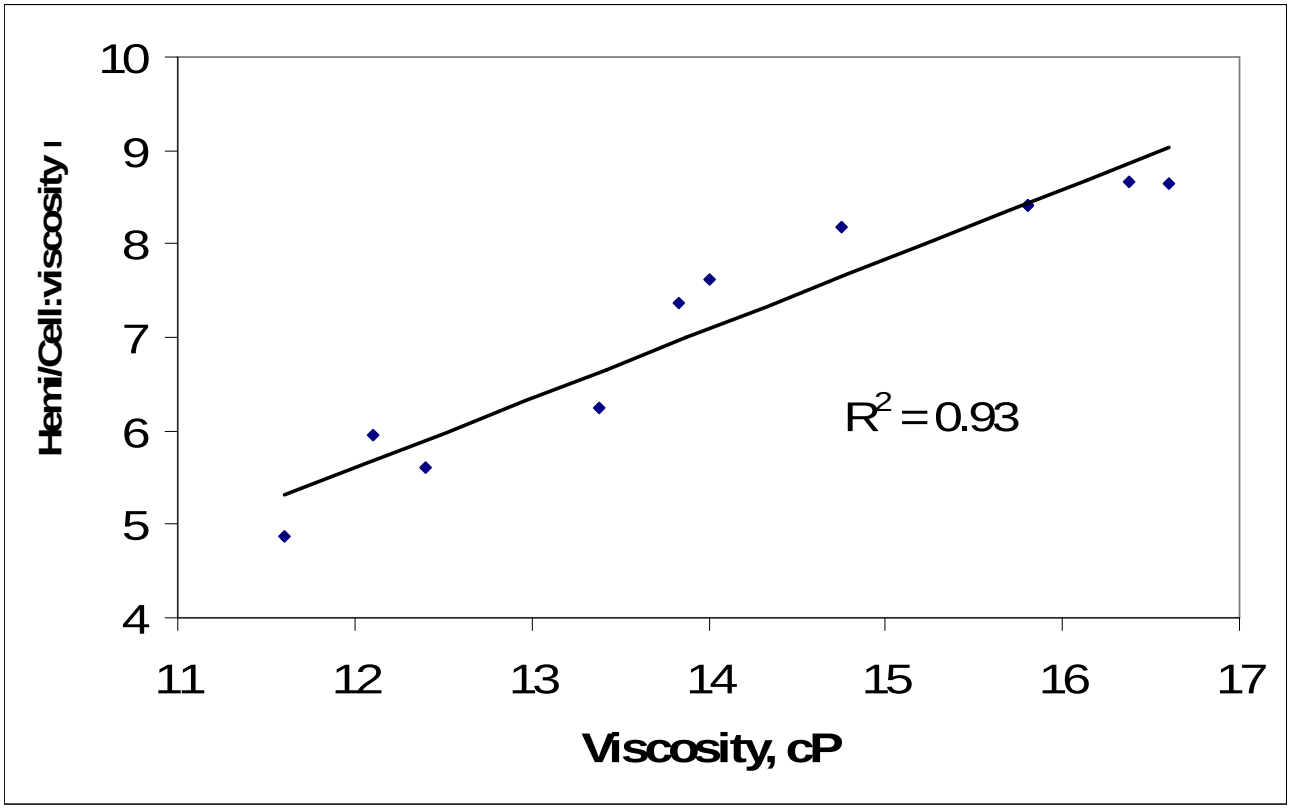
Cellulose/hemicelluloses at different pretreatment time



Molin et al,
NPPRJ 2002

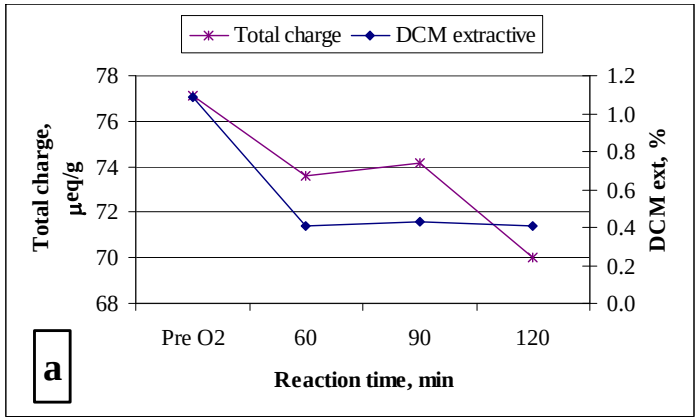
Results – part 1

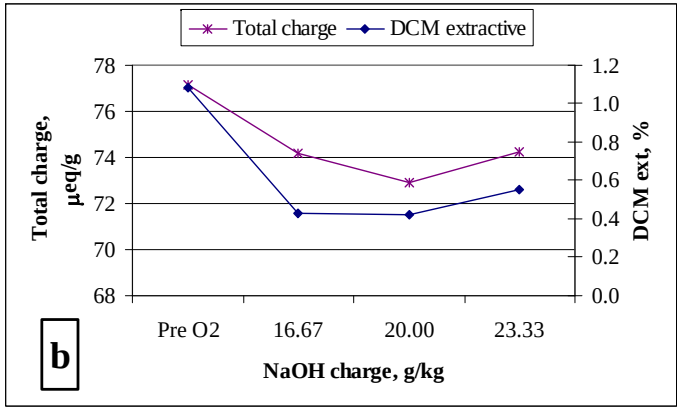
Hemi/Cellulose:viscosity vs Viscosity

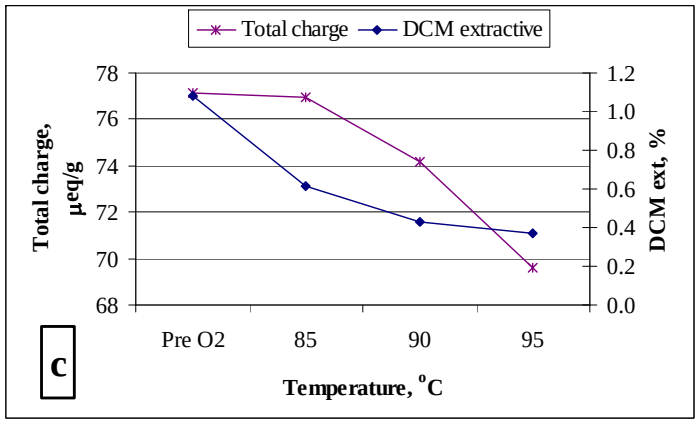


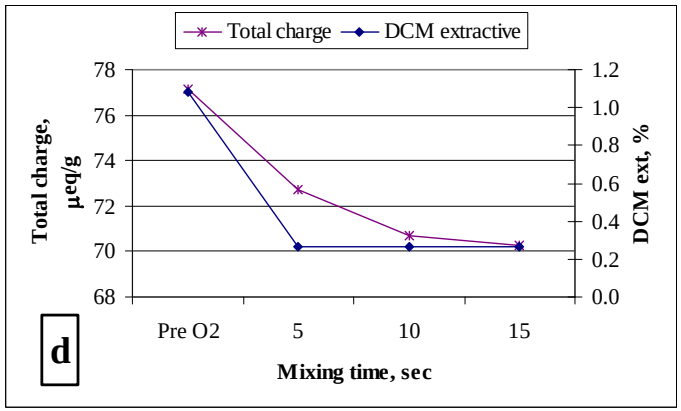
Results – part 1

Effect of OD process on total charge & DCM extractives



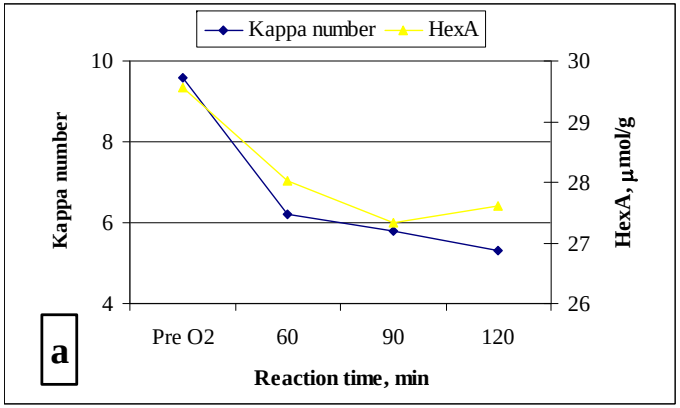


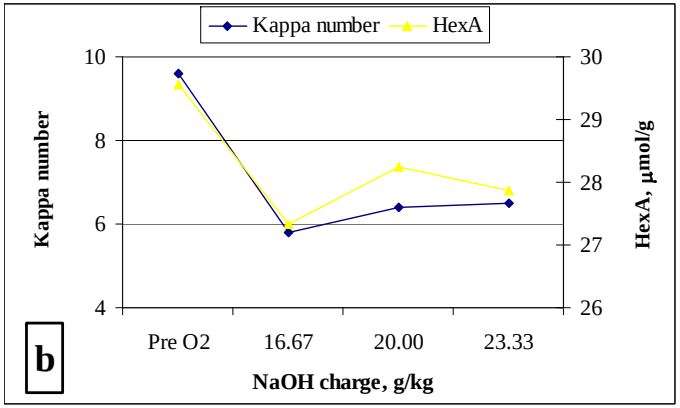


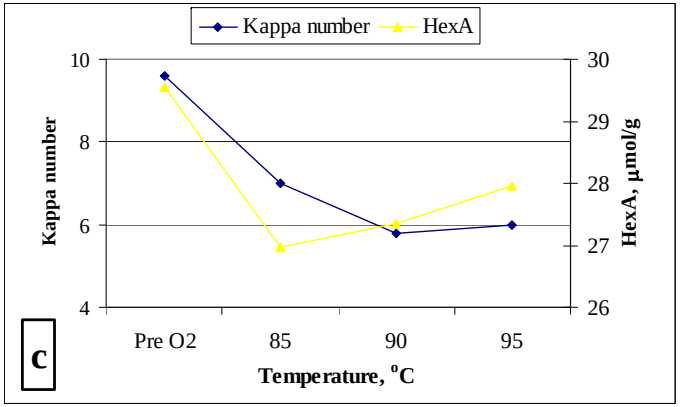


Results – part 1

Effect of OD process on Kappa# & HexA







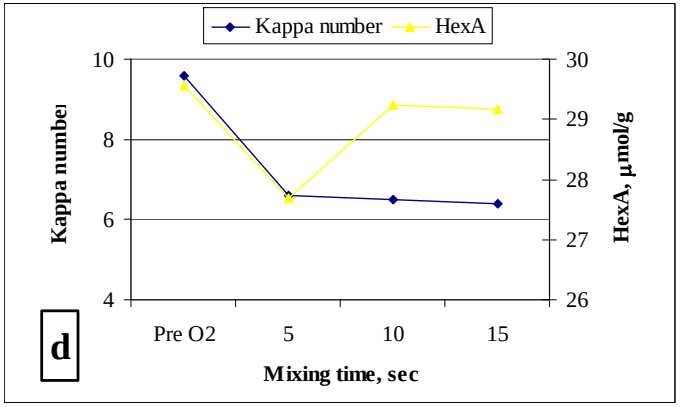
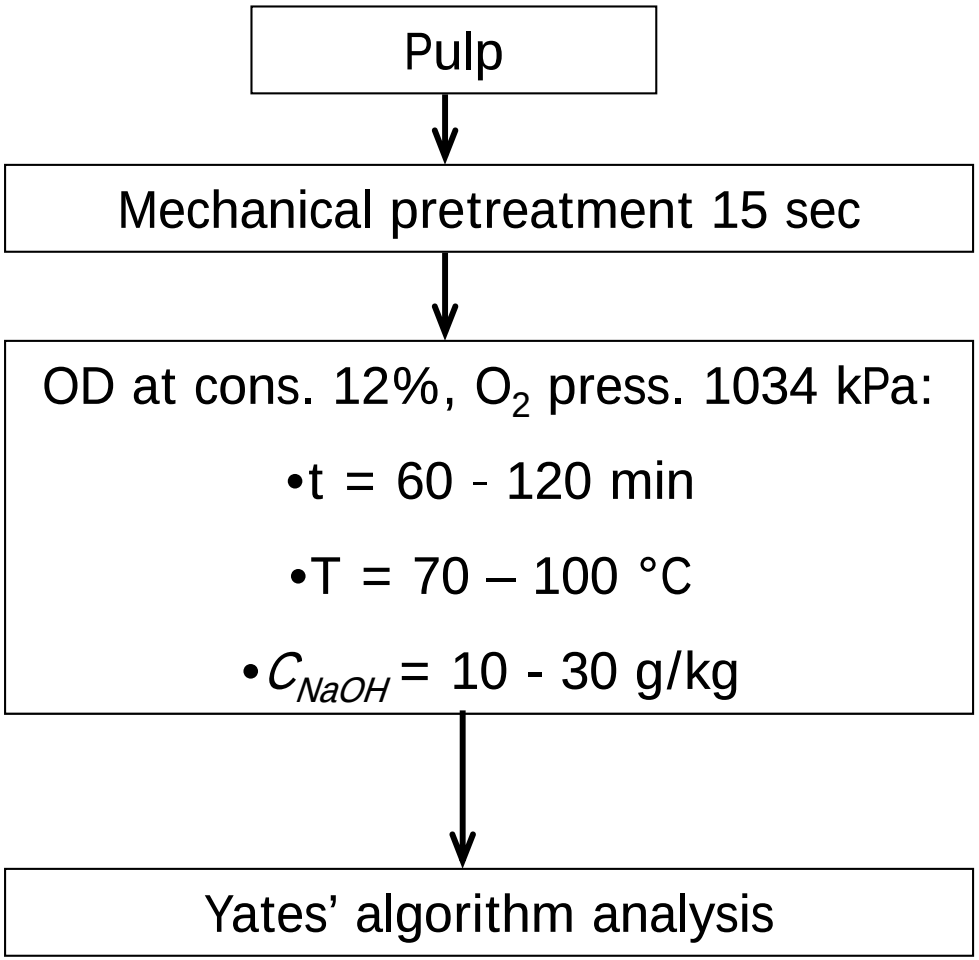


Diagram-experiment



Results – part 1

Yates' algorithm analysis

Exp.	Variables			Variables	Estimated effects			
	t	T	*C*	effect	DZSTS	WZSTS	tensile	Kappa#
y1	-	-	-	average	38	29	20	7.3
y2	+	-	-	t	-2	-2	-2	-0.7
y3	-	+	-	T	-7	-6	-11	-2.3
y4	+	+	-	t T	0	-1	0	-0.1
y5	-	-	+	*C*	-5	-7	-6	-0.5
y6	+	-	+	t *C*	2	1	0	0.4
y7	-	+	+	T *C*	-4	-2	1	-0.4
y8	+	+	+	t T *C*	2	2	1	0.1

t = 60 - 120 min, T = 70 – 100 °C, *C* = 10 - 30 g/kg, 15 sec mechanical pretreatment

Results – part 1

Yates' algorithm analysis

Exp.	Variables			Variables	Estimated effects			
	t	T	*C*	effect	DZSTS	WZSTS	tensile	Kappa#
y1	-	-	-	average	38	29	20	7.3
y2	+	-	-	t	-2	-2	-2	-0.7
y3	-	+	-	**T**	**-7**	**-6**	**-11**	**-2.3**
y4	+	+	-	t T	0	-1	0	-0.1
y5	-	-	+	***C***	**-5**	**-7**	**-6**	-0.5
y6	+	-	+	t *C*	2	1	0	0.4
y7	-	+	+	**T *C***	**-4**	-2	1	-0.4
y8	+	+	+	t T *C*	2	2	1	0.1

t = 60 - 120 min, T = 70 – 100 °C, *C* = 10 - 30 g/kg, 15 sec mechanical pretreatment

Results - part 1

Yates' algorithm for tensile index

Exp.	Variables			Tensile	Calculations			Estimated effects	
	t	T	*C*	Index	1	2	3		
y1	60	70	10.0	29.3	57.1	90.5	159	Grand average	19.8
y2	120	70	10.0	27.8	33.4	68.4	-9.4	t effect	-2.4
y3	60	100	10.0	18.8	44.1	-5.6	-43.5	T effect	-10.9
y4	120	100	10.0	14.7	24.3	-3.8	0.3	t T effect	0.1
y5	60	70	30.0	23.7	-1.5	-23.7	-22.1	*C* effect	-5.5
y6	120	70	30.0	20.4	-4.1	-19.8	1.8	t *C* effect	0.5
y7	60	100	30.0	12.4	-3.3	-2.6	3.9	T *C* effect	1.0
y8	120	100	30.0	11.9	-0.5	2.9	5.5	t T *C* effect	1.4

Results - part 1

Yates' algorithm for DZSTS

Exp.	Variables			DZSTS	Calculations			Estimated effects	
	t	T	*C*		1	2	3		
y1	60	70	10.0	292	575	1115	2104	Grand average	263
y2	120	70	10.0	284	539	989	-49	t effect	-12.2
y3	60	100	10.0	290	568	-49.0	-183	T effect	-45.8
y4	120	100	10.0	249	421	0.0	-5.1	t T effect	-1.3
y5	60	70	30.0	291	-7.9	-36.0	-126	*C* effect	-31.4
y6	120	70	30.0	277	-41.1	-147	49.0	t *C* effect	12.3
y7	60	100	30.0	203	-14.0	-33.2	-111	T *C* effect	-27.8
y8	120	100	30.0	217	14.1	28.1	61.3	t T *C* effect	15.3

Results - part 1

Yates' algorithm for WZSTS

Exp.	Variables			WZSTS	Calculations			Estimated effects	
	t	T	*C*	kPa	1	2	3		
y1	60	70	10.0	242	480	913	1626	Grand average	203
y2	120	70	10.0	238	433	714	-52.4	t effect	-13.1
y3	60	100	10.0	236	410	-42.0	-154	T effect	-38.4
y4	120	100	10.0	198	303	-10.4	-23.0	t T effect	-5.7
y5	60	70	30.0	211	-3.9	-46.3	-199	*C* effect	-49.8
y6	120	70	30.0	200	-38.1	-107	31.6	t *C* effect	7.9
y7	60	100	30.0	151	-10.8	-34.3	-61.0	T *C* effect	-15.3
y8	120	100	30.0	152	0.4	11.3	45.6	t T *C* effect	11.4

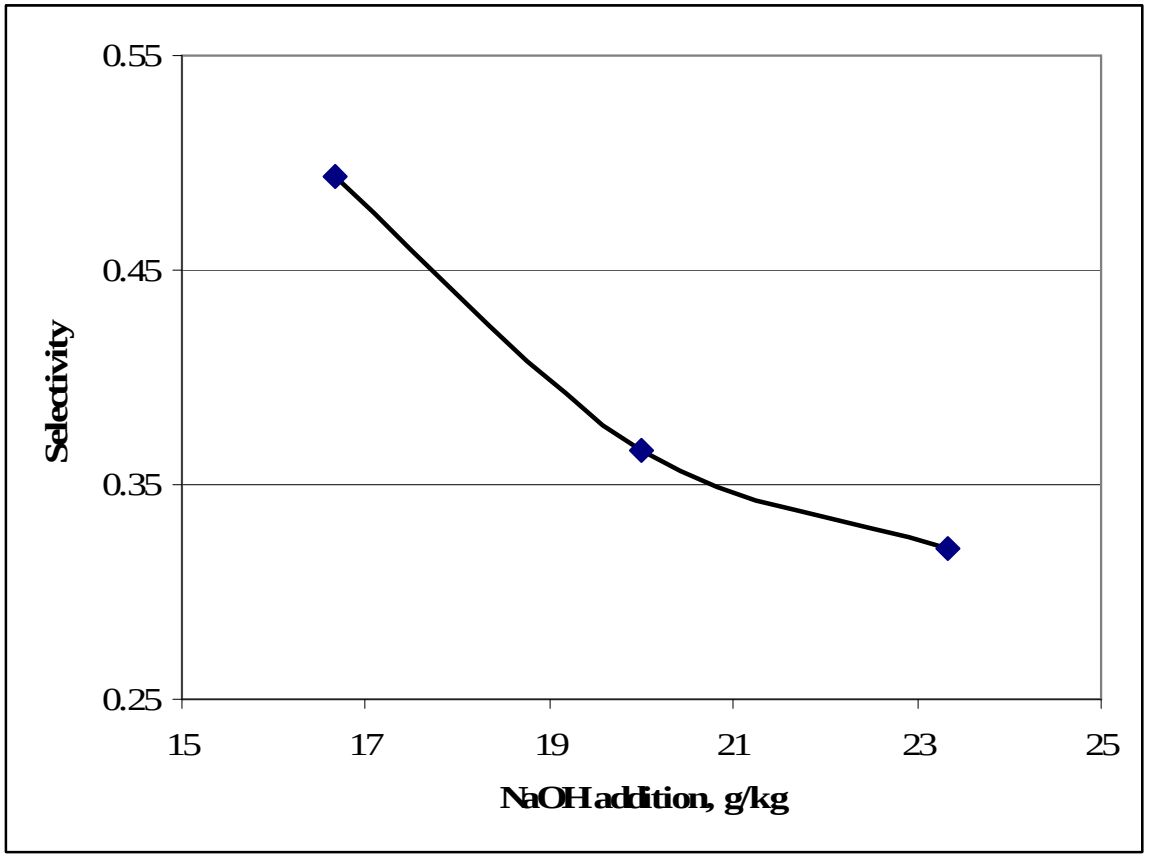
Results - part 1

Yates' algorithm for Kappa number

Exp.	Variables			Kappa #	Calculations			Estimated effects	
	t	T	*C*		1	2	3		
y1	60	70	10.0	8.9	17.0	30.2	58.2	Grand average	7.3
y2	120	70	10.0	8.1	13.2	28.1	-3.0	t effect	-0.7
y3	60	100	10.0	7.3	16.7	-2.2	-9.2	T effect	-2.3
y4	120	100	10.0	5.9	11.4	-0.7	-0.4	t T effect	-0.1
y5	60	70	30.0	8.5	-0.9	-3.8	-2.1	*C* effect	-0.5
y6	120	70	30.0	8.2	-1.3	-5.3	1.5	t *C* effect	0.4
y7	60	100	30.0	5.9	-0.4	-0.5	-1.5	T *C* effect	-0.4
y8	120	100	30.0	5.5	-0.4	0.0	0.5	t T *C* effect	0.1

Results - part 1

OD selectivity – w/o mechanical pretreatment



OD conditions:

- t=90 min
- T=90 °C
- Cons=12 %
- O_2 press=1034 kPa

Yang et al, IECR 2002

Results – part 1

Mill pulp properties (1), *A. mangium*

	Properties	Unit	Pre O_2	Post O_2
1	Kappa number		9.6	4.9
2	Viscosity	cP	23.5	12.4
3	DZSTS	kPa	307	290
4	WZSTS	kPa	269	248
5	Tensile index	Nm/g	6.46	6.95

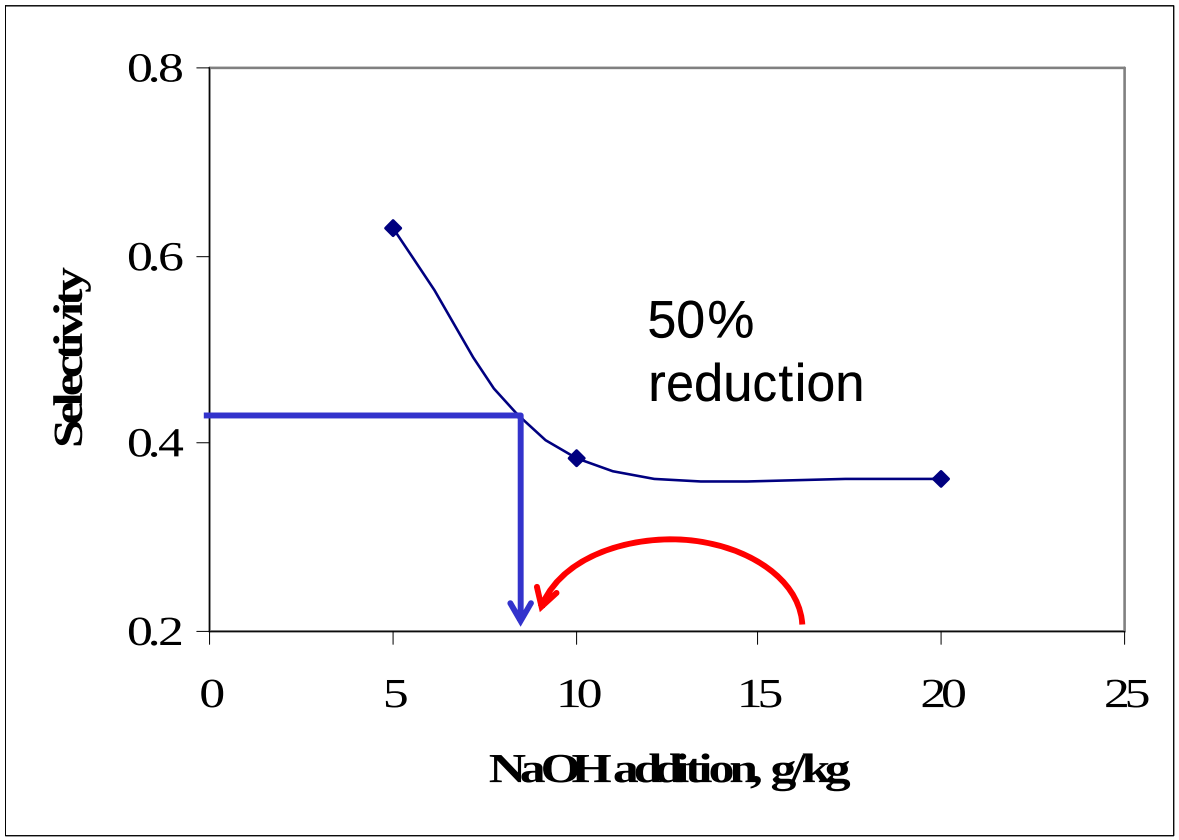
Selectivity
0.42

OD conditions:

- t=120 min
- T=90 °C
- NaOH=16.7 g/kg
- Cons=12 %

Results - part 1

OD selectivity – mechanical pretreatment 15 sec

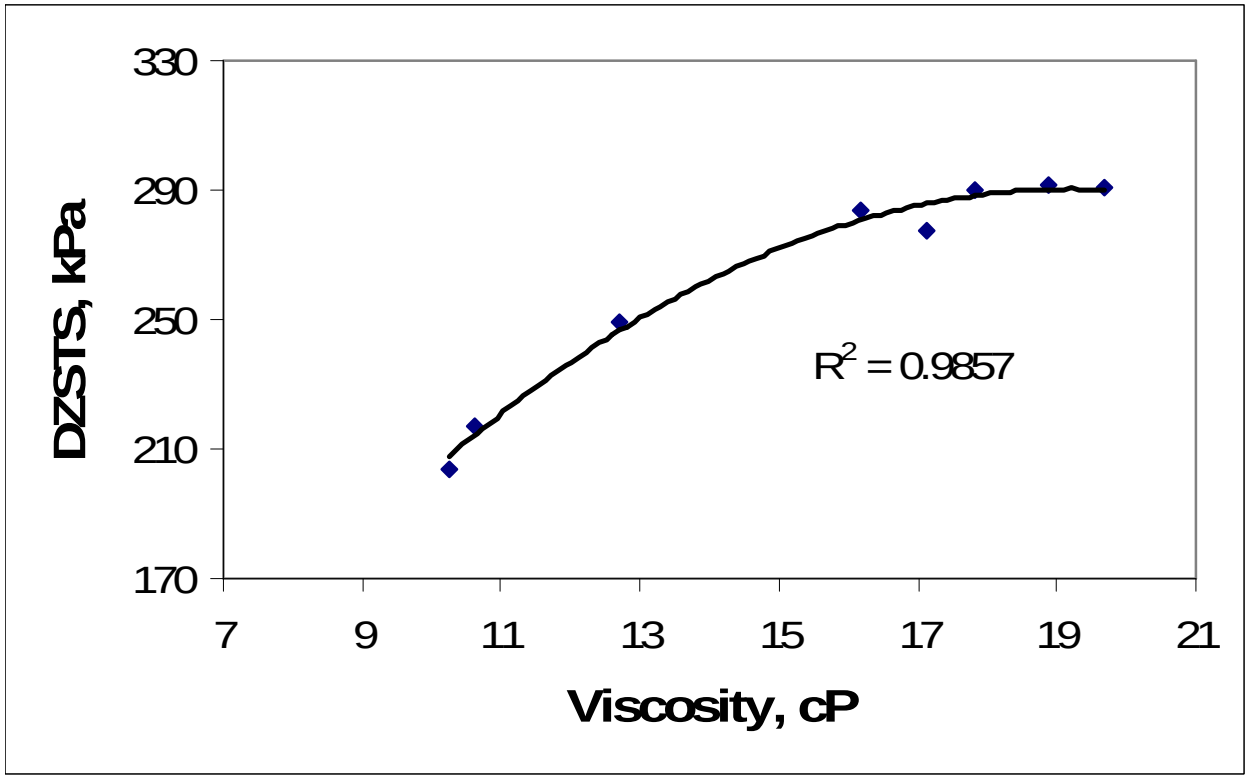


OD conditions:

- t=120 min
- T=90 °C
- Cons=12 %
- O_2 press=1034 kPa

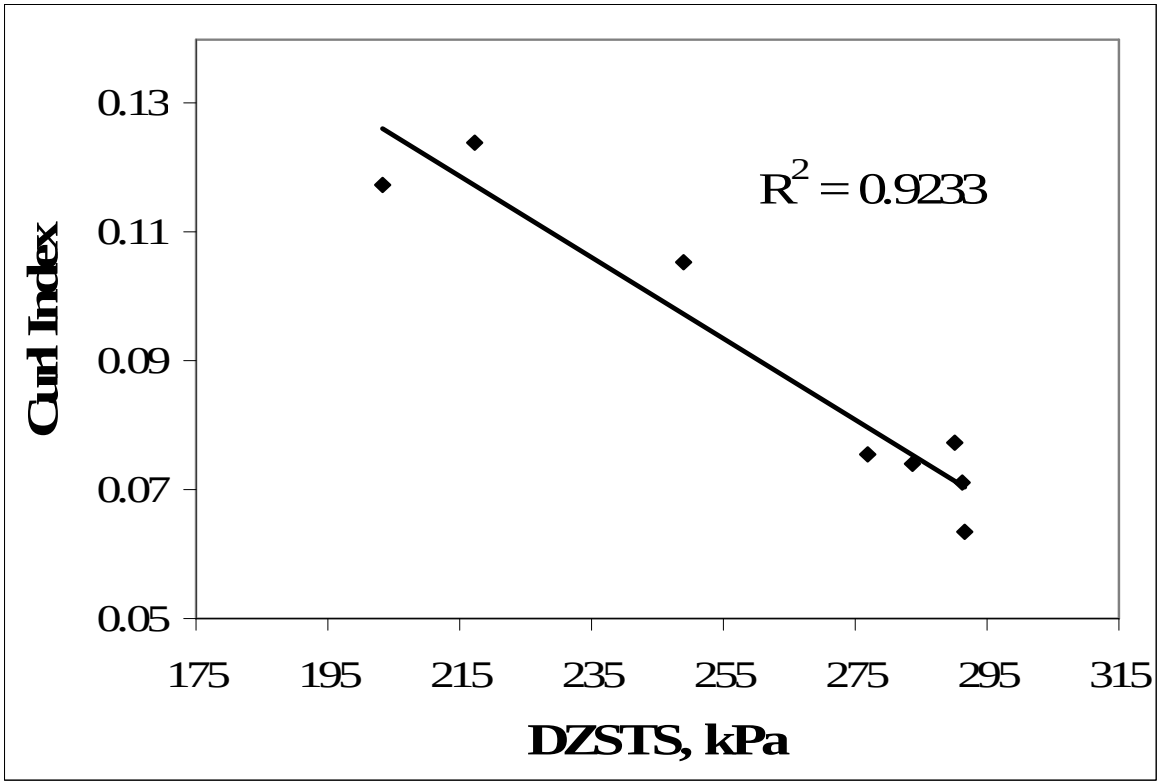
Results - part 1

DZSTS vs viscosity – Yates' data



Results - part 1

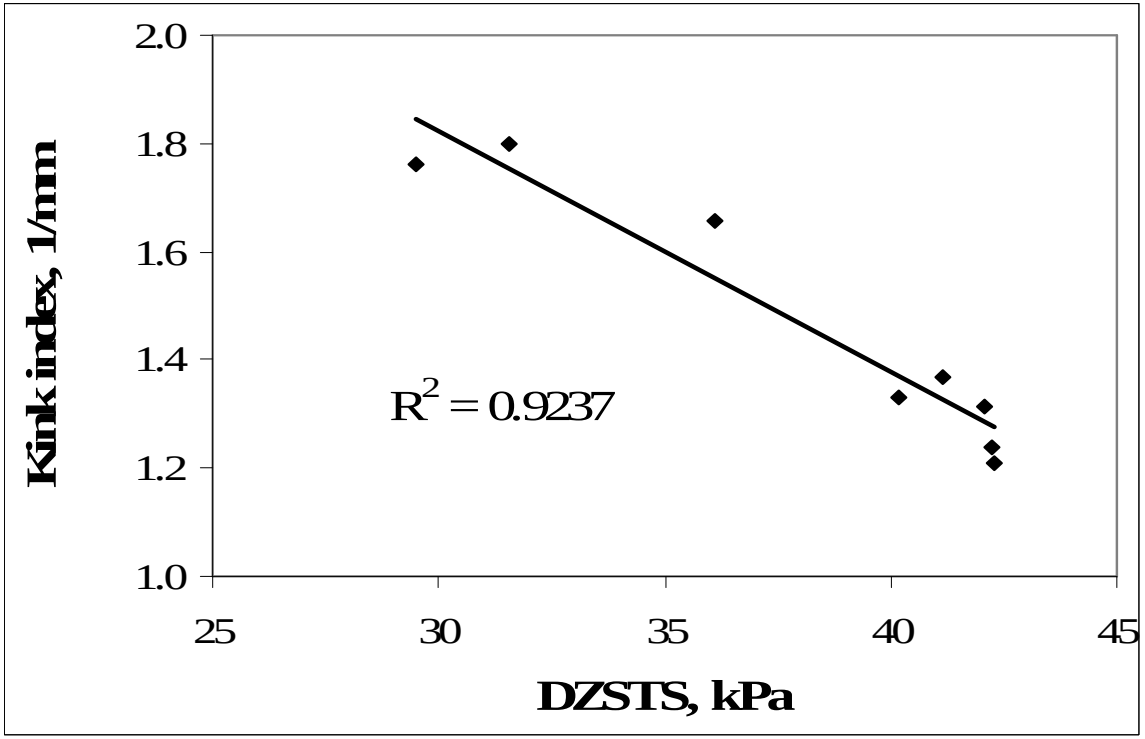
DZSTS vs fiber curl – Yates' data



Mohlin et al,
TAPPI 1996

Results - part 1

DZSTS vs fiber kink – Yates' data



Mohlin et al,
TAPPI 1996

Introduction - 2

- Background
  - *A. mangium* contains extractives twice as much to those of *Eucalyptus* wood (Neto, 2004), and eight times as much to those of MHW (pulp)
- Objective
  - Determine the best pretreatment method prior to OD on extractives removal and selectivity improvement

Results - part 2

Metal profile of A. mangium and MHW kraft pulps

Metal	*A. mangium*, mg/kg	MHW, mg/kg
Cu	4.19	1.69
Fe	7.73	5.34
Mn	2.21	19.4
Mg	38.5	281
Ca	282	2470
Ni	< 0.36	< 0.28
Co	< 0.30	< 0.20

Mg/Mn=40

Mg/Mn=30

Pretreatment in brief

C	1	2	3	4
Pulp	Pulp	Pulp	Pulp	Pulp
$MgSO_4$	Ultrasound 2h	$MgSO_4$	$MgSO_4$	$MgSO_4$
NaOH	washing	70 °C, 2h	NaOH	Mix 5 sec
OD	$MgSO_4$	NaOH	70 °C, 2h	NaOH
	NaOH	OD	OD	OD
	OD			

$MgSO_4$ 0.5%, NaOH 2%, time 1h, temp. 90 °C, cons. 12%, O_2 press. 1034 kPa

Results – part 2

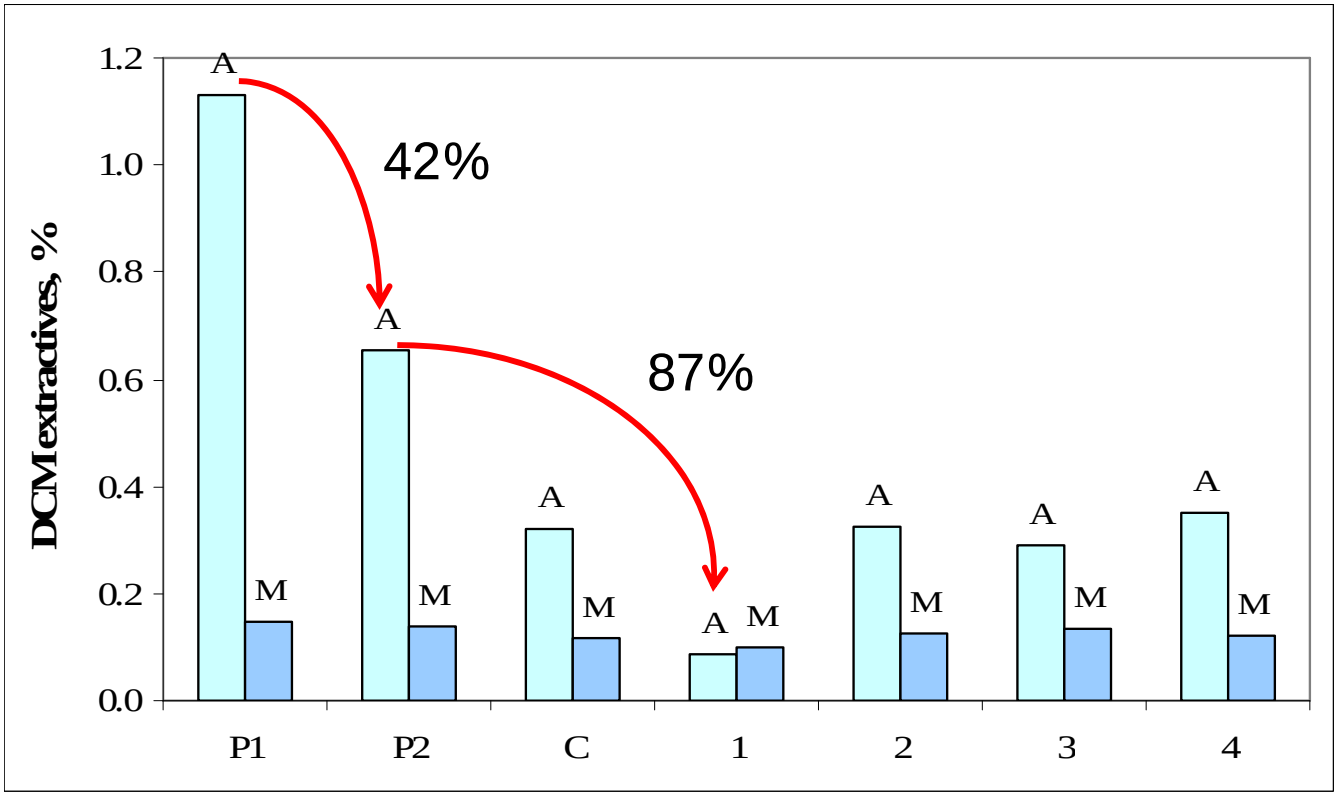
Mill pulp properties (2), pre O_2

	Properties	Unit	*Acacia*	MHW
1	Kappa number		10.7	13.8
2	Viscosity	cP	16.8	10.6
3	DCM extractive	%	1.13	0.15
4	Fiber length	mm	0.69	0.91

8 x

Results - part 2

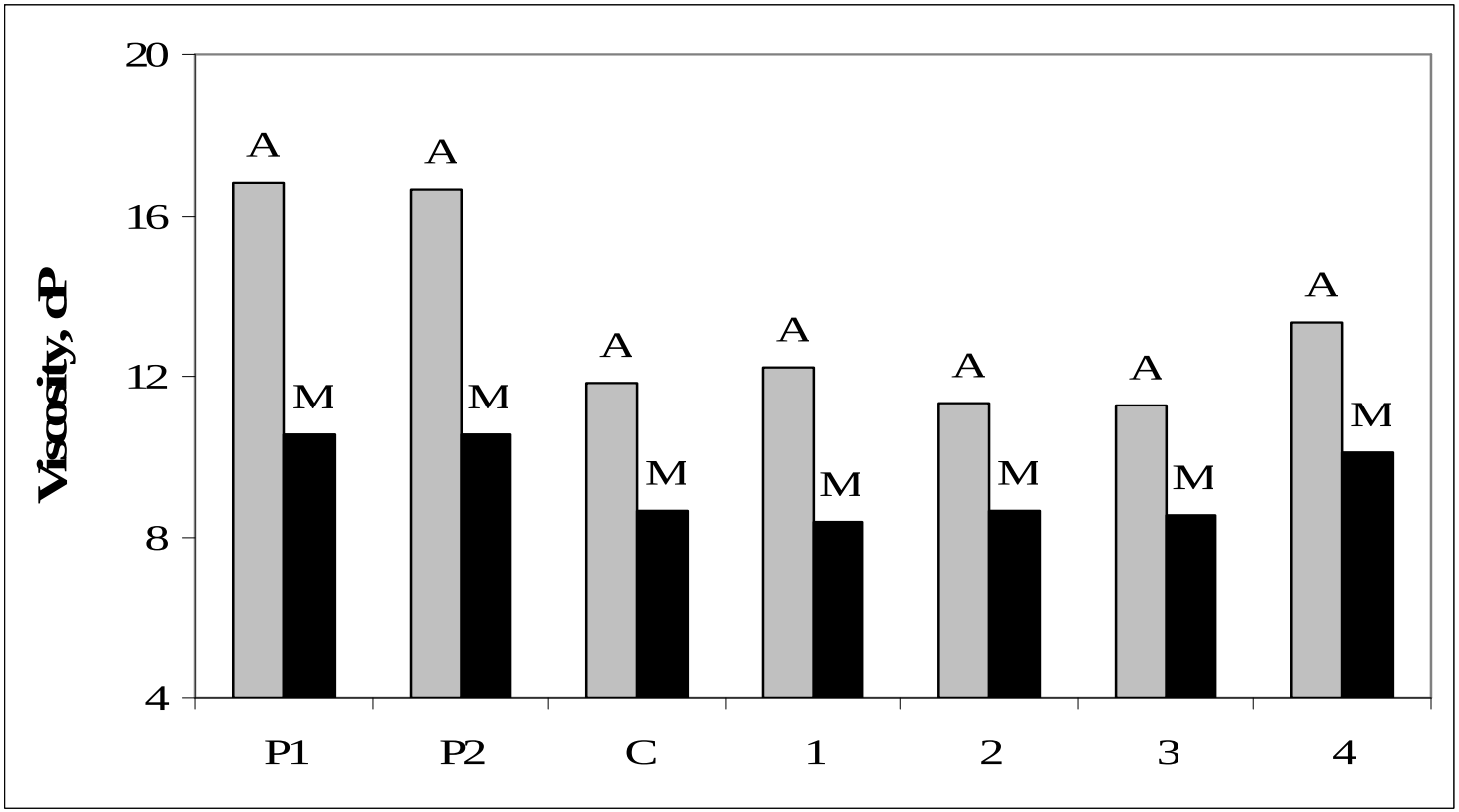
DCM extractives: w/ & w/o pretreatment



P1-pre O_2, P2-pre O_2+ultrasound+wash

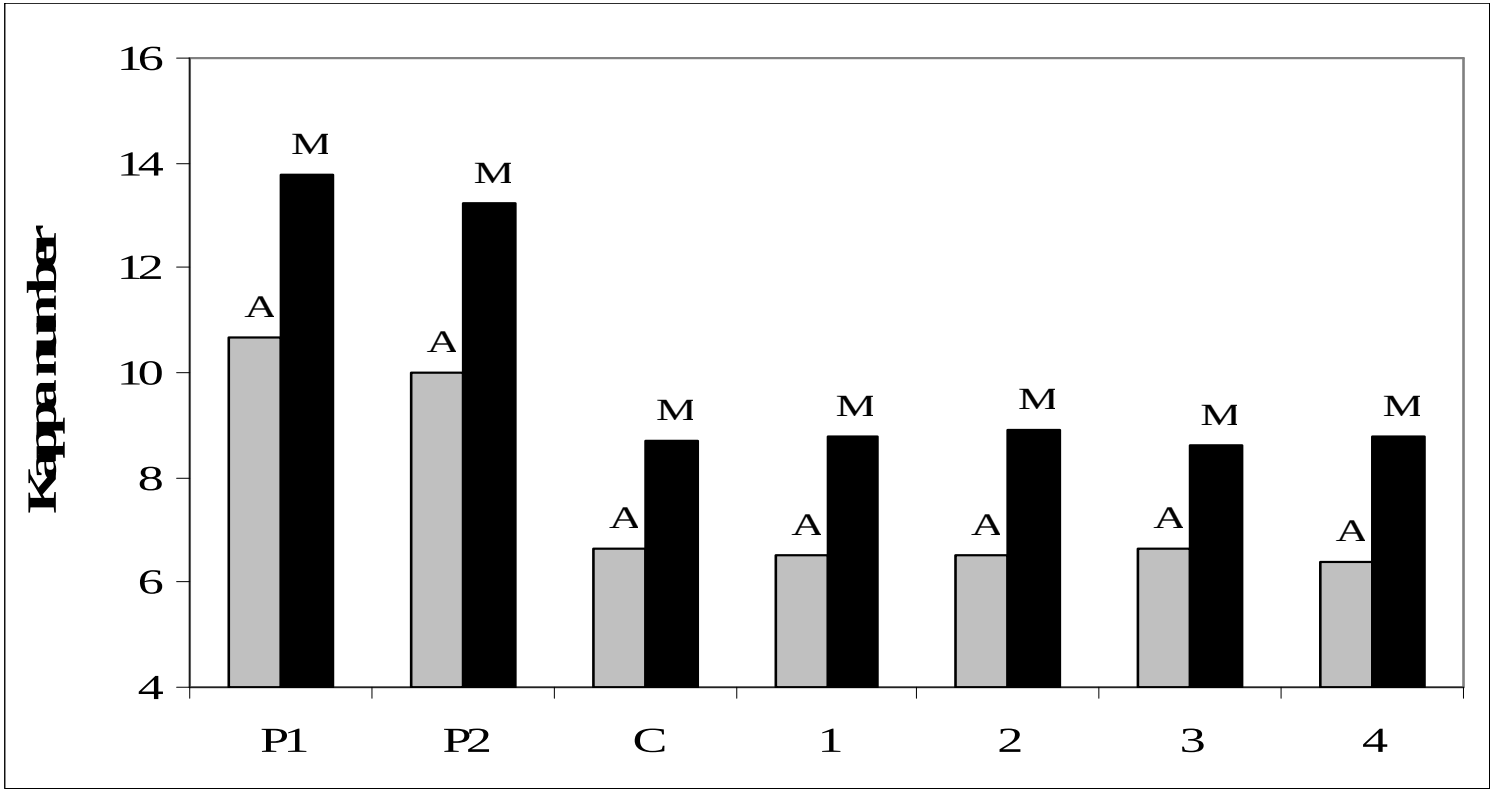
Results - part 2

Viscosity: w/ & w/o pretreatment



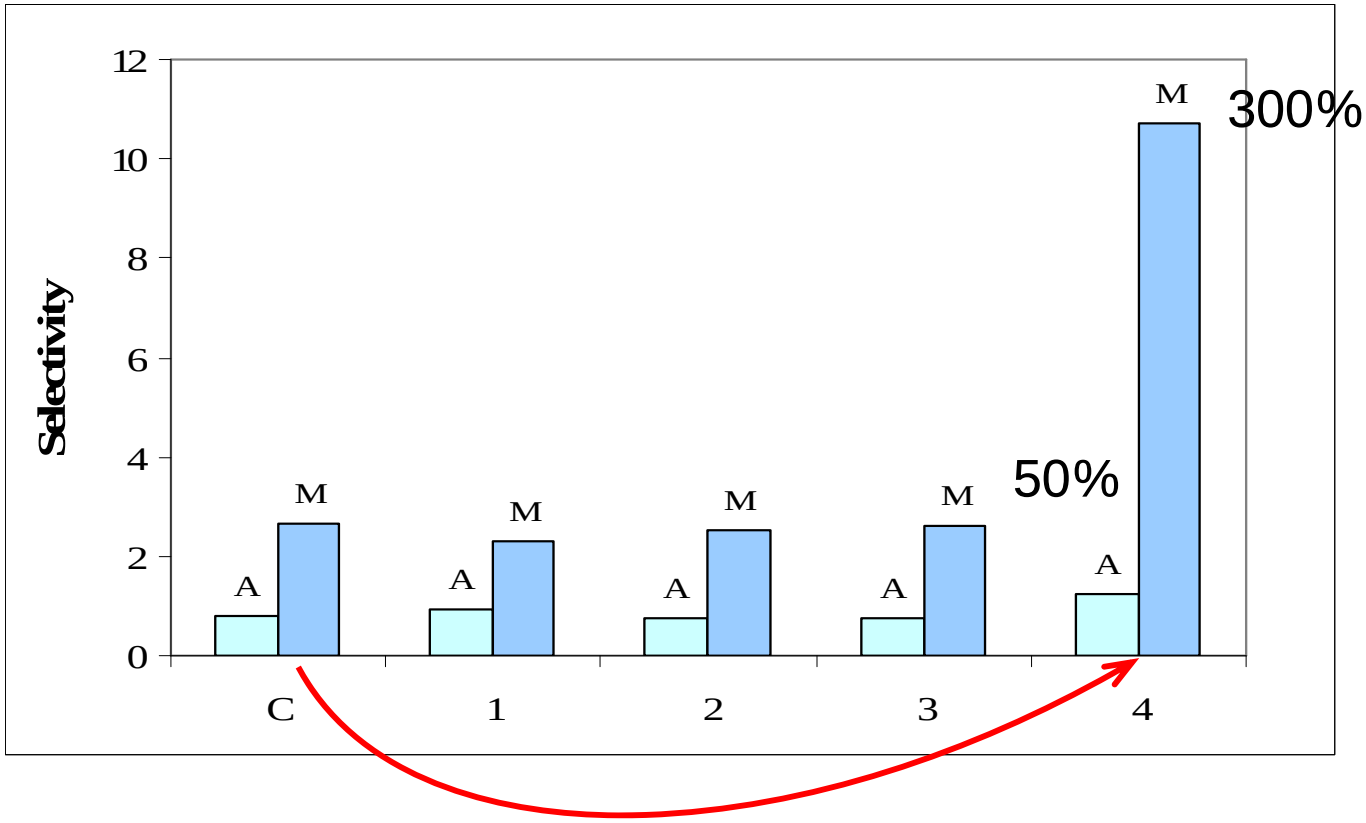
Results - part 2

Kappa number: w/ & w/o pretreatment



Results - part 2

OD selectivity: w/ & w/o pretreatment



Results - part 2

Metal profile of pre O_2 *A. mangium* and MHW kraft pulps

Metal	*A. mangium*, mg/kg	MHW, mg/kg
Cu	4.19	1.69
Fe	7.73	5.34
Mn	2.21	19.4
Mg	38.5	281
Ca	282	2470
Ni	< 0.36	< 0.28
Co	< 0.30	< 0.20

Mg/Mn=40

Mg/Mn=30

Yang et al,
TAPPI 2001

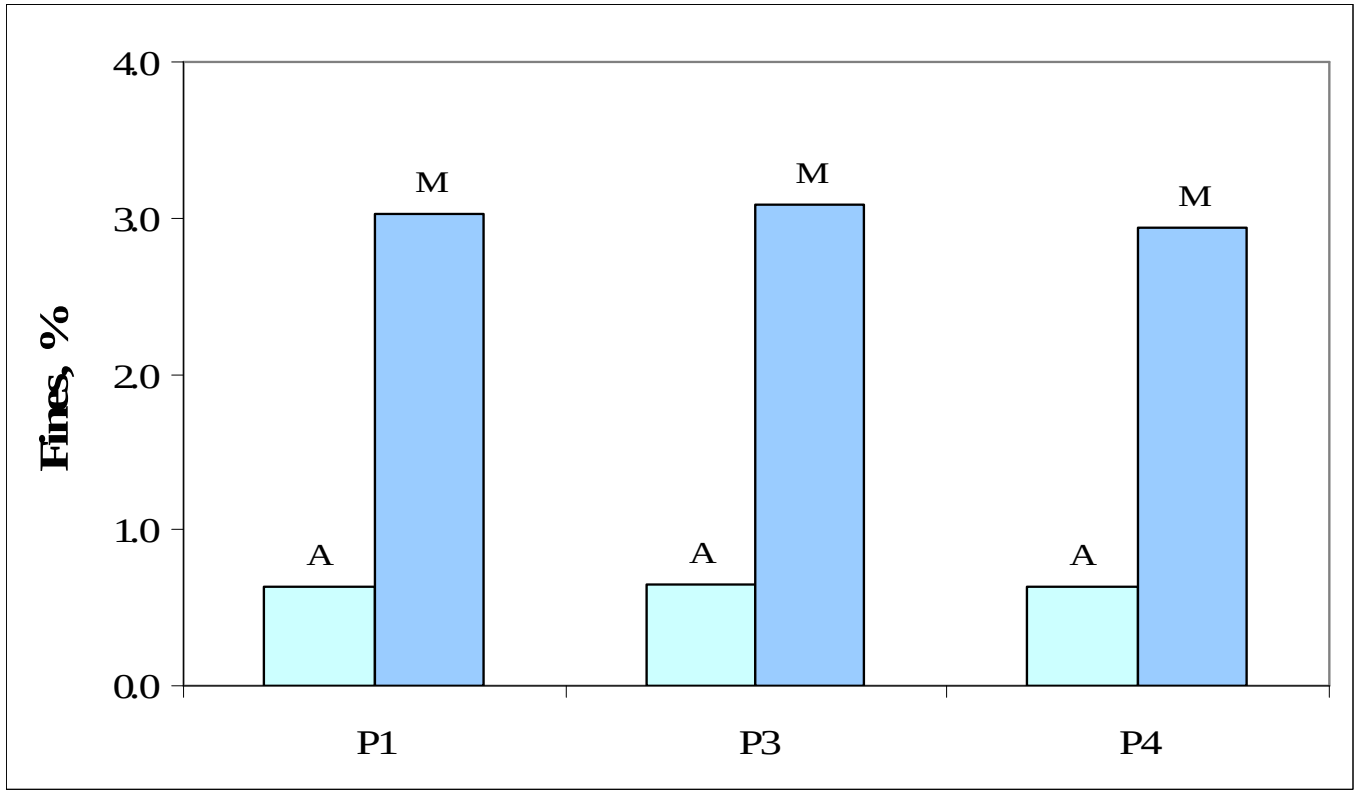
Pretreatment in brief

C	1	2	3	4
Pulp	Pulp	Pulp	Pulp	Pulp
$MgSO_4$	Ultrasound 2h	$MgSO_4$	$MgSO_4$	$MgSO_4$
NaOH	washing	70 °C, 2h	NaOH	Mix 5 sec
OD	$MgSO_4$	NaOH	70 °C, 2h	NaOH
	NaOH	OD	OD	OD
	OD			

$MgSO_4$ 0.5%, NaOH 2%, time 1h, temp. 90 °C, cons. 12%, O_2 press. 1034 kPa

Results - part 2

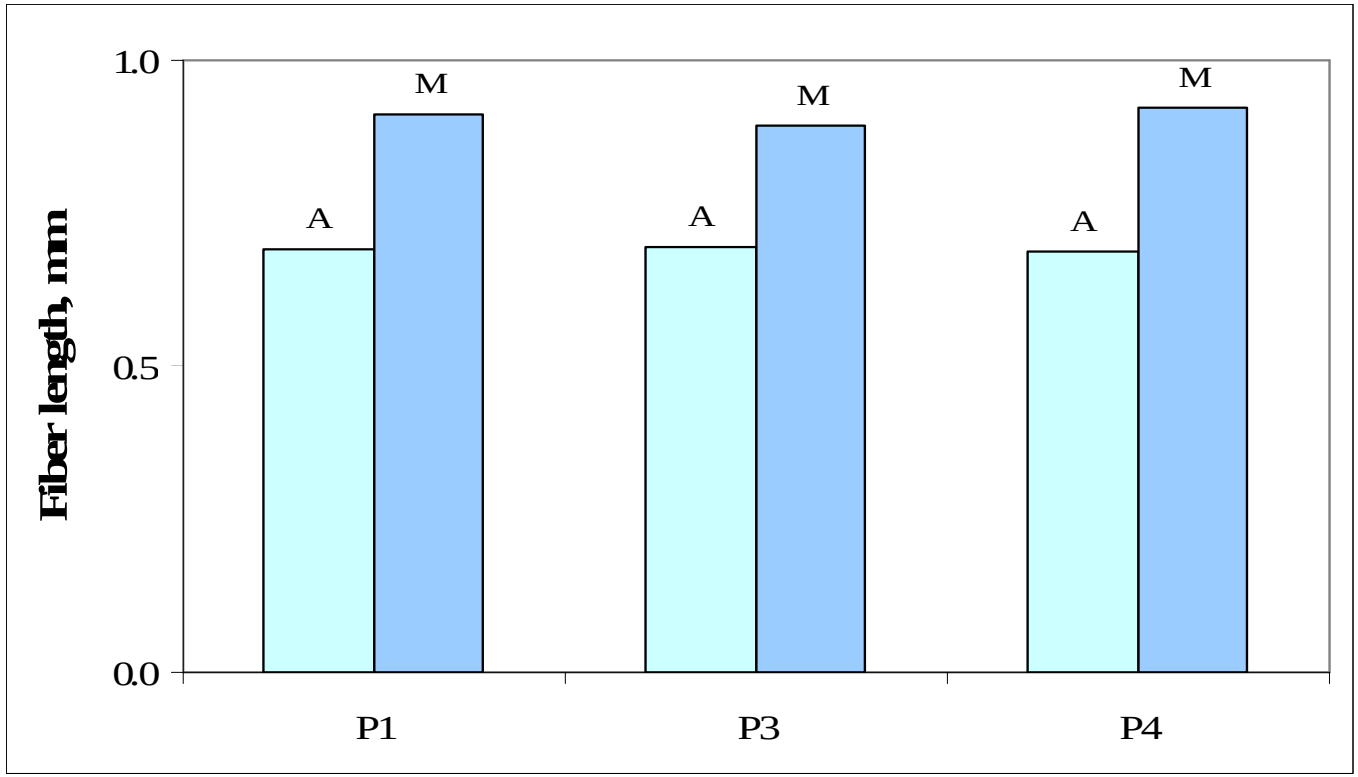
Pre O_2 fines: ultrasonic & mechanical pretreatment



P1-pre O_2, P3-pre O_2+ultrasound, P4-Pre O_2 mechanical pretreatment

Results - part 2

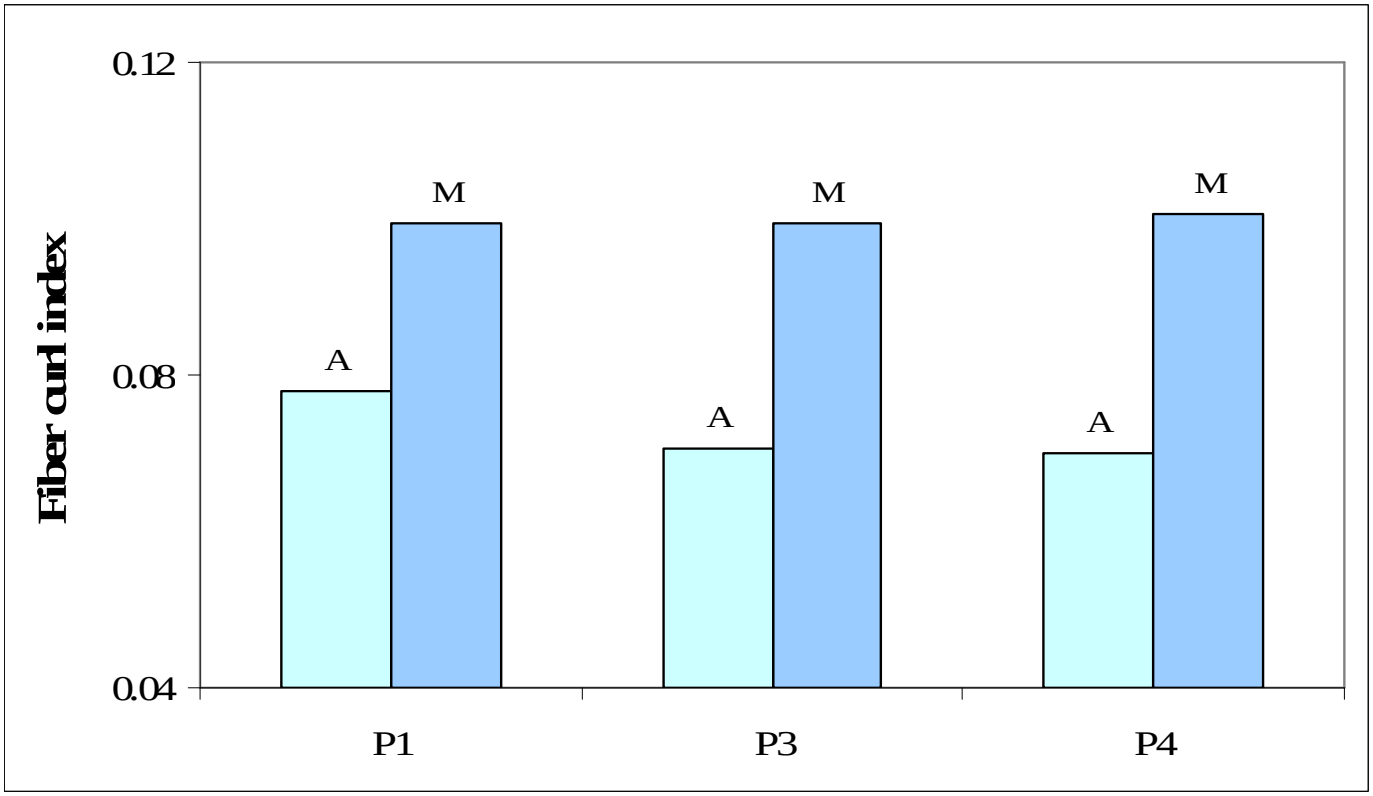
Pre O_2 fiber length: ultrasonic & mechanical pretreatment



P1-pre O_2, P3-pre O_2+ultrasound, P4-Pre O_2 mechanical pretreatment

Results - part 2

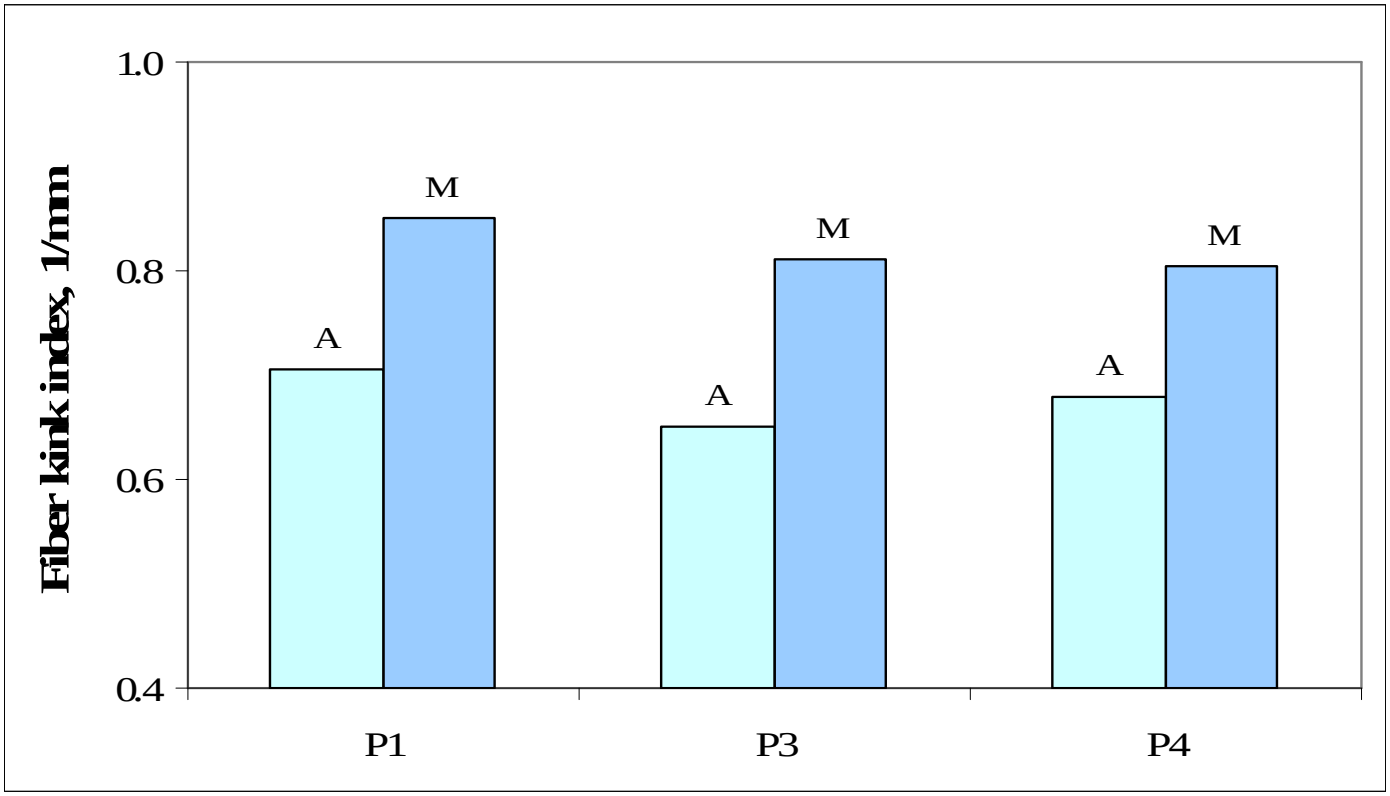
Pre O_2 fiber curl: ultrasonic & mechanical pretreatment



P1-pre O_2, P3-pre O_2+ultrasound, P4-Pre O_2 mechanical pretreatment

Results - part 2

Pre O_2 fiber kink: ultrasonic & mechanical pretreatment



P1-pre O_2, P3-pre O_2+ultrasound, P4-Pre O_2 mechanical pretreatment

Conclusions

- Alkali charge was found to be the most pronounced factor affecting the pulp strength
- Alkali charge can be reduced by 50% by applying 15s mechanical pretreatment prior to OD to get similar selectivity to that of mill
- Extractives removal increased by 60 and 15% for *A. mangium* and MHW pulps, respectively, by applying ultrasonic pretreatment followed by washing prior to OD
- OD selectivity increased by 50 and 300% for *A. mangium* and MHW pulps, respectively, by applying mechanical pretreatment prior to OD