

## Article

# Lignin from Bioethanol Production as a Part of a Raw Material Blend of a Metallurgical Coke

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**Abstract:** Replacement of part of the coal in the coking blend with lignin would be an attractive solution to reduce greenhouse gas emissions from blast furnace (BF) iron making and for obtaining additional value for lignin utilization. In this research, both non-pyrolyzed and pyrolyzed lignin was used in a powdered form in a coking blend for replacing 5-, 10- and 15 m-% of coal in the raw material bulk. Graphite powder was used as a comparative replacement material for lignin with corresponding replacement ratios. Thermogravimetric analysis was performed for all the raw materials to obtaining valuable data about the raw material behavior in the coking process. In addition, chemical analysis was performed for dried lignin, pyrolyzed lignin and coal that were used in the experiments. Produced bio cokes were tested in a compression strength experiment, in reactivity tests in a simulating blast furnace shaft gas profile and temperature. Also, an image analysis of the porosity and pore shapes was performed with a custom made MatLab-based image analysis software. The tests revealed that the pyrolysis of lignin before the coking process has an increasing impact on the bio coke strength, while the reactivity of the bio-cokes did not significantly change. However, after certain level of lignin addition the effect of lignin pyrolysis before the coking lost its significance. According to results of this research, the structure of bio cokes changes significantly when replacement of coal with lignin in the raw material bulk is at a level of 10 m-% or more, causing less uniform structure thus leading to a less strong structure for bio cokes.

**Keywords:** bio-coke; softwood lignin; lignin pyrolysis; blast furnace; compression strength; reactivity; image analysis

## 1. Introduction

Blast furnace (BF) iron making faces important changes. Tightening environmental legislation, increasing prices of GHG emission allowances and competition between the steel manufacturers encourage the steel manufacturers to research and implement new, less GHG –generating processes and raw materials. However, GHG emissions reduction methods should not be carried out at the expense of functionality of the process or the quality of the product.

The BF- basic oxygen furnace (BOF) route is the leading pathway to produce crude steel in a sense of produced tons of steel annually. The share of the steel that is produced via the BF-BOF route is approximately 70%, of which approximately 85% of the raw materials is BF-produced pig iron [1]. In a BF-based iron production, metallurgical coke is a primary fuel of the process. Besides working as a fuel the metallurgical coke also works as a reducing agent for the iron ore and as a bed material for the raw material burden by creating a layer with a permeable matrix for ascending gases and for descending melts (steel and slag) [2]. The consumption of metallurgical coke with the existing BF process technology can be as low as 250 kg/tHM (tons of hot metal), while it has been over 500 kg/tHM

in the 1970s' [3]. The decreasing amount of coke usage in the process emphasizes more and more already high demands of the coke quality especially mechanical strength.

The use of biomaterial as a part of the raw material blend in the coking process can be one of the possible solutions when it comes to the potential new techniques to decrease GHG emissions in the BF-process iron making. The advantage of the bio-based carbon sources in comparison to fossil-based carbon sources is that during its growth the biomass binds the carbon dioxide (CO<sub>2</sub>) that is released at the end of its life cycle. With biomasses, the natural carbon cycle is short as the growth and decay of the biomaterial occurs at the soil surface layer. With the fossil carbon sources, the natural carbon cycle is much longer. The carbon deposits have built up to Earth's crust over the millions of years and the natural degassing of carbon from the deposits is slow. Therefore, the utilization of the fossil carbon perturbs the long-term carbon cycle, while utilization of the bio-based carbon sources does not significantly disturb the balance in carbon cycle [4]. Biomass-based additives to coking coal blend have been studied earlier: Montiano et al. studied the influence of hardwood and softwood sawdust on coking properties of coking mix [5]. Ng et al. studied the effect of charcoal addition to the coking blend [6]. Suopajarvi et al. studied the effect of charcoal and kraft-lignin addition to the produced coke strength and reactivity properties [7]. One of the least studied fractions of biomass as a part of the coking blend is lignin.

Lignin is a complex highly branched biopolymer and is an integral part of the secondary cell walls of plants. Softwood contains from 25% to 35% of lignin, on a dry basis. The production of lignin has become relevant in recent years because of the development of new technologies to separate lignin from the main product. The availability of lignin has increased and will further be increased on the upcoming years because of the kraft-lignin separation from the black liquor in the pulp production with Lignoboost technology [8], as well as the separation of lignin from the wood-based biomaterial via enzyme hydrolysis and yeast fermentation in bioethanol production. In both cases the lignin by-product has been used up to now as a raw material in energy production in combined heat and power (CHP plants). However, for achieving additional value to lignin, also other ways to utilize lignin have been under research in the basis of natural properties of lignin, e.g., the use of lignin as a reducing agent [9].

As an injectable reductant for BF iron making, multiple properties of pyrolyzed lignin were as good as or better than the properties of pulverized coal (PC) according to Farrokh et al. [10]. Suopajarvi et al., have stated that the replacement of the coal in the raw material blend of the coking process with lignin by 2.5% of the total bulk mass leads to 26.3% decrease in the coke cold strength in comparison to reference coke [7]. They have also reported that kraft-lignin loses major share of its mass before the softening stage of the coal thus leading to empty spaces in the coke structure. The same behavior was not observed with the use of charcoal in the coking blend but instead the strength of coke remained even with 7.5–10 m-% replacement of coal with charcoal. The charcoal was pyrolyzed in 600 °C, and, according to thermogravimetric analysis, the charcoal acted mainly as inert material in the coking blend throughout the coal plastic phase in the coking process [7]. The earlier study [7] did not consider the effect of pre-pyrolysis of lignin before using it as a raw material in a coking blend. It is not clear if it is better that lignin or any other biomaterial has an active role during the coke formation or should the behavior of biomaterial be inert. In this paper, the effect of both, non-pyrolyzed and pyrolyzed lignin on the formation and most important properties of coke, will be revealed. Cold compression strength of coke is tested by using a Gleeble 3800 thermomechanical simulator. For coke reactivity analysis, a custom-made thermogravimetric analyzer (TGA) is used. The structural changes in produced cokes acting behind the changing properties are analyzed from the microscopy images by using MatLab-based image analysis software and the results will be discussed. The effect of pyrolysis of lignin on its behavior during the coke formation will be evaluated; does the pyrolyzed lignin behave as an inert during the coke formation or is the behavior more alike with the non-pyrolyzed lignin.

## 2. Materials and Methods

### 2.1. Materials

A medium volatile coking coal with a 62.4% vitrinite concentration was used as main raw material. Gieseler-fluidity and dilatation of the coal are presented in Table 1. As for alternative carbonaceous biomaterial, lignin was used. Lignin was used both in non-pyrolyzed and pyrolyzed form. The pyrolysis of lignin was performed in 350 °C. The pyrolysis temperature was selected based on the earlier reports about behavior of lignin in the pyrolysis process [11,12]. The aim was to set the degradation of lignin on in the pre-pyrolysis before the actual coking process. In the coking process, the lignin degradation was assumed to continue and finally when the structure of lignin begins to reunify by crosslinking of the functional groups (phenols), the coal would have filled up the cracks and voids in the lignin structure resulting to a uniform structure throughout the whole coke. Pre-pyrolysis of lignin also decreases the amount of oxygen (O<sub>2</sub>) rich gas release. According to Diez et al. [13], there is a relationship between the oxygen content of biomass and the rheological properties of the coking blend, which was shown as a decreased Gieseler maximum fluidity of coal blend during the coking process as the oxygen content of biomaterial was increased. Before the pyrolysis, the lignin was dried in 40 °C for nine days in order to decrease the moisture level in the material from 50–60 m-% to 5–10 m-%. The pyrolysis was executed in an Entech model ETF 75/17 V vertical split tube furnace (Entech, Ängersholm, Sweden). The heating rate of the pyrolysis was 5 °C/min from room temperature to 350 °C. The holding time in the final temperature was 8 h, after which the furnace and the lignin was let freely to cool down to a room temperature. The pyrolysis was done under nitrogen (N<sub>2</sub>) gas. The gas flow rate was 1 L/min.

As for comparative inert material in the raw material blend of coking, synthetic graphite powder was used. Graphite powder, synthetic, −20 + 100 mesh, 99.9% (metals basis), was purchased from Alfa Aesar (Karlsruhe, Germany). The comparative raw material was used in the blend to enable to define whether the properties of coke changed because of the use of lignin in the blend or are the changes in coke properties caused by the replacement of coking coal by material that acts as an inert during the coal plastic phase in the coking process.

A chemical analysis was conducted to the coking coal, non-pyrolyzed and pyrolyzed lignin. The chemical analysis of coal was performed at the SSAB Europe Raahe steel plant, in Raahe, Finland. The chemical analysis of non-pyrolyzed and pyrolyzed lignin, was performed at Eurofins, Oulu site according to the existing standards. From the data of ash compositions of raw materials, the basicity index (BI, %) was defined. The BI is, by definition, the ratio between the basic and acid components in the ash of the material and is defined in Equation (1):

$$BI (\%) = (CaO + Fe_2O_3 + MgO + Na_2O + K_2O)/(SiO_2 + Al_2O_3) \times A \quad (1)$$

where A is the ash percentage of the sample and the chemical compounds are the proportions of the certain compound in the ash.

**Table 1.** Dilation and Gieseler-fluidity.

Dilatometer		
Softening temperature	°C	405
Shrinking temperature	°C	434
Temperature of max dilatation	°C	475
Shrinkage	%	22
Dilatation	%	57
Gieseler-Fluidity		
Softening temperature	°C	422
Temperature of max fluidity	°C	459
Re-solidification temperature	°C	490
Maximum fluidity	ddpm	457

## 2.2. Thermogravimetric Analysis

Thermogravimetric analysis was conducted to raw materials that were used in this research to define the amount of volatile matter in the materials that will be released during the coking process. A STA 409 PC Luxx thermogravimetric analyzer (TGA, Netzsch-Gerätebau GmbH, Selb, Germany) was used in the tests. Temperature was raised from room temperature to 1200 °C at a heating rate of 2.5 °C/min in nitrogen gas at a flow rate of (60 mL/min) to maintain an inert atmosphere.

The sample size was approximately 15 mg of fine powder; the size fraction for coal was 70% of 0.5–1.0 mm and 30% of <0.5 mm and for lignin 125–250 µm, which were the size fractions for subsequent coking experiment. The amount of released volatile matter at specific time was calculated with a procedure that is described in Equation (2):

$$\text{VMT} = (M_0 - M_i)/(M_0 - M_f) \times 100 \quad (2)$$

where VMT is the volatile matter in percentage,  $M_0$  is the initial mass,  $M_f$  is the final mass and  $M_i$  is the mass at specific time  $i$ .

## 2.3. Coke Making

Thirteen different types of cokes were produced for analysis: one reference coke that contain good quality, medium volatile coking coal, three lignin-bearing cokes, three pyrolyzed lignin-bearing cokes and three graphite powder bearing cokes. The amounts of replacing agents in the coking blends were 5-, 10- and 15 m-%. The raw materials were ground to powder followed by sieving to a certain grain size for coal, non-pyrolyzed- and pyrolyzed lignin. Graphite powder was fed to raw material mix as it was (−20 + 100 mesh, i.e., 841–149 µm). For coal, two size fractions were used in the blend: 30% of the material were ground and sieved to a <0.5 mm size fraction and 70% to 0.5–1.0 mm fraction. Lignin, both non-pyrolyzed and pyrolyzed, was ground to 125–250 µm size fraction before blending it into a coking charge. The choice of size fractions of coal based on the data from the coking coal size fractions from a commercial coking process. However, the biggest size fractions were cut out because of the limited size of the mini coke oven. The choice of 125–250 µm size fraction for lignin based on the report from Suopajarvi et al., in which the replacement of coking coal with the charcoal with the corresponding size fraction produced the strongest coke in comparison to other charcoal containing cokes in which the particle size of charcoal was different [7]. The amount of raw materials in the charges of different types of cokes are presented in Table 2.

**Table 2.** Size fractions and portions of the raw materials in the blend.

Replacing Agent	Amount of Replacement [m-%]	Coal		Lignin [g]	Pyrolyzed Lignin [g]	Graphite Powder	Targeted Bulk Density [kg/m <sup>3</sup> ]
		0.5–1.0 mm [g]	<0.5 mm [g]				
None	0	9.1	3.9	0	0	0	751.62
Lignin	5%	9.1	3.25	1.11	0	0	778.5
Lignin	10%	9.1	2.6	2.23	0	0	805.38
Lignin	15%	9.1	1.95	3.34	0	0	832.26
Pyrolyzed lignin	5%	9.1	3.25	0	0.65	0	751.62
Pyrolyzed lignin	10%	9.1	2.6	0	1.3	0	751.62
Pyrolyzed lignin	15%	9.1	1.95	0	1.95	0	751.62
Graphite	5%	9.1	3.25	0	0	0.65	751.62
Graphite	10%	9.1	2.6	0	0	1.3	751.62
Graphite	15%	9.1	1.95	0	0	1.95	751.62

The bulk density of the charge was targeted to 750 kg/m<sup>3</sup>. The bulk density of charge in industrial coke oven varies usually from 600 kg/m<sup>3</sup> to 800 kg/m<sup>3</sup>, depending on the raw material blend, location in the coke oven, the grain size and whether the charge is stamped or not [14]. The addition of raw lignin to the coking charge was compensated to be higher, considering the amount of VMT that will be released in the pyrolysis in temperature of 350 °C, so that in both cases (pyrolyzed and non-pyrolyzed)

the bulk density would be the same after VMT release in 350 °C. The pyrolyzed and non-pyrolyzed lignin addition are set to replace the smaller coal fraction that was added to the coking charge, which is presented in Table 2.

The raw materials were measured and carefully mixed together in a beaker glass before feeding the charge into the mini oven of the mini coke battery. Mini ovens and the coke battery were made of graphite. Dimensions and more detailed presentation of the mini ovens and coke battery are presented in Suopajarvi et al. [7]. Mini ovens were covered with graphite powder in order to prevent the free oxygen from reacting with the coking charge. A graphite lid was put on the coke battery and the battery was charged into the Nabertherm HT08/18 chamber furnace (Nabertherm GmbH, Lilienthal, Germany), which has heating resistors on the walls on both sides of the furnace. Two lumps of graphite were also charged into the furnace to the back wall and to the opening in order to prevent the free oxygen in the furnace from reacting with the graphite of the coke battery. Nitrogen was used as a protective gas in the coking process with a flow rate of 1 l/min. The heating rate of the chamber furnace was 2.5 °C/min from room temperature up to 1200 °C with no holding time at the final temperature. Furnace was let to cool to room temperature freely. Before the actual coking experiments, a set of trials was made to define optimal furnace heating rate. The trial cokes were explored visually and scratched by hand for evaluating which heating rate produced the most homogenous and mechanically durable set of cokes.

#### 2.4. Compression Strength of Coke

The cold compression strength measurements were performed with a Gleeble 3800 thermomechanical simulator (Dynamic Systems Inc., New York, NY, USA). The Gleeble 3800 thermomechanical simulator and its functions are explained in more detail by Hojny, [15] and Haapakangas et al. [16]. Ten samples of each coke type were tested for room temperature compressive strength. Before the strength tests, the formed coke cylinders were cut to a specific size: 12 mm of height and 17 mm of diameter on the cross section of the cylindrical samples. The samples have been found to be suitable for the Gleeble 3800 using the standard sample holder. The compression force was linearly increased at an increase rate of 100 N/s so that the final breakdown of the coke structure would occur after around 30 s from the start of the compression, as instructed in the ASTM standard C695-15 [17]. The breaking point of the samples were tested beforehand with a batch of trial samples and the increase rate of stress was defined based on the results.

#### 2.5. Coke Reactivity

For testing the reactivity of the different types of produced cokes, a custom-built TGA (thermogravimetric analyzer) was used. The custom-built TGA is able to utilize gases such as H<sub>2</sub>, H<sub>2</sub>O, CO, CO<sub>2</sub>, N<sub>2</sub> and air. All the gases are preheated to 150 °C before fed to the furnace. Water is pumped to the system with a peristaltic pump and evaporated in 250 °C in an evaporator heater before it is fed to the system in order to prevent condensation. The peristaltic pump was calibrated before each test. The whole system is controlled and monitored with a specially designed computer software. More detailed description and a schematic drawing from the equipment are presented in Iljana et al. [18].

The samples were ground and sieved to a particle size 2.0–4.0 mm. The mass of the samples in the experiments was approximately 2 g. Before reactivity tests, the ground coke samples were dried in a 110 °C overnight in order to remove the sample moisture. The mass of the samples was weighed and they were placed to a spinel crucible with inner height of 28 mm and diameter of 22 mm. The crucible was perforated from on the bottom in order to enable the gas flow through the sample stack. The crucible was placed to the centre of the furnace in an inert (N<sub>2</sub>) atmosphere where it was kept for 10 min before introducing it to the reactive gases in order to stabilize the temperature throughout the sample before the experiment. Both, isothermal and non-isothermal (dynamic) reactivity experiments were made for coke samples. In isothermal experiments, the temperature was fixed to 1100 °C and

the holding time of samples under reactive gas atmosphere was 2 h. In dynamic experiments, the temperature was elevated from 800 °C to 1100 °C with a heating rate of 2 °C/min with a static gas profile. The gas profile was set to correspond a simulated gas profile of a commercial blast furnace (BF) shaft, including hydrogen and water vapor. The same gas profile is reported as a “low-hydrogen shaft gas” in Haapakangas et al. [19] and it is thermodynamically balanced at 1100 °C with thermochemical calculation software, HSC Chemistry 7.0 (Outotec, Pori, Finland). The composition of the gas profile is presented in Table 3. Total gas flow was set to 2 L/min throughout the whole experiment.

**Table 3.** The gas profile in reactivity and threshold temperature tests.

Gas Species	N <sub>2</sub>	CO	CO <sub>2</sub>	H <sub>2</sub>	H <sub>2</sub> O
Share [vol-%]	50	27.9	17.1	2.1	2.9

## 2.6. Optical Microscopy

Polished sections were prepared from each coke type. Five mm slices in height were cut from each type of coke cylinder. Cut slices were mounted to epoxy and polished for microscopy research. The samples were studied under 4× and 20× objective lenses. The images, presented in this paper, were taken under 4× objective lens. After imaging the samples the images were analyzed with MatLab-based image analysis software for porosity, pore shape factors and pore size distributions in the samples. The principle of operation of the MatLab-based image analysis software, used in this research is explained in more detail in Haapakangas et al., 2016 [19] and in Mattila and Salmi [20].

## 3. Results and Discussion

### 3.1. Raw Materials

The ultimate analysis, proximate analysis and ash composition of the coal, non-pyrolyzed lignin and pyrolyzed lignin are presented in Table 4.

**Table 4.** Chemical analysis of coal and dried lignin.

		Coal	Lignin	Pyrolyzed Lignin
<b>Total Moisture (105 °C)</b> [m-%]		9.02	5.3	1.80
<b>Ultimate analysis [m-%], db</b>	C	79.90	62.10	75.80
	H	4.82	6.06	4.40
	O	2.88	30.40	17.80
	N	2.20	1.04	1.40
	S	0.56	0.13	0.09
<b>Proximate analysis [m-%], db</b>	Volatile matter	22.69	66.26	28.67
	Ash content	9.64	0.20	0.50
	Fixed Carbon	67.67	33.55	70.83
<b>Ash composition [%], db</b>	CaO	0.77	24.30	16.40
	MgO	0.54	4.70	3.10
	SiO <sub>2</sub>	65.20	4.30	8.00
	Al <sub>2</sub> O <sub>3</sub>	26.37	1.70	3.00
	Na <sub>2</sub> O	0.38	12.10	9.60
	K <sub>2</sub> O	0.94	7.70	6.40
	Fe <sub>2</sub> O <sub>3</sub>	3.45	4.90	5.80
	P <sub>2</sub> O <sub>5</sub>	0.47	16.10	10.50
	TiO <sub>2</sub>	1.56	0.04	0.10
<b>Basicity Index, BI [%]</b>		0.64	1.79	1.88



According to chemical analysis results, the pyrolysis of lignin had a positive effect on lignin chemical properties in a sense of using it as a raw material in a coking process: carbon content increases, oxygen content decreases, volatile matter decreases and no significant increase in the total amount of ash was observed. In comparison to coal, pyrolyzed lignin has quite similar elemental chemistry, except for the amount of oxygen, which is high in comparison to coal despite the pyrolysis lignin. Ash content of pyrolyzed and non-pyrolyzed lignin is small in comparison to coal. When comparing both, non-pyrolyzed and pyrolyzed lignin to kraft-lignin whose chemical analysis is presented in Suopajarvi et al. [7], the results are mainly similar; the most considerable differences are that kraft-lignin contains a lot more sulfur but on the other hand the phosphorus content is higher with the bioethanol production side-product lignin.

The basicity index of the materials (coal and lignin) revealed that coal had more acid components in relation to basic components, while lignin and pyrolyzed lignin had more components that are basic. The total amount of ash of pyrolyzed and non-pyrolyzed lignin is however very small in comparison to coal. The basic ash chemistry of lignin can be possibly turned into a profit because the basic components of lignin ash, such as CaO, SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and MgO are the key components of BF slag and therefore the addition of lignin on the coal blend of metallurgical coke may reduce the need of use of limestone in the actual BF-process [21]. Other than that, the alkali content, e.g., potassium, of non-pyrolyzed and pyrolyzed lignin is high which is studied to have an increasing effect on the reactivity of the produced coke [22].

### 3.2. Devolatilization of the Raw Materials

TG- and DTG-curves of the raw materials, except for graphite, are presented in Figure 1. The yield of raw lignin was the lowest, approximately 35% from the initial mass in the TG-analysis. The yields of coal and pyrolyzed lignin were 78% and 62%, respectively. The first peaks in the DTG curves indicates the start of the water vapor release at around 100 °C. The moisture content of the coal, dry lignin and pyrolyzed lignin were 9.02 wt %, 5.3 wt % and 1.8%, respectively.

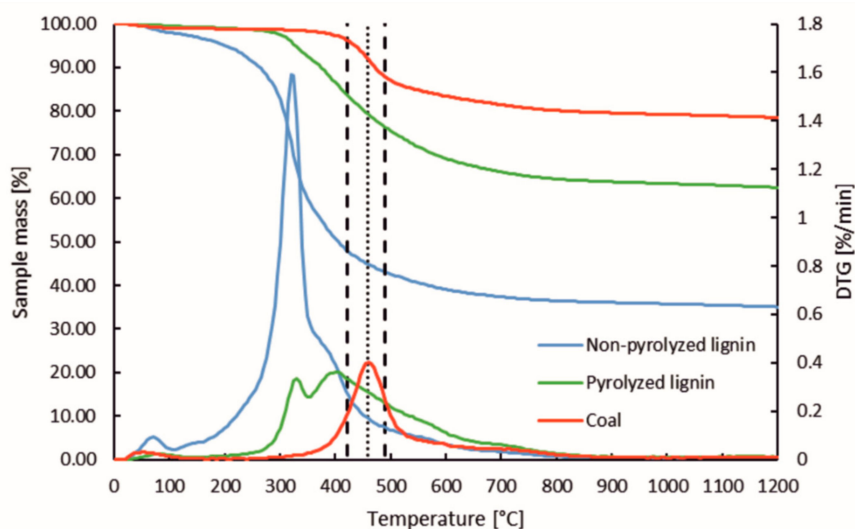


Figure 1. Devolatilization behavior of the raw materials.

In both of the lignin cases, the most dramatic mass loss occurred around 350–450 °C. This is the temperature range in which the reaction kinetics of lignin peaks and most of the VMT is released, according to Basu, 2010 [23]. The degradation of pyrolyzed lignin was more restrained in the 350–450 °C but the first peak in the DTG-curve (around 330 °C) implies that the pyrolysis of the lignin has not been complete throughout the whole lignin stack during the pyrolysis of the lignin. The behaviour of graphite powder was also thermo-gravimetrically tested under coking conditions but the release under N<sub>2</sub> gas was almost non-existent. The minor release near the final temperature of the TGA-experiment

could imply to the combustion of graphite caused by possible impurities either in the graphite itself or in the protective gas ( $N_2$ ).

As presented in Table 1, the coal begins to soften in 422 °C, the fluidity peaks at 459 °C and the resolidifies at 490 °C. In Figure 1, the softening and resolidification temperatures are marked with dashed black lines and the temperature of maximum fluidity of the coal is marked with dotted black line. The peak in the coal DTG curve is at the point where the coal fluidity reaches its maximum value, 457 ddpm, Table 1. The percentage of the mass loss during the coal plastic phase for coal, non-pyrolyzed lignin and pyrolyzed lignin were 39.5%, 7.6% and 20%, respectively. VMT releases of non-pyrolyzed lignin and pyrolyzed lignin before the coal softening temperature were approximately 80% and 43%, respectively. Because the graphitic coke battery is sealed with graphite powder and a graphitic lid, the formed gases do not have totally free access out of the coke ovens, which means that there is a significant amount of oxygen-rich gas present in the beginning and during the coal plastic phase. The same applies with the use of pyrolyzed lignin in the coking blend but not in the same extent as in the case of non-pyrolyzed lignin. Previously Diez et al. have reported that functionality of oxygen has a dominant influence on the fluidity development of the parent coal [13,24]. For the hardwood lignin, the thermal degradation product is mainly syringol (2,6-dimethoxyphenol), which is reported to have a decreasing impact on coal maximum fluidity in the coal plastic phase, but no significant effect on the plastic phase temperatures (solidification, maximum fluidity and re-solidification temperatures) of the coal. The main product of thermal degradation of softwood is guaiacol (2-methoxyphenol), and the amount of syringol is considerably less than in the thermal degradation of hardwood [24,25]. However, the structure of guaiacol resembles a lot of syringol, missing only the other methoxy group from the sixth C (carbon), as presented in Figure 2.

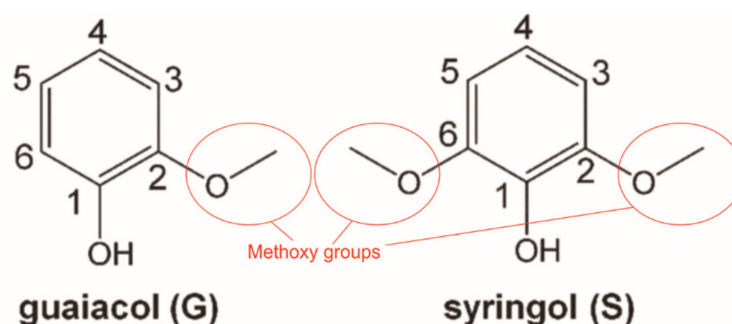


Figure 2. Structure of guaiacol and syringol monomers, modified from Dean et al. [26].

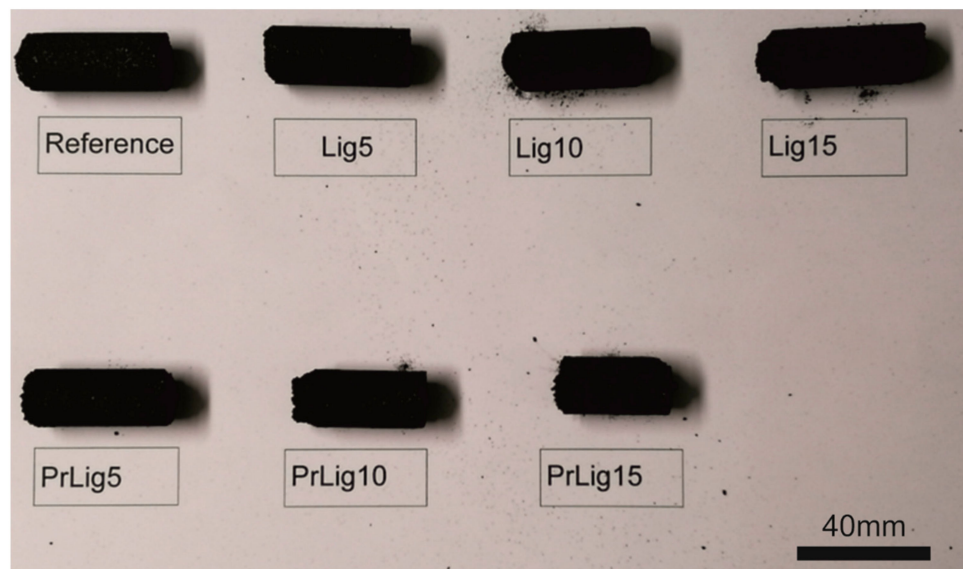
### 3.3. Produced Cokes

In visual evaluation, reference coke and cokes with lowest replacement ratios of coal with non-pyrolyzed lignin and pyrolyzed lignin had a good form without visible cracks either in the parallel or perpendicular direction. They also showed good mechanical strength and did not crack when twisted by hand. The cokes that contained higher amounts of non-pyrolyzed or pyrolyzed lignin, on the other hand, showed significant sensitivity towards abrasive force, the surface of the cokes were coarse and a lot of fine, non-coked matter remained in the mini-ovens when the samples were pulled out. The structure was so fragile that they were relatively difficult to handle without braking the samples. All the lignin containing cokes and reference coke are presented in Figure 3. Abbreviations Lig and PrLig refers to non-pyrolyzed and pyrolyzed lignin, respectively, and the number refers to the m-% of the replacement of coal in the coking blend.

In the coke-making configuration used in this research, where the heat conducts to the raw material charge radially from every direction, the plastic front does not proceed from a certain end of the coking charge to the opposite end but all the locations in the coking charge go through the plastic phase simultaneously. This may cause blockages for releasing gases, which may cause high porosity areas, more empty space between particles and pyrolytic carbon on the edges of pores thus leading to



weaker and more reactive coke structure. The structure of the cylindrical cokes was the weakest on the both ends of the cylinder, while the midsection of the cylinders had relatively good strength and was visually in a good condition.



**Figure 3.** Produced cylindrical cokes.

#### 3.4. Cold Compression Strength of Cokes

The cold compression strength of the samples are presented in Figure 4. According to the results, the coke strength decreases dramatically as the replacement ratio of coal by lignin increases. The decrease in strength properties also occurred with the samples in which some of the coal was replaced by graphite. Reference coke showed good strength throughout the whole batch of samples (10 pcs), resulting to coke strength against compressive stress to be 19.2 MPa in average. Out of the bio-cokes, the samples with the best strength characteristics was found from the batch that contained 5m-% of pyrolyzed lignin. The strength against compression in average was 8.2 MPa after which the structure of the sample broke down. The average strength of the samples that contained 5 m-% of graphite powder was 9.77 MPa. Based on the results, it can be concluded that the effect of pyrolyzed lignin on coke strength properties is mainly caused due to lack of physical interaction between pyrolyzed lignin and coal during the coal plastic phase and the releasing gases from pyrolyzed lignin only have a minor effect on coke strength properties at low replacement ratios. As the replacement ratio increases, the effect of releasing gases from pyrolyzed lignin become more significant, thus the results of the compression strength test differ more between the cokes containing pyrolyzed lignin and the cokes containing graphite powder. Overall, the bio-coke samples that contained pyrolyzed lignin instead of non-pyrolyzed lignin showed better strength towards compressive forces. This can be explained by several factors. Lignin is known to experience several dilatation-shrinking stages when temperature is elevated from room temperature to 600 °C. These variations in lignin volume could lead to empty spaces in the formed coke matrix and result to a weaker coke structure [7,27]. The highest dilatation peak for lignin is reported by [27] to take place around 300 °C and the following shrinkage continues up to 600 °C, which is over 100 °C higher than re-solidification temperature of the coal that was used in this research. Also, the releasing gases (mostly phenols) have a significant decreasing effect on coal maximum fluidity in coal plastic phase [24]. This leads to less mobile particles in the coking blend, less interaction between the particles thus leaving empty spaces inside the coal matrix itself and between the coal matrix and lignin particles. These phenomena stands out in the case of non-pyrolyzed lignin as well as in the cases of higher replacement ratios of pyrolyzed lignin.

As the replacement ratio of coal with graphite powder increases, the strength of coke weakens but the weakening is caused by the graphite inert nature during the coke formation.

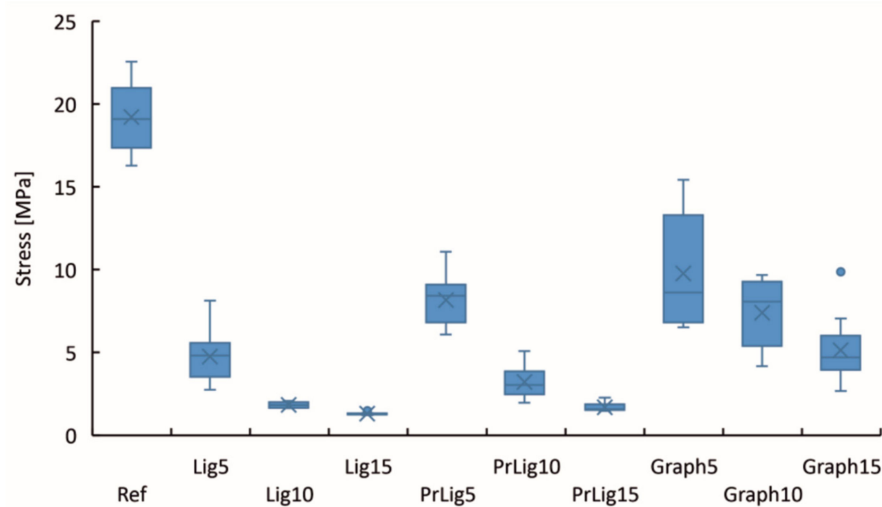


Figure 4. Compression strength of produced cokes.

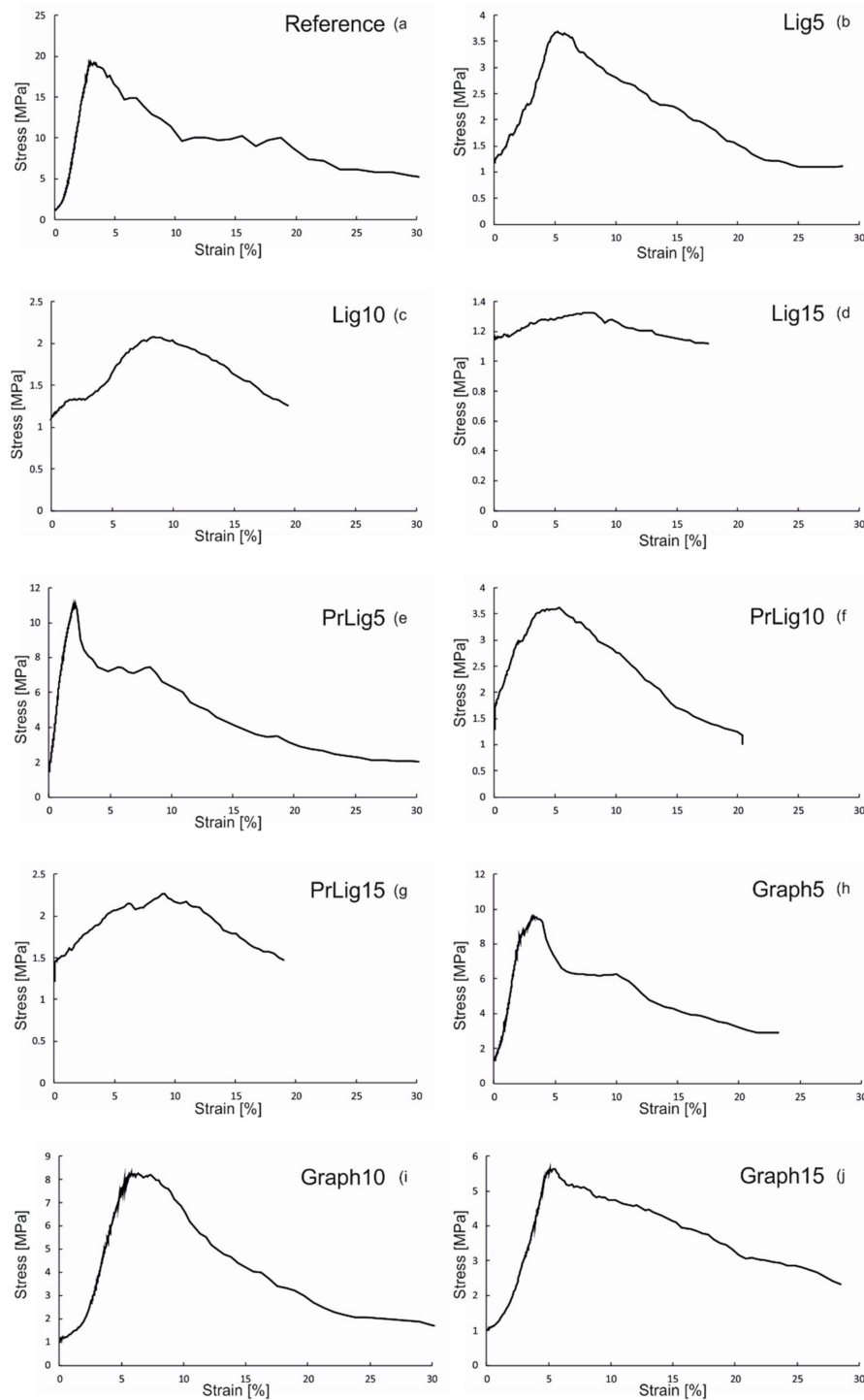
In Figure 4, the x inside the blue box refers to the average of the results and the line refers to the median of the results. The upper edge of the blue box refers to upper quarter and the lower edge refers to the lower quarter of the results. The ends of the vertical line segment refer to extremes of the results. The blue circle (above the Graph15 vertical line segment) refers to anomalous result. Reference refers to the reference coke, Lig, PrLig and Graph refer to lignin, pyrolyzed lignin and graphite, respectively and numbers after the abbreviations 5, 10 and 15 refer to the mass-percentages of coal which is replaced by a certain replacing agent.

According to strength test results, the differences in strength between non-pyrolyzed and pyrolyzed lignin containing cokes become more even in higher addition level of biomaterial. This implies that the level of addition of biomaterial is already so high and has affected negatively on coke structure that the pre-treatment (pyrolysis) of the lignin loses its significance and instead of behaving as an inert in the coking blend, the negative impact of releasing gases becomes more relevant. The deviations of the strength test results are higher in coke grades with small amounts or no lignin (Figure 4). The standard deviation does not take into account the fact that the results of different cokes are in a different magnitude, the average strength of reference coke being 19.2 MPa and of Lig15 coke being 1.2 MPa. Therefore, the results should be also expressed with a variability index, which is not bound to the unit of measurement. Variability indices and standard deviations of the strength test results are presented in Table 5.

Table 5. Standard deviations and variability indices of samples.

Sample	Average	Standard Deviation	Variability Index
Reference	19.21	2.06	10.75
Lig5	4.76	1.59	33.46
Lig10	1.84	0.17	9.33
Lig15	1.30	0.07	5.65
PrLig5	8.17	1.54	18.91
PrLig10	3.22	1.01	31.26
PrLig15	1.69	0.26	15.26
Graph5	9.77	3.28	33.55
Graph10	7.40	1.93	26.14
Graph15	5.14	1.96	38.07

The breaking behaviours of cokes are presented in Figure 5. In the figure, the breaking behaviours of the curves that were the most descriptive for the whole batch of samples were chosen. Some of the samples showed less noticeable peaks in the stress-strain curves while the peaks of some curves were clearly noticeable. However, a certain pattern could be observed from the behaviour under compressive stress for each type of coke.



**Figure 5.** Breaking behavior of the cokes: (a) Reference coke; (b) Lig5; (c) Lig10; (d) Lig15; (e) PrLig5; (f) PrLig10; (g) PrLig15; (h) Graph5; (i) Graph10; (j) Graph15.

Reference coke and cokes with 5 m-% of replacing agent, showed a clear peak in the curve around 5% strain which resembles a lot of brittle fracture behaviour. Also some residual strength can be observed from the curves of samples Reference, PrLig5 and Graph5, even when the strains of the samples increases. This kind of behaviour refers to the elasticity of the structure with empty spaces between solid coke structure, caused by porous media of the cokes. As the curve of PrLig5 resembles a lot of Reference and Graph5, the curves of higher replacement ratios of coal with pyrolyzed lignin (PrLig10 and PrLig15) resemble more of the curves of the samples Lig10 and Lig15. The result suggests that at higher replacement ratios of pyrolyzed lignin, the formation of coke structure becomes more alike with the case of use of lignin as a replacing agent. When the amount of biomaterial in the coke is increased, the peak in the curve becomes less clear and wanders from 5% strain to around 10% strain, which means that the cokes lose their brittle fracture behaviour as the amount of replacing agent in cokes increase. The same kind of behaviour cannot be observed in graphite-containing cokes. The lack of brittle nature in case of cokes is usually a sign of several different structural properties: thin cell walls, irregularly shaped pores, large pores, connected pores and high overall porosity [28]. All the mentioned structural properties are related to increased amount of empty space and decreased amount of supporting structure in the coke structure. Also, the linkages between the particles inside the coke structure play a significant role strength wise, especially when the cokes contain material that does not dissolve as a part of the coke matrix: the weaker the linkages are the less force is needed for breaking down the linkages. The structural changes will be further discussed in Section 3.6., based on the LOM-images taken from the samples.

### 3.5. Reactivity of Cokes

The reactivity of all the coke samples of this study in isothermal conditions is presented in Figure 6. According to the results of the reactivity tests, the reference coke is the least reactive with a mass loss of 22% in 2 h reactivity test in simulated BF shaft gas atmosphere. Samples containing non-pyrolyzed lignin are slightly less reactive than the samples containing corresponding amount of pyrolyzed lignin, but the difference is little. When considering the chemical analysis of raw materials the amount of alkali rich ash is higher in case of pyrolyzed lignin than in case of non-pyrolyzed lignin. However, it should not play a significant role, because the amount of non-pyrolyzed was optimized based on the lignin pyrolysis data so that the amount of replacing agent would be the same at 350 °C, thus the amount of ash would also be the same. At addition-level of 10m-% of biomaterial, the samples with pyrolyzed and non-pyrolyzed lignin addition have identical reactivity curves in the conditions used in this reactivity test. Overall the pyrolyzed lignin and non-pyrolyzed lignin containing bio cokes with corresponding amounts of replacing agent reacted similarly in the simulated blast furnace shaft gas conditions.

The reactivity increases as the amount of biomaterial in the sample increases. This has been noticed and reported also by other authors [5–7]. According to Suopajarvi et al. [7] and Diez et al. [13], higher reactivity of the bio-cokes is attributed to the following factors: the ash composition of the raw materials, oxygen content, the inhibition of fluidity development in the carbonized blend, the presence of porous isotropic particles from the biomass, functionality of the biomass material, and the microporosity of the cokes. Also pore size distribution and shape factor have an effect on the reactivity: larger pores have better accessibility for reactive gas to reach active sites of coke (graphite crystallite edges) or catalytic components which are usually concentrated on the larger pores [29]. Pores with certain pore volume and with irregular pore shapes have a larger edge length in comparison to more regular shaped pores with a corresponding pore volume, thus leading to larger surface area for cokes with irregular pore shapes, which may contribute to the coke reactivity [13]. Babich et al. [22] discovered, however, that the effect of microporosity on the coke reactivity index (CRI) of coke decreases and actually disappears as the amount of alkali in the system is increased.

The results of dynamic (non-isothermal) reactivity tests are presented in Figure 7. The threshold temperature of the Reference sample was the highest but the threshold temperatures of PrLig5 and

Graph15 were approximately the same. However, after the gasification reaction threshold temperature, the reaction of PrLig5 progresses faster than Reference and Graph15 causing the PrLig5 reaction curve to separate from the curves of the other two samples with the same threshold temperature. Lig5, PrLig10 and Lig15 had the lowest threshold temperatures.

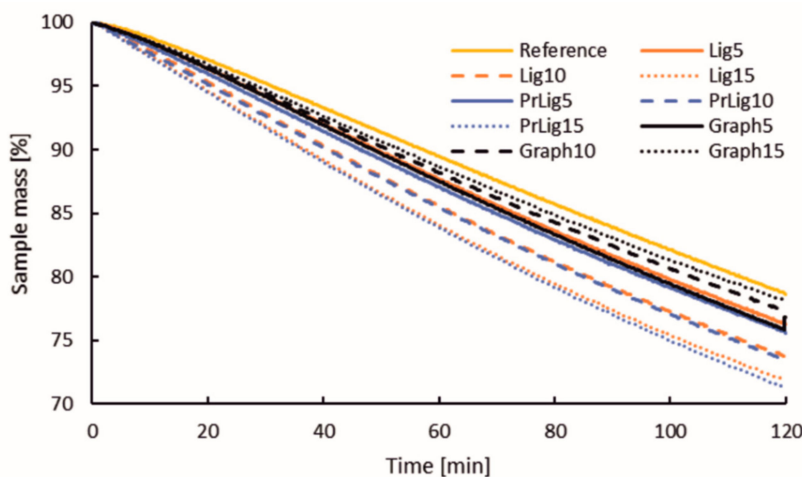


Figure 6. Coke reactivities in isothermal conditions.

However, the mechanism causing the low threshold appears to be different for all the three samples: the gasification of Lig5 starts at early stage of the experiment but after reaching a certain level of gasification, the reaction slows down in comparison to PrLig10 and Lig15. For PrLig10 and Lig15 the gasification constantly accelerates by the temperature elevation, the acceleration of reaction of Lig15 being faster from the two samples. This may refer to more open structure for Lig5 in comparison to PrLig10 and Lig15, thus the reactive gas has a better pathway to active sites of the Lig5 coke. In comparison of PrLig10 and Lig15, the reactive gas seems to have a better access to the active sites of PrLig10, although the difference of the mechanism in comparison to Lig15 does not differ much. At 930 °C the reaction rate of Lig15 is the same as the PrLig10 and further accelerates faster than PrLig10. This is believed to be caused by the higher alkali content of Lig15, as the alkali content is known to have increasing effect on reactivity of coke, especially in water vapor containing reactive gas atmosphere. When the temperature is elevated further and the reaction rate increases, the curves set to same order as in isothermal tests.

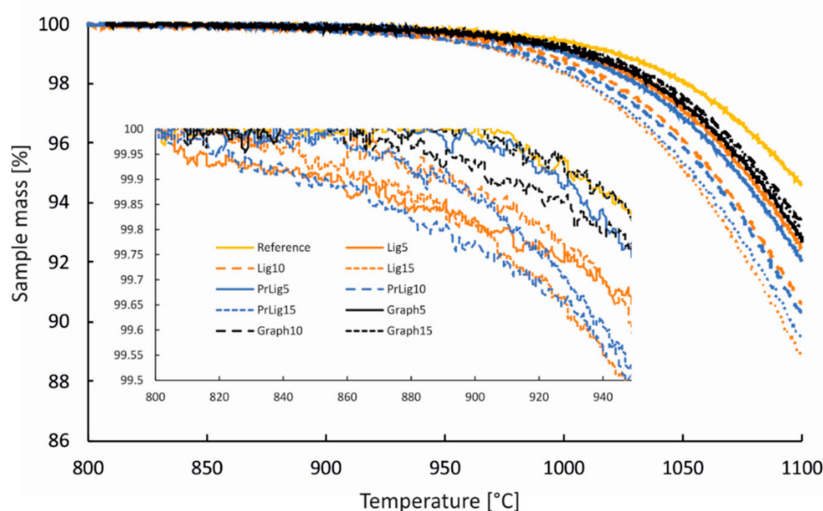
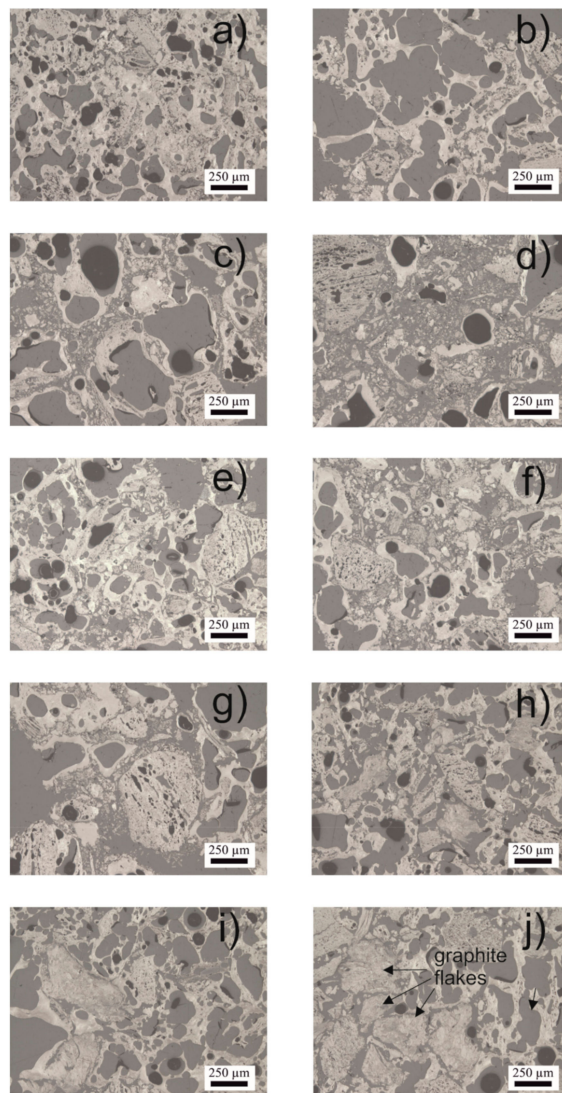


Figure 7. Dynamic reactivity tests of coke samples: All the samples throughout the whole experiment and zoomed illustration of the samples' threshold temperatures.



### 3.6. Light Optical Microscopy and Image Analysis for Cokes

Representative light optical microscopy (LOM) images, taken under 4× objective, for all samples are presented in Figure 8.



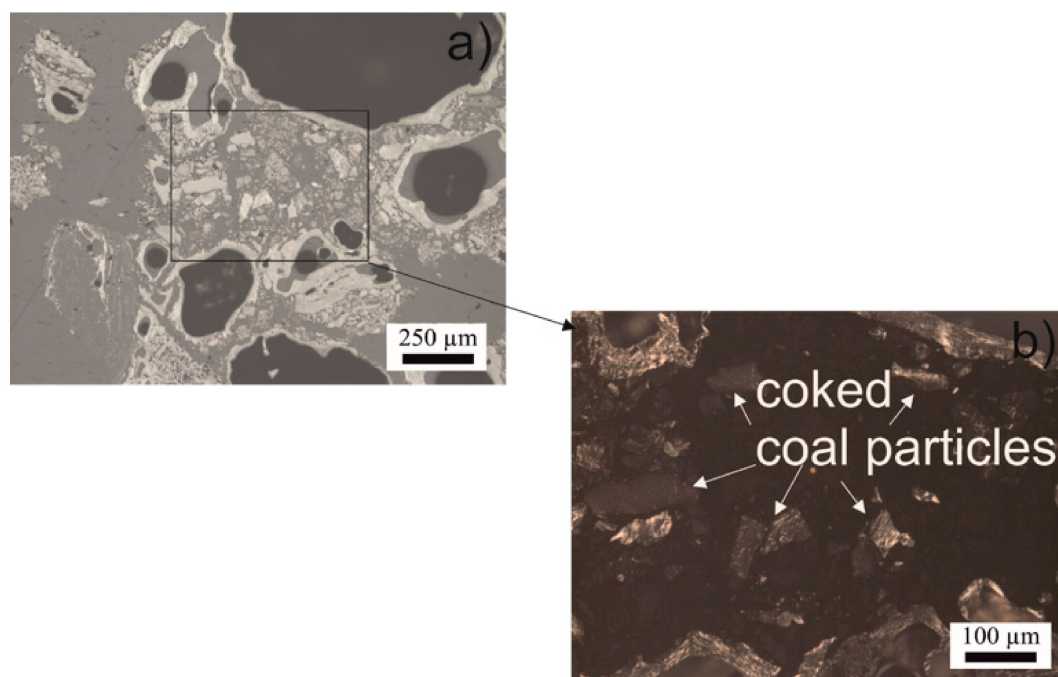
**Figure 8.** LOM images from coke samples: (a) Reference sample; (b) Lig5; (c) Lig10; (d) Lig15; (e) PrLig5; (f) PrLig10; (g) PrLig15; (h) Graph5; (i) Graph10; (j) Graph15.

The reference coke sample (a) had a structure similar to industrial cokes: the structure was compact, filled with mainly medium sized elliptical shaped pores. For Lig5 (b), the structure was more open filled with large irregularly shaped pores with not much inert material inside the pores. Also, the cell wall thickness of Lig5 was considerably smaller than in reference coke structure throughout the whole sample. PrLig5 on the other hand, had a structure more alike with the structure of reference coke. As the replacement ratio of coal with biomaterial increased, the structure of cokes changed: the empty space increased, cell wall thicknesses decreased and a lot of non-reacted material accumulated inside the enlarged pores. This applied to both non-pyrolyzed and pyrolyzed lignin. Also the pore connectedness in coke structure increased when the amount of biomaterial in the coke increased. In Lig15 and PrLig15 samples (images (d) and (g)) the development of pore connectedness has gone the furthest and formed large scale pores have a lot of inert material in the pores. As for the graphite containing cokes, same kind of behavior was not observed when the amount of graphite was increased from 5 m-% to 10 m-% and 15 m-%. The structure itself remained the same but the amount of graphite



flakes in the structure obviously increased when the replacement ratio of coal with graphite was increased. This explains the behavior of graphite containing cokes in the reactivity test where the reactivity rather decreased than increased as the level of graphite in coke increased. The weakening of structure can be explained by the loose linkage of graphite flakes to the surrounding coke matrix. Graphite flakes inside the coke pores can be detected from Figure 8j.

As mentioned, with higher replacement ratios of coal with biomaterial the accumulation of fine, non-reacted material occurred inside the pores of the cokes. These fines were mainly lignin flakes that were not attached to surrounding coke matrix but also a large share of coked coal particles were observed from inside the coke pores. This can be seen from the Figure 9, which is taken from the sample Lig15.



**Figure 9.** Fines inside the pores of Lig15 sample. (a) 4× objective lens and polarizing lens set to 90°; (b) 10× objective lens and polarizing lens set to 0°.

A lot of coke particles, unreacted with the main structure of coke, remain inside the pores. The texture of the coke particles was mainly banded and isotropic but also mosaic areas were found. Isotropic lignin particles are not easy to detect from the Figure 9b, but they appear as dark grey in the figure. The observation confirms the fact that releasing gases from lignin at coke plastic phase decrease the fluidity development and the coal particles are less mobile thus leading to less interaction between coal particles.

The number of pores and pore shape factors for the coke samples are presented in Table 6. All the samples had a large number of small pores at the size range of 0.01–0.2 mm of pore edge length. Only Lig5 and PrLig10 stand out from the results, Lig5 having clearly the smallest amount of pores PrLig10 having the highest amount of pores. The result explains well the low threshold temperature in the reactivity test as well as the different mechanism for low threshold temperature. The pore shapes of the smallest pores are a lot alike between all the samples. However the decrease in pore shape factor from the smallest pore size range to the second smallest size range (0.2–0.41 mm) becomes bigger as the amount of replacing agent in the coke is increased. The most noticeable pattern can be observed from the largest pores. As the amount of replacing agent is increased, the pore shape factor decreases. This contributes to both reactivity and the strength of coke amongst the other things mentioned in this paper.

**Table 6.** Distribution of pores to a certain size ranges and pore shape factors.

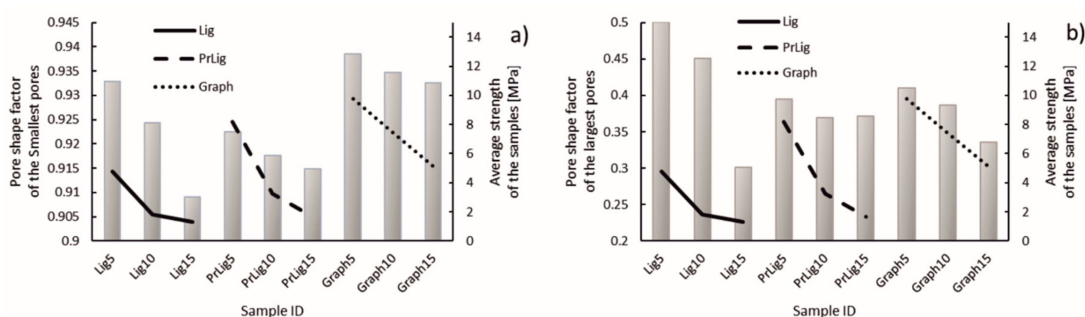
Pore Edge Length [mm]	Number of Pores									
	Reference	Lig5	Lig10	Lig15	PrLig5	PrLig10	PrLig15	Graph5	Graph10	Graph15
0.01–0.20	1971.00	923.00	2062.00	2482.00	2305.00	2879.00	2233.00	1897.00	2120.00	2313.00
0.20–0.41	147.00	73.00	114.00	122.00	141.00	104.00	100.00	114.00	145.00	116.00
0.41–0.82	56.00	39.00	44.00	51.00	79.00	63.00	45.00	49.00	62.00	76.00
0.82–1.22	13.00	5.00	19.00	19.00	23.00	18.00	8.00	21.00	24.00	21.00
1.22–1.63	7.00	4.00	9.00	10.00	8.00	4.00	9.00	7.00	7.00	14.00
1.63–8.5	8.00	11.00	13.00	13.00	14.00	14.00	6.00	15.00	10.00	15.00

Pore Edge Length [mm]	Pore Shape Factor									
	Reference	Lig5	Lig10	Lig15	PrLig5	PrLig10	PrLig15	Graph5	Graph10	Graph15
0.01–0.20	0.94	0.93	0.92	0.91	0.92	0.92	0.91	0.94	0.93	0.93
0.20–0.41	0.75	0.75	0.64	0.63	0.66	0.65	0.67	0.73	0.73	0.69
0.41–0.82	0.61	0.65	0.63	0.52	0.57	0.52	0.59	0.63	0.62	0.59
0.82–1.22	0.52	0.52	0.51	0.50	0.48	0.50	0.67	0.53	0.50	0.50
1.22–1.63	0.50	0.56	0.48	0.46	0.45	0.56	0.65	0.35	0.45	0.42
1.63–8.5	0.35	0.50	0.45	0.30	0.39	0.37	0.37	0.41	0.39	0.34

High amount of small pores and uniform distribution of pores are previously reported to have a positive impact on coke strength [30]. The results of image analysis and the observations made from the LOM images support that outcome. Even though some of the lignin containing samples had higher porosity in the smallest size range in their structure than the Reference sample, the shapes of the large pores were not uniform and the pores were not distributed evenly. Non-regular distribution of pores leads to thin cell wall thicknesses at some locations while at other locations cell wall thicknesses are almost non-existent. This leads to irregular distribution of strength around the coke, thus a weaker structure. Pore shapes also have their contribution on the cell wall thickness: The more irregular the pore shape is the more is the variation of cell wall thickness between neighbouring pores in comparison to pores with perfect elliptical shapes.

Pore shape factor of the largest and the smallest pores have a good correlation with strength test results. The correlation of strength and the shape of the smallest pores for non-pyrolyzed lignin, pyrolyzed lignin, and graphite containing coke samples were 0.86, 0.99 and 0.99, respectively. The correlations of strength with largest pore shape factors in the respective order were 0.79, 0.95 and 0.97. Coke average strengths and the pore shape factors of samples' largest and smallest pores are presented in Figure 10a,b. Irregularity of the pore shape factor of the smallest pores correlates inversely with the reactivity of the cokes. The correlations between pore shape factors of the smallest pores and mass losses were  $-0.97$  and  $-0.99$  for non-pyrolyzed and pyrolyzed lignin containing samples, respectively.



**Figure 10.** Strengths and pore shape factors. (a) Strength of cokes and pore shape factors of the smallest pores; (b) Strength of cokes and pore shape factors of the largest pores of the samples. The grey bars represent the pore shape factors of each sample. Strengths of samples are presented by black curve lines: Solid, dashed and dotted lines represent lignin, pyrolyzed lignin and graphite containing samples, respectively.

A similar correlation was found also between the pore shape factors of the largest pores and reactivity, correlations being  $-0.93$  and  $-0.81$  for non-pyrolyzed and pyrolyzed lignin-containing samples, respectively. With samples containing graphite, the correlation of reactivity with the pore shape factors was direct,  $0.93$  with the shape factor of the smallest pores and  $1.00$  with the largest pores. The results suggest that the increase of graphite decreases the reactivity of the produced coke in the simulated BF gas atmosphere, despite the weakened pore shape factor.

#### 4. Conclusions

The aim of this research was to investigate the use of lignin in the coking blend—how the replacement of some of the coal in the coking blend with lignin effects on the main properties of coke: strength and reactivity. The replacement ratio was varied in order to determine what would be a suitable amount for coal replacement with lignin without significantly harming the coke properties. The effect of pre-pyrolysis of lignin was investigated for getting answers to following questions: Does the pre-pyrolysis of lignin improve the properties of produced coke and what are the mechanisms or factors behind the different effect? Graphite powder-containing cokes were produced to determine whether the effect pyrolyzed lignin addition to the coking blend is more inert like, or is the effect a consequence from properties of lignin.

The cokes were produced on a laboratory scale. Compression strength, reactivity of cokes, VMT release from raw materials in coking process and coke structure (porosity, pore shapes) were tested from each coke grade. The following conclusions could have been drawn from the results of this research:

1. The VMT release was the most significant with non-pyrolyzed lignin, which lost 64.95% of its mass. The pyrolysis of the lignin at  $350\text{ }^{\circ}\text{C}$  improved the properties of the lignin at a perspective of using lignin as a raw material in a coking blend. By small replacement ratios of coal with pyrolyzed lignin, the pyrolyzed lignin acted as an inert on the coke structure similarly to graphite powder. However, when the replacement ratio was increased to 10m-%, the pyrolyzed lignin began to effect on the coke structure and properties similarly to non-pyrolyzed lignin. This is attributed by the extensive release of gaseous compounds (mainly phenols) from the lignin at the coal plastic phase, which is known to decrease the maximum fluidity of coal.
2. Strength of coke decreased dramatically as the level of non-pyrolyzed or pyrolyzed lignin was increased. The structure of coke that contained 5m-% of pyrolyzed lignin implied to strength properties to be more alike with the reference sample. Also the structure of graphite containing samples were alike with the structure of reference coke but the difference between compression strength properties was significant. Also the strength test results imply that at low replacement ratios of pyrolyzed lignin the replacing agent has more inert-like effect on the coke structure but as the ratio increases, the pyrolysis loses its significance and the effect on the coke structure becomes more alike with the non-pyrolyzed lignin.
3. The reactivity test results of cokes were in line with the literature. The cokes with the highest replacement ratios of coal with lignin were the most reactive. No significant difference in reactivity was observed between non-pyrolyzed and pyrolyzed lignin containing cokes with corresponding amount replacement of coal with lignin. Graphite powder had an inverse effect on coke reactivity as the amount of graphite in the coke was increased. The threshold temperatures varied a lot between different types of cokes, samples Lig5 and PrLig10 having the lowest threshold temperatures for gasification reaction. This was explained by the open structure of Lig5 and large amount of pores in the case of PrLig10.
4. The microscopy images and the image analysis results supported the results from reactivity and cold compression strength test. The structure opens as the amount of lignin in the blend was increased. The enlarged pores had significant amount of fine material, separate from the actual coke matrix in the samples containing 10- and 15m-% of lignin and pyrolyzed lignin. The weakening cold compression strength and increased reactivity of cokes as the amount of

lignin in the coking blend was increased are attributed, at least partly by the mentioned structural changes. The observations were confirmed by the results of image analysis. The pore shape factor decreased i.e., the irregularity of pores increased, as the amount of lignin in the samples was increased. The changes in pore shape factors correlated highly with the results of the reactivity and cold compression test, correlations being near to 1 or −1.

**Author Contributions:** A.K. mainly took care of the designing and the execution of the experiments. Sample preparation, data analysis and writing was mainly done by A.K. H.S. contributed to preparation of the research plan and to writing. O.M. contributed to planning and preparation of the research plan. J.U. contributed to planning and execution of the Gleeble 3800 experiments. T.F. contributed to writing.

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