The role of organic matter lost in kraft pulping material balances

A. Luonsi*, S. Lento, S. Halttunen*** and K. Ala-Kaila******

* Pirkanmaa Regional Environment Centre, P.O.Box 297, FIN-33101 Tampere, Finland
(E-mail: *antero.luonsi@vyh.fi*)

** Häme Polytechnic, Visamäentie 35, FIN-13100 Hämeenlinna, Finland

*** Tampere University of Technology, FIN-33101 Tampere, Finland

**** Metsä-Botnia Ltd, P.O. Box 165, FIN-26101 Rauma, Finland

Water Science and Technology **Vol 47 No 10 pp 61–69** © IWA Publishing 2003

Abstract Efficiency improvement in a pulp mill includes minimisation of environmental discharges simultaneously with the development of pulp quality and production economy. Material balances in production processes, including fate of sidestreams, are key in proceeding these matters. Different approaches of determining the material balances increase understanding of process behaviour. We have focused on measuring sidestream (carryovers, washing water, filtrate) dissolved organic matter (DOM) in fibreline unit process blocks of softwood ECF bleached kraft production. The DOM was analysed by traditional wastewater methods (volatile solids, organic carbon, chemical oxygen demand). The measured data was combined with primarily simulated water balances and routine operational mill data in a simulation model. From this balance, yield estimate included, lost organic matter through complete degradation (CD) and volatile organic compounds (VOC) can be calculated throughout the fibreline. The sensitivity of this considerable amount (23–35 kgDVS/adt in total) to various factors is discussed in this paper.

Keywords Dissolved organic matter; material balances; softwood ECF bleached kraft production

Introduction

Water effluent is the major target over solid waste and air emissions when extreme environmental loading minimisation of pulp and paper mills are planned. Axegård and Backlund (1999) forecast that the bleached kraft mill of the year 2020 could be free of water effluent, at least from the standpoint of overall mill energy balances. Because the target of water effluent free bleached kraft processing is not self evident, diversity of approaches is useful in studying the appropriate route for water effluent minimisation in order to achieve a balanced process of product quality, economy and overall environmental loading.

Full material balances over a mill process are required as a basis for the diverse evaluation of plans targeting the goals mentioned above. From an economical and environmental standpoint the need to emphasise yield loss minimisation, i.e. maximum lignin removal specificity, increases. The amount of dissolved organic matter (DOM) in sidestreams of a fibreline (carryover, washing water, filtrate) is closely related to yield loss. Our approach for managing organic matter in softwood bleached kraft (ECF) production has been to proceed from a characterisation of wastewater fractions to characterisation of all liquid streams, i.e. sidestreams in the fibreline. In the characterisation, traditional wastewater analyses [dissolved volatile solids (DVS), dissolved organic carbon (DOC), dissolved chemical oxygen demand ($DCOD_{Cr}$)] was used. This characterisation of DOM has then been combined with the primarily calibrated water balance and routine mill operational data in a simulation system. The study of organic matter balances has been proceeded up to the elemental level (C, H, O, other) of organic matter within the unit process block of oxygen delignification reactor and wash press (Luonsi and Halttunen, 2000).

In these studies we found that there is a considerable loss of organic matter from the balance of production process, which we interpreted by complete degradation (CD), also including the escape of volatile organic compounds (VOCs) in the production process (Luonsi and Halttunen, 1997). The usual ignorance of this fraction may be due to the low share it represents from the perspective of total material flows in the production. Another reason may be the utilisation of varying analytical methods (like COD_{Cr}, Kappa number, absorbance, etc.) for different fractions of organic matter, which in certain circumstances may falsely cover the lost quantities. We also found (Luonsi *et al*., 1998) that the dissolved volatile solids, particularly in liquid acid fractions, may be underestimated due to escaping dissolved easily volatilising solids (DEVS) in the first step of standard volatile solids analysis. Even dissolved organic carbon (DOC), often recommended due to its accuracy and straightforward nature compared, for example, to DVS analysis, would not solve this problem because it is only a fraction of the DOM which has to be followed for instance through washers in the fibreline.

In this paper the focus is particularly on the sensitivity of the amount of CD+VOC in relation to DEVS compensation, washing efficiencies as well as to estimated yield and specificity of lignin removal.

Materials and methods

Methods of liquid stream characterisation measurements are given in Luonsi and Halttunen (1997) and Luonsi *et al*. (1998). Volatile solids analysis made from filtered (SB-filter to remove fibres) samples (DVS) was used for describing DOM. Modified PROCELL simulation model was used in calculating the various cases of process status description over the whole (ECF) fiberline. The extent of covering the DEVS lost in DVS analysis as well as yield estimate and lignin removal as a fraction of yield loss (specificity) were the major variables used. The major criteria for accepting a simulation result were a ≤10% difference to the DVS measured in major sidestreams and a certain range of washing efficiency values in drum washers of the actual bleaching stages. As a result of the calculation, the quantity of CD and VOC was achieved. Variation of lignin removal specificity was studied both with PROCELL and additionally also with a simplified Excel simulation over the block of major bleaching stages, D+E_O. Before and after this particular block the best coverage of mill routine information was available.

Elemental level study for oxygen delignification (Luonsi and Halttunen, 2000) brought up prospects which will need to be studied with extensive sets of simulation runs in the future. However, due to limited effects (e.g. ~1 kappa unit) on the mass flow from oxygen delignification to actual DE_ODE_PD bleaching, this study concentrates on the sensitivity simulations based on the status description of oxygen delignification which was achieved in the original calibration of the fibreline (Luonsi and Halttunen, 1997).

The particular cases given here as examples of those simulated for sensitivity can be described as follows:

1. Maximum achievable compensation of DEVS for the DVS in acid filtrates.
2. Compensation of DEVS in acid filtrates only to the extent maintaining washing efficiency values within 2 and 4.
3. Demand 2 added by applying maximum yield in D_0 and E_1 stages.

Results and discussion

The operational conditions, according to mill data in the successive unit processes of the fibreline at the time samples were taken for the standard case of calibration (Luonsi and Halttunen, 1997), are given in Table 1.

The measured DOM balance as kgDVS/adt in liquid sidestreams is shown in Figure 1. The DOM values are given before and after the washer. For simplicity the calculated DOM

Table 1 Chemical doses and kappa number in unit processes according to daily mill reports and yield utilised in the standard case of calibration

	COOK	O_2	D_0	E_1	D_1	E_2	D_2
Eff. Alkali (%)	20.5						
O_2 (kg/adt)		10.8		5.2			
NaOH (kg/adt)		10.8		18.9		4.5	
ClO_2 (act.Cl) (kg/adt)			19.8		23.4		9.9
H_2O_2 (kg/adt)						1.8	
Kappa number out	25	17	13.6	5.7	3.7	0.7	0.2
Lignin removal (%)		32	20	58	35	80	71
Yield (%)	47	98	98.8	98	99.5	99.45	99.7

balance over the reactor with yield loss and complete degradation+VOC is not shown. The net (measurable) DOM from the reactor ($carryover_{in}$ + yield loss – (CD+VOC)) to the washer is shown in parentheses.

Sensitivity of lost quantity (DC+VOC) in the block of D0 and E1 stage

Small yield losses like those in actual bleaching stages are very difficult to measure accurately by direct methods even in parallel process studies in the laboratory (Lazaar, 1998). Also, gaseous determinations in the mill are laborious and costly. Both of those were thus out of reach in our study. Therefore yield loss, complete degradation (CD) and volatile organic compounds (VOC) in the mill processes were determined through balance calculations. In order to show the minimum level of the discharge comprised from CD+VOC in the process, the balance of the most comprehensively defined block of D_0 and E_1 was studied. Around this block kappa is routinely measured and thus lignin removal can be calculated. Also measurable DOM in all incoming and outgoing streams was available. Yield loss originates from lignin and other organics (carbohydrates, extractives) which dissolve and transform. When yield loss in this situation is assumed to be equal to lignin removal (i.e. 100% specificity of lignin removal), absolute minimum for the discharge of CD+VOC can be determined. In Table 2 measured values have been used for kappa, carryover and filtrate. Maximum DEVS measured (Luonsi *et al.*, 1998) in D_0 and D_1 filtrates were used although the potential for DEVS in the calibration situation was different and lower due to a 10°C higher process temperature. At higher temperature the part of the DEVS were volatilised and lost already in the mill.

As can be seen from the table, there is a 1–11% deficiency in the outgoing streams compared to incoming streams in the hypothetical situation of 100% specificity of lignin removal. The other studied, similarly a stable production situation with oxygen delignification, confirmed this result by giving a higher value than 5.0 kg/adt with the measured standard DVS values. In case 2 (Table 2) the balance would be zero if the DEVS loss in D_0-filtrate were 39%, i.e. higher than the extreme DEVS measured by DOC (Luonsi *et al.*, 1998). In this case, a yield loss specificity down to 76% satisfies the 10% accuracy limit which most probably will be exceeded in reality. This reasoning is considered to be adequate to prove the existence of considerable CD+VOC.

According to Figure 2 the CD+VOC fraction would also exist in the extreme case of yield loss comprised of lignin only (specificity 100%) and DEVS fully covered. However, the most probable area of lignin removal specificity used in the balance calculations was in the area of 60–70%, close to the curve achieved with DVS values corrected partially with the quantity of identified volatile compounds.

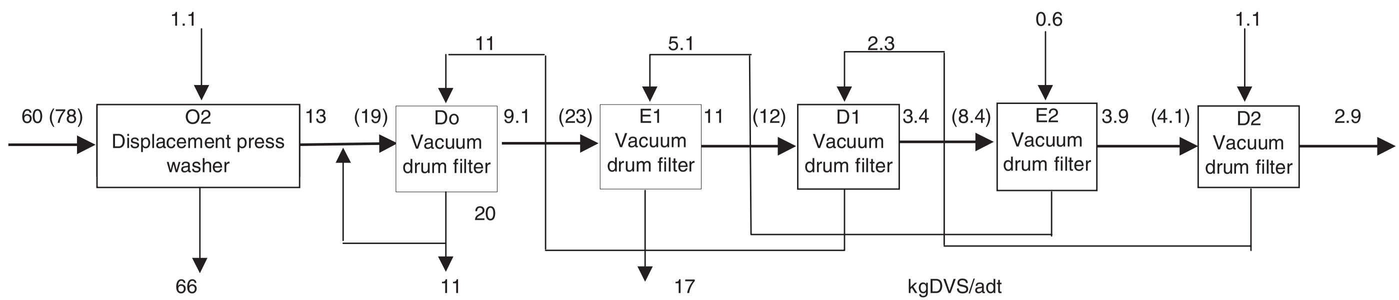

Figure 1 Calibrated DOM balance of ECF fibreline in the case based on the original DVS results

Table 2 Determination of the balancing discharge stream, CD+VOC, in the block of D_0 and E_1-stage without (case 1) and with (case 2) consideration of maximum measured dissolved easily volatilising compounds in DVS measurement in acid filtrates. Assumed lignin specificity 100%

Stream	Case 1, in	Case 1, out	Case 2, in	Case 2, out
Carryover in	12.7		12.7	
Yield loss minimum				
= lignin removal, kappa 17–5.7	16.1		16.1	
Washing water to E_1 (=E_2-filtr.)	4.9		4.9	
Washing water to D_0 (=D_1-filtr.)	10.8		13.1	
Carryover out		11.0		11.0
E_1-filtrate		17.1		17.1
D_0-filtrate		11.4		18.2
Total In/Out	44.5	39.5	46.8	46.3
Balance = complete degradation + VOC		5.0		0.5

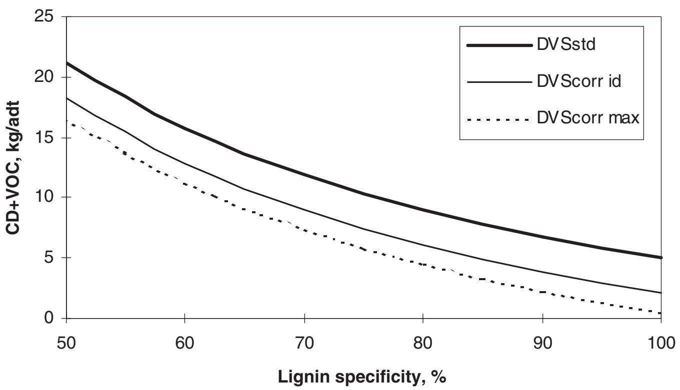

Figure 2 Complete degradation and volatile organic compounds (CD+VOC) versus lignin specificity in the block of the first acid (D_0) and first alkaline (E_1) stage of actual ECF-bleaching based on kappa and standard DVS-measurements. The curve in the middle is based on DVS values corrected up to the amount of identified volatile organic compounds. The dotted line is based on full DEVS coverage

Dissolved easily volatilising solids (DEVS) coverage in filtrates

The amount of DEVS ranged from 17–37% of the DOM in acid filtrates and 4–9% in alkaline filtrates according to a separate study (Luonsi *et al.*, 1998). Volatile compounds from D_0-filtrate were also identified by gas chromatography. Methanol and formic acid comprised the majority of the identified volatiles (94%) representing a discharge of 4–5 kg/adt. The calculated carbon content of these measured specific volatile compounds covered 63% of the loss measured with DOC.

Based on this study new simulations were made in order to reach the corrected DVS values of acid filtrates in particular. In other measured streams, the 10% accuracy criterion was maintained. The new targeted values for filtrates (30% loss of coverage in D_0, 20% both in D_1 and D_2) are shown in Figure 3 in addition to these measured and standard DVS calibrated as well as those from three developed cases.

The calibrated values represent the minimum. In the new simulations the maximum achievable addition of DOM in the acid filtrates was 78, 71 and 100% in the D_0, D_1 and D_2 stages, respectively. At the same calibration the change in E_1 and E_2 stage filtrates was 1 and –4%, respectively, and thus satisfies the 10% accuracy criterion. However, this corrected situation led to a very high calculated washing efficiencies in the D-stages. From this case it was concluded that further adjustments were needed with higher priority on washing efficiency values.

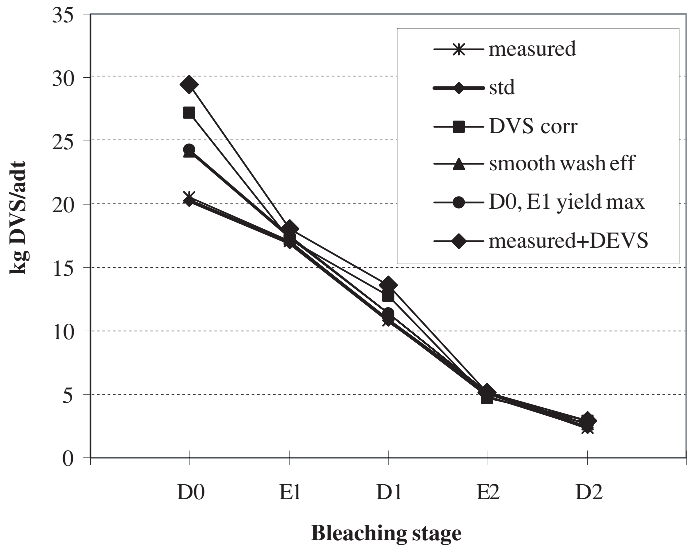

Figure 3 Dissolved organic matter as kgDVS/adt in washing filtrates in selected cases

Maximum attainable DEVS coverage and Norden washing efficiency of 2.0–4.0 as calibration targets following results were achieved. Washing efficiency profile of 3.5, 2.5, 3.5, 2.5 and 2.0 could be achieved in DE_ODE_PD sequence washers, respectively, with 42%, 22% and 47% of targeted DEVS covered in the acid stages. In the alkaline E_1 and E_2 stage the increase of calibrated DOM was 2 and 6%, respectively, compared to the measured values. The latter values satisfy well the requirement of covering the marginal DEVS escape in alkaline filtrates.

Effects of yield estimate and lignin removal specificity on the amount of lost quantity (CD+VOC)

Further simulations were made in order to evaluate the validity and sensitivity of the considerable CD+VOC in reactors of a fully balanced fibreline. An increase of yield has to be compensated with a decrease in CD+VOC in order for the situation to be unchanged in the washer. In such testing the level of lignin specificity in yield loss is one characteristic which can be used as an evaluation criterium. With yield profiles given in Table 3, the respective lignin share of yield loss is shown in Figure 4 and the resulting CD+VOC is shown in Figure 5.

When defining the carryover as the amount of non-fibrous organic matter that accompanies the pulp, it is assumed that carryover does not include lignin which is measured with kappa number analysis. In practice, the fraction of adsorbed organics, which is not washed out in the kappa determination with the excessive quantity of pure water but which is washed with the weak alkaline washing liquor in carryover measurements, forms a potential overlap in measurements of organics. In this calculation procedure the potential overlap causes overestimation of yield loss through over estimation of lignin in pulp and thus requirement for higher CD+VOC. However, the quantity of this overlap is assumed to be marginal.

Table 3 Yield profile used in different cases of calibration simulations

	O_2	D_0	E_1	D_1	E_2	D_2
Std and DVS corr.	98	98.8	98	99.5	99.42	99.7
DVS smooth wash eff.	98	99	98.1	99.5	99.42	99.7
Yield, D_0 E_1 max.	98	99.4	98.25	99.5	99.42	99.7

From Figure 4 the influence of increasing yield on the specificity of delignification in the D_0 and E_1 stage can be seen. The yield increase in D_0 and E_1 stages was tested in a situation where the smooth profile of Norden washing efficiency, E, was used as one major calibration criterion. In this case DVS values could be corrected only partially for escaped DEVS as given above. The high yield of 99.4% and the resulting extremely high lignin specificity (>85%) in the D_0 stage undoubtedly represents an unrealistically high efficiency. It must be remembered that the idea of the D_0 stage being the preparative stage in lignin removal (20%) and E_1 being the actual stage for removal (58%) was used. Utilisation of this idea was supported with the results of lignin measurements (by abs. 280 nm) where only about 35% of measured DVS could be covered by the measured lignin in the D_0 stage filtrate while the percentage in the E_1 stage filtrate was about 50% and in the O_2 filtrate was about 65%.

The considerable transformation and complete degradation of lignin and other organics as well as low lignin dissolution out of the fibre in the D_0 stage is partly explained with more than 40% recycle of the D_0-filtrate back for dilution water to bring the pulp to the D_0-stage. A considerable fraction of chlorine dioxide is consumed to degrade the DOM in the recycling liquor and thus the DOM degrading and preparative lignin processing role of the stage is emphasised. In conclusion of the above, the extremely low CD+VOC (7 kg/adt; Figure 5) in the tested cases represents a value that already exceeds the practically possible minimum.

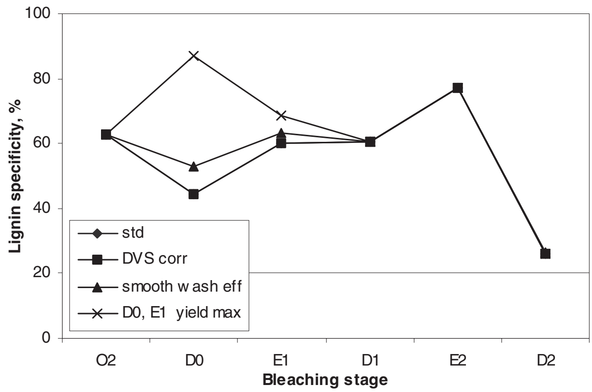

Figure 4 Share of lignin in yield loss (lignin specificity) along fibreline in selected cases

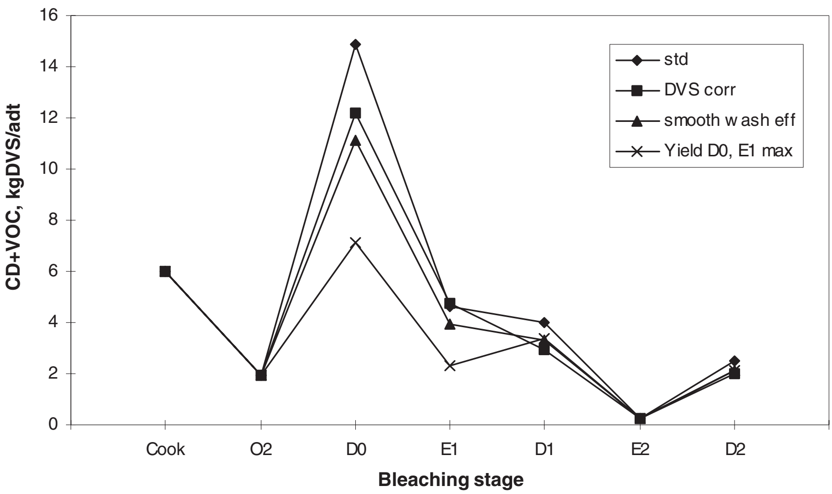

Figure 5 Complete degradation and volatile organic compounds (CD+VOC) in fiberline in selected cases of calibration

The results showed that the amount of overall CD+VOC in D_0 and D_1-stages decreased about 20–25% from the original standard DVS case when DEVS were considered as fully as possible in filtrates of acid stage washers. When other factors were kept as constant as possible in this simulation washing efficiency values in acid stages increased beyond acceptable. However, lower washing efficiency values than those could be applied when DEVS coverage, yield and lignin specificity were taken as variables. The effects on CD+VOC can be seen in Figure 5.

In the block of D_0 and E_1 the applied yield loss in the two appropriate cases of "smooth E" and "D_0 and E_1 yield maximum" was 27 (2.9%) and 22 kg/adt (2.4%), respectively. Thus, the specificity of lignin removal was 59 and 73%, respectively. Net carryover in the block was 2.1 kgDOM/adt, washing waters 11.4 and 5.2 kgDOM/adt and filtrates 13.5 and 17.5 kgDOM/adt, respectively. According to this balance the lost quantity of CD+VOC was 15 and 10 kgDOM/adt, respectively. If adding full DEVS coverage to the D_0-filtrate without even DEVS coverage in the incoming D_0-washing water (D_1-filtrate) value and without balancing the other streams, the extreme minimum value for CD+VOC with this biased calculation would give 7.5 kgDOM/adt in this block in the latter case. This example of varying yield estimate emphasises that the quantity of CD+VOC cannot be neglected in any case.

The above specificity evaluation gives an indication that from the CD+VOC profiles in Figure 5, the lowest, related to extreme yield and specificity values (Figure 4) is unlikely and the value of the "smooth E"-case for the D_0-stage CD+VOC (10–11 kg/adt) is the most obvious. The reduction of the CD+VOC value compared to the standard DVS calibration case without DEVS consideration is 4–5 kg/adt, which was also the quantity of identified volatile compounds in D_0 filtrate (Luonsi *et al.*, 1998).

Yield loss in the whole actual bleaching (DE_ODE_PD) of "smooth E" and "D_0 and E_1 yield maximum" cases was 40 (4.3%) and 34 kgDOM/adt (3.6%), respectively. Carryover in from O_2-bleaching was 13 kgDOM/adt and carryover out from the D_2 stage was 2.9 kgDOM/adt. Thus the yield loss and net carryover together was 50 kgDOM/adt and 44 kgDOM/adt, respectively. Washing waters to the E_2- (partly condensates) and D_2-stage (from dewatering and drying) brought 1.7 kgDOM/adt into the fiberline. The DOM in the D_0 and E_1 filtrate was 13.5 and 17.5 kg/adt, respectively. From these balances CD+VOC in these cases was 21 and 15 kg/adt, respectively. The lignin removal from kappa 17 to 0.2 in these cases was 24 kg/adt showing 59–69% overall specificity in actual bleaching. No further criteria were available to define the obvious situation more accurately within this frame. Additionally, if taking the DEVS coverage fully into account in the D_0-stage filtrate without balancing other streams, there would be 2.5 kg/adt more DOM in the filtrate and thus the lost DOM quantity would be 18.5 and 12.5 kg/adt, respectively. Even with this latter biased way of balance calculation the fate of DOM as CD+VOC remains equally considerable discharge stream as those of acid filtrate and alkaline filtrate. Each of these three streams represent 1.3–2.2% yield loss from the pulp entering actual bleaching.

The faced difficulty of satisfying both the washing efficiency and full DEVS coverage for DOM measured by DVS in acid filtrates leaves water balance, potential kappa- and carryover DVS-measurement overlap, evaluation method of DEVS, as well as washing efficiency calculations through DVS measurement data, as those aspects requiring further evaluation and development if higher accuracy is required.

The overall quantity of complete degradation and VOC in the studied fibreline was between 23 and 35 kgDVS/adt. In order to narrow the achieved range considerably, various kinds of actions would be beneficial: (1) comprehensive evaluation of standard characterisation methods of process streams and wastewaters for creating one appropriate set overall; (2) comprehensive sampling and analysing programme including well calibrated mill measurements. A project covering all these demands, would require considerable resources.

The balances were studied up to the elemental level in the oxygen delignification stage (Luonsi and Halttunen, 2000). The effects of the findings on the actual DE_ODE_PD bleaching stages remain to be studied. In any case, the description of operational status in the whole fibreline depends on the prioritisation of potentially contradicting criteria. Therefore multidisciplinary evaluation of the results is the key for finding the state description of the process closest to the real.

Conclusions

Combination of measured dissolved organic matter (DOM) in sidestreams of bleached kraft mill fibreline with the predetermined water balance and the routine mill operational data in a simulation model opens the way for studying full organic matter balance in the fibreline and thus enables evaluation of the fate of the DOM.

The considerable loss of DOM from the fibreline balance was shown. The extreme cases of this study showed that the overall quantity of complete degradation and volatile organic compounds in the studied softwood ECF bleached kraft fibreline was between 23 and 35 kgDVS/adt of pulp. The result within this range depends on prioritisation of calibration criteria, such as compensation of dissolved easily volatilising solids lost in DVS analysis, washing efficiency of drum washers, as well as yield estimate and lignin specificity used in calculation.

The methods of this study, when effectively utilised with good professional awareness, provide a useful tool in developing and optimising bleached kraft pulping process operation and environmental discharges. This tool enables intensive cooperation between pulping specialists and wastewater specialists.

Acknowledgements

Professor Matti Viitasaari (late) is highly acknowledged for encouragement and advice throughout the project. Vesa Mikkonen, M.Sc. is acknowledged for his valuable advice through his theoretical and practical process knowledge. Special thanks go to senior professional Aarne Granroth for discussions about the background for pulp mill operations and decision making. Thanks are also due to Dr Maaret Kulovaara for discussions on the nature of organics.

References

Axegård, P. and Backlund B. (1999). Opportunities for maximum resource efficient production of bleached kraft pulp. In: *The Second Biennial Johan Gullichsen Colloquium*, 9–10 September, Dipoli, Espoo, Finland.

Lazaar, D. (1998). Personal communication.

Luonsi, A. and Halttunen, S. (1997). Development of simulation system to combine kraft process and wastewater treatment – Calibration of bleached kraft model through dissolved organic matter in fiberline. *Wat. Sci. Tech.*, **35**(2–3), 15–23.

Luonsi, A., Lehtonen, M., Deleuze, S., Pönni, S. and Halttunen, S. (1998). Loss of volatile organics from kraft bleaching filtrates in the evaporation/drying phase of the analysis for dissolved total solids (DTS) and dissolved volatile solids (DVS). *Wat. Sci.Tech.*, **38**(4–5), 281–288.

Luonsi, A. and Halttunen, S. (2000). Operational status of oxygen delignification described through elemental dissolved organic matter analysis. *Int. Pulp Bleaching Conference*, 27–30 June, Halifax, Canada. Book of Poster Presentations, pp. 47–54.