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Optimization of Pitch Removal by Dissolved Air Flotation in a Eucalyptus Kraft Mill

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Abstract: Wood extractives cause production and environmental problems as well as decreasing the quality of the final product in pulp and paper manufacturing. These disturbances are commonly referred to as pitch problems in this industry. The complex composition of wood extractives is the reason why the nature of pitch problems is different for the various wood species. Also, there is a strong dependence on pulping, bleaching, and papermaking processes. Nowadays, the most common way of handling pitch is to use chemicals in order to fix the extractives to the fibers and thus remove them from the process with the final product. However, this causes serious problems in the final product and also increases problems when paper is recycled. Thus, fixation is not considered to be a sustainable operation for the future. Alternative methods to remove the extractives from the process water must be developed to overcome pitch disturbances and increase pulp quality. This is especially important in mills with closed water loops where the accumulation of extractives in the process waters can occur.

In this paper an internal process water kidney, based on dissolved air flotation (DAF), is considered. The objective was to remove extractives from a kraft mill process using *Eucalyptus globulus* as the raw material. The results show that with the dual system, polyethylene oxide and phenol formaldehyde resin (PEO/PFR), it is possible to remove

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80% of the extractive compounds by DAF. Three different techniques, hemacytometry, gas chromatography and turbidity measurement, were used to evaluate the removal efficiency. The applicability of a fast measurement, such as turbidity, to optimize the DAF operation during a future mill operation was studied.

Keywords: Pitch control, Dissolved air flotation, Extractives, Eucalyptus kraft mill, PEO

INTRODUCTION

Eucalyptus globulus is extensively used for paper pulp manufacture in many regions such as Australia, Brazil, and Southern Europe. Pitch problems are encountered despite the relatively low extractives content of the eucalyptus species. Wood extractives are released during pulping and bleaching and form unstable colloidal systems that can destabilize to form deposits, causing operational and quality problems in pulp and paper manufacture. The term pitch is applied to both wood extractives and deposits that form during the pulping and papermaking processes. Pitch deposition is a complex phenomenon. In pulping, wood extractives increase the consumption of pulping chemicals, impair the color and brightness of unbleached pulp, and cause tacky deposits on pulping equipment. Furthermore, detrimental pitch is carried over to the paper machine resulting in strength loss, impurities and holes in the final product (1, 2).

The pitch-induced problems have increased during recent years with the trends to use more environmentally friendly processes in pulp and paper mills, such as elemental and total chlorine-free bleaching and closure of water circuits. Therefore, the effect of detrimental substances and the alternatives for removing and controlling problematic compounds from process waters are topics that continuously appear in the literature (3).

The complexity of wood extractives is the reason why the nature of pitch problems differs for the various wood species, and it depends on the pulping, bleaching, and papermaking processes. The conventional methods for pitch control are extensive debarking, seasoning, the use of pitch control additives, and a wide range of various improvements in pulp and paper manufacture (1, 4, 5).

Nowadays the most common way of handling pitch problems in the industry is the use of chemicals to fix the extractives to the fibers and then remove them with the final product (6–8). However, it may cause serious problems in the final product and also increases the problems whenever paper is recycled. Therefore, fixation is not considered as a sustainable operation for the future. Another alternative is to increase stability against pitch aggregation and deposition. For example, the use of hemicelluloses in thermo-mechanical (TMP) pulping has been recently proposed to inhibit pitch aggregation and deposition. This research has been carried out at laboratory scale but it has not yet been proved at industrial scale (9, 10).

Consequently, alternative methods to remove or separate the extractives from the process water must be developed to overcome pitch problems. Two main approaches are described in the literature: the use of biotechnology or the use of physico-chemical processes. The most important group of methods for pitch control is based on a biotechnological approach in which the main components of pitch deposits have been identified and microbial and enzymatic preparations are used to degrade such components. Many papers have been published in recent years about using these biotechnological approaches to control pitch problems, by treating the pulp with enzymes or the wood with different microorganisms (11–16). However, they are not yet feasible for all types of pulp processes.

At present, microbial and enzymatic preparations for the control of triglyceride-containing pitch deposits, during the manufacture of mechanical and sulfite pulp, are commercially available. However, biotechnological products for pitch control in other pulping processes, such as alkaline pulping, are still under development. These products include a bio-pretreatment of wood with fungi before pulping for the removal of sterols involved in pitch deposit formation in chlorine-free pulps. Simultaneously, tailor-made enzymes are being produced using protein-engineering techniques, enabling the specific removal of pitch contaminant compounds from the pulps (17, 18). One remaining challenge that still has to be overcome is the thermal stability of enzymes, since process waters are, in many cases, over 70°C (19).

Fewer studies have been published in relation to the use of separation technologies of pitch compounds. However, these could provide technical and economical solutions for pitch problems in pulp and paper manufacture.

In recent years different membrane technologies have been introduced to the pulp and paper industry for internal process water treatment, e.g., microfiltration, ultrafiltration and nanofiltration. Some recent studies show the feasibility of using these techniques to remove extractives from several process water filtrates (20, 21). However, substances that are adsorbed onto membranes during filtration, e.g., phenolic and hydrophobic compounds, cause changes in the permeability characteristics of the membranes, which result in membrane fouling (22). Therefore, at present, this alternative is still not technically and economically viable.

Dissolved air flotation (DAF) is one alternative that could provide a good method to obtain better pitch control in eucalyptus kraft mills. DAF, with suitable chemicals that aggregate the colloidal extractives before their removal, lowers the amount of extractives in the circulation water. Low molecular weight organic cationic fixing agents and poly-aluminum chlorides are effective coagulants of colloidal wood pitch in mechanical pulping filtrates. These have been proposed in the literature for the removal of pitch from the process water, in the form of resin sludge, by flotation. However, the behavior of kraft filtrates from *Eucalyptus globulus* is very different and there are no successful results described in the references (23, 24).

Another approach proposed in the references to aggregate the extractives, in order to remove them by DAF, is the use of polyethylene oxide (PEO), a nonionic polymer, with phenol formaldehyde resins (PFR) as co-factors (Netfloc® system). This system was jointly developed at Domsjö sulfite mill by MoDo and Kemira. This process has been tested in other pulping processes such as thermomechanical pulping (TMP), chemi-thermomechanical pulping (CTMP), and kraft using mixed tropical hardwoods. Netfloc® systems also remove nonprocess elements, e.g., metals, from filtrates in chemical and mechanical pulp mills, which improve peroxide stability and oxygen delignification. This process has also been successfully used in Nordic kraft mills with TCF (total chlorine-free) and ECF (elementary chlorine-free) bleaching, using softwood as the raw material (25, 26).

However, the system PEO/PFR does not work for all types of process waters, and there are no previous successful studies described in the literature in relation to *Eucalyptus globulus*. PEO is also used as a retention aid in Canadian paper mills using a mechanical pulp furnish. It is claimed that it may be used in closed water systems, since it is a nonionic polymer, and therefore its efficiency should not be affected by anionic trash. However, it is not widely applied because it shows a big variability on wet-end performance in different mill environments, which depends on the quality of the white water (27–30). This fact may explain why the Netfloc® system is not always viable for pitch control. Thus a preliminary study on a laboratory scale is always necessary to check the compatibility of the system with a given process water and to assess its efficiency to aggregate the detrimental substances present in those waters.

This paper is focused on the removal of extractives from the process water of a kraft mill producing TCF market pulp from *Eucalyptus globulus* wood. In this specific case, no biotechnological approach is available, since they are still under development. Therefore, it was decided that the best alternative was the aggregation of extractives and their removal by DAF. However, the technical viability of the agglomeration of *Eucalyptus globulus* extractives present in a kraft TCF process has to be assessed before a mill trial. Therefore, this study is focused on the selection and optimization of the best chemicals to destabilize the extractives, causing their aggregation and facilitating the removal of the aggregates by DAF. Different chemicals, including the system PEO/PFR, have been studied.

First a feasibility study was carried out at laboratory scale, and since the results were very promising, a second set of experiments was carried out at a mill site to evaluate the proposed treatment with real industrial process water conditions.

EXPERIMENTAL

To obtain a viable DAF treatment process it is necessary to optimize the use of chemicals. The smallest chemical doses that aggregate the colloidal substances have to be determined in order to reduce chemical costs and to optimize the coagulation and flocculation processes, as well as the separation process. This study was performed in two steps. First, the chemical dosage and the chemical addition order were studied on a laboratory scale, then the feasibility of the proposed separation process was studied, using real industrial process waters in a pulp mill.

Procedure and Analysis on a Laboratory Scale

The first step was to obtain a representative pitch dispersion in order to perform the DAF test on a laboratory scale. It was required both to prepare a pitch dispersion with a composition similar to the real pitch present in the mill process waters, and to obtain a sufficient amount to perform all the experiments with the same pitch dispersion in order to avoid variations. Therefore, the protocol started with the extraction of the lipophilic material from milled wood received from the mill, then it was hydrolyzed, and finally the lipophilic material was re-extracted and the final pitch dispersion was prepared.

In order to obtain the required amount of extractives it was necessary to carry out the extraction in a pilot plant extractor. The extractives were obtained by soxhlet solvent extraction from eucalyptus hardwood. Twenty-five litres of acetone and 1.5 kg of milled wood were used for each pilot scale extraction. Using acetone, a high yield of extraction was obtained.

Once the lipophilic material was obtained, the second step was to hydrolyze it to simulate the lipophilic material present in the kraft pulping process. This was carried out using a 0.5 N potassium hydroxide solution in 90% methanol. However, this dispersion also contains polar compounds, and a second extraction, with hexane, was necessary in order to remove them.

After hydrolysis and hexane extraction, the hexane was removed in a rotator evaporator and the dry extracts were dissolved in acetone at 30 g/L concentration to have a stock solution of lipophilic extractives with a similar composition to those present in the kraft process waters. This solution was kept at 4°C until it was used.

Dissolved air flotation tests were carried out in a laboratory unit Flotatest FTH3 from Orchidis Laboratoire. The temperature was kept constant at 70°C in all the experiments. DAF jars were filled with 1 L of sample. Rapid mixing (180 rpm) of the flocculation chemical with the water was carried out for 30 seconds followed by slow agitation (60 rpm) for 6.5 min. The air-saturated water was introduced and the samples were left to stand for 10 min to allow the agglomerates to be floated to the surface. The sample from the purified

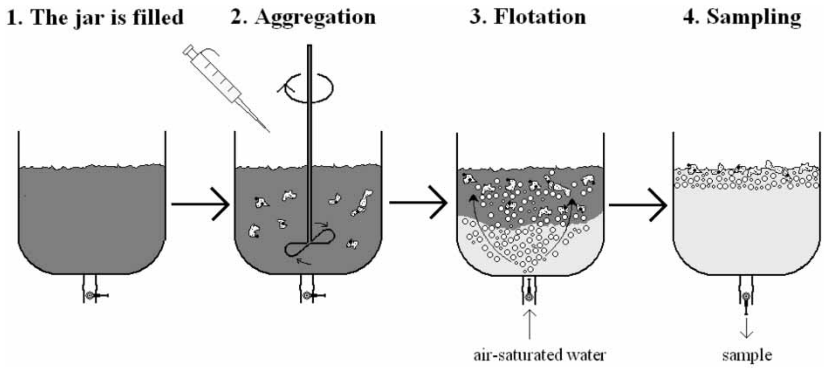

Figure 1. A simplified flow-scheme of the aggregation and dissolved air flotation-process.

water was taken from the bottom of the bottle for analysis. Figure 1 shows a schematic diagram of the laboratory DAF set-up experiments.

In order to have at least two different analysis methods for the identification and quantification of colloidal extractives, an assessment of the turbidity was made and the extractives content was determined by gas chromatography (GC).

Determination of lipophilic extractives by gas chromatography (GC) was carried out according to the following procedure. A water sample of 2 mL was acidified to pH 3.5 in a test tube with 0.05 M sulphuric acid. Bromocresol green was used as the indicator. The sample was extracted with methyl *tert*-butyl ether (MTBE) containing an internal standard. The supernatant was evaporated with nitrogen and dried in a vacuum oven at 40°C for 25 min followed by silylation with 80 μL of BSTFA (bis-(trimethylsilyl)-trifluoroacetamine) and 40 μL of TMCS (trimethylchlorosilane). The solution was kept in an oven at 70°C for 35 min. The sample was analyzed by gas chromatography on a short column (31).

Turbidity was measured by photometric determination using a Filterphotometer PF-11 supplied by Macherey-Nagel.

Results with Laboratory Pitch Dispersions

In order to select the best dosages and the order of addition, a set of laboratory tests was performed with the pitch dispersion obtained in the previous protocol. In the literature there is a controversy over the best ratio of PFR/PEO and the flocculation mechanisms of this system. Both Lindström et al. (1984) and Xiao et al. (1996) stated that in the flocculation of latex particles the optimum ratio of PEO/PFR is 1:1. Xiao et al. found a dependence between the molar mass of copolymer and the optimum PEO/PFR. Copolymers with lower molar masses elevate the optimum PEO:PFR ratio. Yoon and Deng (2004) studied the flocculation of a clay suspension. They reported that the maximum flocculation was not very sensitive to the ratios of 1 to 5, but the ratios of 3 obtained the highest flocculation. According to Lindström et al., the order of addition was not critical, but somewhat better flocculation was achieved when PEO was added last. In order to obtain detailed information we decided to study both the dosage and the addition order of PEO and PFR.

The chemicals were supplied by Kemira. In all experiments a certain dosage of $MgSO_4$ was also introduced in order to have high ionic strength and to improve the performance. The solutions were prepared at 50% for the $MgSO_4$, at 1% for the PFR, and at 0.05% for the PEO. These solutions were used for these experiments at different dosages and orders of addition to obtain the best conditions to remove contaminants from a pitch dispersion at 100 mg/L concentration, as shown in Table 1. Samples were heated to 70°C and their pH adjusted to 10. Waters after DAF experiments were analyzed by measuring turbidity and by determining the lipophilic extractives by GC.

$MgSO_4$ was added first at the desirable level and after that two addition sequences were tested, PEO/PFR and PFR/PEO. Table 2 summarizes the obtained results at the different dosages and sequences. Turbidity results are expressed as percent of turbidity reduction from initial values, and GC values are referred as the percent reduction of sitosterol in pitch samples.

The best results were obtained with the PFR/PEO sequence at 200 mg/L $MgSO_4$ and at a PEO/PFR ratio of 1:3. With these conditions, removal of sitosterol from the waters was higher than 80%. This is the common addition order when this dual system is used for other applications.

PEO may form bridges via hydrogen bonding between the ether oxygen and the hydroxyl groups present in the extractives. When ionic strength increases with the addition of a higher dosage of $MgSO_4$, the thickness of the electric double layer of the colloidal particles will decrease and, as a consequence, the PEO chains adsorbed on these particles are larger than the electric double layer and can interact with other particles. Then very few positions are free to interact with the phenolic hydroxyl groups of the PFR and the formation of complex colloidal-PEO-PFR is impeded. This justifies

Table 1. Concentrations of chemicals for eucalyptus extractives removal (mg/L)

	$MgSO_4$			
	100		200	
PEO	5	10	5	10
PFR	5 10 15	10 20 30	5 10 15	10 20 30

Table 2. Results of analysis from waters after DAF treatment

	PEO/PFR		PFR/PEO	
$MgSO_4$/PEO/ PFR (mg/L)	Decrease in turbidity (%)	Sitosterol removal (%)	Decrease in turbidity (%)	Sitosterol removal (%)
100/05/05	78	74	32	75
100/05/10	90	75	45	79
100/05/15	91	81	75	81
100/10/10	71	74	65	—
100/10/20	92	77	76	72
100/10/30	83	—	78	90
200/05/05	44	58	82	82
200/05/10	57	59	85	78
200/05/15	52	70	87	83
200/10/10	60	72	86	70
200/10/20	77	62	98	78
200/10/30	39	61	98	88

why the removal efficiency decreases when $MgSO_4$ dosage increases in the instances when PEO is added before the PFR.

When PFR is added first to the suspension it does not interact with the colloidal particles due to its anionicity. Thus, PEO is able to interact with the phenolic hydroxyl groups of the resin forming a complex that may interact with the extractives and producing a flock that floats easily. As a consequence, the removal efficiency increases when PFR is added before PEO. In these cases it is also reasonable that with the increase of the ionic strength, the thickness of the electric double layer of extractives particles is reduced and, therefore, the layer of adsorbed complex PEO–PFR is wider than the thickness of the electric double layer. Thus both interactions with other particles and the removal efficiency increase. Furthermore, in some references it is proposed that PEO and PFR form a network that captures particles during movement through the dispersion.

It was then decided that further experiments at the pulp mill would be carried out using this order of addition: $MgSO_4$/PFR/PEO.

Mill Experiments

The promising results obtained at laboratory scale led to a set of industrial trials at Ence Pulp Mill in Pontevedra. This mill produces 340,000 t/yr of TMP eucalyptus pulp, bleached entirely using an oxygen delignification process. The process consists roughly of five different stages: washing

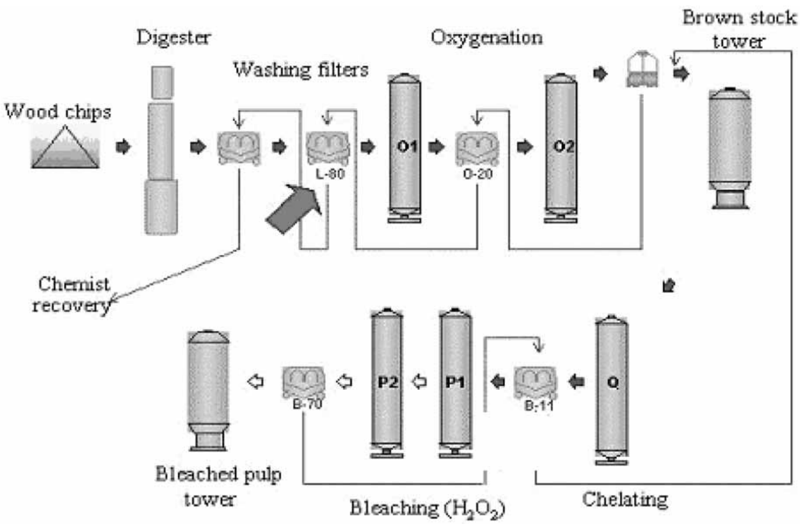

Figure 2. Sampling point presented in a simplified flow diagram of the eucalyptus kraft mill.

filters, oxygenation, chelating, peroxide bleaching, and storage of pulp. A simplified flow diagram of the mill can be seen in Fig. 2.

The pitch removal from the process filtrate has been studied. The output of the washing filter L-80 was chosen (process water from the last cleaning filter after the cooking pulp process, Fig. 2). As has been discussed, the laboratory test showed that the best order of chemicals was PFR/PEO and the best ratio of PEO:PFR was 1:3. In order to optimize the PEO:PFR ratio with real process waters from the mill, it was decided to test also 1:2 and 1:4. In the lab test the benefits of a high $MgSO_4$ dosage were also observed, therefore an extra test was performed at higher $MgSO_4$ dosage for an optimum PEO:PFR ratio of 1:3. The dosages used are summarized in Table 3.

DAF effluents were immediately characterized by turbidity and hemacytometry to minimize the effects of any changes with time. Hemacytometry

Table 3. Chemical dosages in the mill experiments (mg/L)

	$MgSO_4$			
	200			400
PEO		10		10
PFR	20	30	40	30

(blood cell-counting chamber) was available at the mill site. It is a known technique to determine dispersed pitch particles by counting them under an optical microscope. The spherical shape of the pitch particles allows colloidal pitch to be distinguished from other particles (35). GC was carried out later on in the laboratory. Figure 3 shows the obtained results. As can be observed, a good correlation between residual turbidity and the amounts of colloidal pitch and lipophilic extractives in the effluent samples was obtained. Evidently, any of the methods could be used to evaluate the efficiency of DAF to purify a process effluent at the mill site in the future. However, the fastest one is turbidity.

In all cases the removal efficiencies were higher than 60%. The best results were obtained with the dosage of 200/20/10, at which 75% of the extractives were removed, confirming the high removal efficiency obtained at laboratory scale. Results were slightly worse than in the laboratory experiments. This might be due to the fact that polyphenolic compounds, present in the process water, interfere with the polymer and decrease its efficiency. On the other hand, experiments at the mill were carried out at 80°C while lab experiments were carried out at 70°C. The higher temperature decreases the amount of oxygen dissolved in the pressurized water, which may also contribute to the lower removal efficiency. The reason why the best PEO:PFR-ratio at mill scale (1:2) differs from the ratio obtained at lab scale (1:3) can be explained by the different sample and process conditions. The

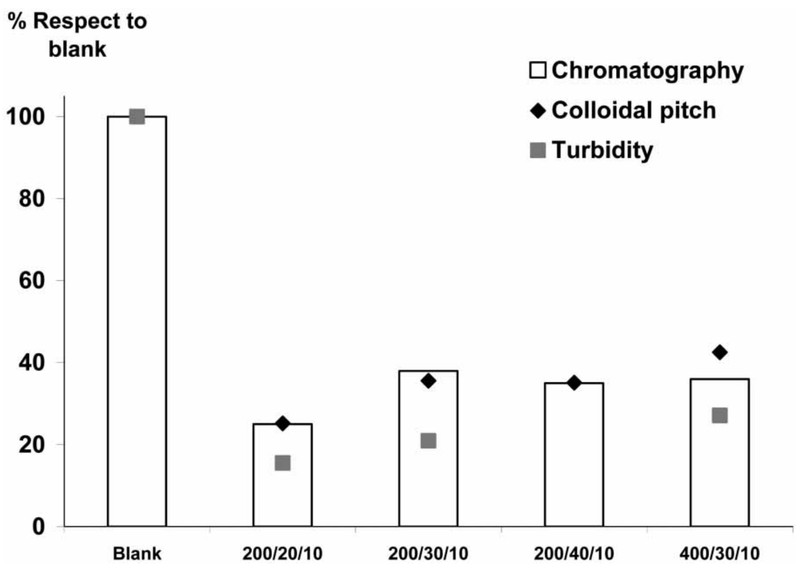

Figure 3. Comparison of turbidity, amount of colloidal pitch and amount of lipophilic extractives in the L-80 water after DAF treatment.

flocculation mechanism induced by PEO/PFR requires the formation of the PFR–PEO complex. The complex formation increases the rigidity of the polymer and keeps a more extended conformation, which is able to form bridges among the particles. In the case of mill samples, the PEO does not only interact with the PFR but also interacts with many other compounds, e.g., lignin and all organic compounds with phenolic groups in their structure. The presence of these compounds in the waters that interact with the PEO decreases the PFR requirements because they act as cofactors for the PEO chains, forming complexes with good flocculation ability (36).

Finally, it was decided to perform a comparative test with other chemicals, e.g., polyacryl amide (PAM) and polydiallyl-dimethyl ammonium chloride (p-DADMAC). These polymers aggregate colloidal particles via different mechanisms. Polyacryl amide acts by bridging individual pitch particles in the suspension. Poly-DADMAC neutralizes the charges and may form patch-like cationic sites on particles so that they can collide with each other and flocculate. PAM and p-DADMAC were tested at the best dosage (250 mg/L) obtained in laboratory prescreening tests, based on turbidity measurements. Results are presented in Fig. 4. It can be observed that the removal efficiency is much lower for these polymers than for the PEO/PFR system and therefore they are not suitable for this application. The low removal efficiency of p-DADMAC may be due to its partial neutralization at the high level of anionic trash present in the water, or because the flocks formed are too small

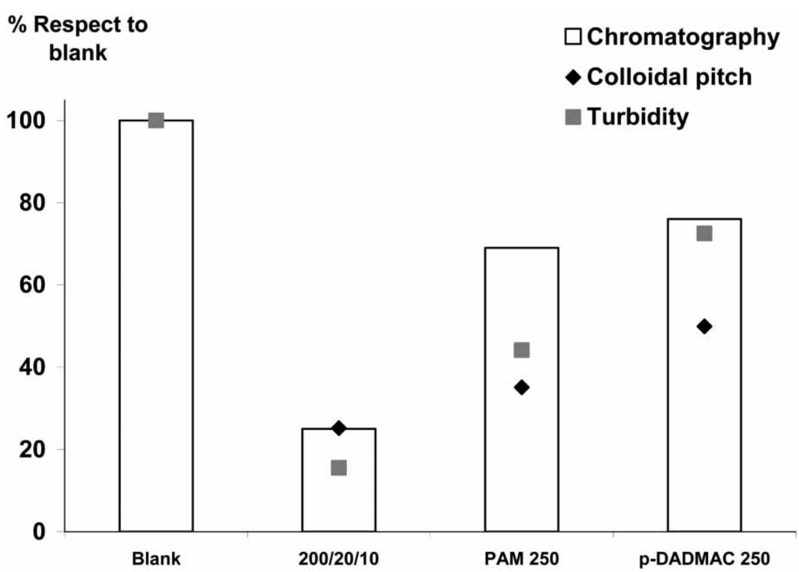

Figure 4. Comparison of DAF treatment using different chemicals.

to be efficiently removed from the waters by flotation. On the other hand, PAM was slightly more efficient. This could be due to the formation of larger flocks due to its higher molecular weight. However, the removal efficiency was still low. The importance of an optimum flock size is clear, and this justifies the high efficiency achieved with the PEO/PFR system that produces large flocks.

The secondary aim of these trials was to select the best routine analysis for the control, by operators, of a potential future industrial installation. The accuracy and reliability of pitch quantification was determined by turbidity and colloidal pitch measurements. Analysis of extractives by chromatography was considered the most accurate method to determine the residual concentration of pitch in the process water. The results obtained with other methods were compared with the extractives concentration determined by GC. As seen in Figs. 3 and 4 and discussed earlier, the difference between good and poor removal of pitch was observed by measuring both turbidity and counting colloidal pitch particles.

A more detailed comparison of different methods can be obtained by plotting the results obtained from pitch determination of L-80 effluent by turbidity and colloidal pitch methods vs. extractives concentration obtained by GC (Fig. 5). To facilitate the interpretation of the results, all the values were treated as percent respect to the sample without any chemical treatment. In order to compare in one plot all the methods, the differences between the values and averages for each method are plotted. The reference

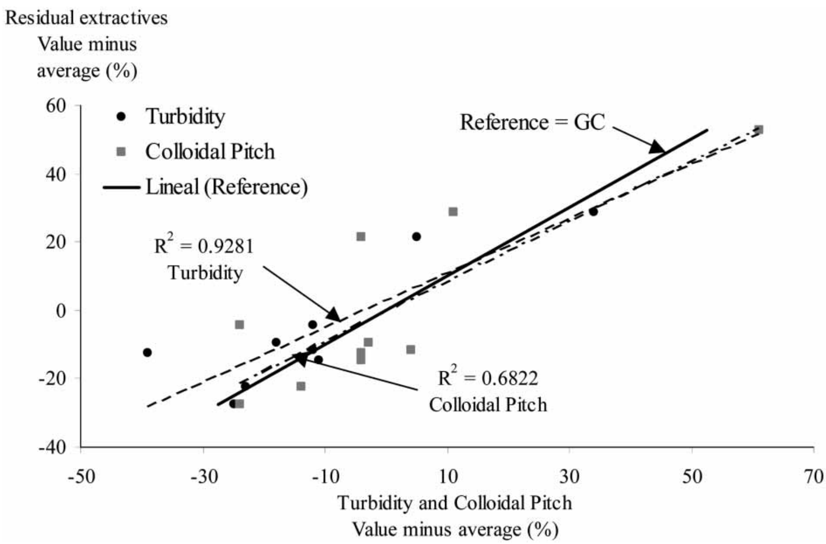

Figure 5. Comparison of analytical tools to determine pitch removal efficiency.

curve represents a case when values determined with a certain method correspond perfectly to the values obtained by chromatography. In practice a systematic error in a method is not harmful for mill operations as long as a trend in results can be foreseen. In this case it would mean that although the trend line is far away from the reference curve, it does not matter as long as the r-squared value is close to 1. By that means, determination of colloidal pitch by turbidimetry is more reliable than hemacytometry. Turbidity measurements with portable equipment can thus be used for a fast optimization of chemical dosages in the DAF unit.

CONCLUSIONS

The technical viability of the removal of pitch compounds by dissolved air flotation from the process water in a eucalyptus TCF kraft mill has been proved.

The removal efficiency of detrimental substances depends highly on the chemicals used. The results obtained on a laboratory scale show that with the dual system PEO/PFR it is possible to remove 80% of the extractive compounds. Best results were obtained with 200 mg/L $MgSO_4$, 10 mg/L PFR and 30 mg/L PEO. On a mill scale, efficiencies of 75% were reached with 200 mg/L $MgSO_4$, 10 mg/L PFR and 20 mg/L PEO.

The three measurements used to evaluate the removal efficiency of extractive compounds, turbidity, hemacytometry, and gas chromatography, allow the trend of extractives removal to be monitored. Turbidity can be used for a fast optimization of chemical dosages on a mill scale.

The protocol used at lab scale to obtain wood extractives for the evaluation of pitch control strategies has been validated.

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