Pyrolysis Characteristics of Industrial Lignin for Use as a Reductant and an Energy Source for Future Iron Making

Dongwen Xiang, Fengman Shen,* Xin Jiang, Haiwei An, Haiyan Zheng, and Qiangjian Gao

ABSTRACT: The purpose of this study is to explore the possibility of using industrial lignin instead of pulverized coal as a reducing agent for the production of direct reduced iron (DRI), thus reducing CO₂ emissions. The pyrolysis characteristics and kinetics of pulverized coal and industrial lignin were studied by nonisothermal thermogravimetry. In the three stages of pyrolysis, the weight loss rate of industrial lignin is higher than that of pulverized coal. The volatile matter of industrial lignin is easier to release than that of pulverized coal, but the coking process is longer than that of pulverized coal. The activation energies of pyrolysis of Lu’an anthracite (LA), Shen’mu bituminous coal (SM), alkali lignin (AL), and magnesium lignosulfonate (ML) were 71.10, 70.30, 55.20, and 37.34 kJ·mol⁻¹ at the middle-temperature stage, and 133.64, 98.31, 57.78, and 46.68 kJ·mol⁻¹ at the high-temperature stage, respectively. After pyrolysis, a few nanometer thick carbon film structure appears in alkali lignin coke, which is conducive to the reduction of iron ore powder.

1. INTRODUCTION

The current primary problems in the ironmaking industry are energy consumption and CO₂ emissions. According to relevant studies, the CO₂ emissions by the iron and steel industry accounts for 6.7% of the total global CO₂ emissions and 16% of the total industrial CO₂ emissions.¹–³ In 2018, an average of 1.85 tons of CO₂ was emitted for every ton of steel produced.⁴ CO₂ is the main culprit causing the greenhouse effect, so reducing CO₂ emission is an urgent task for the development of the iron and steel industry in the future. At present, the mainstream electric arc furnace (EAF) steelmaking in the world generally uses 50–70% scrap steel with 50–30% direct reduced iron (DRI). The world’s DRI production over the years is shown in Figure 1.⁵ In 2018, the world’s DRI production was 100.49 million tons, exceeding the landmark of 100 million tons for the first time. Facing the increasing production capacity of EAF steel and the shortage of scrap resources in China, DRI has been paid more and more attention by the iron and steel industry and will usher in a good opportunity for development.

However, the essence of the coal-based direct reduction process is to use coal, a nonrenewable energy resource, which does not reduce CO₂ emission in essence. Therefore, this study hopes to find biomass to replace coal as a reducing agent, thus reducing the use of coal. According to statistics, 200 million tons of black liquor produced by China’s paper industry every year contains about 20 million tons of industrial lignin.⁶ Under the harsh process conditions in the paper industry, chemical treatment will lead to the chemical transformation of lignin’s natural structure, including structural depolymerization, redox, and condensation.⁷,⁸ This transformation makes the structure of lignin highly complex and difficult to understand, which seriously hinders the exploration of its applicable and effective value-added methods.⁹ The utilization rate of industrial lignin is extremely low, and it is generally burned as low-grade fuel or

Figure 1. World DRI production over the years.
made into low-value-added products such as flocculants and dispersants. Lignin and lignosulfonate have been studied by many researchers, and the focus of these studies has been on their modification. However, the research on using lignin or lignosulfonate as a reducing agent for producing DRI is still insufficient. If industrial lignin can be applied to the production of DRI, that is, iron ore powder can effectively promote the pyrolysis of industrial lignin, while the pyrolysis products can promote the reduction of iron ore powder. It can not only save coal resources and reduce CO2 emissions but also make effective use of the wastes generated by the pulp and paper industry, which has a very important practical significance for the development of environmental protection.

This work is mainly in the early exploration stage. Pyrolysis experiments are carried out on anthracite (LA), bituminous coal (SM), alkali lignin (AL), and magnesium lignosulfonate (ML) to explore the possibility of industrial lignin as a reducing agent to produce DRI. The main contents of this work are as follows: (1) The release characteristics of the volatile matter of four reducing agents are discussed. (2) The differences in the agravic section of the four reducing agents during pyrolysis are analyzed. (3) The activation energy of pyrolysis of four reducing agents in different temperature ranges is calculated, and the pyrolysis mechanism function is determined. (4) The surface morphology of the products after pyrolysis is observed, and it is found that industrial lignin has certain advantages as a reducing agent. We know that the process of lignin reducing iron ore powder is not lignin itself as a reducing agent, but reducing substances such as hydrogen, carbon monoxide, and coke produced by lignin pyrolysis play a reducing role. Therefore, the study of pyrolysis kinetics is of great significance for further understanding the pyrolysis mechanism of industrial lignin, predicting the reaction rate and reaction difficulty.

Industrial lignin is a very promising renewable and environmentally friendly reducing agent conducive to the green development of the iron and steel industry. The practical reduction application effect of industrial lignin on iron ore powder will be discussed in other articles.

2. RESULTS AND DISCUSSION

2.1. Higher Heating Values (HHV) of Reducing Agents. It can be seen from Table 5 that the volatile matter content of AL is 60.44%, and that of ML is 57.82%, which is much higher than that of pulverized coal (13.38% for LA and 28.28 for SM), but the fixed carbon content is much lower than that of pulverized coal. The content of oxygen and sulfur in industrial lignin is higher than that in pulverized coal. Most of the sulfur can be removed in ironmaking or steelmaking processes. According to the famous Mendeleev formula, the higher heating value (HHV) of the four reducing agents is calculated, and the results are shown in Table 1.

\[
\text{HHV} = 4.18[81C + 300H - 26(O - S)]
\]

Table 1. Higher Heating Value of Different Reducing Agents

| samples | HHV (kJ kg\(^{-1}\)) |
|---------|---------------------|
| AL      | 25 669.63           |
| ML      | 13 483.38           |
| LA      | 30 943.01           |
| SM      | 29 014.94           |

output of 30 943.01 kJ·kg\(^{-1}\), and the lowest heat output of ML is 13 483.38 kJ·kg\(^{-1}\), which is mainly due to the high carbon content in LA and the low carbon content in ML.

2.2. Thermogravimetric Analysis. The pyrolysis process of pulverized coal and industrial lignin is very complicated, including a series of chemical reactions and physical changes. The thermogravimetric results of pulverized coal and industrial lignin under a nitrogen atmosphere are shown in Figure 2. It can be found that the pyrolysis process of pulverized coal and industrial lignin is basically similar, that is, they all go through three stages. The pyrolysis process can be divided into stage I, stage II, and stage III according to the initial temperature \(T_i\) and the ending temperature \(T_e\) of volatile matter release. The temperature ranges of the three pyrolysis stages of different reducing agents are shown in Table 2 and Figure 3.

Stage I of pyrolysis is that, when the pyrolysis temperature is low, a drying and degassing process. The weight loss of pulverized coal in this stage is mainly due to the release of water, some gases (\(\text{CH}_4\), \(\text{CO}_2\), and \(\text{N}_2\)) in the pores, and the thermal decomposition of some chemical bonds with weak bond energy. The weight loss of industrial lignin is due to the volatilization of free water and bound water, as well as the volatilization of a small amount of carboxylic acid during glass transition. In this stage, the weight loss rate of ML is 21.2%, which is much higher than that of the other three reducing agents, mainly because of the highest moisture content in ML.

Stage II of pyrolysis of pulverized coal and industrial lignin is mainly the rapid release of volatile matter. The TG curve in Figure 2 shows rapid weightlessness. At this time, the reaction mechanism and control links begin to change. The pyrolysis process of pulverized coal in this stage is mainly the escape of gas and tar, and the formation of semi-coke. The reason is that the side chains of aromatic fused ring compounds, the noncovalent molecules, and some oxygen-containing functional groups are broken and decomposed in pulverized coal, thus forming \(\text{CO}_2\), \(\text{CO}\), \(\text{CH}_4\), \(\text{H}_2\text{O}\), \(\text{H}_2\) phenols, aliphatic hydrocarbons, and other substances. In industrial lignin, carbohydrate compounds are decomposed, ether bonds and part of carbon–carbon bonds are broken, resulting in the formation of low molecular phenols, alkanes, alcohols, and aldehydes, as well as most of \(\text{CH}_4\), \(\text{CO}_2\), and a small amount of \(\text{CO}\). The order of the weight loss rate in this stage is AL (33.78%) > ML (28.7%) > SM (14.24%) > LA (6.69%). There are two reasons for this phenomenon: (1) The volatile matter content of industrial lignin is much higher than that of pulverized coal. (2) Industrial lignin is mainly composed of the carbon bond \((\text{R} - \text{O} - \text{R})\) with low bond energy (about 380–420 kJ·mol\(^{-1}\)) and is easy to break during pyrolysis, while pulverized coal is mainly composed of poly cyclic aromatic hydrocarbons connected by the carbon–carbon bond with large bond energy (about 1000 kJ·mol\(^{-1}\)), which is not easy to break during heating. We can also find that the weight loss rate of SM is higher than that of LA, which is related to the oxygen-containing functional groups in pulverized coal. SM has...
a low degree of coalification and high oxygen content, so the oxygen-containing functional groups with lower bond energy will also increase, eventually leading to a higher weight loss rate of SM.

Stage III of pyrolysis is carbonization, in which semi-coke is gradually transformed into coke. At this stage, pulverized coal mainly goes through the polycondensation reaction and produces more H2 and CO. There are two main sources of H2, one is the polycondensation dehydrogenation of aromatic and hydrogenated aromatic structures24 and the other is the secondary pyrolysis reaction, such as C2H6 → C2H4 + H2, C2H4 → CH4 + C, and CH4 → 2C + 2H2.25 There are also two sources of CO, one is due to the breakage of carbonyl and oxygen-containing heterocyclic rings and the other is the reaction between CO2 and semi-coke.26 Industrial lignin mainly goes through the carbon-forming reaction and the decomposition or condensation reaction of the aromatic ring structure and generates CO2 and a large amount of CO.27,28 The weight loss rate of industrial lignin in this stage is also higher than that of pulverized coal. The order of the weight loss rate from large to small is ML (17.1%) > AL (16.65%) > SM (9.69%) > LA (2.93%). This also fully shows that industrial lignin is easier to pyrolyze and will produce more gas at this stage, which is conducive to the reduction of iron ore powder.

In addition, it can be found from Figure 2 that there will be a small weight loss peak at the high-temperature stage, mainly due to the following three possible reason: (1) decomposition of minerals (mainly carbonate);29 (2) condensation of semi-coke into coke at high temperatures, resulting in the release of
a small part of hydrogen; and (3) reaction of alkali metal salt with the carbon in semi-coke. 31

It can be seen from Figure 3 that a very interesting phenomenon appears in the pyrolysis temperature ranges of the four reducing agents. In stage I of pyrolysis, the order of temperature range is LA (719 K) > SM (651 K) > ML (513 K) > AL (496 K), while in stage III of pyrolysis, the temperature range shows a completely opposite phenomenon: LA (540 K) < SM (708 K) < ML (831 K) < AL (851 K). This shows that industrial lignin is better than pulverized coal in drying and degassing, while it takes longer than pulverized coal in the coking process. In this study, the heating temperature range is 303–1273 K, and a large coking temperature range means that the coking starting temperature is lower, that is, industrial lignin is easier to coke than pulverized coal.

It is well known that lignin is a kind of complex organic matter with many functional groups. The main structural units of lignin mainly include three kinds of phenylpropane monomers with different properties (coniferyl alcohol, coumaryl alcohol, and sinapyl alcohol types). The industrial lignin used in this study was obtained by the alkaline pulping process, which is closer to the characteristics of natural lignin. Recent studies have shown that pulverized coal is mainly composed of aromatic hydrocarbons, aliphatic hydrocarbons, and a small amount of oxygen-containing functional groups. Therefore, industrial lignin has a higher content of oxygen-containing functional groups than pulverized coal. Moreover, due to the low bond energy of oxygen-containing functional groups, the structure in industrial lignin is easy to break and generate gases such as CO and CO2.

The research shows that the CO and CO2 yield increases linearly with the increase in the O/C atomic ratio of coal. 31 In this study, the O/C atomic ratios of LA, SM, AL, and ML are 0.10, 0.22, 0.50, and 1.30, respectively. The O/C atomic ratio of industrial lignin is higher than that of pulverized coal, resulting in a higher content of CO and CO2, which is beneficial to the reduction of iron ore powder. Therefore, the oxygen-containing functional group is also one of the characteristics of the reducing agent, and detailed experimental data and analyses are our future work.

2.3. Pyrolysis Characteristics of the Reducing Agent. The pyrolysis characteristic parameters obtained from Figure 2 are shown in Table 3. It can be seen from Table 3 that the $T_e$ of ML is only 526.3 K, and that of AL is 542.9 K, which is far lower than those of SM (681.2 K) and LA (749.1 K). In addition, the $T_e$ and $T_{max}$ of industrial lignin are also significantly lower than those of pulverized coal. The $(d/w$/ $d$t)$_{mean}$ values of AL, ML, SM, and LA are 2.05, 1.79, 0.93, and 0.27%·min$^{-1}$, respectively, the $(d/w$/ $d$t)$_{max}$ values are 2.90, 2.68, 1.42, and 0.37%·min$^{-1}$, and the $P$ values are 12.57, 11.31, 5.35, and 0.01 10$^{-4}$%·K$^{-3}$·min$^{-2}$. This indicates that the volatile matter of industrial lignin is easier to release than that of pulverized coal, and the pyrolysis reaction is also easier. The $T_e$, $T_d$, and $T_{max}$ of ML are lower than those of AL, but the $P$ values of the two are basically the same, which indicates that the difficulty of the release of the volatile matter of the two is basically the same.

2.4. Kinetic Analysis. As is known, the difficulty of the chemical reaction can be reflected by activation energy, that is to say, the reaction is difficult when the activation energy is large. On the contrary, the reaction is easier when the activation energy is small. The purpose of this work is to determine the degree of difficulty in the pyrolysis of pulverized coal and industrial lignin according to the activation energy.

According to the analysis and discussion on the pyrolysis process of pulverized coal and industrial lignin in Section 2.2, it can be seen that the control mechanism of pyrolysis is different at different temperature ranges. Because the single kinetic model cannot describe the whole pyrolysis process well, this study adopts the segmented method to fit the different stages of pyrolysis to deeply understand the control mechanism of pulverized coal and industrial lignin in the pyrolysis process. Since the pyrolysis process of pulverized coal and industrial lignin is mainly affected by moisture in stage I, it will not be discussed here. This study focuses on the pyrolysis mechanism of stages II and III. The reaction mechanism functions of the
four reducing agents at stages II and III are fitted and calculated, and the results are shown in Figure 4 and Table 4. The results show that stage II accords with the third-order chemical reaction model, and the mechanism function is \(G(\alpha) = [(1 - \alpha)^{-2} - 1]/2\). The reaction mechanism of stage III accords with the fourth-order random nucleation and growth model and the mechanism function is \(G(\alpha) = [-\ln(1 - \alpha)]^4\).

It can be seen from Figure 4 and Table 4 that the linear fitting results are good. In stage II of pyrolysis, the order of activation energy of the four reducing agents is LA (71.10 kJ·mol\(^{-1}\)) > SM (70.30 kJ·mol\(^{-1}\)) > AL (55.20 kJ·mol\(^{-1}\)) > ML (37.34 kJ·mol\(^{-1}\)). The order of activation energy in stage III is LA (133.64 kJ·mol\(^{-1}\)) > SM (98.31 kJ·mol\(^{-1}\)) > AL (57.78 kJ·mol\(^{-1}\)) > ML (46.68 kJ·mol\(^{-1}\)). It can be found that the activation energy of industrial lignin is lower than that of pulverized coal in stages II and III, which indicates that industrial lignin is easier to pyrolyze. This result is also consistent with the analysis in Section 2.2. For the same reducing agent, the activation energy of stage III is larger than that of stage II, which indicates that pyrolysis in stage III is more difficult. This is because the bond energy of the material structure in the high temperature is relatively large and is not easy to break.

2.5. Surface Morphology Analysis. The surface morphology of the four reducing agents after pyrolysis was analyzed by scanning electron microscopy (SEM), as shown in Figure 5. The morphology of industrial lignin after pyrolysis is significantly different from that of pulverized coal. The coal coke is in the form of particles with rough surfaces and different sizes. A few nanometer thick carbon film structure appears in AL coke. However, the ML coke has a larger and thicker sheet structure. AL coke has a large specific surface area, but ML coke does not seem to have an advantage over coal coke.

3. CONCLUSIONS

Industrial lignin can replace pulverized coal as a reducing agent for the production of DRI. The pyrolysis of the four reducing agents all go through three stages: the low-temperature drying and degassing stage, the medium-temperature volatile matter rapid release stage, and the high-temperature carbonization stage. The volatile matter of industrial lignin is easier to release.
than that of pulverized coal during pyrolysis. The drying and degassing temperature range of industrial lignin is smaller than that of pulverized coal, while the coking temperature range is larger than that of pulverized coal. The pyrolysis activation energy of industrial lignin is lower than that of pulverized coal. A few nanometer thick carbon film structure appears in alkali lignin coke, which increases the specific surface area and is very beneficial to the reduction of iron ore powder.

4. METHODS AND MATERIALS

4.1. Materials. The reducing agents used in the experiment include alkali lignin (AL), magnesium lignosulfonate (ML), Lu’an anthracite (LA), and Shenmu bituminous coal (SM). LA and SM are provided by an iron and steel company, while AL and ML are provided by Huawei Youbang Chemical Co., Ltd. Before the experiment, the samples were placed in an oven and dried at 378 K for 24 h.

4.2. Apparatus and Experimental Procedures. The pyrolysis characteristics of pulverized coal and industrial lignin under a nitrogen atmosphere were studied on a thermogravimetric analyzer (STA409CD, Netzsch Group, Germany). In this work, about 10 mg of the sample was placed in an alumina pan and heated at 10 K min$^{-1}$ up to a temperature of 1273 K. The carrier gas (N$_2$) flow rate was maintained at 30 mL min$^{-1}$ for each experiment. A separate blank run was conducted using an empty pan under identical conditions and these data were used for baseline correction during the evaluation of the sample thermal gravimetric analysis (TGA) profile. To calculate the kinetic parameter for the sample pyrolysis work, we have taken the time—temperature data while heating up the samples from 303 to 1273 K.

According to the GB/T 212-2008 method, the proximate analysis of pulverized coal is carried out. The analysis of O, N, and H elements was determined by an ONH836 (Laboratory Equipment Corporation) and that of S and C elements was
The pyrolysis process of pulverized coal and industrial lignin can be expressed by eq 3

\[ \text{A(solid)} \rightarrow \text{B(solid)} + \text{C(gas)} \]  

(3)

The pyrolysis process of pulverized coal and industrial lignin is a complex multiphase chemical reaction. According to the law of mass action and the Arrhenius equation, many scholars have proposed different kinetic treatment methods. According to the form of the kinetic equation, it can be divided into a derivative method and an integral method. The pattern matching method is one of the most commonly used analysis methods in the field of kinetics of nonisothermal processes. The integral method will not produce numerical errors due to derivative, and the data is not easy to be distorted in the process of calculation. Therefore, the Coats–Redfern integral method is adopted in this paper.

The basic theory of classical chemical reaction kinetics is based on the isothermal process and the homogeneous reaction. Using the thinking method of infinitesimal differential, assuming that the change in temperature can be ignored at an infinitesimal interval time, then the nonisothermal process can be regarded as an isothermal process, and the chemical reaction rate equation can be expressed by eq 4.

\[
\frac{d\alpha}{dt} = kf(\alpha) 
\]

(4)

where \( \alpha \) is the conversion rate, \( \% \); \( t \) is the pyrolysis time, min. \( k \) is the reaction rate constant, \( \text{min}^{-1}. \) \( f(\alpha) \) is the chemical reaction mechanism that depends on the elementary reaction, and its functional form depends on the reaction type and reaction mechanism.

The expression of the conversion rate \( \alpha \) is as follows

\[
\alpha = \frac{w_0 - w_t}{w_0 - w_{\infty}} 
\]

(5)

where \( w_0, w_t \) and \( w_{\infty} \) are the initial mass of the sample, the mass at time \( t \), and the mass at the end of the reaction, respectively, mg.

The reaction rate constant \( k \) is expressed by the classical Arrhenius equation

\[
k = A\exp\left( -\frac{E}{RT} \right) 
\]

(6)

where \( A \) is the frequency factor, \( \text{min}^{-1} \); \( E \) is the activation energy, \( \text{J mol}^{-1} \); \( R \) is the gas constant, 8.314 \( \text{J mol}^{-1} \cdot \text{K}^{-1} \), and \( T \) is the absolute temperature, K.

The expression of the heating rate \( \beta \) is as follows

\[
\beta = \frac{dT}{dt} 
\]

(7)

From eqs 4 to 7, we can get the following results

\[
\frac{d\alpha}{dT} = \frac{A}{\beta} \exp\left( -\frac{E}{RT} \right) f(\alpha) \]

(8)

The integral equation can be obtained as follows

\[
G(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \int_0^T \exp\left( -\frac{E}{RT} \right) dT
\]

\[
= \frac{A}{\beta} \int_0^T \exp\left( -\frac{E}{RT} \right) dT 
\]

(9)
Table 6. Expressions of $G(\alpha)$ and $f(\alpha)$ for the Kinetic Model Functions Usually Employed for the Solid-State Reaction

| shorthand | reaction model | integral formula $G(\alpha)$ | differential formula $f(\alpha)$ |
|-----------|----------------|-------------------------------|----------------------------------|
| P1        | Mampel power   | $a$                           | 1                               |
| P2        | Mampel power   | $a^{1/2}$                      | $2\alpha^{1/2}$                  |
| P3        | Mampel power   | $a^{1/3}$                      | $3\alpha^{1/3}$                  |
| P4        | Mampel power   | $a^{1/4}$                      | $4\alpha^{1/4}$                  |
| A1        | Avaramie Erofeev| $[-\ln(1 - \alpha)]^{3/2}$   | $2/3(1-\alpha)[-\ln(1-\alpha)]^{3/2}$ |
| A2        | Avaramie Erofeev| $[-\ln(1 - \alpha)]^2$       | $1/2(1-\alpha)[-\ln(1-\alpha)]^2$ |
| A3        | Avaramie Erofeev| $[-\ln(1 - \alpha)]^3$       | $1/3(1-\alpha)[-\ln(1-\alpha)]^3$ |
| A4        | Avaramie Erofeev| $[-\ln(1 - \alpha)]^4$       | $1/4(1-\alpha)[-\ln(1-\alpha)]^4$ |

Nucleation Models

Chemical Reaction

- first order
  - $-\ln(1 - \alpha)$
  - $1 - \alpha$
- second order
  - $(1 - \alpha)^{-1} - 1$
  - $(1 - \alpha)^2$
- third order
  - $[(1 - \alpha)^{-2} - 1]/2$
  - $(1 - \alpha)^3$

Geometrical Contractions

- contracting area
  - $(1 - \alpha)^{1/2}$
  - $2(1 - \alpha)^{1/2}$
- contracting volume
  - $(1 - \alpha)^{1/3}$
  - $3(1 - \alpha)^{1/3}$

Jander Equation

- one-dimensional
  - $a^2$
  - $-1/2a^{-1}$
- two-dimensional
  - $[1-(1-a)^{1/2}]^{1/2}$
  - $4(1-a)^{1/2}[1-(1-a)^{1/2}]^{1/2}$
- three-dimensional
  - $[1-(1-a)^{1/3}]^{1/2}$
  - $6(1-a)^{1/3}[1-(1-a)^{1/3}]^{1/2}$

The Coats–Redfern integral method was used to deal with the exponential integral by the asymptotic series expansion, and the separation of variable integral could be obtained

$$\ln\left(\frac{G(\alpha)}{T^2}\right) = \ln\left(\frac{AR}{\beta E}\right) - \frac{E}{RT} \tag{10}$$

where $G(\alpha)$ is the integral form of the kinetic mechanism function of the solid reaction.

For the zone of the general reaction temperature and activation energy, the expression is $\frac{2RT}{E} \ll 1$. Therefore, eq 10 can be simplified as follows

$$\ln\left(\frac{G(\alpha)}{T^2}\right) = \ln\left(\frac{AR}{\beta E}\right) - \frac{E}{RT} \tag{11}$$

When the correct reaction mechanism $G(\alpha)$ is determined, the relationship between $\ln\left(\frac{G(\alpha)}{T^2}\right)$ and $1/T$ must be in a straight line. The activation energy can be obtained by the slope of the straight line, and the frequency factor can be obtained by the intercept.

The forms of commonly used solid reaction kinetic mechanism functions are shown in Table 6.\textsuperscript{35–50}

### AUTHOR INFORMATION

**Corresponding Author**

Fengman Shen – School of Metallurgy, Northeastern University, Shenyang 110819, Liaoning, P. R. China; Phone: Phone: +86-24-83681506; Email: shenfm@mail.neu.edu.cn

**Authors**

Dongwen Xiang – School of Metallurgy, Northeastern University, Shenyang 110819, Liaoning, P. R. China; orcid.org/0000-0001-5630-2401

Xin Jiang – School of Metallurgy, Northeastern University, Shenyang 110819, Liaoning, P. R. China

Haiwei An – School of Metallurgy, Northeastern University, Shenyang 110819, Liaoning, P. R. China

**Notes**

The authors declare no competing financial interest.

### ACKNOWLEDGMENTS

Financial supports by the National Science Foundation of China (NSFC 51874080, NSFC 51974073, and NSFC 51774071) and the Natural Science Foundation of Liaoning (2019-MS-132) are much appreciated.

### REFERENCES

1. Bataille, C.; Åhman, M.; Neuhoff, K.; Nilsson, L. J.; Fischedick, M.; Lichtenböhmer, S.; Rodriguez, B. S.; Ryan, A. D.; Stiebert, S.; Waisman, H.; Sartor, O.; Rahbar, S. A review of technology and policy deep decarbonization pathway options for making energy-intensive industry production consistent with the Paris Agreement. J. Cleaner Prod. 2018, 187, 960–973.

2. Ahman, M.; Nilsson, L. J.; Johansson, B. Global climate policy and deep decarbonization of energy-intensive industries. Clim. Policy 2017, 17, 634–649.

3. World Steel Association. Steel’s Contribution to a Low Carbon Future and Climate Resilient Societies. https://www.worldsteel.org/en/dam/jcr:2306a7a7-331c-491a-99a6-a093fb6ca96a/Position_paper_climate_2018.pdf.

4. World Steel Association. Steel’s Contribution to a Low Carbon Future. https://www.worldsteel.org/zh/dam/jcr:66fed386-fd0b-485e-aa23-b8a5e7533435/Position_paper_climate_2020_vfinal_CN.pdf.

5. 2018 World Direct Reduction Statistics. https://www.midrex.com/wp-content/uploads/Midrex_CHARSbookprint_2018Final-1.pdf.

6. Cai, M. L.; Bai, S. J.; Liu, M. H. Current status of treatment and resource utilization of papermaking black liquor. East China Paper 2016, 49, 39–42.
(7) Nieminen, K.; Kuitunen, S.; Paananen, M.; Sixta, H. Novel insight into lignin degradation during Kraft cooking. Ind. Eng. Chem. Res. 2014, 53, 2614–2624.

(8) Crestini, C.; Lange, H.; Sette, M.; Argyropoulos, D. S. On the structure of softwood Kraft lignin. Green Chem. 2017, 19, 4104–4121.

(9) Wen, J.; Sun, S. L.; Xue, B. L.; Sun, R. C. Recent advances in characterization of lignin polymer by solution-state nuclear magnetic resonance (NMR) methodology. Materials 2013, 6, 359–391.

(10) Li, Z. B.; Wang, G. Q.; Zou, L. S. Research Progress of Lignin Flocculant. Fine Spec. Chem. 2008, 23, 17–19.

(11) Ouyang, X.; Ke, L.; Qiu, X.; Guo, Y.; Pang, Y. Sulfonation of alkali lignin and its potential use in dispersant for cement. J. Dispersion Sci. Technol. 2009, 30, 1–6.

(12) Guo, D. L.; Wu, S. B.; Lou, R.; Yin, X. L.; Yang, Q. Effect of organic bond na groups on pyrolysis and CO2-gasification of alkali lignin. Bioresources 2011, 6, 4145–4157.

(13) Wang, W. L.; Ren, X. Y.; Li, L. F.; Chang, J. M.; Cai, L. P.; Gong, J. Catalytic effect of metal chlorides on analytical pyrolysis of alkali lignin. Fuel Process. Technol. 2015, 134, 345–351.

(14) De Wild, P. J.; Huijgen, W. J. J.; Gosselink, R. J. A. Lignin pyrolysis for profitable lignocellulosic biofinery. Biofuels, Bioprod. Biorefin. 2014, 8, 645–657.

(15) Ferdous, D.; Dalai, A. K.; Bej, S. K.; Thring, R. W. Pyrolysis of lignins: Experimental and kinetics studies. Energy Fuels 2002, 16, 1405–1412.

(16) Shrestha, B.; Le Brech, Y.; Ghislain, T.; Leclerc, S.; Carre, V.; Aubriet, F.; Hoppe, S.; Marchal, P.; Pontvianne, S.; Brosse, N.; Dufour, A. A multi-technique characterization of lignin softening and pyrolysis. ACS Sustainable Chem. Eng. 2017, 5, 6940–6949.

(17) Klapiszewski, L.; Artur, J.; Beata, S.; Danuta, M.; Adam, V.; Teofil, J. Activation of Magnesium Lignosulfonate and Kraft Lignin: Influence on the Properties of Phenolic Resin-Based Composites for Potential Applications in Abrasive Materials. Int. J. Mol. Sci. 2017, 18, No. 1224.

(18) Antov, P.; Mantanis, G. I.; Savov, V. Development of Wood Composites from Recycled Fibres Bonded with Magnesium Lignosulfonate. Forests 2020, 11, No. 613.

(19) Shen, J. X.; Li, F. S.; Wang, H. G.; Shen, Y. P.; Xu, W. J. Comparative analysis of theoretical calorific value of biodiesel blend fuel. China Oils Fats 2017, 42, 45–48.

(20) Wang, W. L.; Ren, X. Y.; Li, L. F.; Chang, J. M.; Cai, L. P.; Gong, J. Catalytic effect of metal chlorides on analytical pyrolysis of alkali lignin. Fuel Process. Technol. 2015, 134, 345–351.

(21) Zhang, X. Z.; Liu, T. Q.; Zhang, W. L.; Guo, D. L.; Wang, L. F.; Chen, W. M. Effect of pyrolysis conditions on pyrolysis and gasification characteristics of black liquor. China Pulp Pap. Ind. 2016, 37, 77–81.

(22) Guo, D. L.; Wu, S. B.; Liu, B.; Yin, X. L.; Yang, Q. Catalytic effects of NaOH and Na2CO3 additives on alkali lignin pyrolysis and gasification. Appl. Energy 2012, 95, 22–30.

(23) Hassan, H.; Lim, J. K.; Hameed, B. H. Recent progress on biomass co-pyrolysis conversion into high-quality bio-oil. Bioresour. Technol. 2016, 221, 645–655.

(24) Sun, Q. L.; Li, W.; Chen, H. K.; Li, B. Q. TG-MS study on pyrolysis behavior of Shennu coal macerals. J. China Univ. Min. 2003, 32, 646–669.

(25) Wang, R. The Investigation of the Combustion and Pyrogenation. Dissertation; Zhejiang University: Hangzhou, 2005.

(26) Wu, Q. The Study of the HL Lignite’s Pyrolysis Characteristics. Dissertation; Northwestern University: Xian, 2016.

(27) Wang, W. L.; Shi, Y. J.; Dang, Z. P.; Tang, N.; Huang, J. L.; Wang, S. H. Study on pyrolysis characteristics of alkali lignin with the additive of calcium salts. J. Shaanxi Univ. Sci. Technol. 2018, 36, 1–6.

(28) Hu, S.; He, Y. L. Ultrafine micronerosious and mesoporous activated carbon fibers from alkali lignin. J. Mater. Chem. A 2013, 1, 11279–11288.

(29) Yan, J. D.; Cui, H.; Yang, J. L.; Liu, Z. Y. Research on pyrolysis behavior of Yanzhou coal using TG/MS. J. China Univ. Min. Technol. 2003, 32, 311–315.