PYROLYSIS KINETICS OF WASHED PRECIPITATED LIGNIN

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This article describes the pyrolysis behavior of precipitated washed lignin in a Laminar Entrained Flow Reactor between 700 and 1000°C and at different residence times. Lignin was precipitated by acidification of softwood black liquor using CO_2. After acid washing, the solid material was dried and sieved (80-100 µm). This material was then fed into the reactor at a rate of about 0.1 g/min. The formed gases were analyzed with respect to CO, CO_2, and CH_4, and char was collected and weighed. A traditional first order Arrhenius kinetic expression, based on the temperature of the particles with respect to residence time, was adapted to the experimental results. The activation energy was found to be 32.1 kJ/mol. The low ash content in the washed lignin gave a very low solid material residue after the reactor.

Keywords: Kraft lignin; Pyrolysis; Reaction kinetics; Laminar Entrained Flow Reactor

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INTRODUCTION

There is currently great interest in different alternatives for utilizing the energy surplus in modern pulp mills, or in increasing the capacity in old mills with a limitation in the recovery boiler. One way to achieve this is to remove some of the lignin in the black liquor by precipitation, and use it later as a fuel for separate combustion in, for example, a lime kiln or a heat and power plant.

Biomass conversion technologies range from traditional direct fired biomass combustion, designed for steam production, to advanced integrated biomass gasification combined cycle systems with high projected efficiencies. Gasification processes produce large amounts of chemical substances that can be used as substitutes for conventional fuels, mainly H_2, CO, and CH_4. For optimal design of chemical reactors and combustors, an understanding of the interactions between chemical and physical mechanisms during gasification is of fundamental importance. The first step in all thermal conversion systems, both gasification and combustion, is pyrolysis. A thorough determination of the behavior in this step is therefore needed. The objective with this study is to determine the pyrolysis kinetics of washed precipitated kraft lignin.

Lignin Pyrolysis

Lignin pyrolysis, like other biomass pyrolysis processes, involves a complex set of chemical reactions. When lignin is heated up, the chemical bonds in the solid decompose and produce a volatile fraction, tar and a solid residue called char. The volatile product, syngas, consists mainly of H_2 and CO, but CH_4, tar and hydrocarbon gases are formed as well. The char is primarily composed of carbon due to the high temperatures observed during pyrolysis. The thermal decomposition of organic compounds can be explained by two kinds of reactions: primary and secondary reactions. Research has previously been conducted on the pyrolysis of biomass and its constituents, cellulose, hemicellulose, and different kinds of lignin (including black liquor due to its importance in the pulp and paper industry), e.g. Caballero et al. (1996), Conesa et al. (2001), and Ferdous et al. (2002), mainly using different TGA (ThermoGravimetic Analyzer) equipment. Ferdous et al. (2002) also conducted studies of kraft lignin in a fixed bed reactor.

Primary Reactions

Primary reactions are the fast initial decomposition reactions of lignin. These reactions form volatile gases (H_2, CO, CO_2, CH_4, HCs, etc), tar, and char. If the temperature is below 700ºC, then the primary reaction is usually all that is needed to calculate kinetic parameters.

Secondary Reactions

Secondary reactions occur when the temperature is higher than 700-800ºC. Secondary reactions are reactions between the materials produced in the primary reaction. The importance of secondary reactions increases with the residence time of the volatile compounds in the hot zone of the reactor (Caballero et al. 1996).

Equipment

Different kinds of equipment have been used to study pyrolysis; low heating rate equipment such as the TGA (Brown et al. 2001), and high heating rate equipment such as fixed bed reactors (Conesa et al. 2001) and others (Caballero et al. 1996) have been employed. The TGA equipment can handle very low weights of material (in the range of 1 mg) but has the drawback of a supporting holder that also is heated up, thereby changing the estimated temperature increase (especially important when high heating rates are used). The fixed bed reactor can handle more material (0.5 g at each experiment was used by Ferdous et al. 2002), but there is a drawback of having temperature gradients inside the bed. In this study, a Laminar Entrained Flow Reactor (LEFR) was used. It was designed to study fast pyrolysis and gasification kinetics.

Pyrolysis Kinetics

The kinetics of the thermal degradation of lignocellulosic materials is generally influenced by heat and mass transfer processes. Both affect the activation energy and the pre-exponential factor. Furthermore, the pyrolysis reaction of lignin is strongly influenced by temperature, heating rate, and the nature of the carrier gas. Pyrolysis of lignin is a solid-state reaction. Considered as a first order reaction with isothermal conditions in a homogeneous phase, the kinetic expression is:

$$\mathrm{d}\alpha / \mathrm{d}t = k \cdot f(\alpha) \tag{1}$$

$$f(\alpha) = (1-\alpha) \tag{2}$$

$$\alpha = (m_i - m_t) / (m_i - m_f) \quad (3)$$

$$1\text{-}\alpha = m_t / m_i \quad (4)$$

In these equations, k is the rate coefficient, α is the apparent conversion of the degradable part of the lignin, m_i is the initial mass, m_t is the mass at time t, and m_f is the mass at infinite time. The kinetic parameters of isothermal pyrolysis can be calculated from equation 5.

$$-\ln(1-\alpha) = k \cdot t + C \quad (5)$$

The rate coefficient is the kinetic constant expressed by the Arrhenius equation (Equation 6), which is commonly used to calculate the activation energy and the frequency factor.

$$k = A \cdot \exp(-E_a / \boldsymbol{R} \cdot T) \quad (6)$$

E_a is the activation energy [J/mol], $\boldsymbol{R}$ is the common gas constant equal to 8.314 [J/mol K], T is the temperature [K], and A is the frequency factor [s^{-1}]. Lopez Pasquali and Herrera (1997) found a range between 12.46 and 42.60 kJ/mole for the activation energy of lignin from hardwood using a thermo gravimetric technique (TG/TGA). For wheat straw and corn stalk pyrolysis in a plasma heated Laminar Entrained Flow Reactor (LEFR), Shuangning et al. (2005) found an activation energy between 31-33 kJ/mol and a frequency factor of 10^3 1/s. Due to differences in the structure of lignin, activation energy and reaction rates are also assumed to change depending on species and treatment methods.

EXPERIMENTAL

Raw Material

The raw material used in this investigation was precipitated washed kraft lignin from softwood. The precipitation was accomplished by acidification of black liquor using CO_2. The precipitate was further treated with acid wash water to remove much of the inorganic material such as sodium and potassium. The precipitation process was developed and described by Öhman (2006). The properties of the precipitated washed kraft lignin differed from those of natural lignin due to the chemical structural changes that occurred in the kraft pulping process, e.g. its molecular weight was lower than that of the corresponding native lignin and it also contained more phenolic hydroxyl and carboxyl groups (Sjöström 1993). The composition of the precipitated washed lignin is shown in Table 1, and an estimation of the metal distribution is found in Table 2 (Öhman and Theliander 2006).

Table 1. Principal Components of Washed softwood Kraft Lignin

Element	Washed lignin (wt % dry)
C	63.9
H	5.9
O	27.8
N	0.1
Others (metals,ash)	2.3

Table 2. Metal Concentrations in Washed Kraft Lignin

Element	Washed lignin (mg/kg dry weight)
Al	29
Ca	18
Fe	64
K	192
Mg	58
Mn	21
Na	1500

Raw Material Preparation

Precipitated washed kraft lignin was dried at 60º C in an oven for 48 hours. After drying the lignin was crushed and sieved to obtain a particle size range of 80-100 µm.

Experimental Equipment

To investigate the pyrolysis of precipitated washed kraft lignin, the Chalmers Laminar Entrained Flow Reactor (LEFR) was used. It is a laboratory-scale reactor that works at atmospheric pressure and in temperatures up to 1100ºC. Additional operational parameters are given in Table 3. The five-zone heating element of the Chalmers LEFR provides flexibility and high heating rates of 4000-13000ºC/s while maintaining precise experimental control of reaction conditions (Brown et al. 2001). The small lignin particles used in the LEFR (80 -100 µm) ensured that the temperature gradient inside the particles was small and, thus, complete devolatilization was reached very fast. The time required for complete devolatilization was estimated to be less than 0.08 s for furnace temperatures higher than 700ºC (Sricharoenchaikul et al. 2001).

Table 3. Operational Parameters for the Laminar Entrained Flow Reactor

Temperature	600 - 1100ºC
Pressure	1 bar
Biomass flow rate	0.1 – 2 g/min
Primary gas flow rate	0.1 – 1.2 l/min
Secondary gas flow rate	2 – 40 l/min
Quench gas flow rate	1 – 30 l/min
Main gas flow rate	1 – 30 l/min

Figure 1 shows the main system of the Chalmers LEFR, operating with a downward flowing gas stream. The primary flow was injected at the top of the reactor together with the raw material. The secondary flow was preheated to the reactor temperature and injected through a flow straightener coaxially with the primary gas flow. This ensures quick heating of the smaller primary flow and a temperature in the whole gas flow that is uniform and equal to the reactor temperature. The feeder system, consisting of a screw feeder and a hopper, located at the top of the reactor, controlled the particle flow rate into the reactor. When entering the reactor, the particles were rapidly heated up by the secondary flow and the hot walls. The reaction zone length can be varied between 0.2 and 1.2 meters. The inner tube diameter was 70 mm. After the reaction zone, the particles and gases were quenched with nitrogen in a water-cooled collector tube to stop the reactions. Then, large particles were removed by a cyclone in the bottom part of the reactor and collected in a char bin. Fine particles were removed from the product gas by a glass fiber filter.

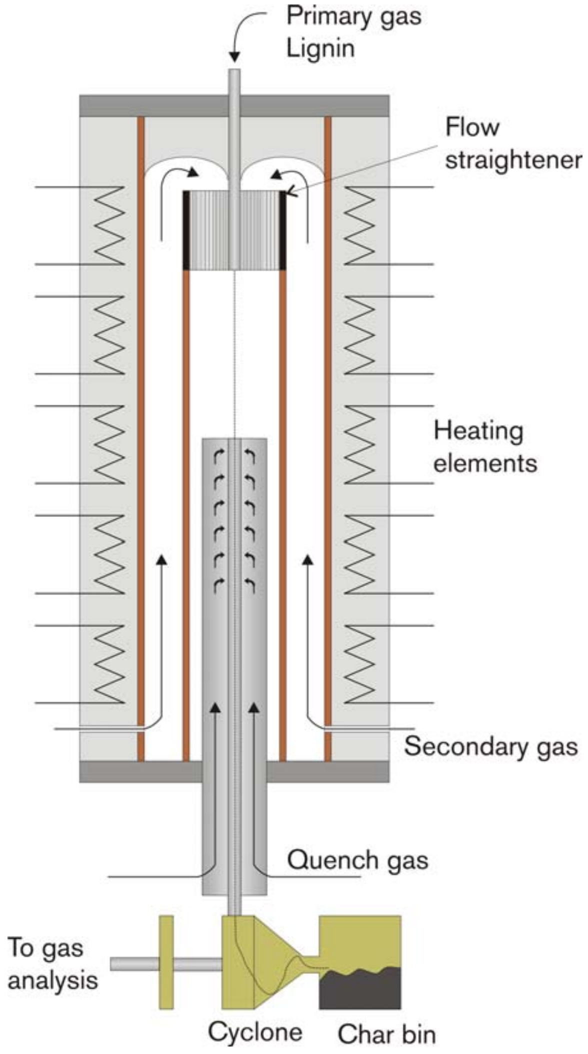

Fig. 1. Chalmers Laminar Entrained Flow Reactor (LEFR)

The detected gases were CO, CO_2, and CH_4. When the exhaust gases were expected to have higher concentrations than the maximum ranges of the analyzer, a diluting gas flow was added before the product gas was allowed to enter the gas analyzer.

Procedure

Experiments were conducted in the Chalmers LEFR at temperatures between 700 and 1000ºC and residence times between 0.7 and 4.2 s. Most of the runs were replicated to verify the obtained values; the average was the common value used for the results presented in this work. The length of the reaction zone was used to vary the residence time. The feed rate of precipitated lignin during the runs ranged between 0.1 and 0.3 g/min. Nitrogen was used in the primary, secondary, and quench flows. Gas flow conditions were recalculated for each run in order to keep the velocity constant when changing the temperature.

The duration of each run varied from 6 to 12 minutes in order to ensure steady state. At the end of each run, the cyclone, particle filter holder and char bin were sealed and removed to a nitrogen purged glove box in order to prevent the reactive char residue from oxidizing or combusting spontaneously on exposure to air. The contents were then weighed.

RESULTS AND DISCUSSION

Char Residue

Figure 2 shows the char residue observed during thermal degradation of lignin for temperatures between 700 and 1000ºC at different residence times (only one value from 700°C is presented due to experimental difficulties). It can be seen that the amount of char decreased with longer residence times and higher temperatures, probably due to higher conversion rates. Char yield decreased with higher reactor temperatures and shorter residence times. At lower temperatures, the residence time had a large effect on the char yield, but the char yields did not seem to be significantly affected by residence time at higher temperatures (900ºC and at 1000ºC). This is explained by the fact that the solid phase reactions are faster and were therefore almost complete already after 1-2 seconds.

Product Gas Yield

Figure 3 shows the effect of different temperatures and residence times on the production of CO. Production increased with both residence time and temperature. As can be seen in Fig. 4, the production of CO increased more than the production of CO_2, i.e. the ratio between the gases decreased. However, the ratio between CH_4 and CO was practically constant (Fig. 5), with a decrease at the longest residence time (the experiment at 800°C showed the decrease already between 1 and 2 seconds). The ratios, for both CO_2/CO and CH_4/CO, decreased with increasing temperature, but the residence time dependence was similar for all temperatures.

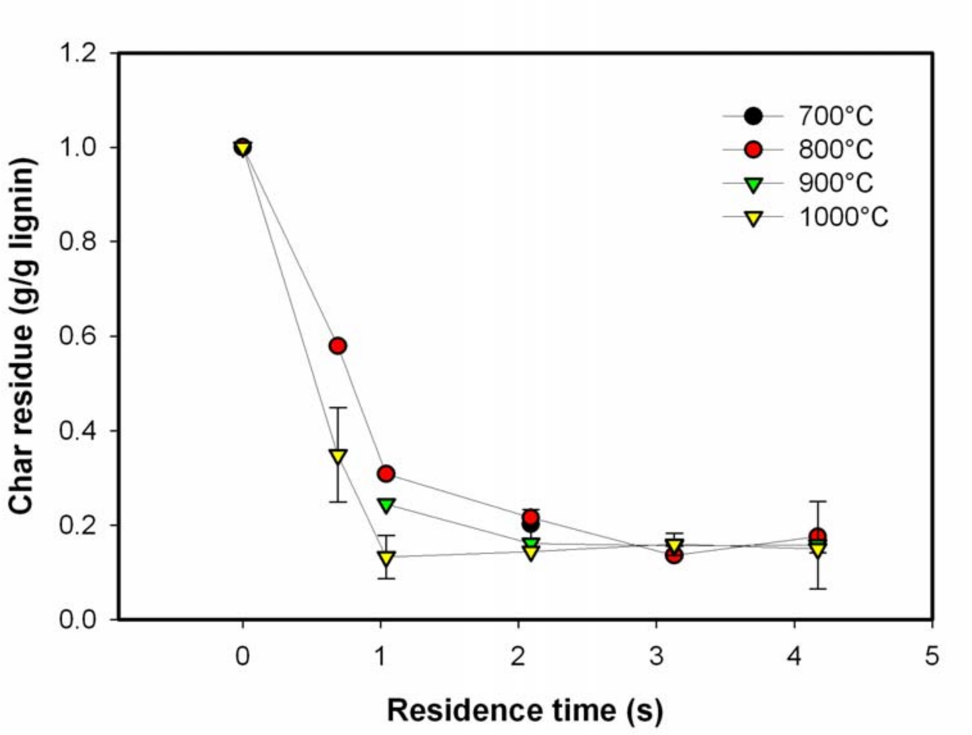

Fig. 2. Remaining char at different temperatures and residence times.

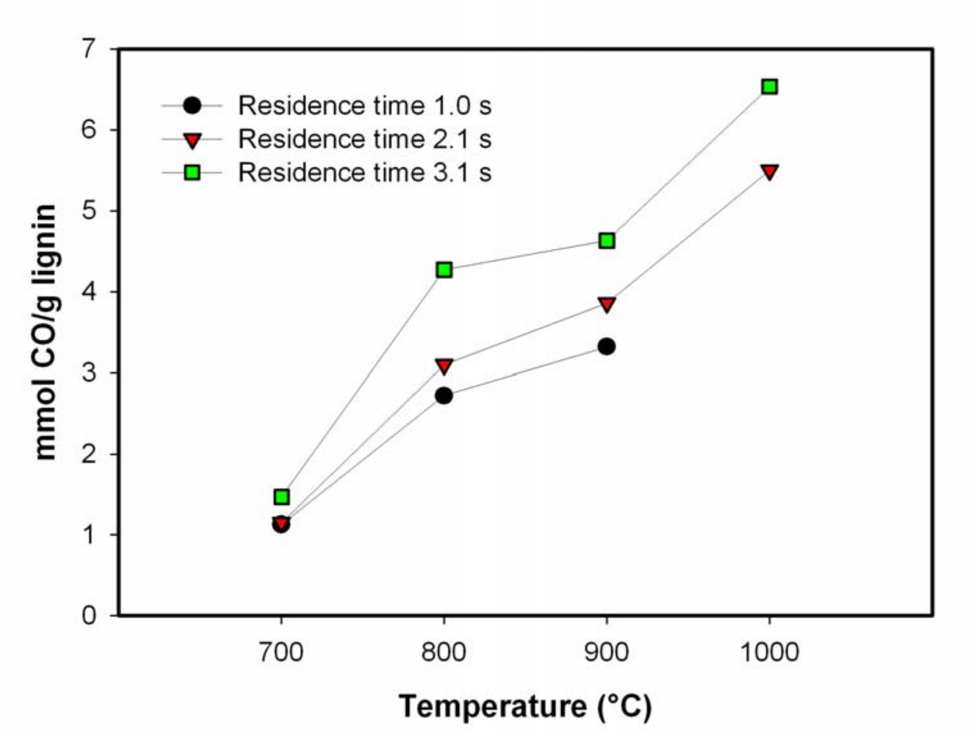

Fig. 3. Production of CO at different temperatures and residence times during pyrolysis of kraft lignin.

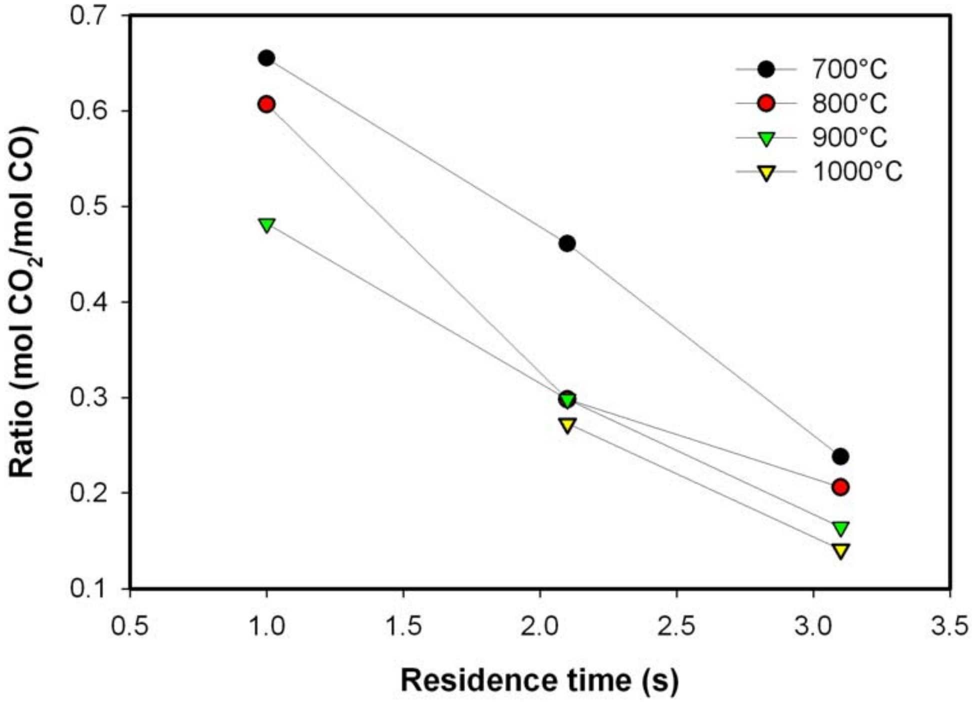

Fig. 4. Relative gas production (CO_2/CO) when softwood kraft lignin is pyrolyzed at different temperatures.

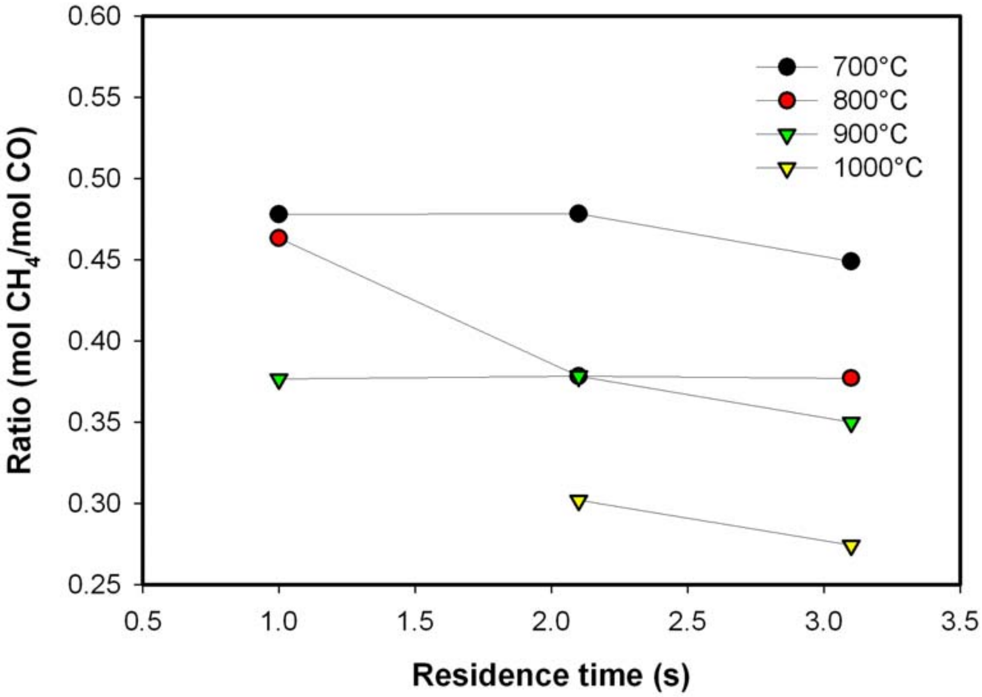

Fig. 5. Relative gas production (CH_4/CO) when softwood kraft lignin is pyrolyzed at different temperatures.

Kinetic Parameters

In order to calculate the rate coefficient (*k*), the activation energy (E_a), and the frequency factor (*A*), some assumptions were made (in addition to the assumption of a first order reaction rate). The mass at infinite time, m_f, was assumed to be zero due to the extremely low ash content of the washed precipitated lignin. Fast pyrolysis occurs in a LEFR in less than one second, and based on our experimental runs, slower reactions occur at longer residence times. This has been taken into account in analyzing the results. The shortest residence time used in the experimental runs was 0.7 s (20 cm). The rate coefficient, *k*, was determined between the residence times of 0 and 1.04 s according to the changed slope of remaining char with time obtained. Figures 6 through 8 show the values obtained for the rate coefficient for each of the reactor temperatures used. At 900°C (Fig. 7), it was not possible to successfully collect the char formed because of the high formation of tars. Therefore, the reaction rate can only be estimated from two points and must be used with this in consideration.

With the rate coefficients obtained for different temperatures, a linear regression of the derived kinetic data could be performed (Fig. 9). From this, the activation energy (E_a) was determined to be 32.1 kJ/mol, which is in accordance with earlier research (e.g. Lopez Pasquali and Herrera 1997; Shuangning et al. 2005). This result is in the lower range of the values obtained for ALCELL hardwood lignins (34-284 kJ/mol) in a study by Murugan et al. (2008). The frequency factor (*A*) was determined to be 37 s^{-1}; this deviates from earlier investigations, but the difference is probably due to the equipment used and the limited number of residence times investigated.

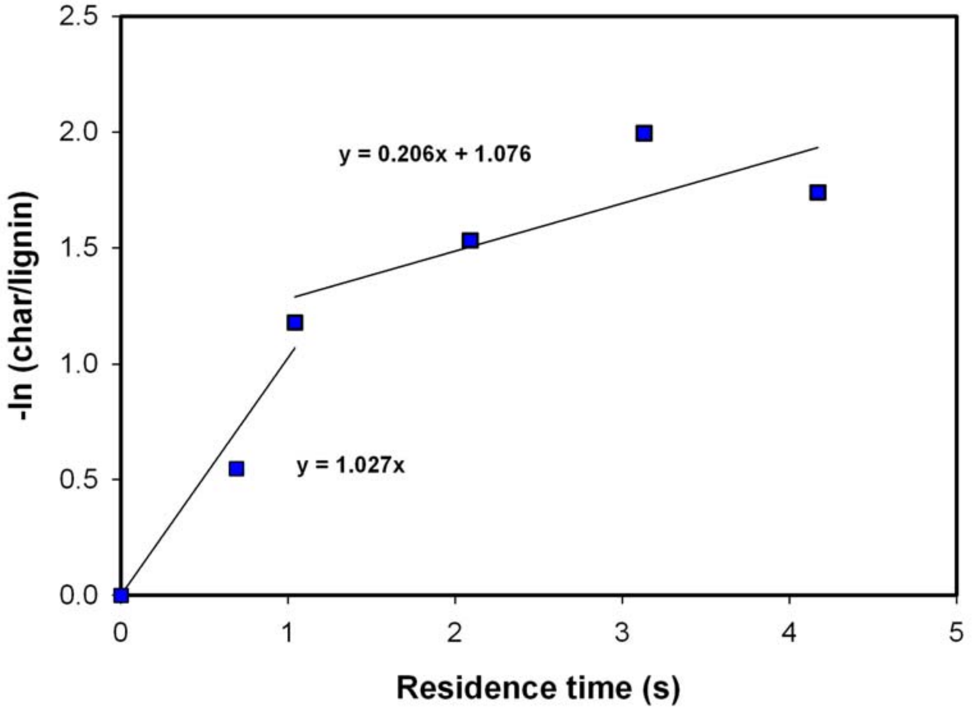

Fig. 6. Rate coefficient at 800ºC.

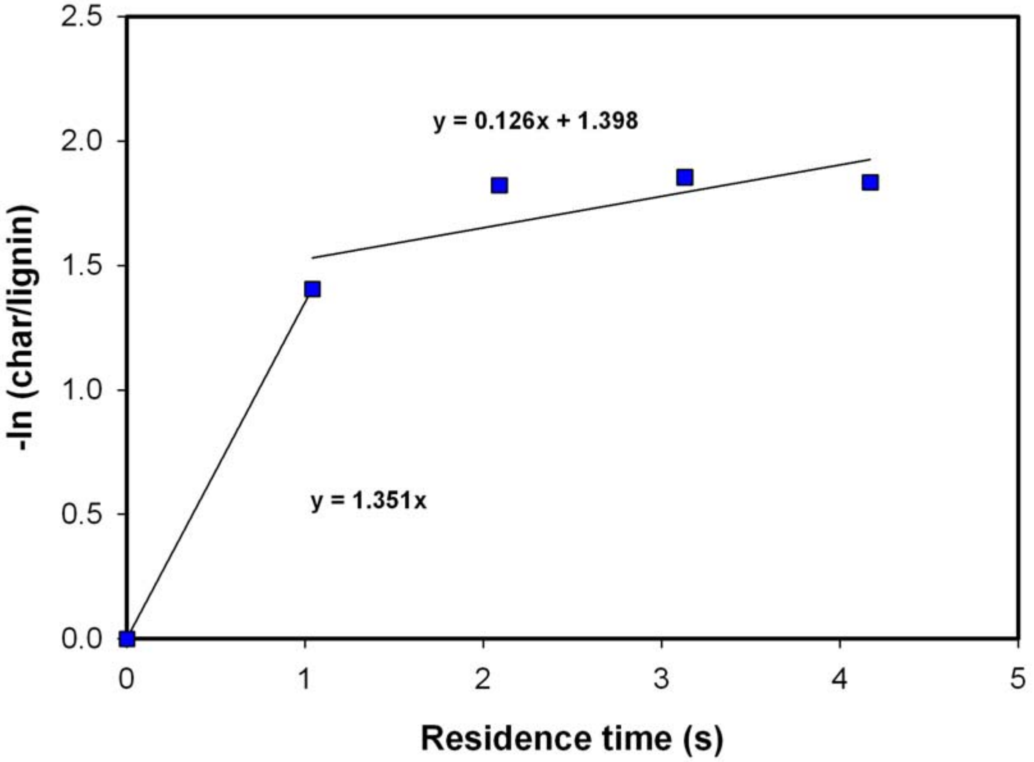

Fig. 7. Rate coefficient at 900ºC.

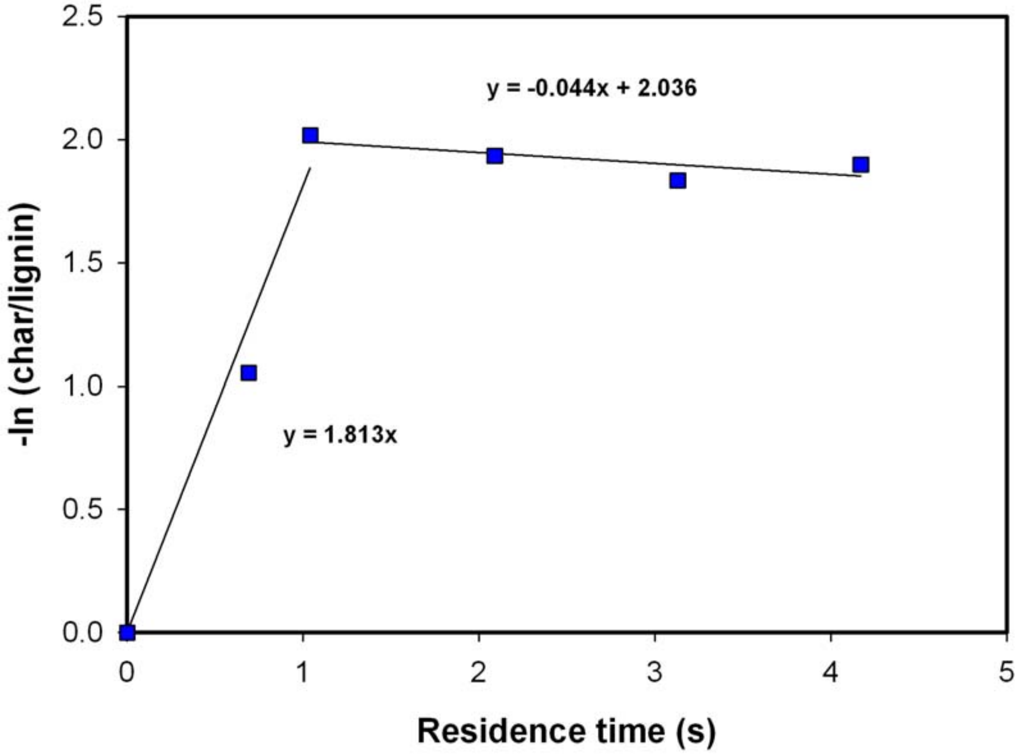

Fig. 8. Rate coefficient at 1000ºC.

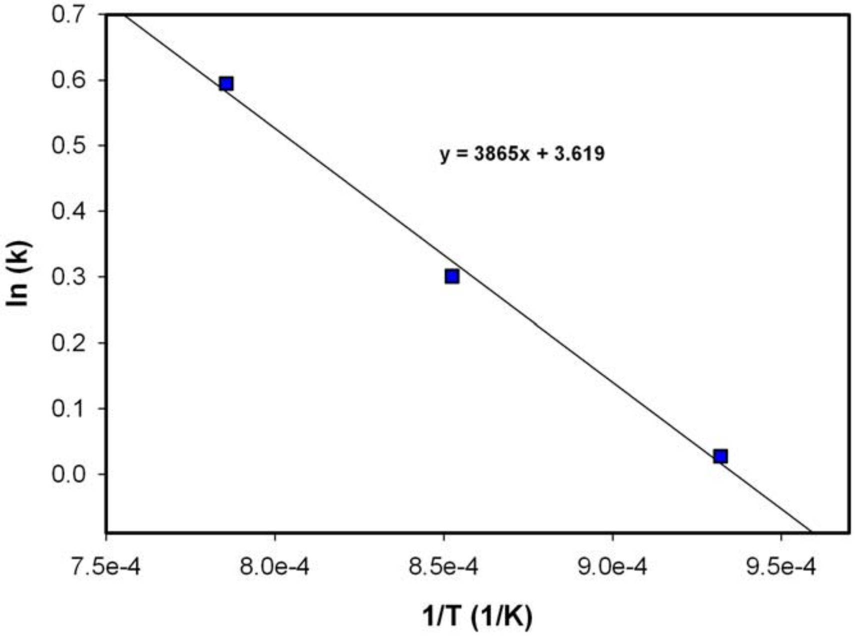

Fig. 9. Linear regression of the rate coefficients at different temperatures during primary pyrolysis and devolatilization.

The secondary pyrolysis, indicated in Figs. 6 to 8, had a declining reaction rate coefficient with temperature, indicating that the reaction rate, defined as the amount reacted in relation to the total initial amount, decreased when the amount of material decreased, i.e. there was only a limited amount of easily accessible material for the pyrolysis reactions. At 1000°C, all pyrolysis had already occurred at one second, and the slope was, therefore, almost horizontal (Fig. 8).

CONCLUSIONS

1. The conversion of washed precipitated softwood kraft lignin into volatile matter, as determined in the Chalmers Laminar Entrained Flow Reactor at temperatures between 700 and 1000ºC, was 69–87 % by weight.
2. It can be concluded from the experimental results that large amounts of CO and minor amounts of CH_4 were produced during the pyrolysis of washed precipitated lignin. Product gas composition was strongly influenced by temperature and residence time. The production of all investigated gases, CO, CO_2, and CH_4, increased with temperature, but the production of CO increased the most (the ratios CO_2/CO and CH_4/CO decreased with temperature).
3. The activation energy (E_a) for the first reaction, occurring from 0 to 1.04 s, was determined to be 32.1 kJ/mol and the frequency factor (A) to be 37 s^{-1}.
4. The remaining char yield depended on temperature and residence time. Data obtained in the experimental runs indicates that the amount of char was not further reduced by higher temperatures or longer residence times after a temperature of 900ºC and residence times longer than 2 s.

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