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**Hapetetun ligniinin käyttö dispergointiaineena**

**Användning av oxiderad lignin som dispergeringsmedel**

**Use of oxidized lignin as a dispersant**

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US 5811527 A, KR 20100002916 A, US 3726850 A, US 4611659 A,

OUYANG, X. et al. Oxidative degradation of soda lignin assisted by microwave irradiation, Chinese Journal of Chemical Engineering, Vol. 18, 2010, 695-702

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The present invention concerns a process for oxidizing lignin at alkaline conditions. This oxidized lignin can be used as a dispersant in various end-products, for example as a renewable plasticizer in cement-containing products, such as concrete, where the ability of the oxidized lignin to endure alkaline conditions is an advantage. Further, the invention concerns a concrete mixture containing aggregate, cement, water and a plasticizer formed of oxidized lignin, and a process for producing such a concrete mixture. The oxidized lignin can be manufactured using a process, where the lignin starting material is reacted with an oxidizing agent in solution in alkaline conditions.

Tämä keksintö koskee menetelmää ligniinin hapettamiseksi alkalisissa olosuhteissa. Tätä hapetettua ligniiniä voidaan käyttää dispergointiaineena erilaisissa lopputuotteissa, esimerkiksi sementtiä sisältävien tuotteiden, kuten betonin, uusiutuvana plastisaatorinä, jolloin hapetetun ligniinin kyky kestää alkalisia olosuhteita on etu. Keksintö koskee edelleen betoniseosta, joka sisältää runkoainetta, sementtiä, vettä ja plastisaattoria, joka muodostuu hapetetusta ligniinistä, ja menetelmää tällaisen betoniseoksen valmistamiseksi. Hapetettu ligniini voidaan valmistaa käyttämällä menetelmää, jossa ligniinilähtöaine saatetaan reagoimaan hapettimen kanssa liuoksessa alkalisissa olosuhteissa.

# USE OF OXIDIZED LIGNIN AS A DISPERSANT

## Background of the Invention

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### Field of the Invention

The present invention concerns a process for oxidizing lignin at alkaline conditions. This oxidized lignin can be used as a dispersant in various end-products, for example as a renewable plasticizer in cement-containing products, such as concrete, where the ability of the oxidized lignin to endure alkaline conditions is an advantage.

### Description of Related Art

Concrete is one of the most commonly used industrially manufactured materials in the world, and manners of improving its strength and durability are constantly under research. Aggregate and cement are the main components of concrete, but also water is required, and usually, various additives are used, for example to improve the fresh-stage or hardening properties of the final product.

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Water plays a dual role in concrete production; it provides the concrete mixture with certain rheological properties, and it participates in the essential hydration reaction, and is required to bring the cement into a paste-like form. However, concrete is particularly strong when it contains only low amounts of water. Thus, a lower water-to-concrete ratio yields a stronger, more durable concrete, while a higher ratio gives a freely-flowing cement-mixture with a higher slump.

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To obtain both a strong concrete product and advantageous cement flow-properties, plasticizers (or dispersants) are often added into the concrete mixture to improve the workability, i.e. to decrease the yield stress (or shearing resistance), of the concrete mixture, while using low water contents.

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Petroleum-based polyelectrolytes, known as superplasticizers, have typically been considered to be the most efficient plasticizers. However, there exists a constant need to replace petroleum-based products with renewable alternatives.

- 5 Superplasticizers act by adsorbing to the cement particle surface and cause electrostatic and steric repulsions between individual cement particles to achieve full dispersion. The active functional groups of the superplasticizers, i.e. the sulfonic (-SO<sub>3</sub>H) and the carboxylic (-COOH) groups, are responsible for achieving the electrostatic repulsion by interacting with the active sites on the cement particles, while the branched structure of the  
10 polyelectrolyte achieves steric repulsion by forcing the cement particles apart.

Water-soluble lignosulfonates, which are by-products of sulfite pulping, are also used due to their highly branched and sulfonic charged structure, but their effect is limited.

- 15 At the present, the main source of lignin is the alkaline sulfate (i.e. kraft) process. The soda process, on the other hand, is the predominant process used for chemical pulping of non-wood materials. Also 2<sup>nd</sup> generation bioethanol production from lignicellulosics provides a source of lignin.
- 20 Presently only a fraction of the lignin formed during the pulping is separated from the spent pulping liquors and employed in specialty products. Instead, the remaining liquors (and lignin) serve, for example, as biofuel in pulp mills. Thus, there is a clear need for further lignin exploitation methods.
- 25 Kraft or soda lignins (among other potential lignins) would be both cost-effective and environmental alternatives to petroleum-based or lignosulfonate-based plasticizers in concrete mixtures. In unmodified form they, however, lack the sufficient efficiency required for their use as plasticizers or dispersants.
- 30 Modification of lignin has been attempted in the past, such as by sulfonating the lignin (as in CN102241818A and CN101885823A), or by adding amine or ammonium groups to lignosulfonates (as in US6238475B1 and WO2001036344A2). Such modifying processes generally include also an oxidizing step, but this step is not carried out under effective conditions, since it is merely intended to provide a suitable basis for further modifications.

This known oxidation of lignin has been described in, for example, US3910873A, but this process was not developed for the requirements of the concrete industry, and can still be improved.

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### **Summary of the Invention**

It is an object of the present invention to provide renewable plasticizers for the concrete industry.

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It is a further object of the invention to provide a novel process for oxidizing lignins in alkaline conditions.

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Particularly, it is an object of the present invention to provide a process for oxidizing lignins to render these lignins suitable for use as plasticizers in concrete.

These and other objects, together with the advantages thereof over known materials and processes, are achieved by the present invention, as hereinafter described and claimed.

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The invention is based on the finding that oxygen oxidation in alkaline conditions can be used as means to increase the hydrophilic properties of lignin for dispersing applications. Oxidized lignins have shown good dispersing properties especially in reducing the shear stress of cement slurry. Thereby, oxidized lignin is a suitable renewable alternative to replace petroleum-based plasticizers (water reducing agents) in concrete technology.

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Thus, the present invention concerns a process for oxidizing lignin, where the lignin starting material is reacted with an oxidizing agent in solution. The oxidation of the lignin under alkali conditions causes minor degradation of lignin and increases its carboxyl content (i.e. the content of carboxyl groups in lignin macromolecule or as separate small molecular weight acids ), thus rendering it more hydrophilic. The invention also concerns the use of this oxidized lignin in cement-containing products, such as concrete.

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More specifically, the process of the present invention is characterized by what is stated in the characterizing part of Claim 5.

Further, the use of the present invention is characterized by what is stated in Claim 11 and the concrete mixture of the present invention is characterized by what is stated in Claim 1.

- 5 Considerable advantages are obtained by means of the invention. Thus, the present invention provides a new type of plasticizer (or cement dispersant) that is based on entirely renewable raw materials, i.e. lignins.

10 The plasticizing effect of this plasticizer, obtained by the plasticizer reducing the shear stress of e.g. a cement slurry, is far better than the effect of unmodified lignin. Also the yield stress of the cement slurry produced using such a plasticizer (or dispersant) is decreased significantly compared to cement slurries produced using commercial lignosulfonates.

- 15 Further, the oxidized lignin of the invention is inexpensive compared to synthetic alternatives, such as the commonly used polycarboxylate ether-based superplasticizers.

Next, the invention will be described more closely with reference to the attached drawings and a detailed description.

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### **Brief Description of the Drawings**

25 Figure 1 shows the charge of soda wheat lignin samples according to the invention, oxidized at a consistency of 0.75%, using different temperatures (22, 40, 60 and 80 °C) and a constant reaction time (30 min). Unmodified lignin (Soda wheat 0.75%) (0 min) was used as a reference.

30 Figure 2 shows the molecular weight vs. charge of lignin oxidized according to the present invention, using oxidation temperatures of 22, 40, 60 and 80 °C. Unmodified lignin (Soda wheat 0.75%)(No oxidation) was used as a reference.

Figure 3 shows the molecular weight vs. charge of the plasticizer of the invention (Soda wheat 5% oxidized, Soda wheat 15% oxidized and Soda wheat 25% oxidized), using unmodified lignin (Soda wheat 15%) as a reference.

Figure 4 shows the shear stress vs. shear rate of 70w-% of a cement (CEM I), containing different amounts of the plasticizer of the invention (Soda wheat 25% oxidized), using unmodified lignin (Soda wheat 15%) and WRDA 90D as reference plasticizers, or no plasticizer (-).

Figure 5 shows the shear stress vs. shear rate of 66w-% of a cement (CEM II), containing different amounts of the plasticizer of the invention (Soda wheat 5% oxidized, Soda wheat 15% oxidized and Soda wheat 25% oxidized), unmodified lignin (Soda wheat 15%) and WRDA 90D as reference plasticizers or no plasticizer (-).

Figure 6 illustrates the reaction heat of cement (CEM II) containing the plasticizer of the invention (Soda wheat 5% oxidized), Glenium C151 and WRDA 90D as reference plasticizers or no plasticizer (-).

Figure 7 illustrates the slump test results of lignin plasticized concrete at 0 min vs. time to maximum heat flow, the samples containing either the plasticizer of the invention (Soda wheat 5% oxidized, Soda wheat 15% oxidized and Soda wheat 25% oxidized), unmodified lignin (Soda wheat 15%) or WRDA 90D.

Figure 8 illustrates the slump test results of lignin plasticized concrete at 30 minutes after mixing, the samples containing either the plasticizer of the invention (Soda wheat 5% oxidized, Soda wheat 15% oxidized and Soda wheat 25% oxidized), unmodified lignin (Soda wheat 15%) or WRDA 90D.

### **Detailed Description of Embodiments of the Invention**

The present invention concerns a concrete mixture containing aggregate, cement, water and a plasticizer formed of oxidized lignin.

The term “plasticizer” is intended to cover also “dispersants”, depending on their end-use. Thus, the oxidized lignin functioning as a plasticizer in the concrete mixture of the invention can be used as a dispersant in other end-products.

In the context of the present invention, the plasticizer (as lignin dry solids bases) is preferably used in a content of  $\leq 0.63\text{w-\%}$  of the cement dry solids. In the concrete mixture, this corresponds to  $\leq 2.7 \text{ kg/m}^3$  of concrete mixture.

- 5 The used cement is generally selected from inorganic binders, such as Portland cements, Pozzolan cements, Belite cements, Belite-calcium sulphoaluminate-ferrite cements, calcium aluminate cements, aluminate cements, aluminate silicate cements, sulphate aluminate cements, calcium aluminoferrite cements, calcium sulphate cements, calcium sulphoaluminate cements, sulphoaluminate cements, supersulphate cements, lime-  
 10 pozzolanic cements, magnesium cements, magnesium oxy-chloride cements, magnesium oxy-carbonate cements, magnesium phosphate cements, magnesium sulphate cements, calcium phosphate cements, phosphate cements, lime-sulphate activated cements, calcium carbonate cements, gypsum, calcium sulphate hemihydrate, calcium sulphate anhydrite, geopolymeric cements, hydraulic lime cements, or binary, ternary or quaternary blends of  
 15 any of these. A particularly useful type of cement is the Portland cements.

In preparing concrete mixture, the cement is most conveniently used as 200-500  $\text{kg/m}^3$  dosage with water/cement –ratio 0.30-0.75.

- 20 The used aggregate typically consists of conventional stone aggregate, suitable for concrete applications.

- The oxidized lignin, in turn, is preferably obtained by oxidizing a lignin-containing material, which has been obtained from a lignocellulose biomass, such as a wood-based or  
 25 other plant-based source, one example being pulping liquors, or lignin side-streams originating from bioethanol production.

- The invention also concerns a process for manufacturing such a concrete mixture by mixing the aggregate, the cement, the water and the plasticizer formed of oxidized lignin.

- 30 The plasticizer can be added at any point of the mixing process. Most preferably, plasticizer will be added at last.

Further, the present invention concerns a process for manufacturing oxidized lignin, where the lignin starting material is reacted with an oxidizing agent in solution. The reaction is, according to the present invention, carried out in alkaline conditions, i.e. at a pH within the range 8–14, typically using a load of oxidizing agent of 10–95w-%, preferably 10–50w-%, calculated based on the weight of the lignin.

Preferably, the pH of the lignin solution is adjusted to a value of 10–14 prior to addition of the oxidizing agent. Optionally, the pH of the lignin solution may be kept constant, in a range of 11–13 during the oxidation.

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Maintaining a desired pH level can be done, for example, with the help of an addition of alkaline agent, such as sodium hydroxide (NaOH) or sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>), or both, preferably in a content of 20–50w-% of the lignin, most suitably in a content of 23–45w-%, or using buffering. Typically, the alkaline agent is added to the lignin solution before adding the oxidizing agent. Some excess alkaline agent can also be added later, during the oxidation reaction, in order to further adjust the pH to a higher level. The amount of alkaline agent required for this adjustment is, however, dependent on various properties of the lignin solution (e.g. its initial pH, its current pH, its lignin content and its content of further substances).

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Generally, the first step of the process is, however, forming an aqueous alkali lignin solution (or slurry). The starting material is, thus, a lignin-containing material or pure lignin.

In order to produce the lignin-based plasticizer of the invention, the lignin dry solids of the product solution (the oxidized lignin) is selected to be high enough to ensure feasible use of the product. Increase in lignin dry solids in the oxidation causes condensation (in addition to lignin degradation) resulting in an increase in the molar mass of the oxidized lignin. Also, the polydispersity of the lignin increases, which may provide further benefits for the plasticizing purposes. Yet, the negative charge and the molar mass of the lignin based plasticizer product can be controlled by the oxidation parameters.

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Thus, the aqueous lignin solution formed in the first step of the process preferably has a lignin content of 0.5–30w-%, more preferably 5–25w-%, and most suitably 15–25w-%.



According to an embodiment of the invention, the oxidation is carried out on non-purified lignin-containing slurries. Slurries with high lignin contents include, among others, pulping liquors (e.g. black liquor), but it is preferred to separate the lignin fraction from such pulping liquors before oxidizing. The obtained separate lignin fraction does not require further purification (i.e. small amounts of impurities can be allowed), although an optional concentrating step can be carried out if black liquor is used.

In a subsequent step of the process, an alkaline agent can be added to the aqueous lignin solution, prior to addition of the oxidizing agent, to provide the desired alkaline conditions. Optionally, buffering can be used.

The oxidizing agent used in the process is preferably selected from oxygen (O<sub>2</sub>) and air, most suitably from oxygen (O<sub>2</sub>). Oxygen is an inexpensive and environmentally friendly chemical and highly suitable for modifying lignin.

When both an oxidizing agent and an alkali are used in the oxidation process according to the invention, the contents of either of these can be varied to further cause changes in the final oxidized lignin.

The oxidizing agent can be allowed to react with the lignin for a prolonged period of time, such as for 3–120 minutes, preferably 3–60 minutes, and most suitably for 5–30 minutes.

A further advantage is obtained by adjusting the initial temperature to a level of  $\leq 100^{\circ}\text{C}$  for the oxidation reaction, preferably  $25\text{--}80^{\circ}\text{C}$ , more preferably  $40\text{--}80^{\circ}\text{C}$ , and most suitably  $60\text{--}80^{\circ}\text{C}$ .

Generally, the following ranges have been found particularly suitable for use in the oxidation of the present invention:

Lignin concentration in solution, w-%	0.75 – 25.0
Alkali concentration, w-% of lignin	23 – 45
O <sub>2</sub> load, w-% of lignin	12 – 50
O <sub>2</sub> consumption, w-% of lignin	8 – 11
Reaction T (initial), °C	$\leq 100$

Reaction t, min

3 – 30

By controlling the parameters in the oxidation (e.g. lignin dry solids, initial O<sub>2</sub> dose, reaction time and initial temperature), the properties of the product can be controlled (e.g. charge, mmol/g, and molar mass, g/mol).

The oxidized lignin obtained in this manner is particularly suitable for use as a plasticizer in cement and cement-containing products, such as concrete.

The oxidation reaction results in the formation of charged groups in lignin, mainly due to the degradation of the phenolic groups. The formed charged groups can be in the form of carboxylic acid groups, or lactone structures that are formed during the oxidation and hydrolysed to acidic structures under highly alkali conditions, such as the conditions prevailing in cement and concrete. The charged groups can form a part of the lignin macromolecule, or they can be in the form of separate acids. The change in the chemical structure and the composition of the lignin leads to an increase in its hydrophilic properties, which is particularly advantageous for dispersing and plasticizing applications.

Alkaline oxidation is also a mean to produce soluble lignin with a relatively high molar mass. Such a lignin product is particularly useful in plasticizing inorganic binders in construction materials, e.g. mortar and concrete.

The oxidized lignin is preferably used in the manufacture of paste mortar or concrete as such, i.e. as a slurry, without a separate isolation and drying step. If required for an alternative end-use, the oxidized lignin product can, however, be separated and dried.

Thus, the oxidized lignin of the invention is suitable for use in also alternative applications, not only as a plasticizer, but as any type of dispersant. It can be generalized that the most suitable applications are processes where an alkaline pH is used (or possibly neutral). In such environments, it can be ensured that the lignin material is completely dissolved. Said processes where an alkaline pH is used, include the preferred process for the production of cement, and processes for the further use of the cement in producing, for example concrete or mortar.

The following non-limiting examples are intended merely to illustrate the advantages obtained with the embodiments of the present invention.

## EXAMPLES

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### Example 1 – Oxidation

Commercial soda wheat straw lignin (Protobind 1000), a by-product of alkaline pulping process, produced by Green Value was oxidized using pure O<sub>2</sub> at varying lignin dry solids contents (0.75, 5, 15, and 25 w-%) under alkaline conditions at elevated temperatures. The NaOH dosage used was 23-45 w-% of lignin dry solids (initial pH~13). The oxidation was conducted in a 1 L Parr reactor with initial O<sub>2</sub> dose 12-32 w-% of lignin dry solids. A given initial O<sub>2</sub> dose can be set by varying the volume ratio of reactor head space vs. lignin solution combined with varying the initial O<sub>2</sub> excess (from 5 to 40 bars). The temperature in the oxidation experiments conducted using 5, 15, and 25 w-% lignin dry solids was 50 - 80 °C. The O<sub>2</sub> uptake during the reaction period (6 or 30 minutes) was 8-11 w-% of lignin dry solids.

In general, increasing the temperature increased also the O<sub>2</sub> uptake, resulting in an increase of carboxylic acid groups (COOH) and in a decrease in phenolic structures. Yet, lignin oxidation took place already at room temperature (RT).

The samples used in the following tests and subsequent examples included the following:

25	Soda wheat =	unmodified lignin (Protobind 1000), dissolved in 0.1 M NaOH at 0.75 w-% dry solids (Soda wheat 0.75%) or dissolved in 1 M NaOH at 15 w-% dry solids (Soda wheat 15%)
30	Soda wheat 0.75% oxidized =	Soda wheat diss. in 0.1 M NaOH at 0.75 w-% dry solids, init. O <sub>2</sub> dose 23 w-%
	Soda wheat 5% oxidized =	Soda wheat dissolved in 0.5 M NaOH at 5 w-% dry solids, init. O <sub>2</sub> dose 12 w-%
	Soda wheat 15% oxidized =	Soda wheat dissolved in 1 M NaOH at 15 w-% dry solids, init. O <sub>2</sub> dose 16 w-%

Soda wheat 25% oxidized =	Soda wheat dissolved in 2.5 M NaOH at 25 w-% dry solids, init. O <sub>2</sub> dose 32 w-%
WRDA 90D =	commercial lignosulphonate based plasticizer
Glenium C151 =	commercial synthetic plasticizer

### Example 2 – Analyzing the lignin fractions

The analyzed samples included the lignin samples described in the following Table 1. Said table also includes some measured characteristics of the samples.

Table 1. Samples used in the following Examples

Sample name	Plasticizer dry solids in solution, w-%	Initial O <sub>2</sub> /lignin, w-%	Consumed O <sub>2</sub> /lignin, w-%	Mn	Mw	PD	Small acids* of initial lignin, w-%	Amount of negative charged groups at pH6, mmol/g
Soda wheat 15%	15	-	-	2100	3400	1.6	1.6	1.7
Soda wheat 0.75% oxidized	0.75	23	11	1705	2783	1.6	5.7	3.7
Soda wheat 5% oxidized	5	12	10	2300	4200	1.8	6.0	4.5
Soda wheat 15% oxidized	15	16	8	3000	6400	2.1	3.8	3.2
Soda wheat 25% oxidized	25	32	11	3100	7000	2.3	n.d	3.8
WRDA 90D	30	-	-	1700	3000	1.8	9.8	n.d
Glenium C151	15	-	-	5100	15900	3.1	n.d	n.d

Mn = number average molecular weight

Mw = molecular weight

PD = polydispersity

n.d = not determined

\* Separate small molecular weight carboxylic acids ( $\leq C6$ ), degradation products of lignin, detected by capillary electroforesis analysis according to Rovio et al. (Rovio, S., Kuitunen, S., Ohra-aho, T., Alakurtti, S., Kalliola, A., Tamminen, T., *Holzforschung* 65, 575-585, 2011)

The samples included unmodified lignin, oxidized lignin and commercial plasticizers. Average molecular weight classes ( $M_n$ ,  $M_w$ ) of these oxidized and unmodified lignin samples as well as the commercial plasticizers were measured by size exclusion chromatography (SEC), using PSS MCX 1000 and 100 000 columns in 0.1 M NaOH eluent (25°C) with UV (280 nm) and RI detection. The molecular weight distributions and average molecular weights were calculated in relation to polystyrene sulfonate standards, using Waters Empower 2 software. The results are shown in Table 1 above.

The charge of the samples was determined by potentiometric titration from solution. The potentiometric titration of lignin charge was conducted according to Rahikainen et al. (Rahikainen, J. L., Evans, J. D., Mikander, S., Kalliola, A., Puranen, T., Tamminen, T., Marjamaa, K., Kruus, K., *Enzyme and Microbial Technology*, 53 (5) 315–321, 2013) with the exception that the sample titrated was oxidised (or unmodified) lignin solution instead of isolated, dry lignin. The molar amount of NaOH for the blank titration was set according to that initially existing in the lignin sample solution. The results are shown in Figures 1, 2 and 3. For Figure 1 the results are indicating the effect of the oxidation temperature, whereas Figures 2 and 3 provide the molar mass vs. charge.

From the results it becomes clear, among others, that increase in lignin dry solids in the oxidation causes condensation (in addition to lignin degradation), resulting in increase in molecular weight of the oxidized lignin.

Negative charge at pH 6 in oxidized lignin solution is twice as high as that of unmodified lignin. The charge originates mostly from lignin bound carboxylic acids groups as well as from separate small molecular weight acids. The content of the small molecular weight acids contributing to the charge of the oxidized lignin may be up to 10 w-% of the lignin material.

### **Example 3 – Analyzing cement samples containing oxidized lignin**

The lignin oxidized as above (Soda wheat 5% oxidized, Soda wheat 15% oxidized, Soda wheat 25% oxidized) was tested for the plasticizing performance using the cement types CEM I (Megasementi CEM I 42,5 R, provided by FinnSementti) and CEM II (Plussasementi CEM II B-M (S-LL) 42,5 N, provided by FinnSementti) as the test

medium. The shear stress of the test medium with or without plasticizer was measured as a function of shear rate using a viscometer, Bohlin Visco 88. A commercial lignosulphonate product - WRDA 90D (containing 30 w-% of lignosulphonate) was used as reference. Unmodified lignin dissolved in 1 NaOH at 15 w-% dry solids was used as reference as well. Cement-water (dry solids: 70 w-% for CEM I, and 66 w-% for CEM II) dispersions were prepared with and without plasticizer solution using efficient mixing, Heidolph DIAX 600. The plasticizer was mixed into a pre-dispersed cement-water mixture. Several plasticizer dosages (as plasticizer dry solids bases), in a range of 0.20-0.80 w-% of the cement dry solids, were tested. The shear stress as a function of share rate was measured immediately after preparing the sample. The results are shown in Figure 4 (for CEM I) and in Figure 5 (for CEM II).

CEMI and CEM II are both grades of Portland cement that are commonly used in concrete applications.

CEM I has a chemical composition of: CaO 60-61%, SiO<sub>2</sub> 18-19%, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, MgO

CEM II has a chemical composition of: CaO 63-65%, SiO<sub>2</sub> 20-22%, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, MgO

From Figures 4 and 5 it can be seen that oxidation improves the function of the lignin as a plasticizer, i.e. decreases yield stress as well as shear stress of the cement-water mixtures as a function of shear rate.

The lower the shear stress with a given shear rate the better the plasticizing performance of the added product. Additives typically slow down the hydration of the cement, i.e. its reaction with water, whereby low doses of plasticizer are desirable.

Also unmodified lignin functions as a plasticizer, but requires a larger dose to achieve the same yield stress, compared to oxidized lignin. Lignosulfonates require even higher doses.

One of the above cement samples, CEM II, with or without plasticizer, was also tested for its reaction heat, caused by the hydration reaction (which will take place also in concrete mixtures). The heat flow was measured as a function of time using a calorimetric method. The plasticizer according to the invention was Soda wheat 5% oxidized. The dosing of the plasticizer was adjusted to give a cement yield stress of about 10Pa. One reference sample was prepared without plasticizer (-). Used reference plasticizers were: Glenium C151 (a

commercial synthetic plasticizer) and WRDA 90D (a commercial lignosulphonate plasticizer). The results are shown in Figure 6.

The effect of the oxidized lignin on the hydration reaction of cement was superior to  
 5 WRDA 90D *i.e.* oxidized lignin hindered the reaction less than WRDA 90D.

**Example 4 – Measuring the slump of oxidized lignin-plasticized concrete**

The plasticizing performance of the oxidized lignins was verified by using concrete  
 10 (cement + stone aggregate + water) as a test medium.

The slump was determined for the unmodified lignin and oxidized lignin-plasticized concrete. WRDA 90D was used as a reference plasticizer. Concrete was prepared according to EN1766 type C(0,40), with the exception that CEMII B-M (S-LL) 42,5N was  
 15 used as the cement. The oxidized lignin plasticizer was soda wheat lignin, oxidized at various lignin dry solids (5%, 15% and 25%). The reference sample contained unmodified soda wheat lignin (at dry solids of 15%). The contents of these lignins were 2.69kg/m<sup>3</sup>. One sample was also prepared with Soda wheat 15% oxidized, using a dose of 1.35 kg/m<sup>3</sup>. WRDA 90D reference plasticizer dose was 5.06 kg/m<sup>3</sup>.

20 Slump was determined just after preparing the concrete (Slump at 0 min) and after 30 minutes of delay (Slump at 30 min). Also, concrete hardening *i.e.* the cement hydration reaction was followed by calorimetric measurements. The slump measured just after preparing *vs.* time to maximum heat flow during hardening is shown in Figure 7. The  
 25 slump at 30 minutes is shown in Figure 8.

The slump in oxidized lignin plasticized concrete at 0 min was fairly comparable to that of WRDA 90D with 2-fold dosing, and clearly higher than in the case of unmodified lignin (Slump at 0 min). After 30 minutes the slump in oxidized lignin plasticized concrete was  
 30 clearly higher than when using unmodified lignin or WRDA 90D.



## Claims

1. A concrete mixture, **characterized** in that it contains aggregate, cement, water and a plasticizer formed of oxidized lignin, said oxidized lignin having been manufactured in a process where a lignin starting material forming an aqueous lignin solution having a lignin content of 0.5–30w-%, preferably 5–25w-% was reacted with an oxidizing agent selected from the group of oxygen (O<sub>2</sub>) and air in the solution, said reaction having been carried out in alkaline conditions, at a pH within the range 8 – 14, using a load of oxidizing agent of 10 – 95 w-% calculated based on the weight of the lignin and optionally adding an alkaline agent to provide the alkaline conditions, prior to addition of the oxidizing agent.
2. The concrete mixture according to claim 1, **characterized** in that its plasticizer content (as lignin dry solids bases) is  $\leq 0.63\text{w-\%}$  of the cement dry solids.
3. The concrete mixture according to claim 1, **characterized** in that its plasticizer content (as lignin dry solids bases) is  $\leq 2.7 \text{ kg/m}^3$  of the concrete mixture.
4. The concrete mixture according to any of claims 1 to 3, **characterized** in that the cement has 200–500 kg/m<sup>3</sup> content with water/cement –ratio 0.30–0.75.
5. A process for manufacturing a concrete mixture, **characterized** by mixing aggregate, cement, water and a plasticizer formed of oxidized lignin, said oxidized lignin having been manufactured in a process where a lignin starting material forming an aqueous lignin solution having a lignin content of 0.5–30w-%, preferably 5–25w-%, was reacted with an oxidizing agent selected from the group of oxygen (O<sub>2</sub>) and air in the solution, said reaction having been carried out in alkaline conditions, at a pH within the range 8 – 14, using a load of oxidizing agent of 10 – 95 w-% calculated based on the weight of the lignin, and optionally adding an alkaline agent to provide the alkaline conditions, prior to addition of the oxidizing agent.
6. The process of claim 5, **characterized** by adjusting the initial temperature to  $\leq 100^\circ\text{C}$  for the oxidation reaction, preferably to 25–80 °C, more preferably to 40–80 °C, and most suitably to 60–80 °C.

7. The process of any of claims 5 to 6, **characterized** by adjusting the pH of the lignin solution to a value of 10–14 prior to addition of the oxidizing agent.
8. The process of claim 7, **characterized** by adjusting the pH of the lignin solution using an alkaline agent, such as sodium hydroxide or sodium carbonate, preferably in a content of 20–50w-% of the lignin, most suitably in a content of 23–45w-%, or using a buffer.
9. The process of any of claims 5 to 8, **characterized** by maintaining a constant pH in the lignin solution during the oxidation reaction.
10. The process of any of claims 5 to 9, **characterized** by allowing the oxidizing agent to react with the lignin for 3–120 minutes, preferably 3–60 minutes, and most suitably for 5–30 minutes.
11. Use of the process of any of claims 5 to 10 in manufacturing the concrete mixture of any of claims 1 to 4

## Patenttivaatimukset

1. Betoniseos, tunnettu siitä, että se sisältää runkoainetta, sementtiä, vettä ja plastisaattoria, joka muodostuu hapetetusta ligniinistä, jolloin mainittu hapetettu ligniini on valmistettu menetelmällä, jossa ligniinilähtöaine, joka muodostaa ligniinin vesiliuoksen, jonka ligniinipitoisuus on 0,5–30 paino-%, edullisesti 5–25 paino-%, on saatettu reagoimaan hapettimen kanssa liuoksessa, jonka hapetin valitaan ryhmästä happi (O<sub>2</sub>) ja ilma, jolloin mainittu reaktio on toteutettu alkalisissa olosuhteissa, pH-välillä 8–14, käyttäen hapetinta panostuksella 10–95 paino-% ligniinin painosta laskettuna, ja mahdollisesti lisäämällä alkalista ainetta alkalisten olosuhteiden aikaansaamiseksi ennen hapettimen lisäämistä.
2. Patenttivaatimuksen 1 mukainen betoniseos, tunnettu siitä, että sen plastisaattoripitoisuus (ligniinin kuiva-aineesta laskettuna) on  $\leq 0,63$  paino-% sementin kuiva-aineesta.
3. Patenttivaatimuksen 1 mukainen betoniseos, tunnettu siitä, että sen plastisaattoripitoisuus (ligniinin kuiva-aineesta laskettuna) on  $\leq 2,7$  kg/m<sup>3</sup> betoniseoksesta.
4. Jonkin patenttivaatimuksen 1–3 mukainen betoniseos, tunnettu siitä, että sementin pitoisuus on 200–500 kg/m<sup>3</sup> ja veden suhde sementtiin on 0,30–0,75.
5. Menetelmä betoniseoksen valmistamiseksi, tunnettu siitä, että sekoitetaan runkoaine, sementti, vesi ja plastisaattori, joka muodostuu hapetetusta ligniinistä, jolloin mainittu hapetettu ligniini on valmistettu menetelmällä, jossa ligniinilähtöaine, joka muodostaa ligniinin vesiliuoksen, jonka ligniinipitoisuus on 0,5–30 paino-%, edullisesti 5–25 paino-% on saatettu reagoimaan hapettimen kanssa liuoksessa, jonka hapetin valitaan ryhmästä happi (O<sub>2</sub>) ja ilma, jolloin mainittu reaktio on toteutettu alkalisissa olosuhteissa, pH-välillä 8–14, käyttäen hapetinta panostuksella 10–95 paino-% ligniinin painosta laskettuna, ja mahdollisesti lisäämällä alkalista ainetta alkalisten olosuhteiden aikaansaamiseksi ennen hapettimen lisäämistä.
6. Jonkin patenttivaatimuksen 5 mukainen menetelmä, tunnettu siitä, että alkulämpötila säädetään hapetusreaktiota varten  $\leq 100$  °C:seen, edullisesti 25–80 °C:seen, edullisemmin 40–80 °C:seen ja sopivimmin 60–80 °C:seen.

7. Jonkin patenttivaatimuksen 5–6 mukainen menetelmä, t u n n e t t u siitä, että ligniiniliuoksen pH säädetään arvoon 10–14 ennen hapettimen lisäämistä.
8. Patenttivaatimuksen 7 mukainen menetelmä, t u n n e t t u siitä, että ligniiniliuoksen pH-arvo säädetään alkalisella aineella, kuten natriumhydroksidilla tai natriumkarbonaatilla, edullisesti pitoisuutena 20–50 paino-% ligniinistä, sopivimmin pitoisuutena 23–45 paino-%, tai puskurilla.
9. Jonkin patenttivaatimuksen 5–8 mukainen menetelmä, t u n n e t t u siitä, että ligniiniliuoksen pH-arvo pidetään vakiona hapetusreaktion aikana.
10. Jonkin patenttivaatimuksen 5–9 mukainen menetelmä, t u n n e t t u siitä, että hapettimen annetaan reagoida ligniinin kanssa 3–120 minuuttia, edullisesti 3–60 minuuttia ja sopivimmin 5–30 minuuttia.
11. Jonkin patenttivaatimuksen 5–10 mukaisen menetelmän käyttö jonkin patenttivaatimuksen 1–4 mukaisen betoniseoksen valmistuksessa.

Fig. 1

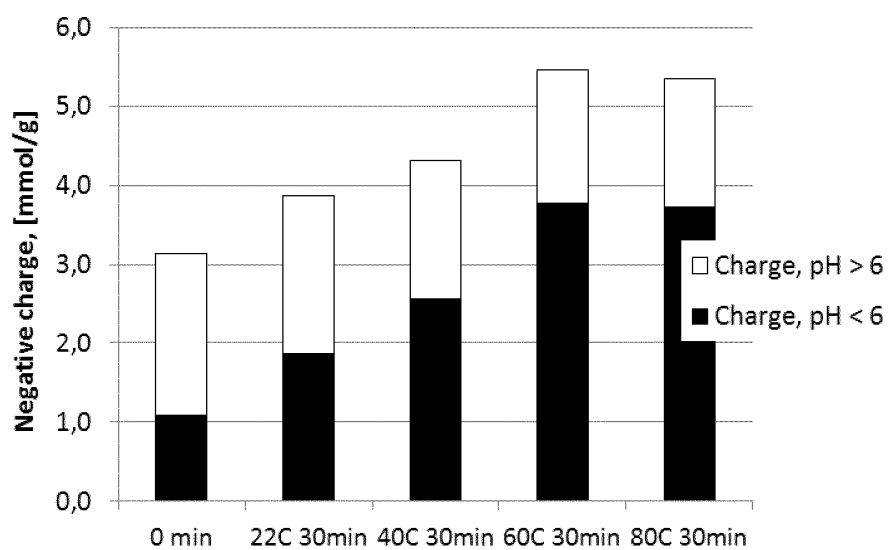


Fig. 2

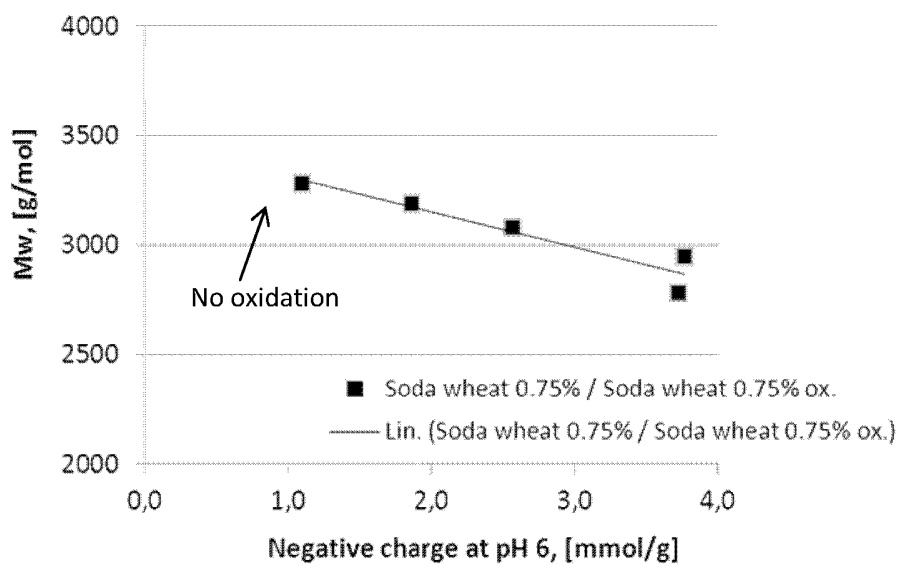


Fig. 3

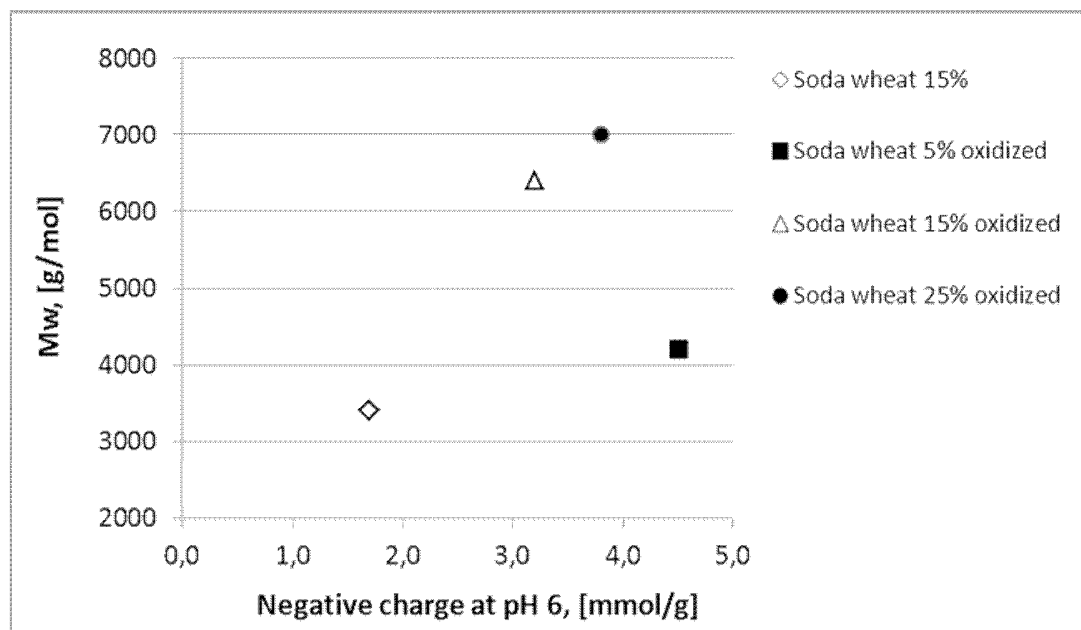


Fig. 4

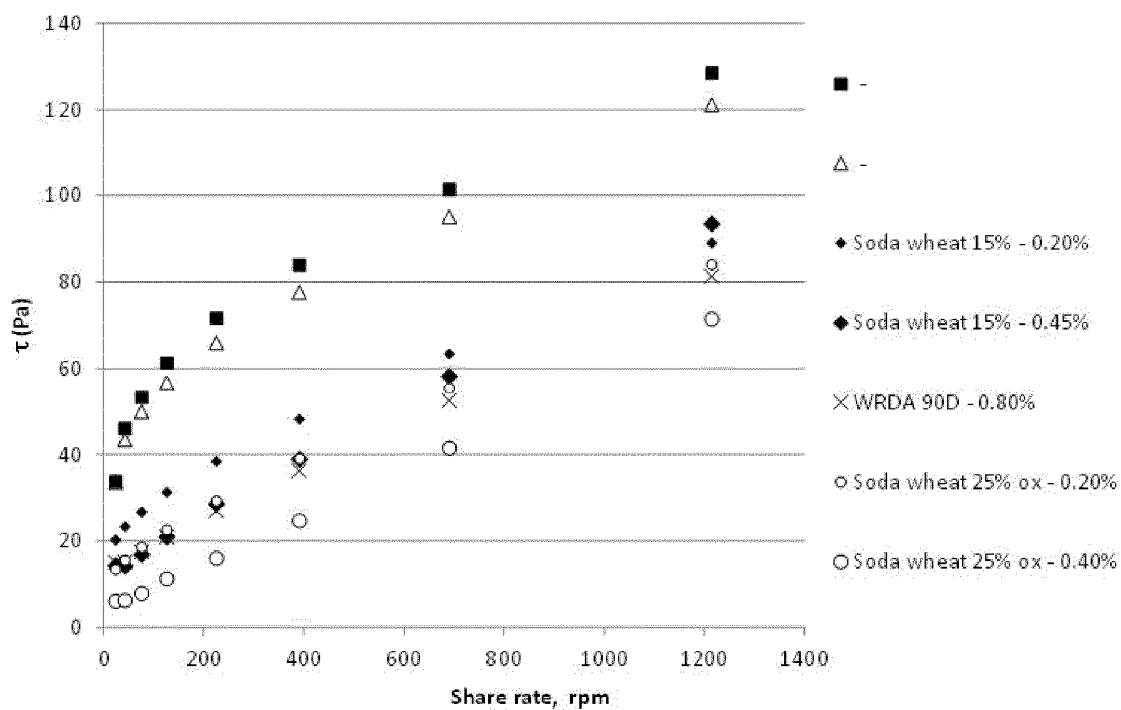


Fig. 5

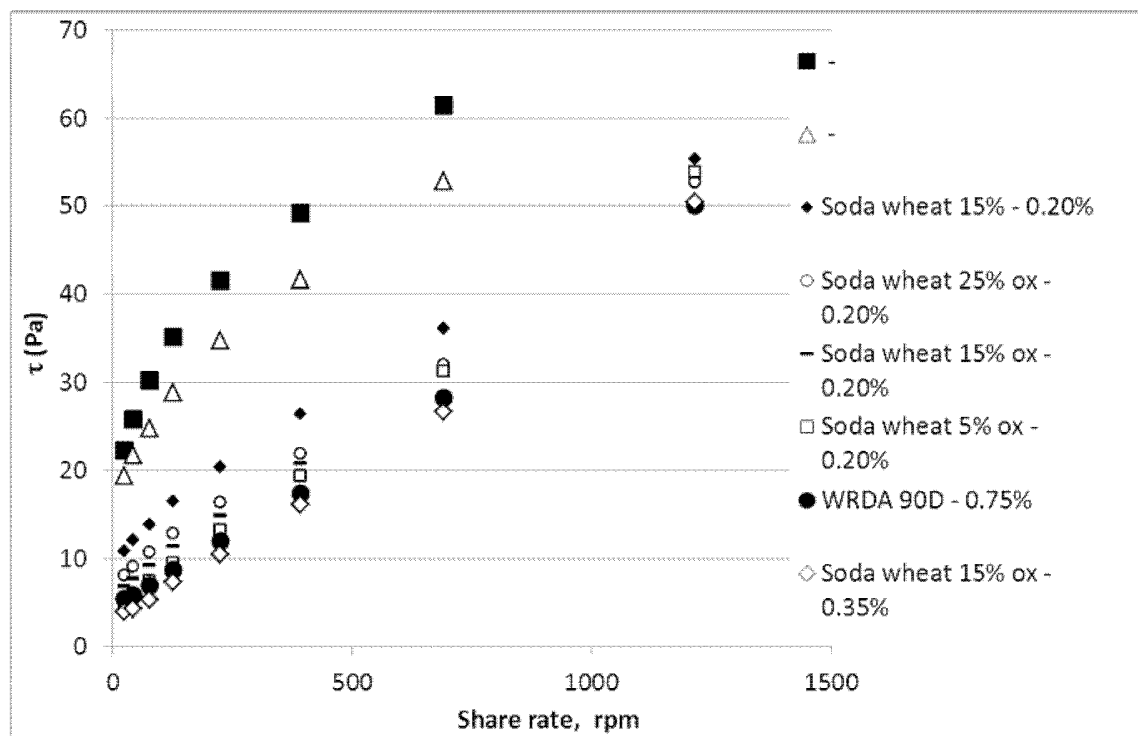


Fig. 6

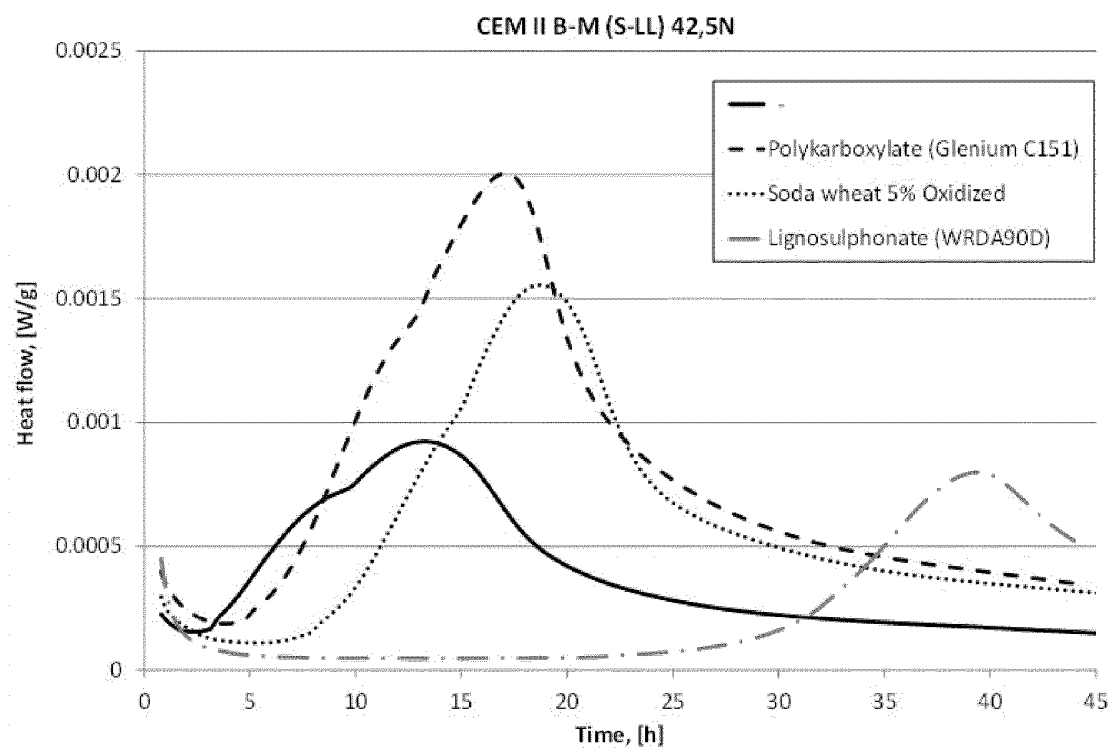


Fig. 7

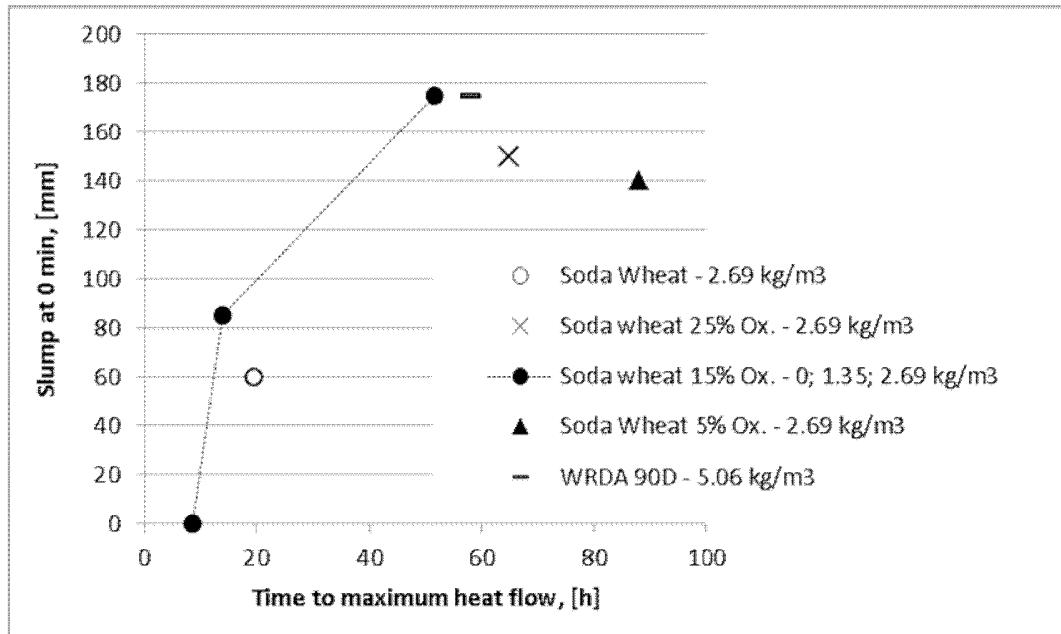


Fig. 8

