



A systematic study of the kinetics of lignin pyrolysis

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ABSTRACT

The pyrolysis kinetics of four types of lignin (Alkali lignin, Hydrolytic lignin, Organosolv lignin, and Klason lignin) were investigated using thermogravimetric analysis (TGA). Kissinger's method was used to derive the kinetic parameters (activation energy, order of reaction and frequency factor). It has been shown that the pyrolysis of all the lignins except Klason lignin was first order with respect to solid decomposition, while for Klason lignin, the reaction had an order of 1.5. The activation energy depends on both separation methods and the plant species from which the lignin was isolated, while the frequency factor did not indicate the dependence of either plant species or separation methods.

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1. Introduction

Lignin is one of the three main components of lignocellulosic materials (the other two are cellulose and hemicellulose). It is the major by-product of second generation bioethanol production and is a major impurity in the separation of cellulose from wood for pulp and paper, therefore attracting considerable interest as a potential source of aromatic hydrocarbons for biofuels and chemicals due to its aromatic nature. Conversion of lignin into valuable products is attracting an increasing attention and this subject is being currently reviewed to be published shortly. The interest in pyrolysis conversion is illustrated by claims of up to 51 wt.% yield of phenol and alkyl phenol from lignin on a dry basis [1].

Various methods have been developed to separate lignin in lignocellulosic materials. Since each separation method modifies to some degree the chemical structure of the naturally occurring lignin, lignin is conventionally named after the method of separation. The separation methods can be divided into two basic categories [2]: dissolution of lignin into a solution; hydrolysis of cellulose and hemicellulose by acids leaving lignin as an insoluble residue.

In the first category, some important lignins are listed as follows, all of which are co-produced in the pulp and paper industry.

- **Alkali lignin.** NaOH solution is used at elevated pressure and temperature to break the linkages with polysaccharides, and then

lignin fragments dissolve in the solvent, forming black liquor. When the alkali losses are made up by Na_2CO_3 , the lignin separated from black liquor is called soda lignin [2]. When the alkali losses are made up by Na_2SO_4 , the lignin separated from black liquor is called Kraft lignin [2].

- **Lignosulfonates.** An aqueous solution containing sulphur dioxide and a salt of sulphurous acid is used to break the linkages with polysaccharides at elevated pressure and temperature. The lignin fragments dissolve in the solvent forming brown liquor. The lignin separated from the brown liquor is called lignosulfonate [2].
- **Organosolv lignin.** An organic solvent such as methanol or ethanol containing a suitable catalyst such as HCl is used to break the linkages with polysaccharides and the lignin fragments dissolve in the solvent. This overcomes the pollution caused by sulphur containing inorganic compounds. Four main processes are now used and the Organosolv lignin is named after each process, Alcell lignin [3], ASAM lignin [4], Organocell lignin [5] and Acetosolv lignin [6].
- **Milled wood lignin.** Wood is milled in a ball-mill for tens of hours to mechanically break the linkages with polysaccharides. The lignin fragments become soluble in some solvents such as 0.2 mol/L NaOH solution and then the dissolved lignin is separated by extraction using dioxane–water mixture [7].

Some important lignins in the second category are listed as follows:

- **Klason lignin.** 72% sulphuric acid is used to hydrolyze nearly all the polysaccharides leaving solid lignin. This method has become one

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Table 1
Kinetic parameters for the pyrolysis of various lignin, cellulose and hemicellulose.

	Method	Temperature range (°C)	Kinetic parameters		
			E (kJ/mol)	n	A (min ⁻¹)
Lignin					
Klason lignin (Douglas fir) [14]	TG (non-isothermal, single heating rate)	25–600	79.8 ± 4.2	1	
Periodate lignin (spruce) [14]	TG (non-isothermal, single heating rate)	20–600	54.6 ± 4.2	1	
Kraft lignin (pine) [11]	Microwave reactor (isothermal)	160–680	25.2	1	4.7 × 10 ²
Milled wood lignin (sweetgum hardwood) [15]	Microreactor (fixed bed)	500–1000	82.0	1	2.0 × 10 ⁷
Kraft lignin (unknown species) [16]	TG (non-isothermal, 3 heating rates)	25–800	129–361	1	3.3 × 10 ⁷ to 1.8 × 10 ⁹
Alcell lignin (unknown species) [16]	TG (non-isothermal, 3 heating rates)	25–800	80–158	1	6.2 × 10 ¹¹ to 9.3 × 10 ²²
Steam exploded lignin (aspen) [17]	TG (non-isothermal, 4 heating rates)	25–800	58.6–291.6	1.09	2.7 × 10 ⁸
Klason lignin (three types of hardwood) [18]	TG (isothermal, 7 constant temperatures)	226–435	12.5, 39.4, 42.6	0.5	
Lignin (unknown type and species) [19]	TG (non-isothermal, single heating rate)	390–500	70.7	1	1.26 × 10 ⁷
Organosolv lignin (Eucalyptus) [20]	TG (non-isothermal, single heating rate)	30–900	19.1–42.5	0.30–0.74	
Lignin (unknown type, birch) [21]	Microreactor (fixed bed)	300–600	75 ± 11	1	1.2 × 10 ⁶
Alkali lignin (bamboo + hardwood) [22]	TG (non-isothermal, 3 heating rates)	25–900	47.9–54.5	1	6.8 × 10 ² to 6.6 × 10 ⁴
Alcell lignin (hardwood) [23]	TG (non-isothermal, single heating rate)	25–300	8.5–67.9	1	
Lignin (unknown type and species) [24]	TG (non-isothermal, 4 heating rates)	25–600	120.7–197.3	1	1.0 × 10 ⁸ to 5.5 × 10 ¹²
Alcell lignin (hardwood) [25]	TG (non-isothermal, 3 heating rates)	25–700	83–195	1	
Cellulose					
Avicel cellulose [26]	TG (non-isothermal, single heating rate)	200–900	244.0	1	8.9 × 10 ⁶
Avicel cellulose [27]	TG (non-isothermal, single heating rate)	200–900	242.6	1	8.9 × 10 ⁶
Hemicellulose					
Xylan [28]	TG (non-isothermal, single heating rate)	200–400	193.0/110.0	1	2.4 × 10 ⁶

Note: the first order of reaction in the table was not derived from the experimental. It was just an assumption made by the authors for facilitating the derivation of activation energy.

of the standard methods for the determination of lignin in wood [8].

- *Hydrolytic lignin*. Dilute acid is used to hydrolyze most of the polysaccharides to produce fermentable sugars, leaving lignin as a solid by-product [9].

Fast pyrolysis is one of the conversion processes for lignin that will potentially lead to more valuable phenol and phenolics. It has been extensively studied in the last few decades, from microscale reactors such as grid reactor [10], microwave reactor [11] and Pyroprobe[®] [12] to fluid bed [13] and fast fluidised twin bed reactors [1]. Most of the previous research focused on product distribution from pyrolysis to achieve higher yields of phenols.

Understanding the kinetics of pyrolysis of lignin is important to better understand the underlying processes and to provide useful information for rational design and scaling-up of pyrolysis reactors. However, there has been no systematic research into the kinetics of lignin pyrolysis. Table 1 lists the kinetic parameters that have been published in the literature. The kinetic parameters for pyrolysis of cellulose and hemicellulose are also included in Table 1 for comparison.

As can be seen from Table 1, only one or two types of lignins were investigated in most publications. This makes it rather difficult to compare the data for different lignins, because different conditions and analytic methods were employed to achieve the data. The most uncertain parameter is the order of reaction, since most researchers assumed a first order reaction and then derived the activation energy and the frequency factor. Large variations exist in the reported activation energy. In order to better fit kinetic prediction with experimental data, some researchers employed distributed activation energy model (DAEM) [16,17,23–25], which is a regression method to correlate the change of activation energy with conversion. Although this model is helpful for engineering computation, it is difficult to use the kinetic data to interpret reaction mechanism due to the empirical nature. Moreover, no detailed discussion was given about the kinetic parameters from a point of view of reaction mechanism in the publications.

Two methods were used to obtain the kinetic parameters, thermogravimetric analysis (TG) and microreactor method. A significant advantage for TG is that heat and mass transfer effects can be avoided, while the transport effect is usually present in microreactors so that accurate kinetic parameters are difficult to achieve. The activation energies obtained using a microreactor in Table 1 are smaller than those obtained using TG, which may arise from the transport effect [16]. For using the TG method, there are two techniques, isothermal and non-isothermal (dynamic). The advantage of the latter is that less experimental data is needed [29].

The aim of the present work is to make a systematic investigation of the pyrolysis kinetics of various types of lignins using dynamic TG technique so that the effects of both separation method and origin on lignin pyrolysis may be better understood through comparison.

2. Experimental

2.1. Materials

Four types of lignin were used: Alkali lignin, Hydrolytic lignin, Organosolv lignin and Klason lignin. Alkali lignin was provided by Asian Lignin Manufacturing (India) with a commercial name Protoband 1000, which was produced from wheat straw and sarkanda grass using a soda process. Hydrolytic lignin was provided by Eteknik (Sweden) with the commercial name Etek lignin. Both Asian lignin and Etek lignin were included in a Round Robin exercise between several European institutes and the results from this will be published separately. Organosolv lignin was purchased from Sigma–Aldrich (UK), which was separated from hardwood. Another Organosolv lignin, Alcell lignin, was provided by Energy Research Centre of the Netherlands (ECN), which was separated from hardwood. Klason lignin was prepared in our laboratory using the standard Klason method [8]. Five Klason lignins were separated respectively from beech, willow, mixed softwood, cassava stalk and cassava rhizome (Cassava is a woody shrub of the *Euphorbiaceae*, cultivated as annual crop).

The Klason lignin was prepared as follows: 5 g of materials was extracted using a sequence of 95% ethanol–toluene (1:2, v/v) for 6 h,

95% ethanol for 4 h and distilled water for 2 h by Soxhlet system. The extracted materials were then pressed and washed with acetone and dried in an oven overnight at 105 °C. 72% sulphuric acid was used to hydrolyze the extractive free sample at a ratio of 20 ml/g at 20 °C with occasional stirring, and then 765 ml of distilled water was added and reflux for 4 h. The resulted solution was filtered and the solid residue was washed with 500 ml of distilled water and dried in the oven at 105 °C for a week.

2.2. TG analysis

The lignin was ground to a particle size less than 38 μm for thermogravimetric analysis. Approximately 2.5 mg of sample was placed into a ceramic sample pan. The thermogravimetric analysis was performed with a Perkin Elmer Pyris 1 TG Analyser. The experiments were conducted in nitrogen at a flow rate of 30 cm³/min. The sample was held at 105 °C for 10 min, and then heated from 105 to 900 °C at a linear heating rate of 2–200 °C/min. Seven different heating rates were used. The reported data was on dry and ash-free basis (see Eq. (2)).

2.3. Derivation of kinetic parameters from TG experiments

The decomposition rate of solid materials can be modelled using Eq. (1) when reaction rate is expressed by the disappearance of the solid.

$$\frac{d\alpha}{dt} = k(1 - \alpha)^n \quad (1)$$

where α is the fraction of solid materials decomposed at time t , which is defined using Eq. (2), n is the order of reaction to the unreacted material, and k is the rate constant given by Arrhenius Eq. (3).

$$\alpha = \frac{W_0 - W}{W_0 - W_{\text{ash}}} \quad (2)$$

where W_0 is the original weight, W_{ash} is the ash content in the sample and W is the weight at time t .

$$k = A \exp\left(-\frac{E}{RT}\right) \quad (3)$$

where A is the frequency factor, E is the activation energy and T is the reaction temperature (K). Substitution of Eq. (3) into Eq. (1) yields

$$\frac{d\alpha}{dt} = A \exp\left(-\frac{E}{RT}\right) (1 - \alpha)^n \quad (4)$$

For a linear heating rate, $\beta = dT/dt$, Eq. (4) becomes

$$\frac{d\alpha}{dT} = \left(\frac{A}{\beta}\right) \exp\left(-\frac{E}{RT}\right) (1 - \alpha)^n \quad (5)$$

A number of methods have been developed for deriving the kinetic parameters A , E and n from dynamic TG experiments based on Eq. (5). Generally, the methods can be divided into integral methods such as those of Coats and Redfern [30] and Ozawa [31] and differential methods such as those of Kissinger [32], Friedman [33], Freeman and Carroll [29] and Borchardt and Daniels [34] depending on whether the integral or differential form of Eq. (5) is used. Integral methods and some differential methods such as Freeman and Carroll [29] and Borchardt and Daniels [34] are based on a single heating rate experiment, which may bring errors into the kinetic parameters for complex reactions. Friedman's [33] and Kissinger's methods [32] use multi-heating rates. Friedman's method calculates the kinetic parameters at various conversions and then takes the average as the parameters of the overall reaction. The DAEM model regresses the activation energy with conversion [16,17,23–25] instead of taking the average. Kissinger's method

derives the activation energy using the peak temperature at which the maximum reaction rate occurs and the order of reaction using the shape of the mass loss–time curve. Kissinger's method was adopted to calculate kinetic parameters in this work.

Kissinger's method is based on the fact that the reaction rate $d\alpha/dt$ will rise to a maximum value with an increase in reaction temperature (for detailed derivation see Ref. [32]). Activation energy E is obtained from the slope of $\ln(\beta/T_m^2)$ against $1/T_m$ ($=-E/R$). The order of reaction n is determined by Eq. (6).

$$S = 0.63n^2 \quad (6)$$

where S is defined by Eq. (7). The value of S can be determined from the derivation of DTG curve. After getting the values of n and E , the frequency factor A can be solved from Eq. (5).

$$S = \left| \frac{(d^2\alpha/dT^2)_{\text{left}}}{(d^2\alpha/dT^2)_{\text{right}}} \right| \quad (7)$$

3. Results and discussion

Fig. 1 shows the relationship between the yield of char and the type of lignin using the TG traces of the heating rate of 200 °C/min as an example (other heating rates have similar characteristics). It is clearly seen that the TG traces are clustered into three groups. The five Klason lignins had a char yield of 40–45% (wt.). Asian lignin, Organosolv lignin and Alcell lignin had a char yield of about 30% (wt.). Etek lignin had a char yield of 22% (wt.).

The nine lignins were separated from different plant species. Organosolv lignin, Alkali lignin, and Etek lignin have similar chemical structures [35,36]. The Klason lignins were isolated using concentrated sulphuric acids, which is believed to cause considerable condensation reactions to the lignin [7]. The difference in chemical structures is believed to be responsible for the different yields of char.

Fig. 2 shows the DTG curves of the lignins at various heating rates. All the curves contain a strong peak, which was attributed to the primary pyrolysis. The peak shifted towards higher temperature with an increase in heating rate. Asian lignin had a shoulder at a lower temperature, which also shifted towards higher temperature with the increase in heating rate. After an isoconversional kinetic analysis [37], the activation energy of all the lignins depends on conversion (α), showing that the pyrolysis of lignins is not a single chemical process. Nevertheless, when isoconversional methods such as Friedman's method were used, the order of reaction usually had a value of greater than 3, which is odd for solid decomposition

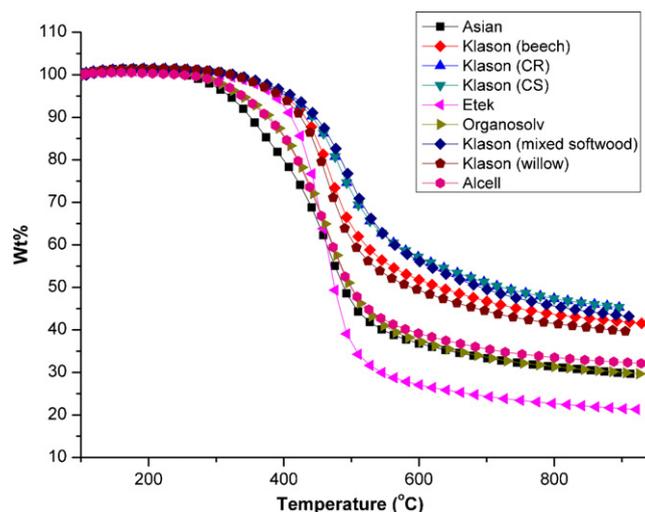


Fig. 1. TGA traces for various lignins at a heating rate of 200 °C/min.

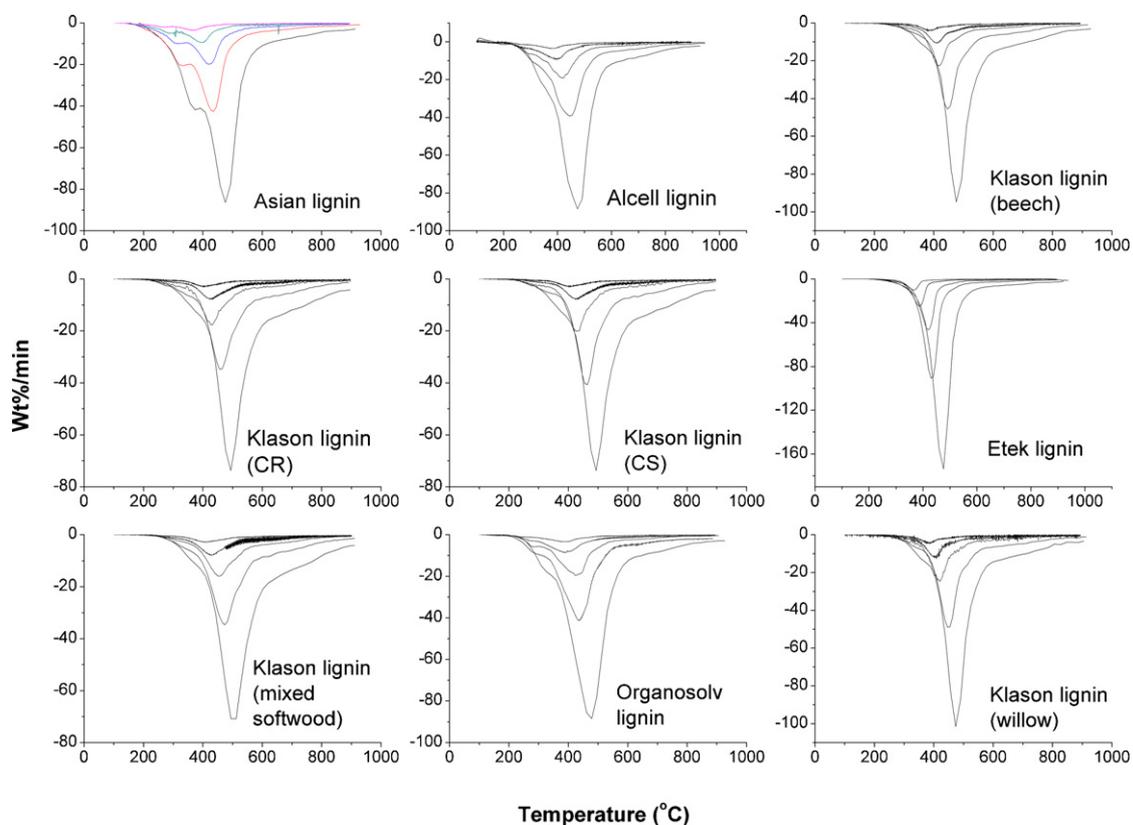


Fig. 2. DTG curves for various lignins at different heating rates. The larger the peak on the curve, the higher is the heating rate.

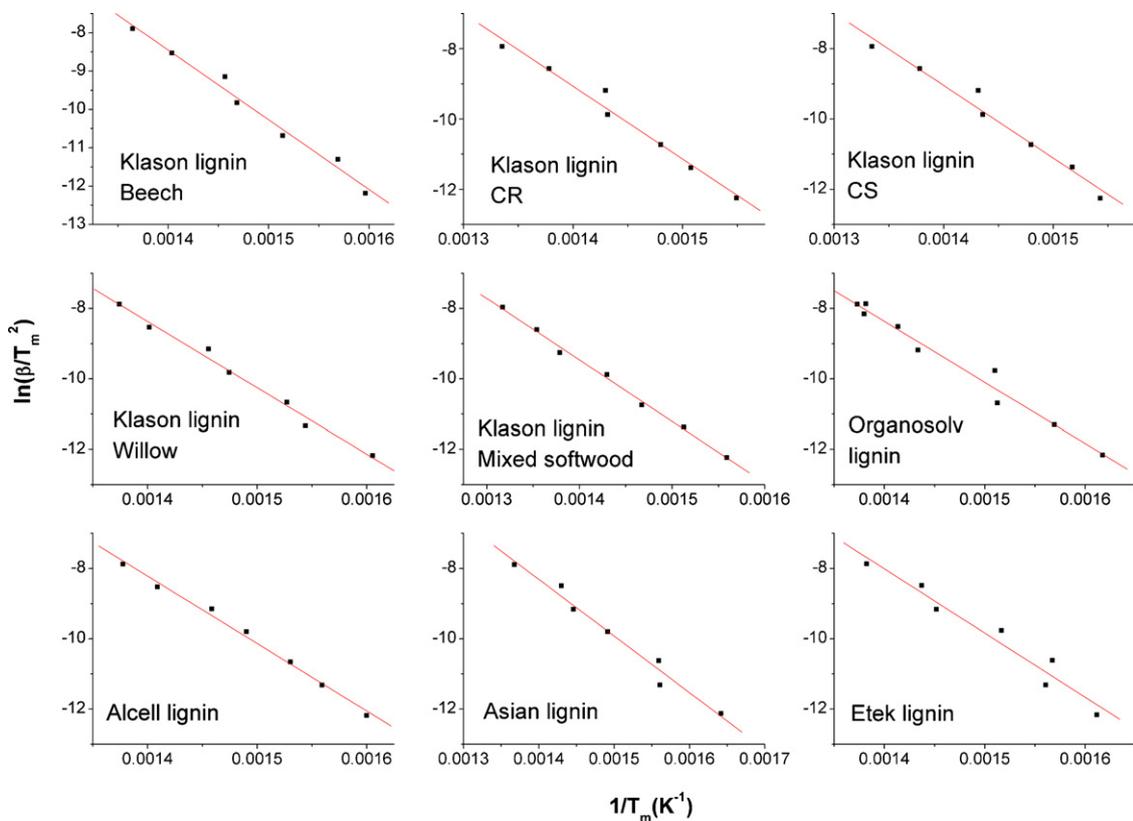


Fig. 3. Plot of $\ln(\beta/T_{m, \max}^2)$ against $1/T_m$ for the lignins in this work. The line represents the linear regression of the points.

Table 2
Shape index of the DTG curves of the lignins at various heating rates.

Heating rate (°C/min)	Lignin								
	Alcell	Asian	Klason (Beech)	Klason (Cassava rhizome)	Klason (Cassava stalk)	Etek	Klason (Mixed softwood)	Organosolv	Klason (willow)
2	0.745	0.758	1.691	1.430	1.632	0.607	1.269	0.607	1.552
5	0.581	0.869	1.124	1.606	1.858	0.640	1.290	0.563	1.662
10	0.567	0.658	1.130	1.908	1.450	0.589	1.342	0.530	1.480
25	0.686	0.563	1.191	1.713	1.161	0.540	1.161	0.640	1.463
50	0.806	0.579	1.056	1.381	1.169	0.686	1.127	0.540	1.404
100	0.818	0.698	1.399	1.474	1.446	0.884	1.432	0.509	1.272
200	0.868	0.823	1.608	1.568	1.599	0.891	1.463	0.791	1.539
Average	0.724	0.707	1.314	1.583	1.474	0.691	1.300	0.622	1.482
SDEV	0.119	0.117	0.254	0.182	0.252	0.142	0.127	0.225	0.123

reactions. On the other hand, the overall pyrolysis behaviour may be represented by the kinetic behaviour at the primary peak since the height of the shoulder was much smaller compared with the primary peak. This paper intends mainly to compare the kinetic behaviour of various lignins with different delignification methods and plant species so that the difference in their chemical structures may be revealed. Therefore, the kinetic parameters at the primary peak temperatures were calculated using Kissinger's method.

The kinetic parameters for the lignins were calculated using the Kissinger's method. The maximum temperature T_m at various heating rates was obtained from the DTG curves. $\ln(\beta/T_m^2)$ was then plotted against $1/T$ for each lignin (Fig. 3). There was a good degree of linearity for each lignin. Table 2 lists the shape index S of all the DTG curves. The value of S was similar at different heating rates for the same lignin, indicating that the order of reaction n did not vary significantly with heating rate. An average of the shape index was used for calculating the order of reaction using Eq. (6). The frequency factor was calculated using Eq. (5) after obtaining the values of E and n . The kinetic parameters E , A and n are given in Table 3.

It can be seen from Table 3 that the activation energies of the lignins were in the range of 130–175 kJ/mol. Unlike char production, the activation energy depends on both plant species and separation methods. The activation energy was different for lignin from different plant species with the same separation method as shown by the five different Klason lignins. The activation energy was also different for the lignins from similar species with different separation methods as shown by comparison Etek lignin with Klason lignin from mixed softwood.

The lignin from straw and grass (Asian lignin) had the lowest activation energy of 134 kJ/mol. The lignin from wood (both hardwood and softwood) had activation energy of 144–159 kJ/mol. The lignin from cassava had the highest activation energy of 172 kJ/mol. The monomers for softwood lignin are mainly *p*-coniferyl alcohol, while hardwood lignin has both sinapyl alcohol and *p*-coniferyl alcohol. The lignin from straw and grass contains a small percentage of *p*-coumaryl and other monomers [38] apart from *p*-coniferyl alcohol and sinapyl alcohol. The variation of the percentage of the

three monolignols may be the reason for the difference in activation energy of pyrolysis. The monomer composition determines the percentage of various linkages in lignin, which need different energies to break down.

It is interesting to compare the kinetic activation energy obtained in this work with the literature value listed in Table 1. Klason lignin has a higher value of 140–170 kJ/mol in this work than the literature value, which ranges from 12.5 to 79.8 kJ/mol. This may be caused by the erroneous assumptions of the first order reaction by other researchers. For the other types of lignin, when a single heating rate experiment was used to derive activation energy in the literature [14,16,20,23], the values are much lower than those of this work. When multi-heating rate experiments were used to derive activation energy in the literature [16,24,25], the activation energy of this work is in the range of the literature values. The only exception is Ref. [22], which used multi-heating rate experiments to obtain an activation energy of 47.9–54.5 kJ/mol, which is much lower than those of this work. The activation energy determined using microreactor had a lower value than those of this work, which may be due to the transport effect [16].

As shown in Table 3, Alcell lignin, Organosolv lignin, Etek lignin and Asian lignin had an order of reaction of 1.0, while Klason lignin had an order of reaction of 1.5. The order of reaction depends strongly on the separation method, but slightly on plant species. These orders agree well with typical solid decomposition reactions [30]. The order of reaction can be explained tentatively as follows: pyrolysis of lignin proceeds in a free-radical pathway [39,40]. There are a larger proportion of ether linkages (β -O-4 and α -O-4) in Organosolv lignin, Alkali lignin and Hydrolytic lignin [7], the ether bonds are liable to break due to its lower bond energy, forming large free radicals. These large free radicals then undergo uni-molecular decomposition, forming products. Klason lignin has much less ether bonds due to its condensed structure [7,41], the free radicals may be formed predominantly by scission of side chains such as the splitting of methyl radicals (CH_3) from methoxyl groups on the benzene ring, and the splitting of hydroxyl radicals (OH) from side propanoid chains. Since these radicals are small, they abstract hydrogen from

Table 3
Kinetic parameters derived for the various lignins in this work.

	Kinetic parameters		
	E (kJ/mol)	n	$\ln A$ (the unit of A is min^{-1})
Alcell lignin (hard wood)	159.5	1.07 ± 0.11	28.50 ± 0.13
Asian lignin (straw and grass)	133.9	1.06 ± 0.11	23.92 ± 0.24
Organosolv lignin (hardwood)	144.2	1.01 ± 0.16	25.68 ± 0.29
Etek lignin (softwood)	151.9	1.04 ± 0.17	27.37 ± 0.37
Klason lignin (beech, hardwood)	151.1	1.43 ± 0.18	26.80 ± 0.20
Klason lignin (cassava rhizome)	172.2	1.58 ± 0.12	29.87 ± 0.24
Klason lignin (cassava stalk)	171.7	1.53 ± 0.16	29.81 ± 0.26
Klason lignin (mixed softwood)	145.2	1.44 ± 0.08	24.78 ± 0.10
Klason lignin (willow)	156.5	1.53 ± 0.08	27.82 ± 0.17

other places to form methane and water. According to the classical theory for the kinetics of chain reactions [42], the former (uni-molecular decomposition) has an order of reaction of 1.0, while the latter (bimolecular reaction) has an order of reaction of 1.5.

The frequency factor did not vary significantly among the lignins. It is also difficult to find any relationship with separation method or plant species. Frequency factor is a reflection of the frequency of collisions between reacting molecules [42]. From the discussion of the reaction order, it is known that the decomposition of Klason lignin involves more free radicals with small sizes, and the decomposition of other lignins involves free radicals with large sizes. The collision number should be larger for free radicals with smaller sizes. However, the free radicals with larger size undergo uni-molecular reactions, while free radicals with small sizes are involved in bimolecular reactions. The lower collision number of large free radicals may be compensated by the higher efficiency of uni-molecular reactions, leading to similar frequency factors.

It is also interesting to compare the kinetic parameters of lignin with those of cellulose and hemicellulose listed in Table 1. Except for Klason lignin, all the other types of lignin have the same reaction order of 1.0 as cellulose and hemicellulose. However, they have different activation energies. Cellulose has the highest activation energy, while hemicellulose has similar activation energy as lignin in this study. Cellulose is a semi-crystalline material, while lignin and hemicellulose are non-crystalline, so the pyrolysis of cellulose must first destroy the lattice of crystals that needs energy, leading to higher activation energy.

4. Conclusions

In this work, the pyrolysis kinetics of nine lignins separated with different methods and from different plant species were investigated using thermogravimetric analysis. The following conclusions were reached from this systematic study.

- Volatiles and char production depends on the lignin separation method. Organosolv lignin, Hydrolytic lignin and Alkali lignin have similar volatiles production, which is greater than from Klason lignin.
- Activation energy depends on both the plant species from which the lignin is separated and the separation method.
- The order of reaction depends strongly on the separation method, but slightly on the plant species. Klason lignin has an order of reaction of 1.5, most probably due to its 'condensation structure'. The other lignins have a first order reaction due to their less modified chemical structure.
- The frequency factor changes to a lesser extent and is independent of both plant species and separation methods, which reflects the free radical nature of the pyrolysis reactions.

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