

A Kinetic Study of CO₂ and Steam Gasification of Char from Lignin Produced in the SEW Process

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The reaction kinetics of gasification are important for the design of gasifiers using biomass feedstocks, such as lignin, produced in biorefinery processes. Condensed and uncondensed lignin samples used in the present study were prepared using the SEW (SO₂-ethanol-water) fractionation process applied to spruce wood chips: the dissolved lignin is precipitated during the recovery of SO₂ and ethanol from the spent fractionation liquor. The gasification of char made from condensed and uncondensed SEW lignin was investigated using thermogravimetric analysis (TGA) at atmospheric pressure using either CO₂ or steam. The main aim of this study was to quantify the reaction rate during the gasification process, which was found to be best described as zero-order. All experiments were performed at constant temperatures between 700 and 1050 °C to obtain the necessary information for describing the reaction rate equation in an Arrhenius form; the heating rate was 20 °C/min for both samples. The experiments led to almost similar results for both samples. The activation energies of CO₂ gasification were approximately 160 kJ/mol and 170 kJ/mol for uncondensed and condensed lignin char, respectively. The activation energies of steam gasification were approximately 90 kJ/mol and 100 kJ/mol for uncondensed and condensed lignin char, respectively.

Keywords: Sulfur dioxide-ethanol-water (SEW) fractionation; Kinetics; CO₂ and steam gasification; Lignin; Thermogravimetric analysis

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INTRODUCTION

The continuing increase in the world's population and the subsequent increase in energy consumption *per capita* have resulted in a dramatic increase in the consumption of fossil fuel during the past few decades. Unfortunately, this has an adverse effect on the environment, with global climate change being of particular concern (Lv *et al.* 2010). Woody biomass, a globally available feedstock, holds great potential as an important raw material for biofuels and renewable chemicals in an integrated forest products biorefinery (IFBR) (van Heiningen 2006). Lignocellulosic biomass is renewable and does not directly compete with food production, so its sustainable utilization would reduce the emission of greenhouse gases and the depletion of natural resources (Di Blasi 2009).

This has resulted in extensive research being undertaken to develop economically feasible methods of producing renewable energy and biofuels from biomass feedstock.

Forest biomass is one of the most viable resources for producing biofuels. One promising process developed as part of the “Bioforest Project” at Aalto University in Finland uses an SO₂-ethanol-water (SEW) fractionation method to produce cellulosic fibers and spent liquor with a high concentration of hemicellulose mono-sugars. The objective of this project is to produce butanol from the hemicellulose mono-sugars when they are combined with the glucose obtained by enzymatic hydrolysis of the fibers using ABE (acetone-butanol-ethanol) fermentation. The SEW liquor is subjected to a conditioning process to remove compounds that inhibit ABE fermentation (Sklavounos *et al.* 2011) and to recover the fractionation chemicals (SO₂ and ethanol). The ABE process utilizes *Clostridia* bacteria to ferment all of the dissolved wood sugars to produce a mixture of acetone/isopropanol, butanol, and ethanol (Iakovlev *et al.* 2011; Rakkolainen *et al.* 2010).

The conditioning process consists of a number of steps (Iakovlev *et al.* 2011; Sklavounos *et al.* 2011) during which lignin is precipitated from the SEW liquor in two different forms, condensed and uncondensed, depending on the fractionation conditions. This paper investigates the reaction kinetics of these lignin fractions during CO₂ and steam gasification at atmospheric pressure.

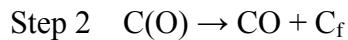
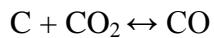
Understanding the kinetics of gasification is necessary for selecting the process and the design of the gasifiers (Mani *et al.* 2011; Zhang *et al.* 2010). Several studies dealing with the kinetics of CO₂ and steam gasification have been reported for chars derived from biomass materials (Khalil *et al.* 2008; Mani *et al.* 2011; Zhang *et al.* 2010).

The gasification of carbonized char from biomass produces “syngas,” a valuable raw material used in several chemical industries; however, the use of this feedstock has not yet been implemented on an industrial scale (Ollero *et al.* 2002). In this study, the reaction kinetics of CO₂ and steam gasification of condensed and uncondensed lignin, derived from spruce wood chips using the SEW process, were investigated using a thermogravimetric apparatus (TGA).

CO₂ Gasification

Mechanism

Several mechanisms have been described for the Boudouard reaction. The Ergun mechanism describes the reaction as a two-step process (Hargrave *et al.* 1988):



where C_f and C(O) represent a free carbon active site and carbon-oxygen complex, respectively. Initially, carbon dioxide is reduced to carbon monoxide, forming an oxidized surface complex. In the next step, the C(O) complex is released as carbon monoxide and a new free carbon active site is formed. Assuming that the sum of C_f and C(O) is constant during the reaction, a steady state is reached, and the CO desorption reaction is rate-determining (Ergun 1956), the following reaction kinetic expression can be derived:

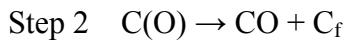
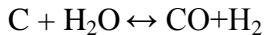
$$r_{c,CO_2} = \frac{k_2 C_t}{1 + \frac{p_{CO}}{K_1 \cdot p_{CO_2}}} \quad (1)$$

where r_{c,CO_2} is the carbon converted from the solid to the gas phase, k_2 is the forward reaction rate in Step 2, C_t is the total number of active sites (free and occupied), K_1 is the equilibrium constant of Step 1 (equal to k_1/k_{-1} , where k_1 and k_{-1} are the reaction rates of the forward and backward reactions in Step 1, respectively), and p is the partial pressure of either CO_2 or CO .

Steam Gasification

Mechanism

The mechanism of the steam gasification reaction is basically similar to the Boudouard reaction. This reaction also proceeds in two steps:



In the first step, hydrogen is released and a carbon-oxygen complex is formed by a water molecule attacking a free active carbon site. In the next step, similar to the Ergun mechanism of the Boudouard reaction, the $C(O)$ complex decomposes to produce carbon monoxide and a new free carbon active site.

Step 2, the decomposition of the carbon-oxygen complex, is the rate-limiting step of the overall reaction, although the effect of this step on the reaction rate may be neglected at high temperatures. In addition, the concentration of product gases is small, and the inhibiting effect is negligible. Using the same assumptions as for CO_2 gasification, the following reaction kinetic expression can be derived:

$$r_{c,H_2O} = \frac{k_4 C_t}{1 + \frac{p_{H_2}}{K_3 \cdot p_{H_2O}}} \quad (2)$$

where r_{c,H_2O} is the carbon converted from the solid to the gas phase, k_4 is the forward reaction rate in Step 2, C_t is the total number of active sites (free and occupied), K_3 is the equilibrium constant of Step 1 (equal to k_3/k_{-3} , where k_3 and k_{-3} are the reaction rates of the forward and backward reactions in Step 1, respectively), and p is the partial pressure of either H_2O or H_2 .

EXPERIMENTAL

Raw Material

Both lignin samples were produced at Aalto University in Helsinki, Finland. Air-dried screened spruce chips were used as the raw material for SEW fractionation. A HAATO 43427 silicon oil bath containing six 220-mL bombs, each of which was filled with 25 g of spruce chips (oven dry), was used for SEW fractionation. The fresh liquor

was prepared by bubbling SO₂ through a 55% (v/v) ethanol-water solution cooled in an ice bath at a low flow rate to dissolve the set amount of either 3% (w/w) or 12% (w/w) SO₂, measured continuously on an electronic balance.

Two different pulping conditions were used, depending on the SO₂ charge in the fresh liquor. For the 3% (w/w) SO₂ concentration, the pulping conditions used were as follows: a liquor-to-wood ratio of 6 L kg⁻¹, a pulping temperature of 150 °C (± 1 °C), and a total pulping time of 120 min, which included the heating-up period. For the 12% (w/w) SO₂ concentration, the pulping conditions employed were as follows: a liquor-to-wood ratio of 3 L kg⁻¹, a pulping temperature of 150 °C (± 1 °C), and a total pulping time of only 30 min, which included the heating-up period. SEW spent liquor was collected by squeezing the pulp suspension contents in a washing sock. In the case of 12% (w/w) SO₂ spent liquor, the pulp, after removal of the SEW spent liquor, was washed twice with 40% ethanol-water at 60 °C and three times with deionized water at room temperature. The wash liquor was then added to the SEW liquor (hereafter known as the MSEW liquor). The 3% (w/w) SO₂-SEW spent liquor and the MSEW liquor were then treated in a rotovap evaporator to remove ethanol and SO₂. The temperature of the water bath was 95 °C, and the vacuum pressure was 300 mbar.

About 65% of the original weight of the liquors was evaporated. The liquor treated in the rotovap (hereafter known as EVAP) contained condensed lignin (a char-like solid) when the level of SO₂ in the cooking liquor was set to 3% (w/w). However, uncondensed lignin was formed in the EVAP liquor when the SO₂ in the cooking liquor was set to 12% (w/w). The latter lignin had the form of a precipitate as a result of its higher degree of sulfonation, which was removed from the EVAP liquor by centrifugation. The values of ultimate and proximate analyses for the two samples of lignin are given in Table 1.

Table 1. Ultimate and Proximate Analyses of Samples

Samples	Ultimate Analysis (wt% Dry)						Proximate Analysis (wt% Dry)		
	C	H	N	Cl	S	Others	Ash	Volatile matter	Fixed Carbon
Condensed lignin	63.8	5.7	0.05	0.02	1.0	29.4	1.4	55	43.6
Uncondensed lignin	60.9	5.8	0.08	0.02	1.2	32	1.0	53.1	45.9

The higher carbon content of the condensed lignin is indicative of more carbon-carbon bonds being formed by condensation reactions.

Raw Material Preparation

A condensed lignin sample with an average dry matter content of 58.6% and an uncondensed lignin sample with an average dry matter content of 39.2% were used to prepare the char. After drying for 24 h at 105 °C, the lignin samples were ground to obtain a fine powder composed of homogeneous particles. The samples were ground separately to omit the effect of particle size on the reactivity of the material (Di Blasi

2009). The samples were thereafter dried once more for 24 h at 105 °C to remove the moisture absorbed during the grinding process.

Experimental Equipment

The gravimetric measurement was performed in a DynTHERM HP analyzer manufactured by Rubotherm GmbH. A sample was loaded in a small ceramic crucible (diameter and height of 9 mm) on a balance with a resolution of 1.0 µg in an environment with a controlled temperature. All of the gasification experiments were performed isothermally. The sample was heated up to the particular temperature of the reaction in a nitrogen atmosphere before the inert gas was replaced by the gasifying media. The mass loss of the sample was recorded during the reaction time. Only a small amount of sample (0.1 g) was used (Higman and van der Burgt 2008) to avoid significant differences in temperature between the TGA set point and the sample caused by the high endothermic reaction heat of CO₂ gasification (+172 kJ/mol) and steam gasification (+131 kJ/mol).

Pyrolysis

Pyrolysis of the samples was conducted using the TGA. In each test 0.10±0.01 g of dried powder was placed into a small ceramic crucible inside the reactor under a flowing N₂ atmosphere (100 mL/min) and was heated up to the reaction temperature at a heating rate of 20 °C/min at atmospheric pressure. This relatively slow rate of heating was adopted to eliminate any atypical heat transfer problems (Khalil *et al.* 2008). Each sample was kept at the particular temperature for 20 min to ensure complete devolatilization (Zou *et al.* 2007). The final pyrolysis temperature was the same as for the isothermal gasification temperature in question for all the experiments and exceeded 700 °C.

CO₂ Gasification Process

CO₂ gasification of the pyrolyzed samples was performed isothermally at three different temperatures, ranging from 850 to 1050 °C (lower temperatures gave very slow reaction rates and were excluded). Carbon dioxide was used as the gasifying media at a flow rate of 50 mL/min and was mixed with the same flow rate of nitrogen gas. Samples from each experiment were kept at the final temperature for 50 min; all experiments were duplicated.

Steam Gasification Process

Almost the same procedure was employed for steam gasification. The steam gasification process was performed isothermally at temperatures between 700 °C and 1000 °C for both of the pyrolyzed samples, with the steam being supplied from an evaporator operating at 200 °C. Distilled water at a flow rate of 0.06 mL/min was injected into the evaporator by an HPLC water-pump; the steam produced was mixed with 50 mL/min nitrogen gas before being fed into the reactor.

RESULTS AND DISCUSSION

Gasification Kinetics

Rate of reaction

Ignoring the effect of desorption of the carbon-oxygen complex, both reactions can be assumed to be zero-order reactions, according to the experimental data for carbon conversion (Figs. 1 through 4), which shows a constant relationship between time and the rate of carbon conversion (Barkia *et al.* 2004; Lee 1993; Rao and Jalan 1972). This is consistent with the kinetic expressions derived (Eqs. 1 and 2) when the partial pressure of the gasifying media (CO_2 or H_2O) is much higher than that of the intermediate products (CO or H_2). In this particular case, the gasifying media are being constantly supplied to the reaction chamber and the gases that are produced are being constantly removed.

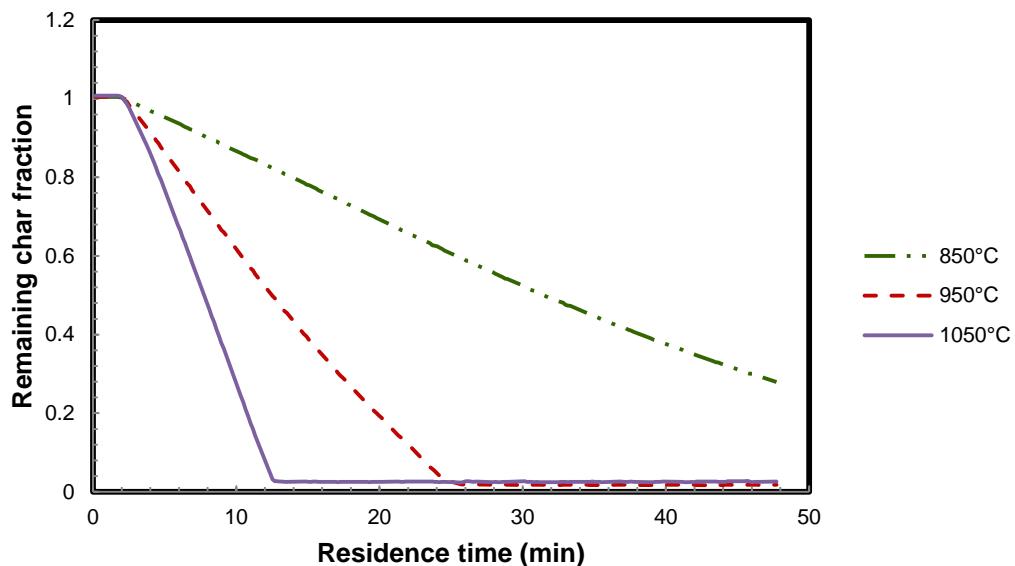


Fig. 1. The amount of remaining char produced from condensed lignin at various temperatures during CO_2 gasification

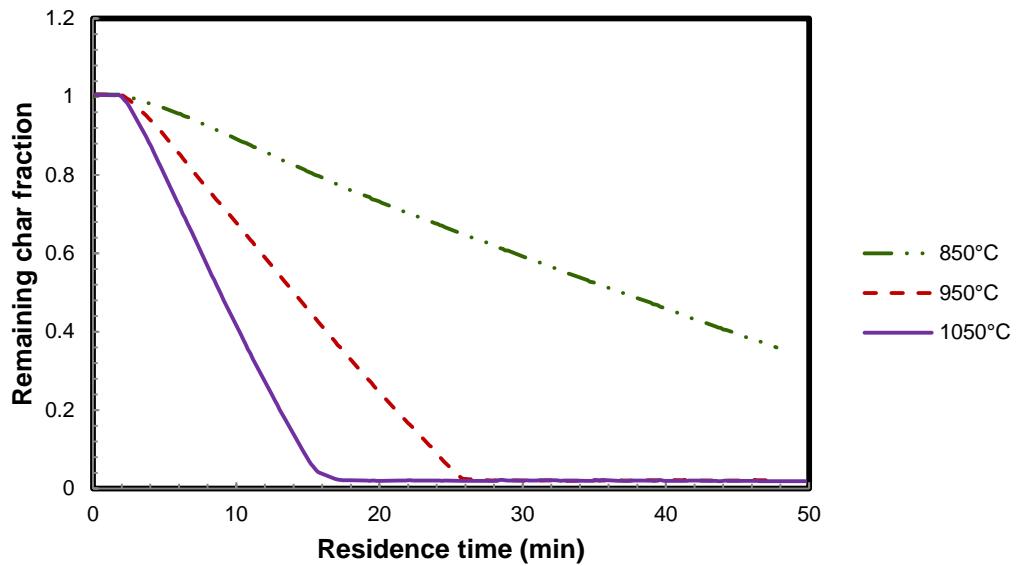


Fig. 2. The amount of remaining char produced from uncondensed lignin at various temperatures during CO_2 gasification

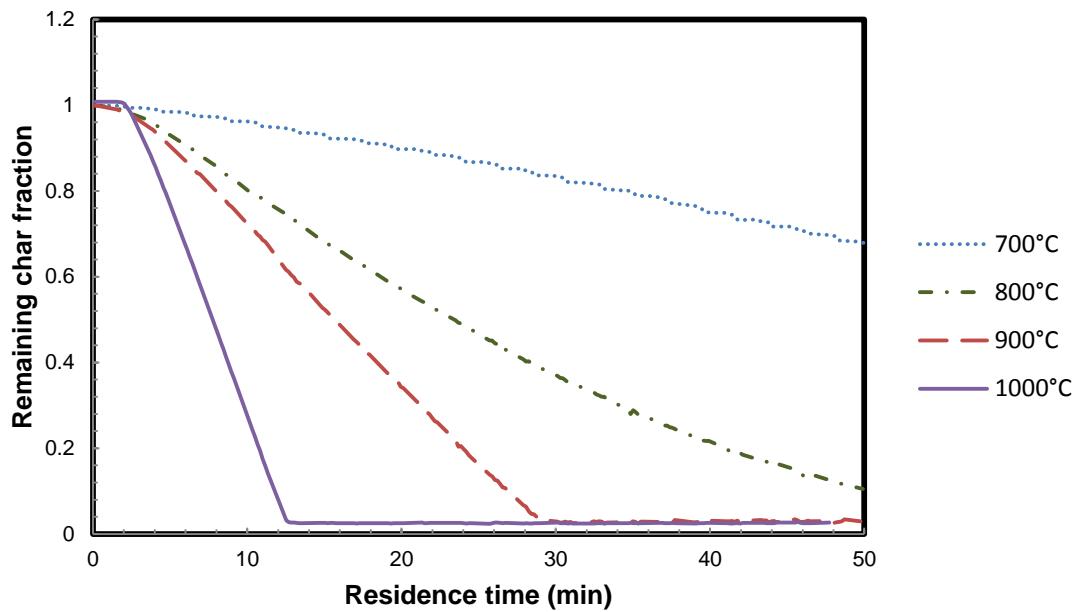


Fig. 3. The amount of remaining char produced from condensed lignin at various temperatures during steam gasification

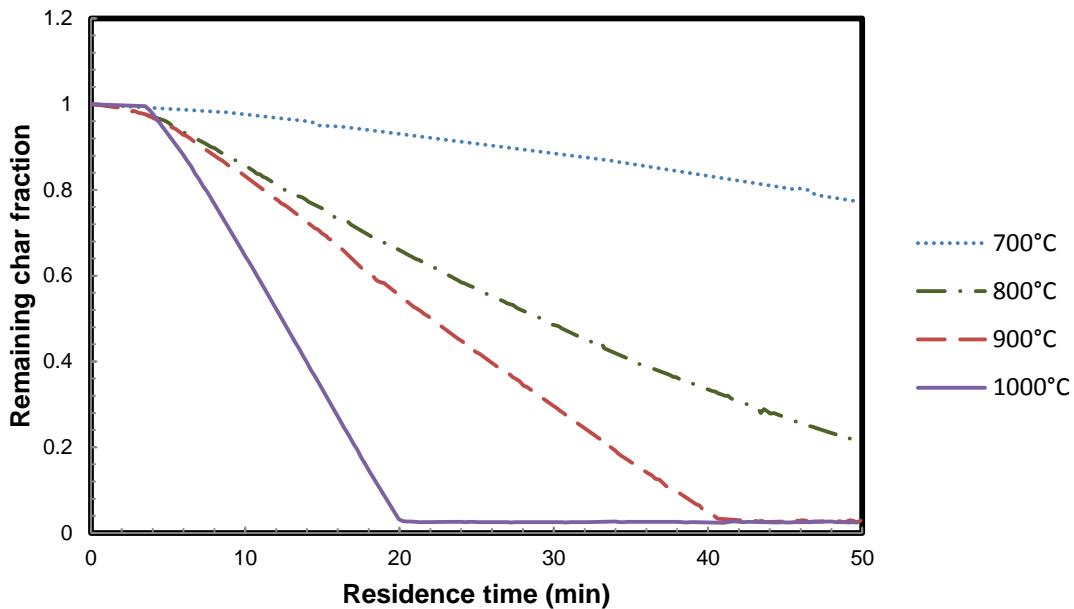


Fig. 4. The amount of remaining char produced from uncondensed lignin at various temperatures during steam gasification. A line representing the average mass loss rate is added at each temperature.

For both reactions, the reaction rate can be described by the rate of char conversion (Eq. 3), where α_c is the reactive fraction of char:

$$r_c = d\alpha_c/dt = d[(m_c - m_i)/(m_0 - m_i)]/dt \quad (3)$$

In Eq. 3, m is the mass and subscript c is char, i is inert (not reacting mainly inorganics), and 0 is initial weight. By neglecting the effect of concentration of products in relation to the concentration of the reacting gases (either CO_2 or H_2O), the reaction rate is constant.

$$r_c = k \cdot C_T \quad (4)$$

The number of sites, C_T , is related to the surface area (sites accessible for the gas) and can, in this particular case, be assumed constant (which was used to derive Eqs. 1 and 2). The reason for the assumption is the fact that the pyrolyzed char has the shape of a cylinder, where the top is directed towards the free gas and the sides are facing the walls of the sample basket. It is therefore likely that most of the reaction will occur from the top and downwards with equal cross sectional area all the time. This is also consistent with the constant reaction rate found in the experiments. Dependency of k on temperature can, at atmospheric pressure, be described in the Arrhenius form according to Eq. 5:

$$r_c = k \cdot C_T = k \cdot A_c \cdot \eta = A \cdot e^{-E/RT} \cdot A_c \cdot \eta \quad (5)$$

where A_c is the cross sectional area of the char, η is number of active sites per area unit which depends on the previous conditions, A is the pre-exponential factor, E is the activation energy, and R is the universal gas constant. The equation can be expressed alternatively as:

$$\ln(k) = -E/RT + \ln(A \cdot A_c \cdot \eta) \quad (6)$$

Based on Eq. (6), the reactivities of chars derived from condensed and uncondensed lignin were plotted against $1/T$ in Fig. 5 for CO_2 gasification and in Fig. 6 for steam gasification. These figures confirm that the relationship between k and T follows the Arrhenius expression, thereby allowing the activation energy (E) and the apparent pre-exponential factor ($A' = A \cdot \eta$) to be determined for both materials. Reactivity parameters for the gasification step for pyrolyzed char from both lignins are shown in Table 2.

Table 2. The Activation Energy (E) and Apparent Pre-exponential Factor (A') of CO_2 and Steam Gasification

Chars	E (kJ/mol)		A' (1/m ² , s)	
	CO_2 Gasification	Steam Gasification	CO_2 Gasification	Steam Gasification
Condensed lignin	111.8	99.2	20600	812600
Uncondensed lignin	93.7	86.1	9000	127300

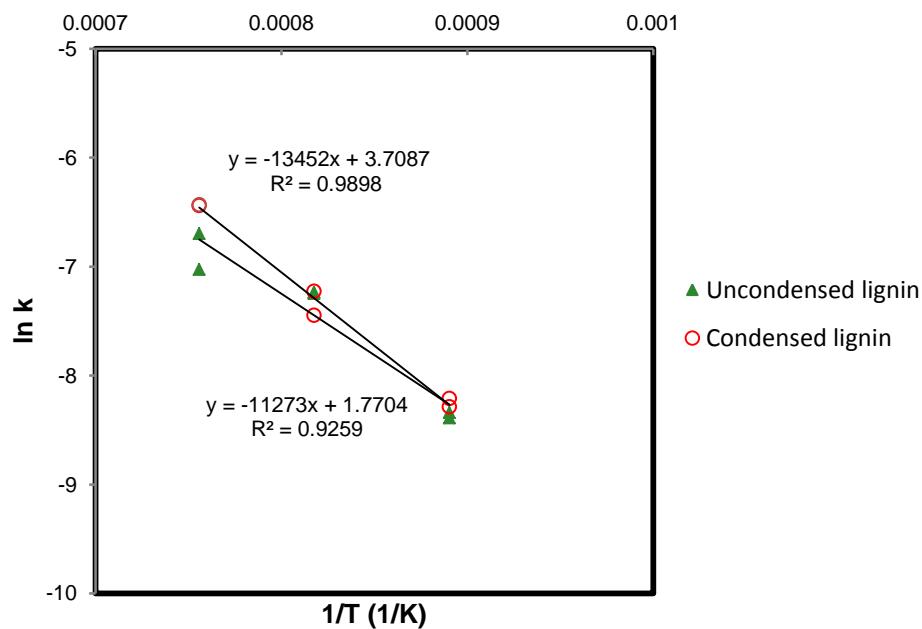


Fig. 5. An Arrhenius plot for CO_2 gasification of char derived from condensed and uncondensed lignin

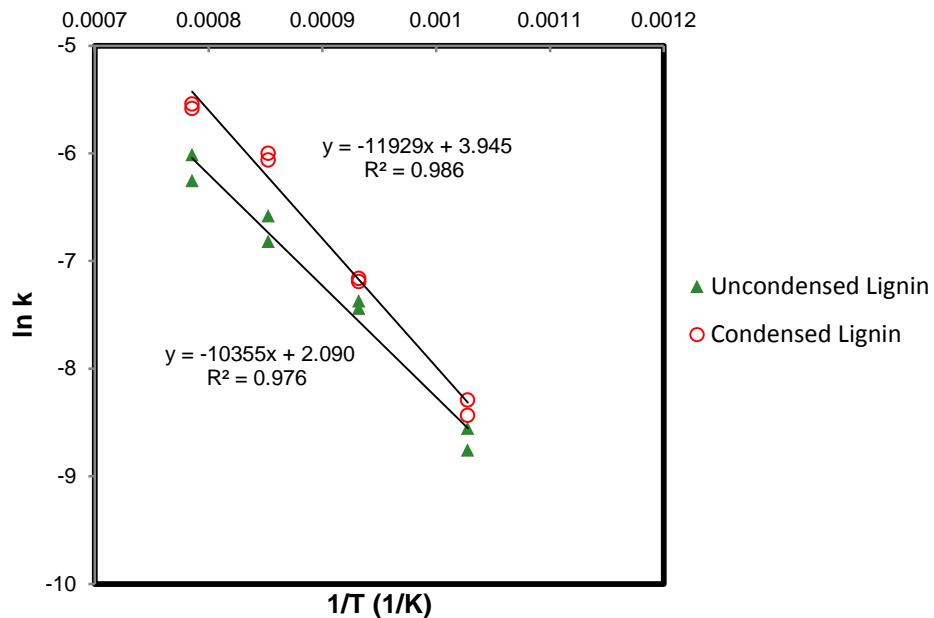


Fig. 6. An Arrhenius plot for steam gasification of char derived from condensed and uncondensed lignin

With respect to the char conversion, the reaction order was found to be zero, which is similar to results calculated by previous studies on other biomass chars (Di Blasi 2009; Mani *et al.* 2011; Wang and Kinoshita 1993). The activation energies for CO₂ gasification (94 to 112 kJ/mol) and steam gasification (86 to 100 kJ/mol) were, on the other hand, relatively low in comparison with other biomass chars. For instance, the activation energy of CO₂ gasification of biomass materials has been reported to be in the range of 200 to 300 kJ/mol, and that of steam gasification has been reported to be between 170 and 250 kJ/mol (Di Blasi 2009; Klose and Wölki 2005; Wang and Kinoshita 1993). However, the values obtained are close to the activation energy of the lignin materials: Iwaki *et al.* (2004), for example, reported activation energies of 100 to 120 kJ/mol for steam gasification. The lower activation energy is probably due to the large amount of alkali metals present in the materials, which catalyze the gasification process (Li and van Heiningen 1990).

Effect of temperature

Temperature affects both the rate constants and the duration of the gasification reaction when biomass char is gasified. Figures 2 through 5 show the carbon conversion obtained at temperatures between 850 and 1050 °C for condensed and uncondensed lignin material. 70% was converted during 50 min at 850 °C, and at 950 and 1050 °C, complete conversion was achieved when CO₂ was used as gasifying media. For steam, the conversion, especially at the lower temperatures, was faster and there was a

conversion of between 20 and 30% already at 700 °C (for CO₂ gasification this number was below 15% at 750 °C).

CONCLUSIONS

1. The CO₂ and steam gasification reactions followed a zero-order reaction rate, based on the carbon conversion and constant partial pressure of the gasifying media. Taking the Ergun mechanism into account, the reaction rate equation was determined to be an Arrhenius expression.
2. The maximum char conversion was achieved for both samples at the highest temperature (1050 and 1000 °C for condensed and uncondensed lignin, respectively). Activation energies in the range of 85 to 115 kJ/mol were determined.
3. The values calculated in this study are comparable to reaction rates determined by other researchers for the gasification of biomass chars and lignin materials at similar temperatures.

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