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ANTHRAQUINONE-AIDED HYDROGEN PEROXIDE REINFORCED OXYGEN DELIGNIFICATION OF OIL PALM (*Elaeis guineensis*) EFB PULP: A TWO-LEVEL FACTORIAL DESIGN

SOO HUEY NG, ARNIZA GHAZALI and CHEU PENG LEH

Bioresource, Paper and Coatings Technology Division, School of Industrial Technology,
University Sains Malaysia, 11800 Minden, Penang, Malaysia

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The study investigates the effect of anthraquinone towards hydrogen peroxide reinforced oxygen delignification on oil palm (*Elaeis guineensis*) empty fruit bunch soda-AQ pulp. The individual and interaction effects of H_2O_2 and anthraquinone and three other process variables – the reaction temperature, time and alkaline charge – were statistically examined by a two-level half factorial experimental design. The factorial models built for four responses – kappa number, pulp viscosity, brightness and selectivity – showed that H_2O_2 had the greatest effect on all responses.

Moreover, the response surface of the factorial models showed that the addition of a low amount of anthraquinone (0.02% on the oven-dry weight of pulp) in the O_P-stage, even without improving kappa number reduction, significantly countered impairment to pulp viscosity by a relatively higher level of H_2O_2 (2.0% on the oven-dry weight of pulp). Besides, a sufficient alkali charge was necessary for H_2O_2 reinforced oxygen delignification and uncontrollable viscosity drop.

Keywords: peroxide reinforced oxygen delignification, anthraquinone, factorial designs, oil palm EFB, delignification, pulp viscosity

INTRODUCTION

In 2008, palm oil, including palm kernel oil, contributed to 30% of the total world oil production. On top of edible oil, massive amounts of lignocellulosic residues are generated by the palm oil industry. Among the various types of oil palm residues, the oil palm fruit bunches, previously steamed and stripped of their fruit for oil production (known as empty fruit bunches, EFB), is the most promising raw material for pulp and paper production, since it has the economical advantage of being readily collected at the palm oil mills, being available throughout the year.[1]

Since the late 1990s, various types of pulps, including cellulose (dissolving) pulp have been produced from oil palm EFB.[2,3] Besides the unbleached pulps, fully bleached pulps, with a brightness of up to 80% ISO, as well as cellulose pulp with a brightness of even up to 90% ISO, may be also produced by TCF bleaching sequences, involving oxygen (O), ozone (Z) and hydrogen peroxide (P) stages.[4,5]

As the lignin content of EFB is quite low – ranging between 17 and 19% –, the kappa number of its chemical unbleached pulps is normally below 15. However, pulp viscosity is considered quite low – the highest value being of about 26 cP for kraft-AQ pulp.[4] Based on a previous study,[6] to attain an ISO brightness above 80%, a TCF bleaching sequence containing the Z-stage is necessary. Since the Z-stage requires very high investment costs for the ozone generator and its auxiliary equipments, as well as rather high operating costs (due to high power consumption), the establishment of a small-scale pulp mill, using EFB as raw material and a simple TCF bleaching sequence without the Z-stage, should be recommended.

According to Sippola and Krause,[7] for enhancing the effectiveness of TCF bleaching of EFB pulp, an improvement of the degree of delignification in the first bleaching stage is essential. Among the chlorine-free bleaching stages, oxygen delignification (O) has the highest potential for the first stage of TCF bleaching, since it allows the removal of up to 50% of residual lignin from the pulp, without significantly reducing pulp strength. However, compared to the conventional chlorination (C) and chlorine dioxide (D) stages, the selectivity of the O stage remains relatively low.[8,9] Previous work[10] has shown that kappa number reduction of the soda-AQ EFB pulp by the O stage should be limited to no more than 38%, for preventing significant losses in pulp viscosity.

For attaining a more efficient TCF bleaching, in the last three decades, numerous studies have been devoted to the enhancement of oxygen delignification, and many attempts involved the addition of hydrogen peroxide (H_2O_2) during the O stage, known as peroxide reinforced oxygen bleaching – O_P. The results have shown that the O_P stage improves the delignification rate and maintains pulp viscosity at an acceptable level.[11-15] However, to preserve a high viscosity, a small amount of H_2O_2 (less than 0.5% on oven-dry pulp) should be added, since any further increase of the H_2O_2 charges reduces viscosity, comparatively with the conventional O stage.[9]

On the other hand, the application of a pre-treatment, such as chelation,[13,14] assures a higher charge of H_2O_2 (1.0% on oven-dry pulp) during the O_P stage, which removes up to 65% of the residual lignin and maintains a substantially higher viscosity of the softwood kraft pulp. Besides, higher pulp viscosity could be preserved by adding a heterocyclic aromatic nitrogen compound in the O_P stage.[14] However, the authors also stated that the addition of 0.3% phenanthroline may cause an increase of about 30% in the NOx discharge from the recovery boiler.

To attain the beneficial effect of H_2O_2 upon delignification and pulp brightness, H_2O_2 charges higher than 0.5% are recommended. However, in the absence of any pre-treatment, a substantial loss of pulp viscosity is inevitable. To minimize cellulose deterioration in a peroxide-oxygen system applied to oil palm EFB soda-anthraquinone pulp, in the present investigation, an attempt was made at adding anthraquinone (AQ) to the system. For multivariable heterogeneous reaction processes, such as pulping and pulp bleaching, the effect of a single independent variable is not comparable, unless all the other conditions remain constant. For a simultaneous determination of the main effects of each independent variable, and also of all possible interaction effects, the application of an experimental design to built mathematical models is easier and more practical than the conventional method based on the process kinetics.[3,16,17]

According to Montgomery,[18] a half factorial design is as good as a full factorial one, for estimating all the main effects and two-factor interactions, on assuming, nevertheless, that the higher interactions are negligible. This design is suitable as a screening experiment to identify and eliminate unimportant factor(s), especially before conducting the response surface study. Thus, in the present investigation, a two-level half factorial design was used to analyze the effect of five bleaching variables – the H_2O_2 charge and percent of AQ, reaction temperature, reaction time, and NaOH charge – on three pulp properties: kappa number, pulp viscosity and brightness.

MATERIALS AND METHOD

Materials

The oil palm empty fruit bunch (EFB) fibre was provided by EcoFibre Bhd., Johore, Malaysia, in the Ecomat® formation. The EFB was soaked in water for one day and washed, in order to remove contaminants (such as sand, dust and oil), then air-dried and kept in plastic bags prior to pulping.

Preparation of unbleached pulp

Pulping of EFB was carried out in a 4 L stationary stainless steel digester (with neither external circulation mixing nor internal agitation), manufactured by NAC Autoclave Co. Ltd., Japan, fitted with a microcomputer-controlled thermocouple.

250 g of oven-dried (o.d.) EFB were placed in the digestion vessel and then sodium hydroxide (25% or calculated as active alkali – 19.4% on the o.d. raw material), anthraquinone (0.1% on o.d. raw material) and distilled water were added, to reach a material-to-liquor ratio of 1:7. The material in the vessel was squeezed to ensure that it was completely soaked in the liquor, for assuring homogeneous cooking. The digester was then heated to 160 °C, at a time-to-temperature of 90 min and a time-at-temperature of 120 min. Upon completion of pulping, the resulting pulp was collected and defiberized in a hydro-pulper for 10 min, for removing the redeposited dissolved lignin from the pulp surface, and thoroughly washed with tap water in a stainless

steel mesh filter. Finally, the pulp was screened through a 0.15 mm Somerville flat-plate screen.

Oxygen delignification

Oxygen delignification was carried out in a 650 mL stainless steel autoclave, equipped with a gas inlet and a stirrer, manufactured by the Parr Instrument Company, U.S.A. Then, 22 g (o.d.) of the above-mentioned pulp were mixed with different ratios of $MgSO_4$, NaOH, H_2O_2 and AQ (as listed in Table 1 for a preliminary study and in Table 2 for the two-factorial designs); these mixtures were adjusted to 10% consistency, by using distilled water. After placing the fibre-chemical mixture in the autoclave, the cover was fastened and the air in the autoclave was replaced by oxygen through the gas inlet, pressure inside the autoclave being kept at 689.48 kPa for appropriate temperature and time values, as shown in Tables 1 and 2. After delignification, the reactor was cooled and the oxygen pressure was released. The pulps were then washed, spin-dried and analysed to determine their properties.

Pulp properties

The oxygen delignified pulps were analysed by the TAPPI Useful Method UM-246 Micro Kappa Number – to find the kappa number, JPRI Standard 3015 (a modified method of TAPPI Standard T230 su-66) – to establish pulp viscosity, and TAPPI T218 om-02 – to determine pulp brightness. Bleaching selectivity was calculated as the ratio of Δ kappa number to Δ pulp viscosity (cP).

Experimental design

Based on the positive results obtained from the preliminary study on the effect of H_2O_2 and AQ addition during oxygen delignification, the following five variables were analysed: percentage of H_2O_2 (P), reaction temperature (T), reaction time (t), alkali charge (A_c) and percentage of AQ (A_q). Also, two-level half factorial (2^{k-1}) designs were used to statistically determine the factors that influence most decisively oxygen delignification. The quality of the oxygen delignified pulps was identified *via* four response variables: kappa number (K_n), pulp viscosity, brightness and selectivity. Table 2 shows the twenty experimental conditions established for the statistical software Design-Expert® by Stat-Ease, Inc. USA, according to 2^{5-1} half fraction designs (32 by 2 = 16 designs) with four blocking plans, plus one central point in each block (4 central points). The real and coded values of the independent variables are shown in Table 2, the latter being calculated with Eqs. 1 through 5:

$$P_{code} = \frac{(H_2O_2 - 1.0\%)}{1.0\ \%} \qquad \text{Eq. 1}$$

$$T_{code} = \frac{(\text{Temp.} - 92.5\ °C)}{7.5\ °C} \qquad \text{Eq. 2}$$

$$t_{code} = \frac{(\text{Time} - 45\text{min})}{15\ \text{min}} \qquad \text{Eq. 3}$$

$$A_{C\,code} = \frac{(\text{NaOH} - 2.0\%)}{0.5\%} \qquad \text{Eq. 4}$$

$$A_{q\,code} = \frac{(\text{AQ} - 0.01\%)}{0.01\%} \qquad \text{Eq. 5}$$

RESULTS AND DISCUSSION

Preliminary study

In the preliminary study on oxygen delignification (the O-stage), several tests with or without H_2O_2 and AQ were carried out. The results revealed that, without H_2O_2 and AQ, the selectivity of oxygen delignification decreased from 2.55 to 1.60, while the alkali charge (A_C) increased from 1.5 to 2.5% (Table 1). Quite notably, a further increase of A_C contributes to decreasing pulp viscosity, even if the kappa number (K_n) is also reduced. Similar to a previous work,[10] EFB soda-AQ pulp delignification by oxygen was limited to 38% (condition II), while the further reduction of lignin, up to 42%, significantly degraded the cellulose.

As already mentioned, many studies[8,9,19] have reported that the conventional O-stages are capable of removing up to 50% of the lignin content, without seriously degrading cellulose. The lower delignifying ability of the O-stage could be due to the elimination of one of the most reactive O-stage sites, the phenolic lignin units.[19] Extended delignification, through anthraquinone addition, to a pulping process is achieved by enhancing the cleavage of the β-O-4 ether linkages in free phenolic lignin structures.[20,21]

As expected, the addition of H_2O_2 greatly improved pulp brightness: comparatively with condition II, the brightness values of conditions IV and V were more than 5 points higher (Table 1). H_2O_2 is a well-known brightening agent that eliminates the chromophoric structures in pulp. The addition of H_2O_2 also increased K_n reduction by up to 14%. Based on selectivity, condition IV, with only 0.8% H_2O_2, gave the best results, while the higher H_2O_2 charge (2 %) of condition V accelerated cellulose degradation, contributing less to K_n reduction, which resulted in a selectivity of only 1.89, while selectivity for condition IV was of 2.31.

The effects of AQ addition during the O-stage were shown by conditions VI and VII. The small amount (0.02%) of AQ added under condition VI favoured K_n reduction and pulp brightness, comparatively with condition II. However, since the pulp viscosity of condition VI was lower than that of condition II, a slightly lower selectivity was observed. Nevertheless, the addition of AQ improved the delignification of the O-stage since, without AQ, K_n was 8.2, with a pulp viscosity of 11.6 cP. for condition III (with 2.5 percent A_C), whereas, under condition VI, with AQ present, K_n was 7.8 and viscosity remained at 12.0 cP.

The positive effects of AQ in the O-stage were not as strong without the presence of magnesium sulphate, as shown by condition VII in Table 1. This indicates that the presence of AQ is unable to retard cellulose degradation, due to the presence of transition metal ions that catalyse the formation of reactive radicals. Since radicals, such as hydroxyl and its ionized radicals (HO· and $O\cdot^-$), attack both the carbohydrate and lignin, a lower K_n was obtained under condition VII, accompanied by low pulp viscosity.

The combined effects of H_2O_2 and AQ during the O-stage were demonstrated by condition VIII (Table 1). Since the reaction time and temperature for this condition were of only 30 min and 90 °C, respectively, K_n was not as low as the values for conditions IV and VI, where either H_2O_2 or AQ were used alone. However, comparatively with the cases where neither H_2O_2 nor AQ was added, the addition of both H_2O_2 and AQ gave a higher bleaching effectiveness and selectivity.

Statistical study on the effects of the bleaching variables

In order to statistically verify the significance of the effects of H_2O_2 and AQ on the O-stage K_n reduction and pulp viscosity, a half two-factorial design was employed. Apart from the H_2O_2 and AQ concentrations, the other three independent variables – reaction temperature, reaction time and A_c – were also investigated. In addition, the interactions between the five variables could be calculated with the software Design-Expert® by Stat-Ease, Inc. USA.

The results for the four response variables – K_n, pulp viscosity, brightness and selectivity – are presented in Table 2 based on a 2^{5-1} factorial design. For each response variable, the effects of the individual variables or the effects of the combinations of two or three variables (combined variables) were presented in a half normal probability plot, with a statistical software. The variables or the combinations of variables that produce notable effects were shown as high absolute values, occurring as outliers (not in the linear plot) in the graph. By selecting these outlier points, the linear line of the probability plot would cover and pass through all the other points near zero (insignificant variables). A factorial model of each response variable was built, based on the selected and combined variables.

Table 3 presents the factorial models built from the variables and combined variables and their corresponding significant coefficient (CE) for the four responses. It could be seen that all factorial models were polynomial equations with second order terms (combined variables or interaction effects). Based on both ANOVA and statistical analysis, each of the four factorial models was significant with values of "prob. >F" below 0.05 and a regression (R^2) close to 1 (Table 4).

Kappa number

The factorial model of K_n (Eq.6), shown in Table 3, revealed that each of the five variables produced a significant effect, with P the most influential variable, followed by A_C and T. Since the significant coefficient (CE) for all five variables takes negative values, the increase of all variables will significantly improve the degree of delignification. A sample of a three-dimensional response surface plot of K_n as a function of P and A_c, shown in Figure 1, indicates that these two variables have the strongest influence on the response. It was also found out that the increases of P and A_C substantially decreased the value of K_n. Since no significant interaction occurred between P and A_C, as determined by its factorial model, the three-dimensional surface plot of K_n showed linear slopes even when the variables moved from the region of low PA_C towards that of high PA_C.

The increase in the amount of P apparently decreased the value of K_n, arising from the increase of the hydroperoxy and hydroxyl radicals (HOO, HO) generated by the decomposition of the added H_2O_2. These radicals act as delignifying species especially when the reaction temperature is substantially high (over 90 ºC).

Table 1
Preliminary study on H_2O_2 and anthraquinone addition during oxygen delignification of EFB soda-AQ pulp

No.	Conditions Re								sponses		
	Alkali charge, %	Temp., °C	Time, min	$MgSO_4$, %	H_2O_2, %	AQ	Kappa number, K_n	Pulp viscosity, cP	Brightness, %	K_n Reduction, %	Selectivity
Unbleached -		-	-	-	-	-	14.2	15	44.26	-	-
I 1.	5	95	60	0.5	0	0	9.1	13	51.88	35.92	2.55
II 2		95	60	0.5	0	0	8.8	12.5	52.7	38.03	2.16
III 2.5		95	60	0.5	0	0	8.2	11.6 55.11		42.25	1.60
IV 2		95	60	0.5	0.8	0	7.5	12.1	58.3	47.18	2.31
V 2		95	60	0.5	2	0	6.8	11.1	62.32	52.11	1.89
VI 2		95	60	0.5	0	0.02	7.8	12	54.9	45.07	2.13
VII 2		95	60	0	0	0.02	7.4	11.6	56.23	47.89	2.00
VIII 2		90	30	0.5	0.92	0.02	8.1 12.8		58.06	42.96	2.77

Table 2
2^{5-1} Design from Design-Expert®

Std. ord.	Coded Variable					Variable					Response			
	P T		t	A_c	A_q	H_2O_2, %	Temp., °C	Time, min.	NaOH, %	AQ, %	Kappa number, K_n	Pulp viscosity, cP	Brightness, %	Selectivity
1 -1		-1	-1	-1	-1	0.0	85.0	30	1.5	0.00	10.2	14.0	47.76	4.00
2 1		-1	-1	-1	1	2.0	85.0	30	1.5	0.02	8.0	12.6	62.88	2.58
3 -1		1	-1	-1	1	0.0	100.0	30	1.5	0.02	8.2	12.4	52.22	2.31
4 1		1	-1	-1	-1	2.0	100.0	30	1.5	0.00	7.2	9.6	62.12	1.30
5 -1		-1	1	-1	1	0.0	85.0	60	1.5	0.02	9.1	13.7	51.33	3.92
6	1	-1	1 -1		-1 2.	0	85.0	60	1.5	0.00	7.6	11.6	63.78	1.94
7	-1	1	1 -1		-1 0.	0	100.0	60	1.5	0.00	8.9	13.2	51.71	2.94
8 1		1	1	-1	1	2.0	100.0	60	1.5	0.02	6.7	10.2	62.21	1.56
9 -1		-1	-1	1	-1	0.0	85.0	30	2.5	0.00	9.0	13.3	50.70	3.06
10 1		-1	-1	1	1	2.0	85.0	30	2.5	0.02	6.9	11.6	62.34	2.15
11 -1		1	-1	1	1	0.0	100.0	30	2.5	0.02	7.6	11.6	53.74	1.94
12 1		1	-1	1	-1	2.0	100.0	30	2.5	0.00	6.2	11.0	63.58	2.00
13 -1		-1	1	1	1	0.0	85.0	60	2.5	0.02	8.2	13.0	53.51	3.00
14 1		-1	1	1	-1	2.0	85.0	60	2.5	0.00	6.8	11.2	61.89	1.95
15 -1		1	1	1	-1	0.0	100.0	60	2.5	0.00	7.4	11.6	53.80	2.00
16 1		1	1	1	1	2.0	100.0	60	2.5	0.02	6.2	11.3	66.63	2.16
17 0		0	0	0	0	1.0	92.5	45	2.0	0.01	7.4	12.0	57.90	2.27
18 0		0	0	0	0	1.0	92.5	45	2.0	0.01	7.2	12.1	59.47	2.41
19 0		0	0	0	0	1.0	92.5	45	2.0	0.01	7.2	12.2	59.36	2.50
20 0		0	0	0	0	1.0	92.5	45	2.0	0.01	7.4	12.4	59.91	2.62

Table 3
Statistical assessment of variable to response

Variable	Kappa number Eq. 6		Pulp viscosity, cP Eq. 7		Brightness, % Eq. 8		Selectivity Eq. 9	
	Coefficient estimation, CE	Prob.>F*	Coefficient estimation, CE	Prob.>F	Coefficient estimation, CE	Prob.>F	Coefficient estimation, CE	Prob.>F
Intercept	7.763	-	11.994	-	57.513	-	2.426	-
P	-0.813	<0.0001	-0.856	<0.0001	5.666	<0.0001	-0.471	<0.0001
T	-0.463	<0.0001	-0.631	<0.0001	0.739	0.0134	-0.399	<0.0001
t	-0.150	0.0154	-	-	0.595	0.0378	-	-
A_c	-0.475	<0.0001	-0.169	0.0105	0.761	0.0114	-0.144	0.0087
A_q	-0.150	0.0154	0.056	0.3115	0.595	0.0378	-	-
PT	-	-	0.019	0.7290	-	-	0.199	0.0010
PA_c	-	-	0.306	0.0002	-	-	0.253	0.0002
PA_q	0.150	0.0154	0.231	0.0017	-	-	0.131	0.0143
TA_c	-	-	0.181	0.0072	-	-	0.143	0.0091
PTA_c	-	-	0.306	0.0002	0.614	0.0331	-	-
Center point	-0.463	-	0.181	-	1.648	-	0.023	-

*Value of Prob.>F below 0.0500 indicates that the model is significant

Table 4
Statistical analysis of reduced models of kappa number, pulp viscosity, brightness and selectivity

Source	Kappa number	Pulp viscosity, cP	Brightness, %	Selectivity
Model Prob.>F[a]	< 0.0001	< 0.0001	< 0.0001	< 0.0001
R^2[b]	0.9718	0.9831	0.9778	0.9603

[a] Value of Prob.>F below 0.0500 indicates that the model is significant
[b] R^2 near 1 is good

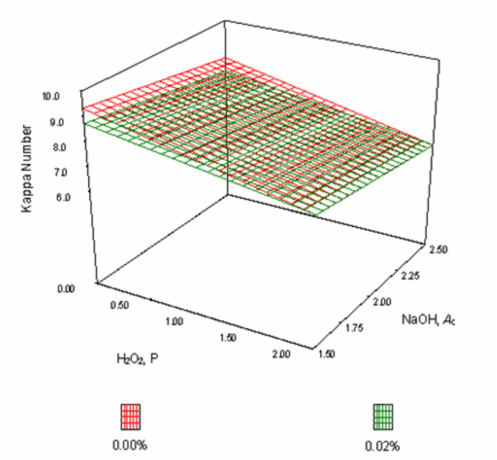

Figure 1: 3D response surface plot of kappa number as a function of H_2O_2, P, alkali charge, A_c and AQ, A_q at constant temperature, T (92.5 °C), and time, t (45 min)

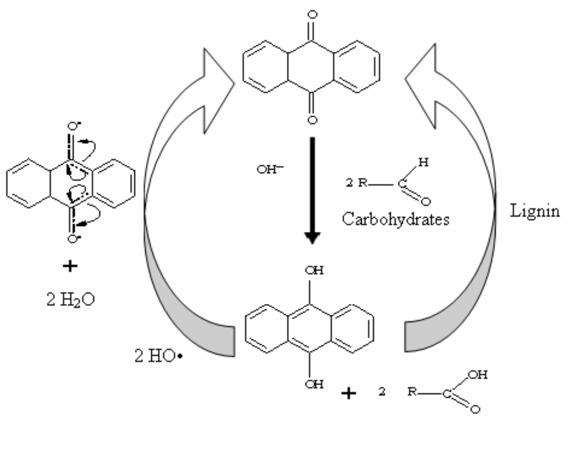

Figure 2: Scheme for anthraquinone-anthrahydroquinone reactions with carbohydrates and lignin during oxygen delignification in the presence of hydrogen peroxide

As generally known, lignin oxidation requires the presence of alkalis, to ionise its free phenolic hydroxyl groups and to initiate a reaction with oxygen, to form soluble acidic degradation products;[22] consequently, within the range of A_C applied in the present study, a higher A_C will result in a higher degree of delignification.

Besides, there is an additionally significant interaction (P A_q) involved in the factorial model. Interestingly, the increase of either one variable of the interaction caused a decrease of K_n. However, the beneficial effect of adding AQ on K_n reduction was diminished when P was approaching a higher level. Therefore, in the region of the highest P value, the increase of the AQ charge showed no further K_n reduction. The conclusion is that, under alkaline conditions, AQ is reduced to anthrahydroquinone (AHQ) through oxidation of the cellulose-reducing end group. Since AHQ is capable of catalyzing the cleavage of lignin β-aryl ether linkages in free phenolic phenylpropane units, it improves delignification. However, as AHQ may be readily oxidized, in the presence of strong oxidants, especially hydroxyl radicals (OH·), generated through stepwise reduction of oxygen and decomposition of H_2O_2 in an O_P stage, the amount of AHQ was decreased by a chemical reaction – as proposed in Figure 2. Thus, the positive effect of AQ on delignification faded, when the amount of H_2O_2 added was increased.

Pulp viscosity

Eq. 7, given in Table 3, shows that pulp viscosity was affected mostly by P and, to a lesser extent, by T and A_C, while the effects of AQ and t were statistically insignificant. Figure 3 shows that viscosity decreased as both P and T increased because, when both P and T took high values, the rate of H_2O_2 decomposition to radical species increased, thus fostering cellulose degradation.

It was interesting to note that the effect of A_C on the O-stage with H_2O_2 was different from the O-stage without H_2O_2.[16] Without H_2O_2, the increase of A_C proportionally increased the hydroxyl ion, which is capable of reacting with cellulose, thus decreasing viscosity. With H_2O_2 added, the decrease in viscosity was higher for low A_C than that for high A_C, especially at high levels of P and T.

This indicated that, with the addition of weak acid H_2O_2 during the O-stage, 1.5% of A_C was insufficient to promote ionization of the hydroxyl radicals (HO·), generated especially by the decomposition of H_2O_2, to the relatively less reactive oxide anion ($O^{\cdot -}$) (pKa = 11.9). Consequently, more cellulose was degraded unselectively. In contrast, pulp viscosity is maintained higher on condition of higher A_c, T and P values, as due to the presence of the conjugated base of H_2O_2 (HOO^-) in high alkalinity, reacting with $HO^{\cdot}$ to produce $O_2^{\cdot -}$, which is less deteriorated to carbohydrate.[23] Therefore, a sufficient amount of alkali should be employed in an O_P stage.

On the other hand, for low P and T levels, a high level of A_C yielded a lower viscosity, comparatively with the low A_C level. Hence, as demonstrated by Figure 3, the changes in viscosity due to changes in P and T were quite notable when the A_C level was low, however the system was more resistant to changes in P and T when a high A_C was applied. Even though A_q alone did not significantly affect viscosity, the interaction effect for P A_q was significant, as shown in Figure 4. With the addition of AQ, the negative effect of P on viscosity was reduced. A quite similar result has also been reported by Ohi *et al.*,[24] namely that the addition of tetrahydroanthraquinone (THAQ) is capable of decreasing the cellulose degradation of linter cellulose under alkaline conditions, at 90 ºC, in the presence of H_2O_2, but without oxygen.

As already mentioned, the hydroxyl radical generated in the O_P-stage has a high potential to react with AHQ. Hence, the AQ added in the system might act as a hydroxyl radical scavenger and reduce cellulose degradation, as a hydroxyl radical able to attack both lignin and cellulose unselectively. On the other hand, the oxidation of the cellulose reducing end groups (mainly generated due to the cleavage of glycosidic bonds of the cellulose chain) by AQ to alkali-stable aldonic acid groups will also retard the further end groups peeling reaction. The result indicated that AQ addition in the O_P-stage, even if without improving K_n reduction, might counteract the negative effect on pulp viscosity, when a relatively higher level of H_2O_2 is employed.

Brightness

The factorial model for brightness (Eq. 8) using the five variables is shown in Table 3. Based on the value of the coefficients of the model and on Figure 5, it is obvious that P had the highest effect on pulp brightness. Since one of the decomposition species of H_2O_2, the hydroperoxide anion (HOO^-), is a well-recognized brightening agent, by diminishing the chromophoric structure in lignin, the presence of H_2O_2 in the O-stage improved the resultant pulp brightness by about 10% ISO. This is a beneficial result, especially for the production of totally chlorine-free (TCF) bleached pulp.

Selectivity

The selectivity of the bleaching process is calculated by dividing the amount of lignin removed (difference of K_n) by cellulose degradation (the difference between cellulose viscosities). Since it is not a direct response, but results from the combination of K_n and viscosity, the effect of the variables on this particular response was complex. Based on the values of CEs in the factorial model (Eq. 9), the most influential variable was P, followed by T and A_C. Increasing all these three variables adversely affected selectivity. Similarly with the results obtained in the preliminary study, the addition of AQ had no positive effect on selectivity. However, as illustrated by Figure 6, the addition of 0.02% AQ improves selectivity for high values of P at high temperature, although the effects recorded were relatively low.

Figure 7 illustrates the relationship between brightness and selectivity for different P levels. Notably, the highest selectivity was obtained in the absence of H_2O_2. Nevertheless, H_2O_2 was necessary in the O-stage to attain higher pulp brightness and to reduce K_n, as discussed above. This means that the addition of AQ will be desirable in the O-stage when H_2O_2 is present.

Verification of factorial models

Table 5 lists the three testing conditions as corroboration points, used for checking the validity of the factorial models built with statistical models. The calculated response values and the actual experimental values are shown in Table 6. Obviously, the experimental values of all responses, except that of the selectivity of conditions IX and XI, were significantly the same with the calculated values, with a difference of no more than 5%. The rather high difference in percentage between the model and the experimental values for selectivity is basically due to its being a function of both K_n and viscosity, and to its quite low value. Hence, selectivity can be greatly affected by small changes in the two variables, while a small difference (higher than 0.2) will cause differences between the model and the experimental values exceeding 5%.

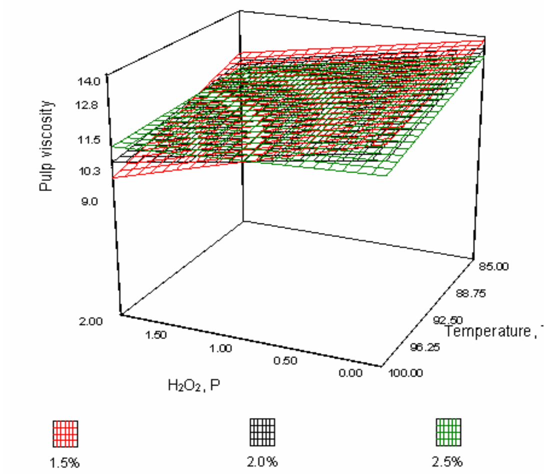

Figure 3: 3D response surface plot of pulp viscosity as a function of H_2O_2, P, temperature, T and alkali charge, A_c at constant time, t (45 min) and AQ, A_q (0.01%)

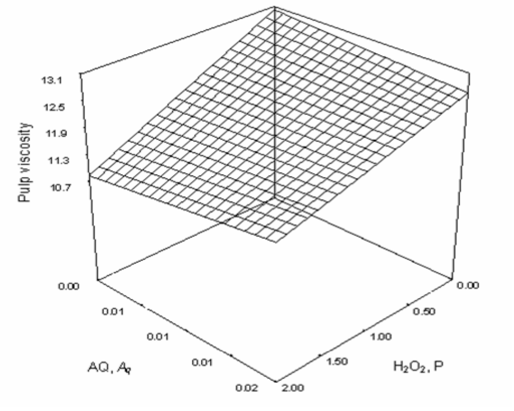

Figure 4: 3D response surface plot of pulp viscosity as a function of H_2O_2, P and AQ, A_q at constant temperature, T (92.5 °C) time, t (45 min) and alkali charge, A_c (2.0%)

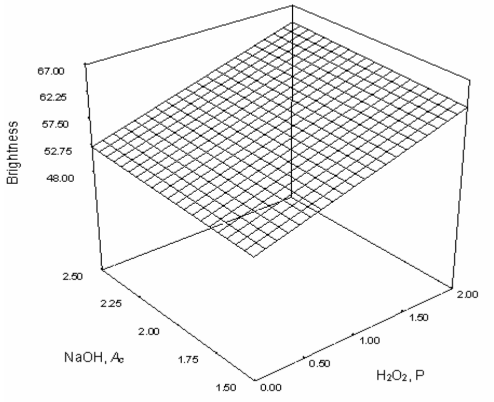

Figure 5: 3D response surface plot of brightness as a function of H_2O_2, P and alkali charge, A_c at constant temperature, T (92.5 °C), time, t (45 min) and AQ, A_q (0.01%)

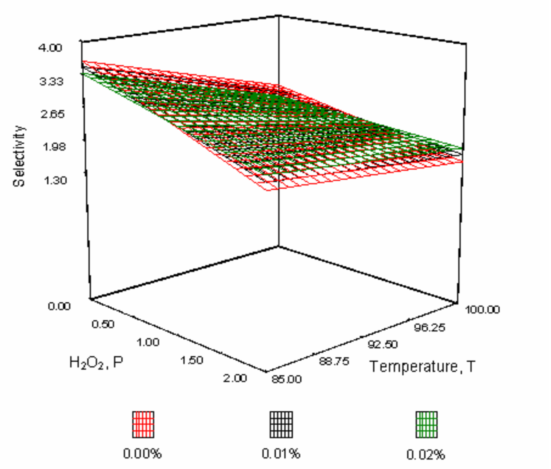

Figure 6: 3D response surface plot of selectivity as a function of H_2O_2, P and temperature, T and AQ, A_q at constant time, t (45 min) and alkali charge, A_c (2.0%)

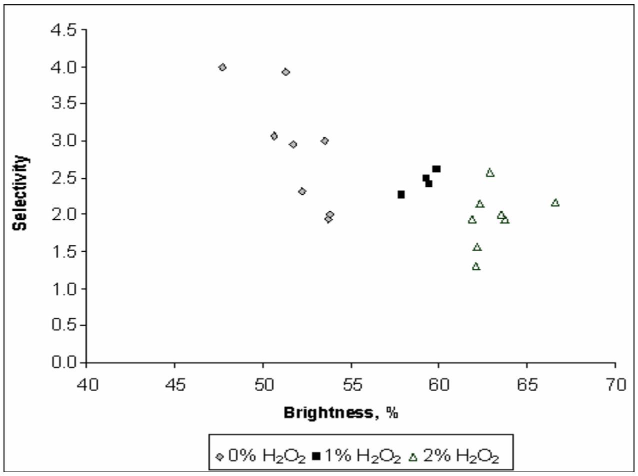

Figure 7: Scatter chart illustrating the relationship between brightness and selectivity at different P levels

Table 5
Experimental conditions for validation of factorial models

Sample	Variable				
	H_2O_2, P (%)	Temp., T (°C)	Time, t (min)	NaOH, A_c (%)	AQ, A_q (%)
IX 0.08		90	30	2.0	0.02
X 0.50		90	30	2.0	0.02
XI 0.75		100	30	2.5	0.02

Table 6
Comparison between predicted and actual experimental values of the four responses

	Sample IX		X	XI
Kappa number	Predicted 8.6		8.3	7.1
	Experimental 8.6		8.2	7.2
	Difference in percentage, %	0	1.22	1.39
Pulp viscosity	Predicted 12.	8	12.6	11.5
	Experimental 13.	3	12.9	11.2
	Difference in percentage, %	3.75	2.33	2.68
Brightness	Predicted 52.	4	54.4	57.6
	Experimental 53		55.1	60.5
	Difference in percentage, %	1.13	1.27	4.79
Selectivity	Predicted 2.9		2.75	2.02
	Experimental 3.3		2.86	1.84
	Difference in percentage, %	12.12	3.84	9.94

CONCLUSIONS

Among the five variables examined in the study, P was the most influential one, while T and A_C were also significant in all factorial models. The addition of H_2O_2 during the O-stage was beneficial, as it reduced K_n and improved pulp brightness. However, at the same time, it also decreased pulp viscosity and selectivity. An impairment to viscosity by a high level of H_2O_2 can be counteracted by the addition of a small amount of AQ, indicating that H_2O_2 and AQ addition during the O-stage appears to enhance bleaching effectiveness, without substantially impairing cellulose degradation. In addition, a sufficient alkali charge was necessary during the O-stage, when H_2O_2 was present, to avoid an uncontrollable viscosity drop. The lower K_n and higher brightness pulp resulting from the tested O-stage bleaching process can enhance the total effectiveness of TCF bleaching of oil palm EFB soda-AQ pulp.

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