

# Bestätigung der Metadaten/Metadata Approval Sheet

Sehr geehrte Autoren,

Bitte prüfen Sie diese Angaben sorgfältig. Sie sind für alle nachfolgenden Publikationswege (Print, Online, Abstracting und Indexing, Suchmaschinen etc.) relevant. Änderungen sind später nicht mehr möglich. Bitte führen Sie eventuelle Korrekturen in den beschreibbaren Feldern in der rechten Spalte aus. Bitte bestätigen Sie die Korrektheit der Daten, indem Sie das Feld unten anklicken.

Vielen Dank für Ihre Mitarbeit, De Gruyter

Dear author,

Please check these data carefully. They are relevant for all following publication processes in Abstracting and Indexing Services, search engines. They cannot be changed after publication. Please fill in your corrections within the editable fields in the right column. Please confirm the correct data by clicking the field below.

Thanks for your kind cooperation, De Gruyter

**Journal-Name:** Nordic Pulp & Paper Research Journal

**Article-DOI:** 10.1515/npprj-2022-0017

**Article-Type:** Miscellaneous

**Article-Title:** Oxidation process concept to produce lignin dispersants at kraft pulp mill

**Subtitle:** none


**Author 1:**

**Surname:** Kalliola

**First Name:** Anna

**Corresponding:** yes

**E-Mail:** anna.kalliola@vtt.fi

**Affiliation:** Sustainable Products and Materials,  
VTT Technical Research Centre of Finland Ltd,  
P. O. BOX 1000, FI-02044 Espoo, Finland


**Author 2:**

**Surname:** Kangas<sup>†</sup>

**First Name:** Petteri<sup>†</sup>

**Corresponding:** no

<sup>†</sup>**E-Mail:** none

**Affiliation:**


**Author 3:****Surname:** Winberg**First Name:** Iris**Corresponding:** no**E-Mail:** iris.winberg@vtt.fi**Affiliation:** Carbon neutral solutions, VTT  
Technical Research Centre of Finland Ltd,  
P. O. BOX 1000, FI-02044 Espoo, Finland


**Author 4:****Surname:** Vehmas**First Name:** Tapio**Corresponding:** no**E-Mail:** tapio.vehmas@vtt.fi**Affiliation:** Knowledge driven design, VTT  
Technical Research Centre of Finland Ltd,  
P. O. BOX 1000, FI-02044 Espoo, Finland


**Author 5:****Surname:** Kyllönen**First Name:** Hanna**Corresponding:** no**E-Mail:** hanna.kyllonen@vtt.fi**Affiliation:** Sustainable Products and Materials,  
VTT Technical Research Centre of Finland Ltd,  
P. O. BOX 1604, FI-40100 Jyväskylä, Finland


**Author 6:****Surname:** Heikkinen**First Name:** Juha**Corresponding:** no**E-Mail:** juha.heikkinen@vtt.fi**Affiliation:** Sustainable Products and Materials,  
VTT Technical Research Centre of Finland Ltd,  
P. O. BOX 1604, FI-40100 Jyväskylä, Finland


**Author 7:****Surname:** Poukka**First Name:** Outi**Corresponding:** no**E-Mail:** outi.poukka@metsagroup.com**Affiliation:** Business Development, Metsä Fibre  
Oy, P. O. BOX 30, FI-02020 Metsä, Finland


**Author 8:**

**Surname:** Kempainen

**First Name:** Katariina

**Corresponding:** no

**E-Mail:** katariina.kempainen@metsagroup.com

**Affiliation:** Group R&D, Metsä Spring Oy,  
Revontulenpuisto 2, FI-02100 Espoo, Finland


**Author 9:**

**Surname:** Sjögård

**First Name:** Pauliina

**Corresponding:** no

**E-Mail:** pauliina.sjogard@andritz.com

**Affiliation:** Recovery and Power, ANDRITZ Oy,  
Hermiankatu 8D, FI-33720 Tampere, Finland


**Author 10:**

**Surname:** Pehu-Lehtonen

**First Name:** Lauri

**Corresponding:** no

**E-Mail:** lauri.pehu-lehtonen@andritz.com

**Affiliation:** Recovery and Power, ANDRITZ Oy,  
Tammasaarenkatu 1, FI-00180 Helsinki, Finland


**Author 11:**

**Surname:** Liitiä

**First Name:** Tiina

**Corresponding:** no

**E-Mail:** tiina.liitia@kemira.com

**Affiliation:** Sustainable Products and Materials,  
VTT Technical Research Centre of Finland Ltd,  
P. O. BOX 1000, FI-02044 Espoo, Finland  
Currently Kemira, R&D Fiber and Bioeconomy,  
Luoteisrinne 2, FI-02270 Espoo, Finland


**Data checked and receipted**  **Date:**

Wenn Sie die Korrektheit der Daten nicht durch einen Haken bestätigen oder keine Änderungen in diesem Formular angeben, gehen wir davon aus, dass die angegebenen Daten korrekt sind.

If you don't confirm the correctness by checking the box or implement your corrections in this form, we have to presume that all data are correct.

# Author Query Form

DE GRUYTER

Journal code: NPPRJ

Article No.: NPPRJ-2022-0017

---

Dear Author,

During the preparation of your manuscript for typesetting, some questions have arisen. These are listed below. Please check your typeset proof carefully, respond to all queries on this form. Please mark corrections and respond to all queries by using the PDF commenting tools.

## Typesetter's queries and/or remarks

Proof page/line	Details required
Q1	Please note that text "author is deceased 3.11.2019" was removed per house style requirements. (p. 1/ line 3)

Many thanks for your assistance.

## Miscellaneous

Anna Kalliola\*, Petteri Kangas<sup>†</sup>, Iris Winberg, Tapio Vehmas, Hanna Kyllönen, Juha Heikkinen, Outi Poukka, Katariina Kemppainen, Pauliina Sjögård, Lauri Pehu-Lehtonen and Tiina Liitiä

# Oxidation process concept to produce lignin dispersants at kraft pulp mill

<https://doi.org/10.1515/npprj-2022-0017>

Received February 22, 2022; accepted March 19, 2022

**Abstract:** This paper presents the concept of an alkali-O<sub>2</sub> oxidation process for producing lignin dispersants in a feasible manner at a kraft pulp mill. The oxidation process uses O<sub>2</sub> gas to increase the anionic charge of lignin and the final oxidised lignin can serve as a concrete plasticiser or versatile dispersant. The integrated process provides several benefits for lignin recovery, the following lignin oxidation, and recycling of chemicals. Firstly, CO<sub>2</sub> precipitated kraft lignin can be used without a sulphuric acid washing step. This simplifies the lignin recovery and no excess sulphur is introduced into mill cycle. As the unwashed lignin is alkaline in nature, the need for fresh alkali in the lignin oxidation is reduced. Moreover, oxidised white liquor, readily available in the mill, can be applied as a partial source of alkali. Finally, membrane filtration of the oxidised lignin solution enables the recirculation of sodium and sulphur back to the chemical cycle and provides a concentrated lignin product. Based on a simulation study, this novel concept significantly decreased the need for purging fly ash at the mill when compared to conven-

tional lignin recovery. It was also demonstrated that the novel lignin dispersants can compete with the tested commercial oil-based plasticisers.

**Keywords:** Concrete plasticisers; Dispersants; Kraft lignin; Oxidation; Oxygen.

## Introduction

Ever increasing interest in recovering multiple value-added products from kraft pulp mills has introduced technologies for lignin isolation and upgrading. For decades, Indulin was the only isolated kraft lignin product available (Li and Takkellapati 2018). More recently, LignoBoost (Tomani 2010, Wallmo et al. 2015) and LignoForce (Kouisni et al. 2016) technologies have been applied for lignin recovery in some kraft pulp mills. Similar recovery technologies, such as SLRP (Lake and Blackburn 2014) and A-Recovery+ (Pehu-Lehtonen and Sjögård 2018), are being introduced by other vendors. In these processes, lignin is typically precipitated from the black liquor using carbon dioxide (CO<sub>2</sub>) followed by further precipitation and washing with sulphuric acid (H<sub>2</sub>SO<sub>4</sub>) providing a lignin with low ash content (Kienberger et al. 2021). A typical softwood kraft mill has an oversupply of sulphur coming into the process from tall oil separation. The recovery boiler's electrostatic precipitator dust i. e. fly ash is mainly composed of sodium sulphate (Na<sub>2</sub>SO<sub>4</sub>) and carbonate (Na<sub>2</sub>CO<sub>3</sub>) and a common way to remove sulphur (S) from the mill cycle is to purge the fly ash as waste. Simultaneously, sodium (Na) is removed from the cycle and Na must be replaced as a make-up chemical in the form of sodium hydroxide (NaOH). When sulphuric acid is used

\*Corresponding author: Anna Kalliola, Sustainable Products and Materials, VTT Technical Research Centre of Finland Ltd, P. O. BOX 1000, FI-02044 Espoo, Finland, e-mail: anna.kalliola@vtt.fi

Petteri Kangas<sup>†</sup>

Iris Winberg, Carbon neutral solutions, VTT Technical Research Centre of Finland Ltd, P. O. BOX 1000, FI-02044 Espoo, Finland, e-mail: iris.winberg@vtt.fi

Tapio Vehmas, Knowledge driven design, VTT Technical Research Centre of Finland Ltd, P. O. BOX 1000, FI-02044 Espoo, Finland, e-mail: tapio.vehmas@vtt.fi

Hanna Kyllönen, Juha Heikkinen, Sustainable Products and Materials, VTT Technical Research Centre of Finland Ltd, P. O. BOX 1604, FI-40100 Jyväskylä, Finland, e-mails: hanna.kyllonen@vtt.fi, juha.heikkinen@vtt.fi

Outi Poukka, Business Development, Metsä Fibre Oy, P. O. BOX 30, FI-02020 Metsä, Finland, e-mail: outi.poukka@metsagroup.com

Katariina Kemppainen, Group R&D, Metsä Spring Oy, Revontulenpuisto 2, FI-02100 Espoo, Finland, e-mail: katariina.kemppainen@metsagroup.com

Pauliina Sjögård, Recovery and Power, ANDRITZ Oy, Hermiankatu 8D, FI-33720 Tampere, Finland, e-mail: pauliina.sjogard@andritz.com

Lauri Pehu-Lehtonen, Recovery and Power, ANDRITZ Oy, Tammasaarenkatu 1, FI-00180 Helsinki, Finland, e-mail: lauri.pehu-lehtonen@andritz.com

Tiina Liitiä, Sustainable Products and Materials, VTT Technical Research Centre of Finland Ltd, P. O. BOX 1000, FI-02044 Espoo, Finland; and Currently Kemira, R&D Fiber and Bioeconomy, Luoteisrinne 2, FI-02270 Espoo, Finland, e-mail: tiina.liitia@kemira.com

52  
53  
54  
55  
56  
57  
58  
59  
60  
61  
62  
63  
64  
65  
66  
67  
68  
69  
70  
71  
72  
73  
74  
75  
76  
77  
78  
79  
80  
81  
82  
83  
84  
85  
86  
87  
88  
89  
90  
91  
92  
93  
94  
95  
96  
97  
98  
99  
100  
101  
102

1 in the lignin precipitation stage, there is increased pres- 52  
2 sure to remove sulphur from the cycle and consequently 53  
3 increased need to add make-up NaOH. Besides the chal- 54  
4 lenge of maintaining the mill Na/S balance, NaOH is a 55  
5 major cost item for lignin recovery (Axelsson et al. 2006). 56  
6 Furthermore, washing stages in the recovery processes 57  
7 comprise a significant part of the investment costs. 58

8 Although kraft lignin has been extensively inves- 59  
9 tigated and recognised as an important alternative to 60  
10 petroleum based chemicals and materials, the market of 61  
11 large volume lignin products is still under development. 62  
12 Kraft lignin is currently used mainly for energy, although 63  
13 some lignin-based products have been commercialised. In 64  
14 these products, lignin is used to replace phenol in phenol 65  
15 formaldehyde (PF) resins for plywood and laminates. Fur- 66  
16 thermore, sulfonated lignin is used as a dispersant, similar 67  
17 to lignosulphonates (Aro and Fatehi 2017, Li and Takkel- 68  
18 lapati 2018). The performance of sulphonated lignins is 69  
19 however low compared to the current state-of-art synthetic 70  
20 products, and only partial phenol substitution is possi- 71  
21 ble in PF resins. The ultimate goal is to create sustainable 72  
22 lignin products that can compete in cost-performance with 73  
23 the current synthetic products, and with a market volume 74  
24 high enough considering the potential lignin production 75  
25 capacity. Scaling-up technologies to achieve technical and 76  
26 economic optimization of lignin applications have been 77  
27 recommended to enhance the commercialization of lignin 78  
28 products. In addition, collaborative research efforts con- 79  
29 necting stakeholders in the value chain are needed (Bajwa 80  
30 et al. 2019, Dessbesell et al. 2020). 81

31 A novel LigniOx technology using alkali-O<sub>2</sub> oxida- 82  
32 tion (of lignin) is a promising method for creating value- 83  
33 added lignin products (Kalliola 2015). The oxidation con- 84  
34 verts water-insoluble technical lignins to water-soluble 85  
35 surfactants, where anionic charge at mild acidic condi- 86  
36 tions stems mainly from carboxylic acids and hydroxyl-*p*- 87  
37 quinones (Kalliola 2015, Tamminen et al. 2018). Oxidised 88  
38 lignin could be used for example as a plasticiser in con- 89  
39 crete (WO2015049424, Kalliola et al. 2015) and gypsum or 90  
40 as a dispersant in paints and coatings (WO2017077198, 91  
41 Kalliola et al. 2017). The market size and market value of 92  
42 these end-products are attractive. Currently, the LigniOx 93  
43 project, partially funded by BBI JU under the H2020 pro- 94  
44 gram of the European Commission, is aiming to scale- 95  
45 up and demonstrate the feasibility of the lignin oxidation 96  
46 technology for these promising markets. 97

47 Anionic dispersants cover most of the dispersant mar- 98  
48 ket. Concrete plasticisers are anionic dispersants that dis- 99  
49 perse cement particles to allow good workability of fresh 100  
50 concrete and ensure good strength properties of the ma- 101  
51 tured concrete. Similarly, anionic dispersants are used 102

in preparing paints and coatings containing a high por-  
tion of different inorganic pigments. Water-soluble lig-  
nosulphonates from sulphite pulping have served the  
market as bio-based plasticisers and dispersants. Some  
sulphonated kraft lignin products are also on the mar-  
kets for dispersants (Aro and Fatehi 2017). Typically,  
the performance of lignosulfonates or sulphonated kraft  
lignin is clearly lower than that of synthetic plasticiser  
products (Ramachandran et al. 1998). Synthetic superplasticiser  
products include, for example, sulfonated naphthalene  
formaldehyde condensates or polycarboxylate ether based  
co-polymers. Polyacrylic acids serve as typical anionic dis-  
persants for pigments in paint and coatings.

Interestingly, oxidised lignins, including oxidised  
kraft lignin, have been shown to outperform lignosul-  
fonate products or even some of the synthetic products  
(Kalliola et al. 2015, 2017, 2018, Fearon et al. 2021). How-  
ever, a feasible industrial process concept for the produc-  
tion of oxidised kraft lignin based dispersants that can be  
integrated into a kraft pulp mill without interfering with  
the chemical balance of the main process has not previ-  
ously been fully investigated and optimised.

The aim of this paper is to introduce a techno-  
economically feasible process concept jointly invented by  
VTT, Metsä Fibre, and ANDRITZ to produce effective lignin  
dispersants at a kraft pulp mill (WO2020157386). This pa-  
per demonstrates the benefits of the oxidation process  
using crude CO<sub>2</sub> precipitated kraft lignin instead of acid  
washed kraft lignin on the Na/S balance of the pulp mill.  
Furthermore, the performance of the oxidised lignin prod-  
uct in mortar and concrete plasticisation is presented.

## Materials and methods

### Oxidation

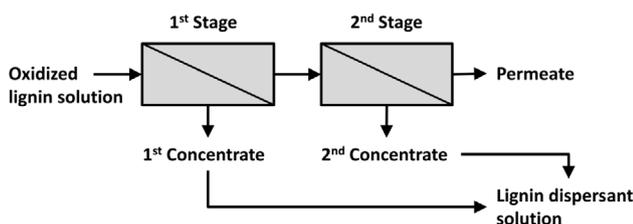
For oxidation, unwashed softwood kraft lignin (UW-SW-  
KL) from Metsä Fibre Rauma mill was isolated by apply-  
ing a lignin recovery pilot from ANDRITZ. Oxidised white  
liquor (OWL) containing 75.5 g/kg of effective alkali and  
95.3 g/kg of total alkali (determined by SCAN-N 30:85) was  
provided by Metsä Fibre. The chemical composition of the  
unwashed lignin and acid washed lignin (also isolated at  
Metsä Fibre Rauma using lignin recovery pilot from AN-  
DRITZ) is presented in Table 7, Appendix.

The oxidation procedure and related measurements  
and determinations were done as previously described  
(Kalliola 2015, Kalliola et al. 2017) in the case of commer-  
cial softwood kraft lignin or soda lignin. A multipurpose  
pressure reactor of size 7-L (Juchheim, Germany) equipped

with a gas stirrer was applied for the oxidation at VTT. At first, lignin material was dissolved in a mixture of water and NaOH (UW-SW-KL-Ox1) or in a mixture of water and OWL (UW-SW-KL-Ox2) at lignin content of 15 %. The effective alkali dose used was 17 % on lignin. The lignin solution was heated up to 70 °C, the reactor was pressurised with O<sub>2</sub>, and a reaction time of 30 min under efficient mixing was used. During the reaction, technical (50 %) NaOH was introduced into the reactor to compensate for the pH drop caused by the acidic reaction products and to further accelerate the formation of anionic charge in lignin. The alkali dose used was 33 % on lignin. O<sub>2</sub> consumption at the end of the reaction was 23-24 % on lignin and pH slightly above value 10.

## Membrane filtration

After oxidation the lignin solution was post-treated by membrane filtration, which aimed to increase the lignin content of the oxidised lignin solution with a high lignin yield. The membrane filtration also provided means to recycle sodium and sulphur back to the mill recovery cycle. Post-treatment of the oxidised lignin solution (UW-SW-KL-Ox1) was carried out by 2-stage membrane concentration using a SEPA CF plate-and-frame crossflow laboratory filtration unit (Sterlitech, USA) with a membrane area of 140 cm<sup>2</sup> and a maximum operating pressure of 69 bar. A polymeric polyethersulfone (PES) nanofiltration membranes, NP010 (Microdyn Nadir, Germany), with a molecular weight cut-off in the range of 1,000–1,200 Da were used in both stages. A scheme illustrating the membrane filtration of oxidised lignin solution is shown in Figure 1. Concentration at the 1st stage was continued until a water recovery (WR) value of 60 % was reached. Concentration of permeate from the 1st stage was continued at the 2nd stage to WR value of 76 %. The overall WR of the concentration was 46 %. The 1st and 2nd concentrates were combined to form the lignin dispersant solution. Lignin concentration in the concentrate fractions and in the permeate was determined.



**Figure 1:** A scheme illustrating membrane filtration of oxidised lignin solution for the production of a dispersant solution.

## Analysis of sodium/sulphur balance of pulp mill

The analysis of Na/S balance of a pulp mill wherein the production of oxidised lignin would be integrated was based on a simulation conducted using a reference model of softwood kraft pulp mill. The model comprises a single-line mill with wood handling, continuous cooking, two-stage oxygen delignification, ECF bleaching (D<sub>0</sub>-E<sub>op</sub>-D<sub>1</sub>-P), pulp drying, seven-stage evaporation with tall oil recovery, recovery boiler, recausticising, bark-fired lime kiln, and condensing turbine. The reference mill is described in detail by Kangas et al. (2014). Minor modifications to the original model of the reference mill were made in studies by Onarheim et al. (2017) and were also utilised here. The overall block flow diagram of the reference mill is shown in Figure 2. The reference mill model was described using Wingems 5.3 modelling tool (Valmet 2022) with a link to Microsoft Excel for data processing and economic computations.

In addition to the reference mill not including lignin recovery (1), five different concepts (2–6) were evaluated:

1. No lignin recovery (reference)
2. Lignin recovery with sulphuric acid washing
  - product: acid washed lignin
3. Lignin recovery without acid washing
  - product: primary lignin cake
4. Oxidation of acid washed lignin
  - product: oxidised lignin
5. Oxidation of unwashed primary lignin cake
  - product: oxidised lignin
6. Oxidation of unwashed primary lignin cake (no permeate recycling)
  - product: oxidised lignin

The additional simplified lignin recovery and oxidation process including membrane filtration were introduced to the reference mill model within the evaporation subunit. Lignin is a major energy source at pulp mills, therefore, only part of the lignin (20 %) was split from the main black liquor stream for oxidation. The remaining 80 % of black liquor is sufficient to cover the energy needs of the mill. Chemicals were introduced and lignin was recovered. The remaining solution was returned to the evaporation train. Recovered lignin (washed or unwashed) was alkali-O<sub>2</sub> oxidised (concepts 4–6) and respective chemicals were used. After the membrane concentration of oxidised lignin solution, part of the permeate (50 %) was recycled to the oxidation reactor and part (50 %) returned to the evaporation train (concepts 4 and 5) or the permeate was fully (100 %) returned (concept 6).

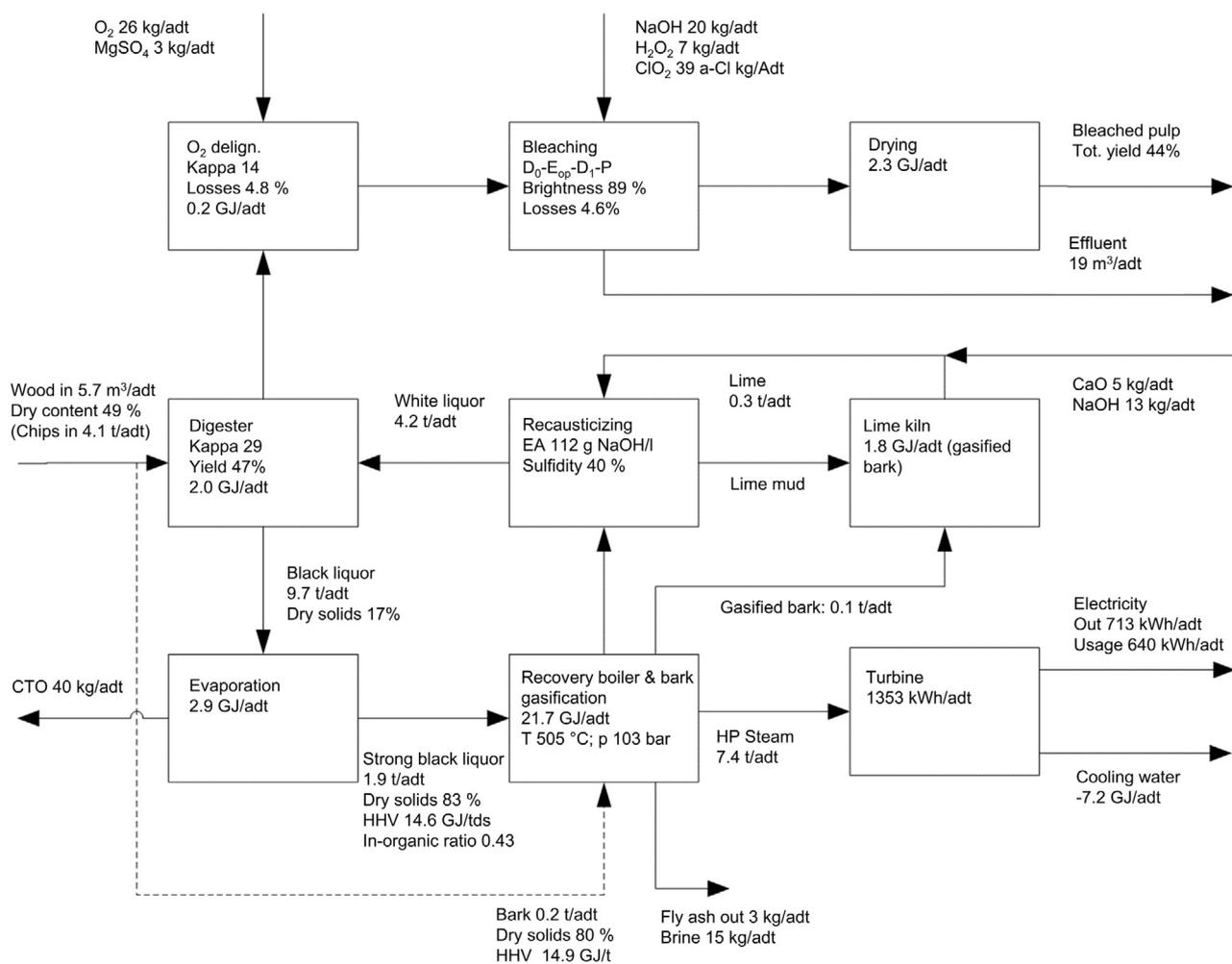


Figure 2: Reference softwood kraft pulp mill, its major areas, and key process parameters.

From the black liquor led to the evaporation plant, 20% was fractionated for the oxidation process. This would correspond to an annual production capacity of 100 000 tonne of lignin product in a pulp mill producing 1 000 000 air dry tonne (adt) softwood pulp annually. Alkaline black liquor was acidified with CO<sub>2</sub> to precipitate lignin. The fractionated lignin precipitate i. e. primary lignin cake was washed with water and sulphuric acid (concept 2). Typical chemical consumptions are 2000 kg of H<sub>2</sub>O/t lignin and respectively 200 kg H<sub>2</sub>SO<sub>4</sub>/t lignin (Tomani et al. 2011). The possibility of production of sulphuric acid from concentrated non-condensable gases was not considered.

The third concept simulated included the precipitation of lignin with CO<sub>2</sub> but omitting the washing with sulphuric acid (concept 3). This should be beneficial for the sulphur balance of the mill and also reduce the investment cost of the recovery process, and operation costs in the ox-

idation stage. On the other hand, the quality of the recovered lignin product might be reduced, resulting in too impure product for some applications. The key parameters of these lignin recovery concepts are given in Table 1.

The lignin oxidation and concentration processes were simulated with the following set-up. Lignin oxidation was conducted by first dissolving the recovered lignin (either acid washed or unwashed lignin) into an alkaline solution. Here, oxidised white liquor was used as an alkali source. Next, lignin was oxidised by introducing O<sub>2</sub> gas to the system while simultaneously feeding fresh NaOH to the reactor. The lignin oxidation process was assumed to use 500 kg effective alkali (NaOH or oxidised white liquor) per tonne of lignin regardless of the lignin being acid washed or unwashed. After oxidation, the solution was concentrated using membrane filtration. WR of 70% from the solution was used, while only 6% of the oxidised lignin passed through the filtration to the permeate. An-

**Table 1:** Key parameters for lignin recovery, lignin oxidation and concentration.

Concept #	Unit	1	2	3	4	5	6
Parameter		No lignin recovery (reference)	Recovery with acid washing	Recovery without acid washing	Oxidation for acid washed lignin	Oxidation of unwashed primary lignin cake	Oxidation of unwashed primary lignin cake (no perm. recycling)
<b>Lignin recovery</b>							
Amount of lignin	%	–	20	20	20	20	20
H <sub>2</sub> SO <sub>4</sub> charge	kg/t L.	–	200	0	200	0	0
Washing water	kg/t L.	–	2000	–	2000	–	–
Na in lignin	g/kg	–	5	50	5	50	50
S in lignin	g/kg	–	25	20	25	20	20
<b>Lignin oxidation</b>							
OWL charge	kg EA/t L.	–	–	–	167	167	167
Lignin content	%	–	–	–	15	15	15
NaOH charge	kg/t L	–	–	–	333	333	333
Yield	%	–	–	–	90	90	90
Permeate recycling	%	–	–	–	50	50	0
<b>Concentration</b>							
WR in filtration	%	–	–	–	70	70	70
Yield, ox. lignin	%	–	–	–	94	94	94
Na to retentate	%	–	–	–	37	37	37
S to retentate	%	–	–	–	38	38	38

EA = effective alkali, L. = lignin, WR = water reduction, perm. = permeate.

nual recovery capacity of 100 000 tonnes of lignin results in approximately 84 600 tonnes of oxidised lignin product. Na and S rejections in the membrane filtration stage were based on concentration experiments. The key parameters of lignin oxidation and concentration processes are also given in Table 1.

For the simulations, no minimum limit was set for fly ash dumping. NaOH was used as the sodium make-up chemical and H<sub>2</sub>SO<sub>4</sub> as the sulphur make-up chemical for balancing the fly ash. The main components of fly ash were Na<sub>2</sub>SO<sub>4</sub> and Na<sub>2</sub>CO<sub>3</sub>. In the simulated concepts, fly ash S/Na ratio (kg/kg) were mainly between 0.45–0.47.

## Application testing

The plasticiser performance of the oxidised lignin solutions was evaluated in mortar and concrete.

Mortar was prepared using standard sand, cement (CEM I 42.5N, MH LA SR3 by CEMENTA Ab or CEM I 52.5N, MEGASEMENTTI by FINNSEMENTTI) and water with a ratio of 1:1:0.4. The dosage of oxidised lignins was 0.20 or 0.60 % (based on lignin) on cement. Plasticiser was added to the mix at the end of the water addition. Commercial lignosulphonate (WRDA 90D by Grace Construction products), polycarboxylate ether (Masterglenium Sky 610 by BASF) and naphthalene (Pantarhit LK FM by HaBe) based plas-

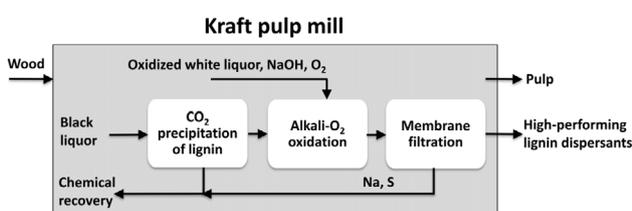
ticisers were used as reference products. Defoamer, tributyl fosfate (TBF) was used in all experiments. The fluidity of the mortar was measured using Haegermann flow table (∅300 mm) method and a mould with a diameter of 100 mm. Flow value represents the spread (diameter) of mortar.

The performance of oxidised lignins was also tested in concrete according to a superplasticiser standard SFS-EN 934-2. Concrete was prepared using fine and coarse stone aggregates, cement (CEM I 52.5N, MEGASEMENTTI by FINNSEMENTTI) and water. Plasticiser dosing 0.36 % (based on lignin) on cement was used. Plasticiser was added to the mix at the end of the water addition. Pantarhit LK FM was used as a reference product. Defoamer, TBF was used in all experiments. The workability of the concrete was evaluated using a slump test. The slump value represents the slump of concrete, which is formed after pulling up the cone (height 300 mm) filled with the material.

## Results and discussions

A schematic presentation of the process concept for producing novel lignin dispersants in a kraft pulp mill is presented in Figure 3. The concept provides several benefits for the lignin isolation process, for the following lignin ox-

1 oxidation process, and for recycling of chemicals. The oxidized lignin product serves as a high-performance concrete plasticiser or versatile dispersant, but also more widely as any other type of surface active agent. In the concept, unwashed kraft lignin is oxidized by oxygen at alkaline conditions partly using oxidised white liquor (OWL) as the source of alkali. Thereafter, the oxidised lignin solution is post-treated by membrane filtration to recycle the chemicals (Na, S) and to concentrate the lignin to produce high-performance dispersants. The process concept allows industrially feasible production of kraft lignin based surface active agents and their integration into a kraft pulp mill. Hereinafter the benefits of the concept are demonstrated in more detail.



23 **Figure 3:** A scheme illustrating combined lignin isolation, alkali-O<sub>2</sub> oxidation and membrane filtration of oxidised lignin for the production of dispersants in a kraft pulp mill.

## 28 Concept for production of dispersant

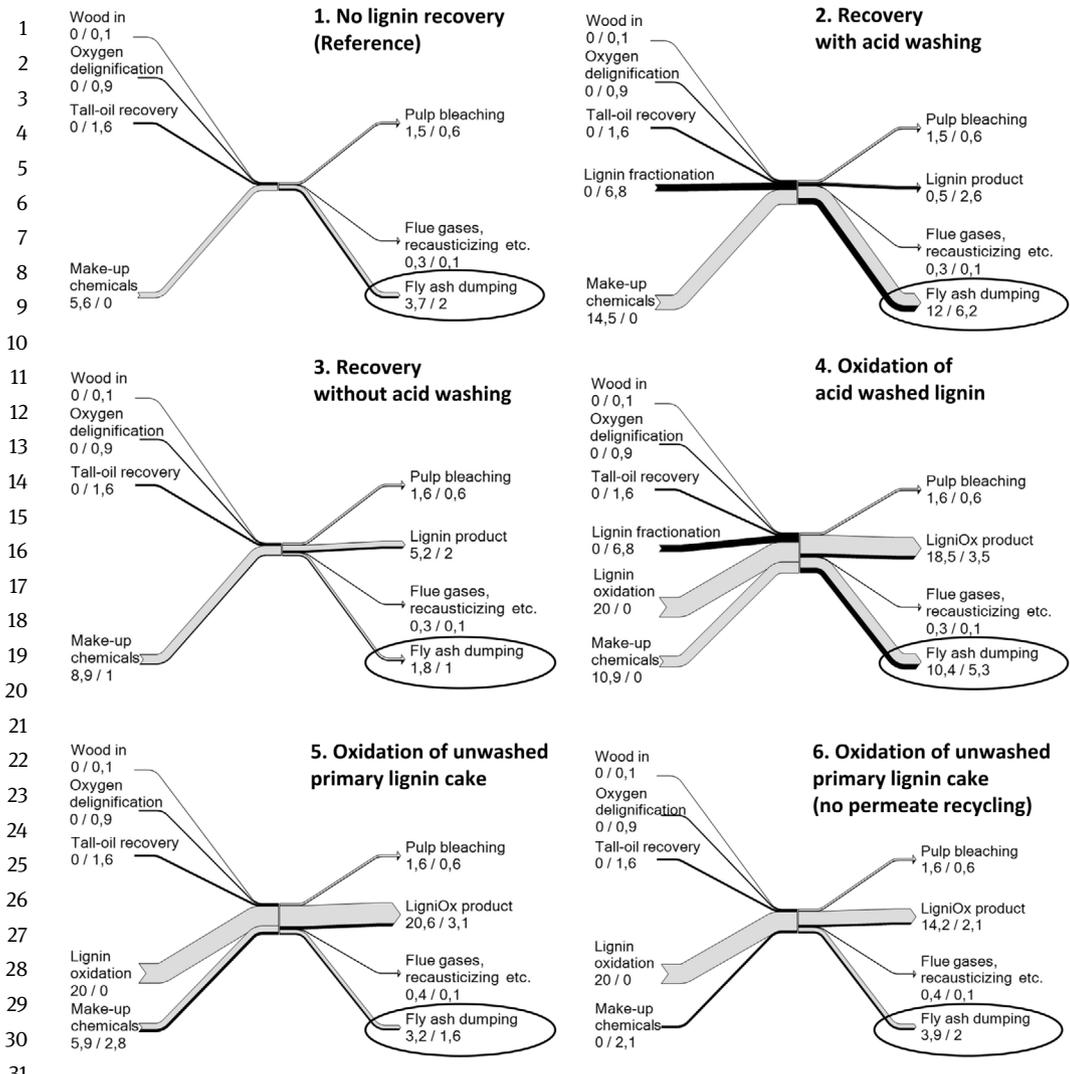
30 In most of the existing lignin isolation processes CO<sub>2</sub> is added to drop the pH of the black liquor from the value of 13–14 to 9–10 (Tomani et al. 2011). Thereby, the phenoxyl groups of the dissolved lignin become protonated and lignin solubility decreases causing lignin precipitation. After precipitation, the solids are separated by filtration, then subsequently re-suspended in water and H<sub>2</sub>SO<sub>4</sub> to decrease pH down to 2.5 for removing lignin bound Na and other impurities. Typically, this conventional lignin recovery introduces 200 kg H<sub>2</sub>SO<sub>4</sub> per tonne lignin to the chemical cycle of the mill (Tomani et al. 2011). The excess sulphur must be purged out of the mill in the form of Na<sub>2</sub>SO<sub>4</sub> and make-up Na needs to be added to the mill. In addition to the environmental load, this is a significant cost factor. These current drawbacks of the lignin recovery processes partly limit the commercialization of the lignin recovery technology at kraft pulp mills. On the other hand, it has been observed via experimental work that the lignin alkali-O<sub>2</sub> oxidation process done under 15 % lignin concentration requires about 500 kg effective alkali per tonne of lignin, and this should not interfere with the chemical balances either.

52 Since the lignin recovery and oxidation processes introduce additional sulphur and sodium to the recovery cycle of a kraft pulp mill, the overall Na/S balance of a pulp mill was evaluated using a process simulation. An annual recovery capacity of 66 700 tonnes of lignin was used in the simulation. The recovered lignin (with and without acidic washing) can be further oxidised, followed by membrane filtration to concentrate the oxidised lignin, and simultaneously recirculating the inorganics and some organics (oxidised lignin fragments and organic acids) back to the chemical recovery cycle. This would result in the production of approximately 56 500 tonnes of oxidised lignin based dispersants annually.

55 The main elements followed in the chemical cycle of a pulp mill are Na and S and the input and output of the chemicals is described here, also illustrated in Figure 4. The main inputs are wood (S 0.1 kg/adt) and process chemicals. Of the process chemicals, H<sub>2</sub>SO<sub>4</sub> is added to tall oil recovery (S 1.6 kg/adt) and MgSO<sub>4</sub> is added to oxygen delignification (S 0.9 kg/adt). The main output from the mill is pulp, which has been bleached (Na 1.5 kg/adt, S 0.6 kg/adt). Losses from the chemical cycle include mainly a white liquor preparation (Na 0.3 kg/adt, S 0.1 kg/adt) and dumping of fly ash from the recovery boiler (Na 3.7 kg/adt, S 2.0 kg/adt). From this chemical balance, it be calculated that in the reference case (1. No lignin recovery), 5.6 kg/adt of sodium makeup was needed and that there is a sulphur excess of 2 kg/adt in the process.

56 The main components in fly ash are Na<sub>2</sub>SO<sub>4</sub> and Na<sub>2</sub>CO<sub>3</sub>. To prevent the build-up of harmful non-process elements, like potassium and chloride, in the chemical cycle of the mill, there is a mill specific minimum for fly ash dumping. However, based on the environmental policies, there also exists mill specific maximum limit for fly ash dumping.

57 Na/S balance of the studied concepts (2–6), and their major sinks and sources are illustrated in Figure 4. The recovery technology based on unwashed lignin (concept 3) was beneficial for the sulphur balance of the mill. The amount of fly ash purged was more than six times higher in the lignin recovery with H<sub>2</sub>SO<sub>4</sub> washing than without the washing (concept 2: Na 12 kg/adt vs. concept 3: Na 1.8 kg/adt). The oxidation technology using membrane filtration had a positive impact on the sodium balance of the mill, as the amount of make-up NaOH was reduced (concept 2: Na 14.5 kg/adt vs. concept 4: Na 10.9 kg/adt) simultaneously decreasing the fly ash purge. Although, lignin oxidation requires fresh alkali in addition to OWL, a significant amount of the additional sodium ended up in the final dispersant product. In the case where unwashed lignin



**Figure 4:** Sodium and sulphur balances of reference softwood kraft pulp mill and different lignin recovery and oxidation options (see Table 1 for key parameters). Grey refers to sodium balance and black refers to sulphur balance, unit of Na/S being kg/adt pulp.

was oxidised (concepts 5 and 6), there was even a small need for make-up sulphur.

The Na/S balance was dependent on the rate of permeate recycling in the oxidation reactor: with a higher rate, more sodium and sulphur ended up in the final oxidised lignin product. In this assessment, lignin washing after oxidation was not considered. If, however, combing washing with the membrane filtration, more inorganics and the washing water is recycled back to the recovery loop.

The assessment revealed that the need for purging fly ash was considerably lower for the production of lignin dispersants using unwashed lignin (concept 5 and 6) than for the production of acid washed lignin or lignin dispersants thereof (concept 2 and 4, respectively). As will be described hereinafter, the lignin dispersants produced using unwashed kraft lignin worked as efficiently as mortar and

concrete plasticisers, and as the lignin dispersants based on conventionally washed kraft lignin (Kalliola et al. 2017).

In summary, the presented concept enables the use of unwashed kraft lignin, which simplifies the lignin isolation process and provides savings to capital and operational costs. In addition, it reduces the environmental load due to decreased fly ash purge provided by the simplified lignin isolation without the introduction of excess sulphur into the process. While the unwashed lignin stream entering the oxidation is already alkaline in nature, it reduces the need for alkali by roughly 15 % in lignin alkali-O<sub>2</sub> oxidation process (WO2020157386). This benefit of lower alkali dosing, shown experimentally, was not considered in the simulation assessment. The concept applies oxidised white liquor, readily available in the mill, as an alternative alkali source for lignin oxidation. This reduces the in-

52  
53  
54  
55  
56  
57  
58  
59  
60  
61  
62  
63  
64  
65  
66  
67  
68  
69  
70  
71  
72  
73  
74  
75  
76  
77  
78  
79  
80  
81  
82  
83  
84  
85  
86  
87  
88  
89  
90  
91  
92  
93  
94  
95  
96  
97  
98  
99  
100  
101  
102

roduction of excess Na into the process, also, providing cost savings. In the oxidation step, O<sub>2</sub> gas can be used from the pressure system designed for the pulp delignification in the mill. Oxidation of the lignin introduces an anionic charge in lignin under the alkaline oxidation conditions. Improvement of the lignin product performance and recirculation of chemicals in the mill is allowed by the filtration of the oxidised lignin solution as demonstrated experimentally. In the novel concept, oxidation of unwashed primary lignin cake instead of black liquor is conducted for several reasons. During the oxidation of black liquor, the inorganic sulphur compounds (such as HS<sup>-</sup>) will be oxidised prior to the organic compounds. This leads to high consumption of O<sub>2</sub> gas. In addition, sulphur compounds in reduced form are preferred for the recovery boiler process. Black liquor is rich in small organic acids and carbohydrate residues, which cause the unwanted cement retardation. The amount of these compounds is reduced by the lignin recovery prior to the oxidation.

All the presented lignin recovery concepts had a negative effect on the energy and electricity production of the mill, due to the smaller amount of combustible organics in black liquor. When the production costs of lignin products are assessed, this negative effect on the net electricity sales should be included as a cost factor for lignin production. In addition, the heat and electricity consumption of the lignin recovery process as well as the lignin oxidation process should be incorporated into the analysis. On the other hand, it has been estimated that 30–40% savings in the consumption of NaOH are realistic, if the oxidation process is combined with the recovery of unwashed lignin compared to the recovery of acid washed lignin (WO2020157386). The chemical savings originate from the lower alkali demand in the oxidation stage, and reduced make-up NaOH. Also, partial use of oxidised white liquor provides cost savings, however, apparently there will be a need for investing in an additional white liquor oxidation unit in the mill. The economy related results discussed were semi quantitative and represented trends of the introduction of these new technologies to the reference softwood kraft pulp mill.

## Dispersant for mortar and concrete plasticisation

Using OWL in combination with NaOH resulted in a lower lignin molar mass when compared to alkali conditions obtained with NaOH as the only alkali source (Table 2). In addition to effective alkali, oxidised white liquor (OWL)

has buffering capacity in the form of carbonate ions. Using OWL in combination with NaOH was beneficial, since it hindered the pH drop during the oxidation period of 30 min and enabled the production of a lower molar mass lignin.

**Table 2:** Molar mass of unwashed softwood kraft lignin before and after oxidation.

	Alkali in oxidation	Mw, Da	PD, –
UW-SW-KL	–	3900	2.8
UW-SW-KL-Ox1	NaOH	3700	2.9
UW-SW-KL-Ox2	OWL+NaOH	3000	2.7

According to the Haegermann flow values of mortar, the plasticisation ability of oxidised lignin prepared using NaOH outperformed lignosulphonate and was higher than that of commercial naphthalene based superplasticiser, however, the oxidised lignin prepared using OWL in combination with NaOH showed the best performance (Table 3) when compared to naphthalene based superplasticiser. The aforesaid better results in the case of using OWL and NaOH instead of using only NaOH for oxidation of unwashed kraft lignin has been also demonstrated earlier by several additional trials (WO2020157386).

**Table 3:** Haegermann flow value of fresh mortar prepared with cement CEM I 42.5N. Commercial lignosulphonate (WRDA 90D), synthetic products (Masterglenium SKY 610, Pantarhit LK FM) or oxidised lignin solutions used as a plasticiser.

	Plasticiser dose, %	Flow value, mm
Ref.	0	117
WRDA 90D	0.40	157
Masterglenium SKY 610	0.20	276
Pantarhit LK FM	0.20	181
UW-SW-KL-Ox1	0.20	188
UW-SW-KL-Ox2	0.20	210

Post-treatment of the oxidised unwashed kraft lignin solution was carried out by membrane filtration. This increased lignin content in the dispersant solution (Table 4), and simultaneously provided a permeate fraction containing the main part of Na and S. Producing a concentrated dispersant solution reduces transportation costs of the final product and recirculation of the permeate to the chemical recovery cycle of the mill enables the reuse of Na and S. Table 4 reports the total mass-based and lignin-based separations by membrane filtration as well as the

lignin concentration in the fractions, including the dispersant solution made by combining 1st and 2nd concentrate. According to the Haegermann flow values shown in Table 5, the high cement dispersing ability of the oxidised lignin is retained after the membrane filtration process and the dispersant solution outperformed the commercial naphthalene based superplasticiser.

**Table 4:** Results of membrane filtration of oxidised lignin solution, UW-SW-KL-Ox1 (Feed).

	Mass, %	Lignin yield, %	Lignin content, %
Feed	100	100	10.2
1st concentrate	–	–	20.3
2nd concentrate	–	–	3.3
Permeate	46	8	1.6
1st + 2nd concentrate	54	92	15.7

**Table 5:** Haegermann flow value of fresh mortar prepared with cement CEM I 52.5N. Commercial synthetic product (Pantarhit LK FM) or membrane filtration fractions of oxidised lignin solution, UW-SW-KL-Ox1 used as a plasticiser.

	Plasticiser dose, %	Flow value, mm
Ref.	0	100
Pantarhit LK FM	0.60	184
Feed	0.60	295
1st concentrate	0.60	280
1st + 2nd concentrate	0.60	290

For the industrial operation, the overall WR of the concentration (46 %) as well as the oxidised lignin concentration in the dispersant solution (15.7 %) should be increased. Thereby, the membrane filtration post-treatment has been further developed and scaled-up in the course of the LigniOx project to support the commercialization of the oxidation technology and the use of these novel lignin dispersants. Also, updating the evaluations for Na/S balance of the pulp mill as well as for the production costs with the data of the most recent achievements will follow.

By applying the membrane filtration, the small organic acids that enter the oxidation process within the unwashed kraft lignin and which are also formed in the secondary oxidation reactions (Kuitunen et al. 2011, Rovio et al. 2011), are separated to the permeate fraction. By removing the small acids, which have been reported to alter the cement hydration kinetics (Ramachandran et al. 1998), the post-treatment actually improved the performance of lignin dispersants used for concrete plasticising.

The oxidised lignin solution as such and after membrane filtration was tested in fresh concrete according to a standard that aims to classify the product as a plasticiser or as a superplasticiser. Both oxidised lignin solutions enabled the targeted water reduction of 12 % in the concrete mix with the plasticiser dosing of 0.36 %, while providing an even higher slump than in the case of the reference concrete mix without water reduction (Table 6). The water reduction value of 12 % corresponds to the requirement of a superplasticiser. In addition, the highest slump after membrane filtration demonstrated that the post-treatment improved the plasticising efficiency of oxidised lignin solution in concrete.

**Table 6:** Results of plasticisation of fresh concrete prepared with cement CEM I 52.5N. Commercial product (Pantarhit LK FM), oxidised or membrane filtered oxidised lignin (1st + 2nd concentrate) used as a plasticiser.

	Water reduction, %	Plasticiser dose, %	Slump, mm
Ref.	0	0	55
Pantarhit LK FM	12	0.36	30
UW-SW-KL-Ox1	12	0.36	60
Membrane filtered UW-SW-KL-Ox1	12	0.36	70

The presented concept for valorising unwashed kraft lignin to sustainable, high-performing plasticiser or dispersant is very promising. Pilot scale demonstration of the oxidation technology as well the field testing of dispersant prototypes are on-going aiming at the commercialization within three years. Production and use of the novel lignin products open new business opportunities for all stakeholders in the value chain. Within the LigniOx project, in addition to kraft lignin, oxidation concepts to produce lignin dispersants from organosolv and hydrolysis residue lignins are investigated.

## Conclusions

LigniOx oxidation solubilises technical lignins using O<sub>2</sub> under alkaline conditions where after the oxidised lignins can be applied as anionic dispersants for several end-uses to enhance the processability and product quality.

The industrially applicable process concept presented in this paper makes the production of these novel lignin dispersants feasible at kraft pulp mill without interfering

with the main process, and provides clear cost and environmental benefits.

The integrated lignin oxidation technology using membrane filtration has a positive impact on the sodium balance of the mill compared to the conventional lignin recovery alone. Additional make-up NaOH is typically needed in kraft pulp mills, and the demand is further increased when lignin recovery with H<sub>2</sub>SO<sub>4</sub> washing is installed. By integrated oxidation technology, the amount of make-up NaOH can be significantly reduced. First of all, the need for purging fly ash from the mill system is lower, because the lignin dispersants can be produced using primary lignin cake after CO<sub>2</sub> precipitation. The alkali introduced to the oxidation affects pulp mill Na/S balance, but the impact on chemical balance and chemical costs can be reduced if oxidised white liquor is used partly as an alkali source. Finally, the recirculation of chemicals (Na, S) back to the chemical cycle of the mill is conducted by membrane filtration of the oxidised lignin solution. The plasticisation performance of the novel lignin dispersants is equal regardless of using unwashed or acid washed kraft lignin, and those can compete with the tested commercial oil-based plasticiser products.

Based on the process simulation, recovering 20 % of the lignin in black liquor, and oxidising this unwashed lignin does not increase fly ash purging in a kraft pulp mill unlike the conventional lignin recovery process alone.

**Acknowledgments:** Several experts at VTT are greatly acknowledged: Mr Juha Kaunisto and Mr Jari Leino for conducting the oxidations, Mr Jaakko Sippola for performing the application testing with mortar and concrete, MSc Atte Mikkelson and Mrs Tarja Wikström for lignin analysis. MSc Miriam Kellock and MSc Elisa Spönlä are acknowledged for helping to edit this manuscript.

Mill staff at Metsä Fibre's Rauma pulp mill is acknowledged for helpful attitude and assistance during lignin isolation trials.

Dr Sakari Kaijaluoto is greatly acknowledged for consulting with the simulation assessment.

**Funding:** This LigniOx project has received funding from the Bio-Based Industries Joint Undertaking under the European Union's Horizon 2020 research and innovation programme under grant agreement n°745246. Programme: H2020 BBI-2016-D03: Valorization of lignin and other side-streams to increase efficiency of biorefineries and increase sustainability of the whole value chain.

**Conflict of interest:** The authors declare no conflicts of interests.

## Appendix

**Table 7:** Chemical and elemental composition of unwashed (UW-SW-KL) and washed (SW-KL) softwood kraft lignin together with their molar mass. Determinations for lignin characterization according to Jääskeläinen et al. (2017).

		UW-SW-KL	SW-KL
Dry matter	%	67.2	64.7
Chemical composition (of dry matter):			
Lignin (insoluble + soluble)	%	72.8	94.7
insoluble (i. e. Klason lignin)	%	67.7	92.8
soluble	%	5.1	1.9
Extractives	%	0.2	1.6
Carbohydrates	%	2.0	0.8
Ash 700 °C	%	22.5	0.8
TOTAL	%	97.5	97.9
Molar mass:			
Mw	g/mol	3900	3600
Mn	g/mol	1400	1500
PD, Mw/Mn	–	2.8	2.4
Elemental compositions (C/H/N/S/O):			
Carbon	%	52.5	65.0
Hydrogen	%	5.0	5.7
Nitrogen	%	0.01	0.02
Sulphur	%	2.5	2.2
Oxygen	%	28.5	23.2
TOTAL (C/H/N/S/O)	%	88.4	96.1
Sodium	%	5.1	1.0

## References

- Aro, T., Fatehi, P. (2017) Production and Application of Lignosulfonates and Sulfonated Lignin. *ChemSusChem* 10:1861–1877. <https://doi.org/10.1002/cssc.201700082>.
- Axelsson, E., Olsson, M.R., Berntsson, T. (2006) Increased capacity in kraft pulp mills: Lignin separation and reduced steam demand compared with recovery boiler upgrade. *Nord. Pulp Pap. Res. J.* 21(4):485–492. <https://doi.org/10.3183/NPPRJ-2006-21-04-P485-492>.
- Bajwa, D.S., Pourhashem, G., Ullah, A.H., Bajwa, S.G. (2019) A concise review of current lignin production, applications, products and their environmental impact. *Ind. Crop. Prod.* 139(1):111526. <https://doi.org/10.1016/j.indcrop.2019.111526>.
- Dessbesell, L., Paleologou, M., Leitch, M., Pulkki, R., Xu, C. (2020) Global lignin supply overview and kraft lignin potential as an alternative for petroleum-based polymers. *Renew. Sustain. Energy Rev.* 123:109768.
- Fearon, O., Liitiä, T., Kalliola, A. (2021) Novel lignin based dispersants for special carbon black. *Pitt. Vernici* 1/2021:4–9.
- Jääskeläinen, A.-S., Liitiä, T., Mikkelson, A., Tamminen, T. (2017) Aqueous organic solvent fractionation as means to improve lignin homogeneity and purity. *Ind. Crop. Prod.* 103:51–58. <https://doi.org/10.1016/j.indcrop.2017.03.039>.

- 1 Kalliola, A. (2015) Chemical and enzymatic oxidation using  
2 molecular oxygen as a means to valorize technical lignins for  
3 material applications. Doctoral dissertation, Aalto University,  
4 92 pp.
- 5 Kalliola, A., Vehmas, T., Liitiä, T., Tamminen, T. (2015) Alkali-O2  
6 oxidized lignin – A bio-based concrete plasticizer. *Ind. Crop.  
7 Prod.* 74:150–157.
- 8 Kalliola, A., Liitiä, T., Vehmas, T., Tamminen, T. (2017) Concrete  
9 Plasticizers and Versatile Dispersants from LigniOx Lignins. In:  
10 7th Nordic Wood Biorefinery Conference, Stockholm, Sweden,  
11 March 28–30, 2017.
- 12 Kalliola, A., Vehmas, T., Liitiä, T., Tamminen, T. (2018) High  
13 performance concrete plasticizers and versatile dispersants.  
14 In: 8th Nordic Wood Biorefinery Conference, Helsinki, Finland,  
15 October 23–25, 2018. pp. 117–121.
- 16 Kangas, P., Kaijaluoto, S., Määttänen, M. (2014) Evaluation of future  
17 pulp mill concepts – Reference model of a modern Nordic kraft  
18 pulp mill. *Nord. Pulp Pap. Res. J.* 29(4):620–634.
- 19 Kienberger, M., Maitz, S., Pichler, T., Demmelmayr, P. (2021)  
20 Systematic Review on Isolation Processes for Technical Lignin.  
21 *Processes* 9(5):804–821. <https://doi.org/10.3390/pr9050804>.
- 22 Kouisni, L., Gagné, A., Maki, K., Holt-Hindle, P., Paleologou, M.  
23 (2016) LignoForce System for the Recovery of Lignin from  
24 Black Liquor: Feedstock Options, Odor Profile, and Product  
25 Characterization. *ACS Sustain. Chem. Eng.* 4:5152–5159.  
26 <https://doi.org/10.1021/acssuschemeng.6b00907>.
- 27 Kuitunen, S., Kalliola, A., Tarvo, V., Tamminen, T., Rovio, S., Liitiä, T.,  
28 Lehtimaa, T., Vuorinen, T., Alopaeus, V. (2011) Lignin oxidation  
29 mechanisms under oxygen delignification conditions. Part 3.  
30 Reaction pathways and modeling. *Holzforschung* 65:587–599.  
31 <https://doi.org/10.1515/HF.2011.100>.
- 32 Lake, M.A., Blackburn, J.C. (2014) SlrpTM – an Innovative  
33 Lignin-Recovery Technology. *Cellul. Chem. Technol.*  
34 48:799–804.
- 35 Li, T., Takkellapati, S. (2018) The current and emerging sources of  
36 technical lignins and their applications. *Biofuels Bioprod.*  
37 *Bioref.* 12:756–787. <https://doi.org/10.1002/bbb.1913>.
- 38 Onarheim, K., Santos, S., Kangas, P., Hankalin, V. (2017)  
39 Performance and costs of CCS in the pulp and paper industry.  
40 Part 1: Performance of amine-based post-combustion CO2  
41 capture. *Int. J. Greenh. Gas Control* 59:58–73. <https://doi.org/10.1016/j.ijggc.2017.02.008>.
- 42 Pehu-Lehtonen, L., Sjögård, P. (2018) A-Recovery+ – the next  
43 generation of chemical recovery cycle. In: 8th Nordic Wood  
44 Biorefinery Conference, Helsinki, Finland, October 23–25,  
45 2018. pp. 213–218.
- 46 Ramachandran, V.S., Malhotra, V.M., Jolicouer, C., Spiratos, N.  
47 (1998) Superplasticizers: Properties and Applications in  
48 Concrete. CANMET, Ottawa.
- 49 Rovio, S., Kuitunen, S., Ohra-aho, T., Alakurtti, S., Kalliola,  
50 A., Tamminen, T. (2011) Lignin oxidation mechanisms  
51 under oxygen delignification conditions. Part 2: Advanced  
52 methods for the detailed characterization of lignin oxidation  
53 mechanisms. *Holzforschung* 65:575–585. 10.1515/HF.2011.088.
- 54 Tamminen, T., Jääskeläinen, A.-S., Borrega, M., Kalliola, A.,  
55 Ohraaho, T. (2018) Improving the properties of technical lignins  
56 for material applications. In: 4th Iberoamerican Congress of  
57 Biorefineries, Jaen, Spain, October 24–26, 2018.
- 58 Tomani, P. (2010) The LignoBoost Process. *Cellul. Chem. Technol.*  
59 44:53–58.
- 60 Tomani, P., Axegård, P., Berglin, N., Lovell, A., Nordgren, D., Ab, I.  
61 (2011) Integration of Lignin Removal Into a Kraft Pulp Mill and  
62 Use of Lignin As a Biofuel. *Cellul. Chem. Technol.* 2:533–540.
- 63 Valmet.com (2022) Valmet WinGEMS process simulator for pulp  
64 and paper industries. [online] Available at: [https://www.  
65 valmet.com/pulp/automation-for-pulp/apc-advanced-process-  
66 controls/valmet-wingems/](https://www.valmet.com/pulp/automation-for-pulp/apc-advanced-process-controls/valmet-wingems/) [Accessed 19 January 2022].
- 67 Wallmo, H., Karlsson, H., Björk, M., Rinne, J., Nikunen, K.,  
68 Kotilainen, A., Korhonen, V. (2015) Successful startup of lignin  
69 extraction at Stora Enso Sunila Mill. In: 6th Nordic Wood  
70 Biorefinery Conference, Helsinki, Finland, 20–22 October,  
71 2015. pp. 185–192.
- 72 WO2015049424: Use of oxidised lignin as a dispersant. Patent  
73 owner VTT Technical Research Centre of Finland Ltd, priority  
74 application filing date 2.10.2013. Granted in Finland (FI 126397,  
75 date of issue 15.11.2016), USA (US 9676667, date of issue  
76 13.6.2017) and China (ZL201480054352.3, date of issue  
77 28.12.2018).
- 78 WO2017077198: Alkali-O2 oxidized lignin as dispersant. Patent  
79 owner VTT Technical Research Centre of Finland Ltd, priority  
80 application filed 6.11.2015. Granted in Finland (FI 128962,  
81 date of issue 15.4.2021), Canada (CA 2999226, date of  
82 issue 18.8.2020), and Europe (EP 3380544B1, date of issue  
83 7.11.2016).
- 84 WO2020157386: Method for producing oxidized lignin in kraft  
85 pulp mill. Patent owners ANDRITZ Oy, Metsä Fibre and VTT  
86 Technical Research Centre of Finland Ltd. Priority application  
87 filed 1.2.2019.
- 88  
89  
90  
91  
92  
93  
94  
95  
96  
97  
98  
99  
100  
101  
102