Full Length Article

The thermal degradation of lignocellulose biomass with an acid leaching pre-treatment using a H-ZSM-5/Al-MCM-41 catalyst mixture

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ABSTRACT

Improvements on the pyrolysis process of biomass fuels are needed to obtain a high-quality of bio-oil. Pre-treatment by acid leaching prior to the pyrolysis process is considered to remove Alkali and Alkaline Earth Metal (AAEM) from the biomass, since AAEM adversely affect the catalytic pyrolysis process. Therefore, the main objective of the present work was to determine and compare the effect of mixed-catalysts consisting of H-ZSM-5 and Al-MCM-41, which are used at different ratios in lignocellulose biomass pyrolysis via Thermal Gravimetric Analysis (TGA) for both, un-leached and leached biomass. In addition, the activation energies have been determined based on the solid-state reaction mechanism. The results from the acid leaching treatment showed that the optimum leaching process was set to 30 min, 30 °C and 5 wt% acetic acid in the leaching liquid. This resulted in 59%, 95%, 99%, and 96% reduction degree of Calcium (Ca), Magnesium (Mg), Potassium or Kalium (K), and Sodium (Na), respectively. The Higher Heating Values (HHVs) for un-leached and leached biomass were 19.42 and 19.14 MJ/kg, respectively, calculated by using the Milne formula. The HHV value is not significantly influenced by the acid-leaching pre-treatment. Thermogravimetric analysis showed similar trends for the mass loss as a function of temperature and four stages could be determined from the thermal degradation of biomass. There was no significant shift in the temperature profiles between un-leached and leached biomass degradations. However, the removal of AAEM significantly affected the degradation of hemicellulose, cellulose, and lignin. A 12.4–18.2% increase of mass losses could be found in Phase 2 for leached biomass, compared to un-leached biomass. The mass losses in Phase 2 also increased with increased heating rates. From the un-leached biomass experiments using a catalyst mixture, the percentage of mass loss increased from 64.95 wt% at 10 K min⁻¹ to 68.33 wt% at 50 K min⁻¹. Moreover, for the leached biomass, it rose from 65.71 wt% at 10 K min⁻¹ to 66.73 wt% at 30 K min⁻¹, before decreasing to 62.44 wt% at 50 K min⁻¹. A lower mass loss in Phase 4 for leached biomass compared to un-leached biomass showed the influence of an AAEM removal. The second order (F2) mechanism was able to illustrate the catalytic pyrolysis process, proven by the result that the coefficient of determination (R²) was higher than 0.99, which was high compared to other mechanisms. An acid leaching pre-treatment led to a reduction in the activation energies. The activation energies for the un-leached biomass were 26.94 and 25.56 kJ mol⁻¹ at a heating rate of 10 K min⁻¹ for a process without and with a catalyst mixture, respectively. The activation energies for leached biomass were 24.05 and 21.80 kJ mol⁻¹. The results also showed that the use of the acid leaching process as a treatment prior to catalytic pyrolysis is positive, since it resulted in high devolatilization and reaction rate.

1. Introduction

The emissions of carbon dioxide from fossil fuels and industry rose by 1.6 percent from 35.7 gigatons CO₂ in 2016 to 36.2 gigatons CO₂ in 2017. Further, the Global Carbon Project reported 2.7 percent increase in 2018, giving a record 37.1 gigatons CO₂ [1]. Displacing fossil fuels with a low-carbon fuel or energy source is one of the ways to reverse the

upward trend in CO₂ emissions. Worldwide, the growth in renewable energies is encouraging [2]. Biomass is considered to be one of the replacement options with a 14% contribution towards the world annual energy consumption [3], in comparison to coal and gases with 12% and 15% contributions, respectively [4]. In addition, biomass as renewable source is able to reduce the emission of carbon dioxide as a greenhouse gas [5]. The production of bio-oil, also known as biofuel, from biomass

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can alleviate the demand for petroleum products [6] and contribute to decarbonisation, especially for the transport sector [7].

The lignocellulose biomass is recognized for its availability to cover the global energy demand [8]. It is also known as scalable, economically viable, and potential carbon neutral feedstock for the production of bio-oil [9]. Thermochemical conversion is known as a method to convert the lignocellulose biomass into liquids, gas fuels, and high-value chemicals [10]. One of the most promising methods that directly can produce bio-oil from lignocellulose biomass is pyrolysis. The pyrolysis process runs in the absence of oxygen. However, the resulted bio-oil from a pyrolysis process contains high oxygenated compounds. Also, the physicochemical properties of the liquid are acidic and thermally unstable, which limits its application in engines and traditional refineries [11]. Therefore, it is advantageous to use catalysts in the pyrolysis process to get a high-quality bio-oil [12].

In order to decrease the content of oxygenated compounds in the bio-oil, zeolites and mesoporous catalysts can be used [13,14]. Numerous researchers [15–19] studied the catalytic pyrolysis of lignocellulose biomass using ZSM-5 and found that ZSM-5 promoted the deoxygenation forming aromatic hydrocarbons [12]. These findings imply that the quality of pyrolysis oil can be upgraded by introducing ZSM-5 in the pyrolysis process. However, due to its porosity, ZSM-5 is not able to break down the heavier oxygenates [20]. The larger molecules from lignin cannot penetrate the internal structure of ZSM-5 and leads to a coke formation. Further, the coke deposition will degrade the catalytic performance of ZSM-5.

As a comparison to the catalytic activity of ZSM-5, Al-MCM-41 as a mesoporous catalyst can facilitate the cracking of large molecules. However, the selectivity to aromatic compounds decrease due to the lack of micropores and the presence of large pores [20]. Hence, studies of catalyst selection and preparation methods remain broad, but the current paper focuses on the application of ZSM-5 and Al-MCM-41. The addition of ZSM-5 and Al-MCM-41 in the pyrolysis of lignocellulose biomass has the potential to break down the large molecules from biomass and resulted in high yield of organic liquid with the increasing quantity of phenols and hydrocarbons [20–26].

On the other hand, inorganic contaminants and ash species contained in lignocellulose biomasses have shown a point of consideration in thermochemical conversion. This is due to these compounds will adversely affect the catalytic pyrolysis process, catalyze undesired dehydration reactions during the pyrolysis process [27,28], as well as increase the yields of thermally derived char and non-condensable gases [29–31]. Therefore, the chemical pre-processing step, such as a dilute-acid leaching method, is preferred before the thermochemical process. The leaching process is expected to remove physiological ash components, alkali earth, and alkali metals that inhibit the thermochemical conversion [32,33]. Several attempts [34–36] have been made to investigate the aqueous fraction of pyrolytic liquids, including wood-derived acids, for demineralization of biomass. Acetic acid was chosen as a model compound for the biomass leaching process, since it is a major acid resulting from biomass pyrolysis [34,37,38]. Hence, the leached lignocellulose biomass is seen as a potential feedstock in the conversion of biomass to bio-oil.

A kinetic study has been conducted in order to have a better understanding of the catalytic performance of materials. Furthermore, a correct design and product yield control will be achieved by obtaining an increase knowledge of the kinetic process [39]. The reaction rates and activation energy can be determined by investigating some variables, such as temperature and the absence or the presence of catalysts [40,41]. Thermogravimetric analysis (TGA) is one of the techniques to determine the kinetic parameters and predict the thermal behaviors of lignocellulose biomass pyrolysis and catalytic pyrolysis [42,43]. TGA is known as a general approach to study the kinetic of decompositions since it has a great virtue of accuracy and the weight loss of the tested sample and reaction temperature are recorded continuously [44].

Over decades, there is vast literature on kinetic evaluation methods

of thermal analysis for biomass pyrolysis [40,45–48]. Zakrzewski [49] investigated the degradation of beech wood and its E_a (activation energy) for different kinetic models using data from thermogravimetric experiments. It was found that the diffuse kinetic models D3 and D4 were comparable with the experimental data, giving the activation energies of 175.8 and 168.3 kJ mol⁻¹, respectively [49]. Thermogravimetric-mass spectrometric analysis on combustion of xylan from beech wood was attempted by López-González, et al. [3]. They found the activation energies for xylan from beech wood were 128 and 125 kJ mol⁻¹ when using heating rates of 10 and 20 K min⁻¹, respectively [3]. Another study by Boukaous, et al. [50] examined the activation energy from the combustion of beech wood. They obtained an activation energy of 99.26 kJ mol⁻¹ for the temperature range of 245–339 °C and 79.51 kJ mol⁻¹ for 431–437 °C [50]. The different kinetic parameter values and conclusions were obtained through various operational conditions and models.

Previous studies by the authors [21,51] have primarily concentrated on the pyrolysis, the quality of products, as well as the kinetic aspects of un-treated biomass. There is a lack in the literature on kinetic studies of treated lignocellulose biomass using leaching. Moreover, for catalytic pyrolysis using a mixture of H-ZSM-5 and Al-MCM-41. Therefore, this study aimed to reduce the contents of the alkaline metals (K, Na) and alkaline earth metals (Ca, Mg) in the biomass as well as determine and compare the effect of a mixed-catalysts consisting of H-ZSM-5 and Al-MCM-41, which were used at different ratios in a lignocellulose biomass pyrolysis via TGA using both un-leached and leached biomass. This paper also presents the kinetic parameters, i.e. activation energies (E_a), calculated using the Arrhenius equation. Furthermore, the solid-state reaction mechanisms from nucleation models to reaction-order models have also been put into consideration to determine the effective mechanism for a catalytic pyrolysis of lignocellulose biomass using a mixture of H-ZSM-5 and Al-MCM-41.

2. Materials and methods

2.1. Lignocellulose biomass and catalysts

Lignocellulose biomass originating from beech wood was purchased from J. RETTENMAIER & SÖHNE GmbH + Co KG, Germany with a particle size of 300–500 µm. The powder catalysts of H-ZSM-5 and Al-MCM-41 were obtained from Alfa Aesar, Germany, and Nankai University Catalyst Plan, China, respectively.

2.2. Methods

2.2.1. Catalysts characterization

Prior to the catalyst characterization, the catalysts were calcined in a muffle furnace at 550 °C for 15 h and then dried in an oven at 110 °C for 12 h. The samples were outgassed at 250 °C for 3 h under vacuum before the measurements. A micromeritics ASAP 2020 instrument was used to measure the N₂ adsorption-desorption and the Brunauer-Emmett-Teller (BET) method was used to determine the surface area. Also, the micropore volume was obtained from the t-plot method. The physicochemical properties of the catalysts are shown in Table 1.

2.2.2. Physicochemical composition of lignocellulose biomass

The samples were prepared according to the EN ISO 14780 standard

Table 1
Properties of H-ZSM-5 and Al-MCM-41 catalysts.

Catalyst	Si:Al ratio (SAR)	BET Surface Area (m ² g ⁻¹)	Micropore Volume (cm ³ g ⁻¹)
HZSM-5	30	314.7320	0.1492
Al-MCM-41	25	957.5100	–

Table 2

Results of the test runs with different acetic acid concentrations and different temperatures at a l/s-ratio of 10:1.

Experiment Condition	Element Content (mg/kg d.b. ^a)				Leaching Efficiency ^{**} (wt%)			
	Ca	Mg	K	Na	Ca	Mg	K	Na
Un-leached lignocellulose	1790	385	1020	54				
A temperature of 90 °C, a residence time of 120 min, Acetic acid in leaching liquid:								
10 wt%	717 ± 42	10.1 ± 0.9	11.1 ± 1.6	< 2.0	60 ± 2	97 ± < 0.1	99 ± < 0.1	> 96
5 wt%	739 ± 45	16.1 ± 0.5	14.4 ± 3.2	2.4 ± 0.4	59 ± 3	96 ± 0.1	99 ± < 0.1	96 ± 1.0
1 wt%	987 ± 18	43.7 ± 1.8	13.9 ± 0.9	2.1 ± < 0.1	45 ± 1	89 ± < 0.1	99 ± < 0.1	96 ± 0.1
0.3 wt%	1098 ± 103	82.6 ± 5.0	34.2 ± 11.1	< 2.0	39 ± 6	79 ± 1.0	97 ± 1.0	> 96
A residence time of 30 min, 10 wt% acetic acid in leaching liquid, with temperatures of:								
30 °C	716 ± 16.6	14.0 ± 0.2	11.5 ± 0.4	< 1.6	60 ± 0.9	96 ± 0.1	99 ± < 0.1	> 97
60 °C	639 ± 66.2	12.7 ± 0.6	11.8 ± 0.5	< 1.6	64 ± 3.7	97 ± 0.2	99 ± < 0.1	> 97
90 °C	725 ± 4.6	10.5 ± 0.3	10.7 ± 0.5	< 1.6	59 ± 0.3	97 ± 0.1	99 ± < 0.1	> 97
A residence time of 30 min, 5 wt% acetic acid in leaching liquid, with temperatures of:								
30 °C	739 ± 73.5	20.8 ± 0.9	14.0 ± 1.4	1.9 ± 0.4	59 ± 4.1	95 ± 0.2	99 ± 0.1	96 ± 0.7
60 °C	773 ± 9.3	19.0 ± 0.7	13.3 ± 0.5	1.7 ± 0.1	57 ± 0.5	95 ± 0.2	99 ± 0.0	97 ± 0.3
90 °C	783 ± 13.6	17.1 ± 1.0	12.4 ± 0.9	2.0 ± 0.0	56 ± 0.8	96 ± 0.3	99 ± 0.1	96 ± 0.1

^a d.b.: dry basis.^{**} leaching efficiency = (1 – element concentration in the treated biomass/element concentration in the untreated biomass) * 100.**Table 3**

Properties of un-leached (L1) and leached lignocellulose (L2) biomasses for TGA experiments.

Analysis	L1	L2
<i>Proximate analysis</i>	<i>d.b.^a wt. %</i>	<i>d.b.^a wt. %</i>
Volatiles	84.2	88.3
Moisture	14.1	4.3
Ash	0.8	0.30
Fixed carbon ^b	0.9	7.1
<i>Ultimate analysis</i>	<i>d.b.^a wt. %</i>	<i>d.b.^a wt. %</i>
Carbon (C)	48.5	49.1
Hydrogen (H)	6.3	5.9
Oxygen (O) ^b	44.65	44.80
Nitrogen (N)	< 0.10	0.18
Sulphur (S)	0.026	0.012
<i>Elements</i>	<i>mg/kg d.b.^a</i>	<i>mg/kg d.b.^a</i>
Calcium (Ca)	1790	739
Magnesium (Mg)	385	20.8
Sodium (Na)	54.3	1.9
Potassium (K)	1020	14.0

^a d.b.: dry basis.^b Calculated by difference.

[52]. The moisture content of biomass was determined according to the EN ISO 18134 standard [53]. In addition, the EN ISO 16948 standard [54] was used to determine the C, H, and N contents. The ash content (loss of ignition at 550 °C) was determined according to the EN ISO 18122 standard [55]. The concentrations of major and minor elements as well as of S in the samples were determined by elemental analyzer LECO RC-612-C and multistep pressurized digestion of the samples, followed by detection applying inductively coupled plasma-optical emission spectroscopy (ICP-OES) (Arcos, Spectro). The chemical composition of un-leached lignocellulose biomasses (L1) is presented in Table 3.

2.2.3. Acid leaching experiment

The leaching was performed in aqueous solutions consisting of deionized water and acetic acid. The equipment consisted of a heated plate with a magnetic stirrer, a glass reactor (volume: 2L), a

Fig. 1. Test run set-up for the acid leaching experiment.

temperature measurement device inside the reactor, and a reflux condenser to recover liquids evaporated during leaching at enhanced temperatures. A Buchner funnel and a water jet pump were used to remove the leaching liquid from the biomass. In Fig. 1, the test run set-up for the leaching experiment is shown. The experiments were carried out in triplicate and standard deviation for each set of triplicates was calculated.

A leaching liquid of deionized water and acetic acid was prepared. The concentration of acetic acid in the leaching liquid was varied between 0.3 and 10 wt%. The leaching liquid was filled into the reactor and heated up to the desired reaction temperature using a continuous stirring. Then, the biomass was added in small batches (to avoid formation of granulates) under the stirring. Also, the stirring continued for the defined residence time. Thereafter, the stirrer and the heater were shut down and the reactor was cooled down to about 30 °C (to enable further handling). The suspension was shaken to re-suspend all solids and poured into the Buchner funnel and sucked with a water jet pump

through the filter. Then, the Buchner funnel was filled up again with fresh (deionized) water and the water was sucked through the water jet pump to displace the acid from the biomass cake. This was repeated until a constant pH value of 6–7 in the liquid downstream the water jet pump was reached.

2.2.4. TGA experiment

Prior to TGA experiments, the sample was dried in an oven at 110 °C overnight to reduce the water content. The samples were prepared by using fixed biomass loading and catalyst mass loading ratio (biomass: catalyst ratio of 1:1). The un-leached lignocellulose biomass was labelled L1, while the leached one was labelled L2. The variation of H-ZSM-5:Al-MCM-41 ratios were labelled as follows: H (1:0), HA-71 (7:1), HA-31 (3:1), HA-11 (1:1), HA-13 (1:3), and A (0:1).

The experiments were carried out in a Netzsch STA 449 F3 Jupiter equipment using the TGA/DTA configuration. Approximately 60 mg of the biomass/catalyst mixture was used for each run. A temperature program with specified heating rates, inert atmosphere flows, steam ratios and residence times were prepared with Proteus, the software of STA 449 F3 Jupiter. The following temperature program was used for each TGA run with Nitrogen (N₂) as an inert atmosphere.

- From the ambient temperature to 110 °C, at a heating rate of 10 °C/min, for sample drying (moisture removal);
- Isothermal drying at 110 °C, for 10 min (until constant mass is reached);
- Temperature raising from 110 to 900 °C (for pyrolysis and subsequent release of volatiles) at different heating rates (10, 20, 30, 50 °C/min), and
- Isothermal transformation at 900 °C for 10 min (to enhance the devolatilization process and production of char).

From an ambient temperature to 900 °C, an argon at a flow rate of 50 ml/min was used to keep the reacting atmosphere inert. The mass loss and mass loss rate were recorded online as functions of time and temperature. The TGA experiments were carried out in duplicate and showed good reproducibility.

2.2.5. Kinetic method

The solid-state reaction kinetics is studied by using the change in extent of reaction (α).

$$\alpha = \frac{m_0 - m_t}{m_0 - m_\infty} \quad (1)$$

where m_0 , m_t , and m_∞ are the initial masses of the samples, the mass of sample at time t , and the mass of sample at the end of a reaction, respectively.

By using the extent of reaction, the solid-state reaction rate can be described as follows:

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \quad (2)$$

The integral rate law is obtained by integrating the above equation:

$$g(\alpha) = kt \quad (3)$$

Introducing the Arrhenius equation for replacing $k(T)$ will give the temperature dependence of the rate constant as the following equation:

$$g(\alpha) = A \exp\left(\frac{-E_a}{RT}\right)t \quad (4)$$

where A and E_a are the pre-exponential factor and activation energy, respectively. The detailed integral method is describe elsewhere [56]. The calculation of E_a can be carried out by introducing various expressions for $g(\alpha)$ in Eq. (2). Data acquisition and data processing were carried out using Microsoft Excel. The different kinetic models for $g(\alpha)$ [41,57–62], commonly known as solid-state reaction mechanism, are

listed in Supplement S1.

3. Results and discussion

3.1. Leaching of alkali and alkaline earth metallic (AAEM) species

Kesalahan! Sumber referensi tidak ditemukan. show the results of the leaching tests at different acetic acid concentrations at a liquid to solid (l/s)-ratio of 10:1, a temperature of 90 °C, and a residence time of 120 min. It is apparent that a decrease of the leaching efficiency for Ca was observed to be connected to a reduction of the acetic acid concentrations. Leaching efficiencies of 60% and 59% and a decrease in Ca contents from 1790 mg/kg to 717 and 739 mg/kg were achieved when using 10 wt% and 5 wt% of acetic acid concentrations, respectively. Further reductions of the acetic acid concentrations led to a larger decrease in the leaching efficiencies and promoted an increase of the Ca contents. A leaching efficiency of 45% and a Ca content of 987 mg/kg were obtained when using a 1 wt% of acetic acid concentration, while an efficiency of 39% and a Ca content of 1098 mg/kg were reached when using a leaching process with a 0.3 wt% of acetic acid concentration. This finding provides an evidence that an acid leaching process is effective to lower the Ca content. As a comparison, Oudenhoven, et al. [63] investigated the leaching process for pine-wood, straw, and bagasse with demineralized water and the results showed that it was only possible to remove 20% of calcium using this process [63].

A decrease of the leaching efficiencies for Mg content was also noticed with a reduction of the acetic acid concentrations. By using an acetic acid concentration of 10 wt%, the leaching efficiency reached 97% with a significant reduction of the Mg content from 385 mg/kg to 10.1 mg/kg. A leaching process using a 0.3 wt% acid concentration gave an efficiency of 79% as well as a Mg content of 82.6 mg/kg. This was higher than that from a process using an acid concentration of 10 wt%. Although the differences of the leaching efficiencies when using 10 wt% and 5 wt% acetic acid concentrations in the leaching liquid slightly differed, a strong decrease when using 1 wt% and 0.3 wt% acetic acid prevailed.

The above findings contradict the results by Davidsson, et al. [64]. They found that the removal of alkali metals (Ca and Mg) when using acid leaching reached 70% at temperatures below 600 °C [64]. However, in the current study a 60% removal of Ca and a 97% removal of Mg was achieved at a temperature of 90 °C. A study by Wu, et al. [65] also attained a lower percentage of Ca removal (5–30 wt%) when using a water leaching process, as compared to the current study. Specifically, they only reached an 80% removal of the Mg content. The alkali earth metal (Ca and Mg) are hardly water-soluble [65]. Hence, higher leaching efficiencies are expected from an acid leaching compared to a water leaching. Nevertheless, the results of the current study agrees relatively well with the results of Davidsson, et al. [64] study showing that the acid leaching process does not completely remove the alkali metals. This is due to a strong bond of the compounds to the material. In the case of this study, 40% of Ca remained in the biomass after the completed leaching process.

The K content was reduced from 1020 mg/kg to a level below 15 mg/kg, corresponding to a leaching efficiency of 99%, when applying a minimum of 1 wt% acetic acid. The leaching efficiency decreased to 97% (on average 34.2 mg/kg) when using a 0.3 wt% acetic acid. For Na, leaching efficiencies of at least 96% were achieved for all tested concentrations of acetic acid. This resulted in a reduction of the Na contents from 54 mg/kg to values of less than 2.4 mg/kg. As compared to the leaching process with demineralized water [63], the leaching efficiency in this study was able to completely remove Na and K and reaching up to 96–99% efficiencies. Oudenhoven, et al. [63] obtained lower efficiencies than the present study, amounting to 75–90%.

The findings of Liu and Bi [66] supports the present findings. They

investigated the removal of Ca, Mg, Na, and K from pine barks by acid leaching using a 0.5 M HCl solution for 48 h at a temperature of 20 °C. They found that the removal efficiencies for Ca, Mg, Na, and K were 90, 98, 100, and 92%, respectively [65]. Although the results from the present study were lower than the findings of Liu and Bi [66], the present finding showed comparable results when using a weak acid, CH₃COOH, instead of a strong acid, e.g. HCl. Furthermore, the residence time was short, 2 h, as contrasted to 48 h in Liu and Bi's [66] study.

The influences of the temperatures and residence times on the leaching efficiency were investigated. The residence time was set to 30 min for all test runs, while the temperature was varied from 30 °C to 90 °C. The test runs were performed with acid concentrations of 10 wt% and 5 wt%, to reach the leaching efficiencies, as shown in the previous tests. The results of these test runs are shown in Table 2.

As shown in Table 2, there was no significant influence of the temperature on the Ca content at a residence time of 30 min. The leaching efficiencies varied between 59% and 64% when using a 10 wt% of acid concentration. Accordingly, a reduction of the Ca contents was observed from 1790 mg/kg to 725 and 639 mg/kg. In a process using an acid concentration of 5 wt%, the leaching efficiency was slightly lower than using an acid concentration of 10 wt%. The efficiency decreased with an increased temperature, from 59% with a Ca content of 739 mg/kg at 30 °C to 56% with a Ca content of 783 mg/kg at 90 °C.

For Mg, a trend of increasing leaching efficiencies with increasing temperatures was observed. In the case of a 10 wt% acetic acid, the Mg contents were reduced from 385 mg/kg to 10.5 and 14.0 mg/kg (leaching efficiencies 96–97%). The leaching efficiencies in the process when using an acid concentration of 5 wt% was slightly lower, namely 95–96%, as the Mg contents were reduced from 17.1 to 20.8 mg/kg.

The highest leaching efficiencies for K was noticed at all temperatures. The K contents in the treated biomass decreased with the increasing temperatures, namely from 1020 mg/kg to 14.0 and 12.4 mg/kg with an acid concentration of 5 wt% and to the range of 10.7–11.8 mg/kg with an acid concentration of 10 wt%.

The contents of Na in the leached biomass were reduced from 54.3 mg/kg to below 1.6 mg/kg when using an acid concentration of 10 wt% at all temperatures. This resulted in leaching efficiencies of more than 97%, while the Na content in a process with an acid concentration of 5 wt% scattered between 1.7 and 2.0 mg/kg and leaching efficiencies from 96% to 97% result.

Wigley [67], who investigated the influence of acid leaching with 1% nitric acid (HNO₃) on the torrefaction of *Pinus radiata*, found that 4 h was the minimum time for leaching of *P. radiata*. A shorter time than 4 h was assumed to be not sufficient to allow for the leaching solution to penetrate deeply into the biomass micropores, while a long residence time of 8 h gave no further reduction on the AAEM content. The present study provided an effective leaching method, giving more than a 55% of leaching efficiency for Ca and more than 95% efficiencies for Mg, K, and Na for a 30 min leaching process. Furthermore, leaching with a weak acid, CH₃COOH, would avoid environmental penalties, as compared to a process using strong acids, e.g. HNO₃. Nonetheless, in regards to the influence of temperatures, the above results are in the lines with the results by Wigley [67]. He found that an increase of the temperature from 30 °C to 90 °C had no significant advantage on the reduction of the AAEM content. Moreover, that an increase of the leaching temperature to 150 °C initiated a hydrolysis reaction, which was not a desirable effect [67].

The results of the present study suggest that the reduction of the residence time to 30 min as well as the decrease of the temperature to 30 °C have no significant influence on the leaching efficiency for both acetic acid concentrations (10 wt% and 5 wt%). The obtained leaching efficiencies from these processes were in the same range (59–99 wt%) as the results for a residence time of 120 min and a temperature of 90 °C.

To summarize, with respect to economic aspects, the leaching parameters to produce leached biomass for the TGA experiments were set to 30 min, 30 °C and 5 wt% acetic acid in the leaching liquid. At these parameters a significant reduction of the AAEM content in the leached biomass could be achieved (Ca: 59%, Mg: 95%, K: 99%, and Na: 96%).

3.2. Physicochemical parameters

The physicochemical analysis was carried out for the leached biomass. The results are compared to the physicochemical analysis for the un-leached biomass. As shown in Table 3, the samples contain low nitrogen (< 0.2 wt%) and sulfur (< 0.03 wt%) contents. This indicates that the risk for emission of toxic gases (NO_x, SO_x) is low.

The Higher Heating Value (HHV) is used to express the calorific value of the biomass, which indicates the amount of energy available from the biomass. The value is calculated by using the Milne formula [68]. The estimated HHV values of L1 and L2 samples are 19.42 and 19.14 MJ/kg, respectively. These values are higher than the HHV values of wood, which was investigated by Jahirul, et al. [69] (16 MJ/kg). A study of Acar and Ayanoglu [70] showed similar HHV values for beech wood as found in the present study. They measured the HHV values of beech wood with a bomb calorimeter according to the ASTM D2015 standard [71] and obtained a HHV value of 19.2 MJ/kg [70].

The L2 sample was expected to have higher HHV values compared to L1, as concluded by Jenkins, et al. [72], Sheng and Azevedo [73], and Jenkins, et al. [74]. This is due to the low contents of minerals in the biomass, which leads to high HHV values. The HHV value represents mass-based measurement. However, the results of the present study showed that the HHV value is not significantly influenced by the acid-leaching pre-treatment. The HHV value of leached biomass (L2) was 0.28 MJ/kg lower than the value of un-leached biomass (L1), even though it should be noted that the mineral content in L2 is clearly decreased. This is shown in Table 3 by the decreased value of ash as well as for the Ca, Mg, Na, and K contents.

3.3. Analysis of TG-DTG curves

Fig. 2(a) and (b) show TG and DTG curves at different heating rates for pyrolysis of un-leached and leached lignocellulose biomass, respectively. All test runs showed similar trends with respect to the mass loss as a function of temperature. Four stages are observed for both biomasses: Phase 1, a drying stage; Phase 2, a devolatilization stage, which started approximately at 160 °C. El-Sayed, et al. [75] revealed that during this phase, cellulose and hemicellulose degradations occurred. Raveendran, et al. [76] added that the small fraction of lignin component might be given off during this phase. A Phase 3 followed approximately at 360 °C, where lignin and heavier hydrocarbons are decomposed; and Phase 4, a residual stage, where a slight mass loss up to the end temperature (900 °C). According to Fig. 2, the TGA and DTG curves of un-leached and leached biomass follow the usual shape for lignocellulose biomass materials [77]. This behaviour is in agreement with the previous findings [78,79] during the investigation of biomass degradation under inert (N₂) atmosphere.

The important characteristic parameter for pyrolysis performance analysis are shown in Fig. 3. T-onset is defined as the start of the biomass devolatilization, determined by the extrapolation of the DTG curve. The temperature which corresponds to the maximum weight loss of hemicellulose is labelled as T_{hc}, while the T_{peak} represents the maximum mass loss rate and the corresponding temperature. When the weight of the biomass remains unchanged, the temperature represented is marked as the T_{offset} value. The thermal properties of lignocellulose biomass, un-leached and leached, for different heating rates are summarized in Table 4.

As shown in Table 4, the devolatilization of un-leached lignocellulose biomass starts at a temperature of 228 °C for a heating rate

Fig. 2. TG and DTG curves of (a) un-leached (L1) and (b) leached lignocellulose (L2) biomass at various heating rates.

of 10 K min^{-1} . This T-onset decreased with an increased heating rate. The lowest T-onset, 166°C , was observed at a heating rate of 50 K min^{-1} . In thermogravimetric analysis of un-leached biomass, the temperatures which corresponds to the maximum weight loss of hemicellulose were noticed at the heating rates of 10 and 20 K min^{-1} and was absent at temperatures of 30 and 50 K min^{-1} . The trend for the T-peak was similar to the T-onset, which showed decreasing values when the heating rates increased. However, the temperature for T-offset increased with an increased heating rate.

Similarly, a decrease of the T-onset was also observed for leached biomass at increased heating rates. At the heating rates of 10 and 30 K min^{-1} , the T-onsets for leached biomass (221 and 196°C , respectively) were slightly lower than those for un-leached biomass (228 and 197°C , respectively). Then, the temperature corresponding to a maximum mass loss of hemicellulose was only noticed at a heating rate of 10 K min^{-1} . For the T-peak, a decreasing trend was detected from the

heating rates of 20 K min^{-1} with 323°C to 50 K min^{-1} with 290°C . The T-peak at 10 K min^{-1} was insignificantly different from the value at 20 K min^{-1} . Compared to the data for un-leached biomass, there was a decreasing value of the T-peak for leached biomass at heating rates of 10 and 20 K min^{-1} . A shift from 330°C for un-leached biomass to 323°C for leached biomass was noticed at 10 K min^{-1} and from 326°C to 323°C at 20 K min^{-1} . Also, there was an increase in the T-offset value, giving 363°C at 10 K min^{-1} and 447°C at 50 K min^{-1} .

In contrast, the study by Jenkins, et al. [74] found that there was a delayed value for leached rice straw, compared to un-leached rice straw. The T-peak value for leached biomass occurred around 325°C , while for un-leached biomass, it occurred at approximately 280°C [74]. Interestingly, Lv, et al. [80] found that the thermal behaviour of the acid-washed biomass showed a similar phenomenon to that of un-washed cellulose, corncob, and rice husk. It is expected that the thermal characteristics of biomass are strongly correlated to the biomass

Fig. 3. Definition of the characteristics of thermogravimetric curves.

Table 4

Thermal properties of un-leached (L1) and leached (L2) lignocellulose biomass without catalyst and with H-ZSM-5:Al-MCM-41 ratio of 3:1 (HA-31) at different heating rates.

Sample	Heating Rate (K/min)	Thermal properties without catalyst				Thermal properties with HA-31 catalyst			
		T-onset (°C)	T-hc (°C)	T-peak (°C)	T-offset (°C)	T-onset (°C)	T-hc (°C)	T-peak (°C)	T-offset (°C)
L1	10	228	291	330	364	230	268	330	362
	20	208	280	326	384	204		313	386
	30	197		307	416	184		304	435
	50	166		287	438	167		288	486
L2	10	221	278	323	363	237	281	332	368
	20	209		323	394	209		324	392
	30	196		311	412	183		304	414
	50	166		290	447	166		296	371

components, which are also different between biomass species. The finding of the present study suggests that the removal of AAEM through an acid-leaching process promoted a slightly shifting of T-hc and T-peak toward lower temperatures (278–323 °C), compared to the values from un-leached biomass (280–330 °C). However, there was significant difference of mass losses (12.4–18.2%) between leached and un-leached biomass.

A different mass loss had evolved from different heating rates. Table 5 presents and compares the mass losses from un-leached and leached biomass at different heating rates in its respective phases. The moisture removal process was observed during the Phase 1 for both the un-leached and leached lignocellulose. The mass losses percentage for Phase 1 is in the range of 0.48–3.14%, Table 5. It implies that the lignocellulose biomass, either un-leached or leached, can be used directly in thermochemical processes, such as a catalytic pyrolysis, where the moisture content of the biomass is lower than 10 wt% [81]. The low moisture content will increase the heating value of lignocellulose biomass and enhance the quality of bio-oil [75]. Similarly, some studies [82–84] found that the rate of pyrolysis from room temperature to around 200 °C was very slow and resulted in a less than 5% mass loss, corresponding to the moisture content release process. Since the 50–70% mass loss occurred in a temperature range of 160–450 °C, the kinetic study was focused on the process during Phase 2.

During the Phase 2, the thermal degradation hastens as the heating rate is increased. Although the mass loss percentage decreased from 68.62 wt% at 10 K min⁻¹ to 68.34 wt% at 20 K min⁻¹, a strong increase of the mass loss percentage to 75.54 wt% at 50 K min⁻¹ prevailed. The decreased value of the mass loss percentage in Phase 3 shows that the lignin decomposition was hindered by the increase of the heating rates. The highest percentage of mass loss, 12.05 wt%, was achieved at a heating rate of 10 K min⁻¹, while the lowest value (5.20 wt%) was

obtained at a heating rate of 50 K min⁻¹. Additionally, there was a decrease in mass loss percentage for Phase 4, which represent the residual solid from the process, as the heating rate increased from 20 K min⁻¹ (19.88 wt%) to 50 K min⁻¹ (16.43 wt%). However, a 2.07 wt% increase in mass loss percentage was noticed from 10 K min⁻¹ to 20 K min⁻¹.

A similar trend in Phase 2 occurred for the leached biomass, as a 84.72% of weight loss was observed at a heating rate of 10 K min⁻¹ and increased to 87.97% at a heating rate of 50 K min⁻¹. An increase of 12.4–18.2% was noticed for the mass loss percentage for leached biomass compared to un-leached biomass. This finding implies that a pre-treatment leaching process prior to a thermal conversion led to a high devolatilization. Nevertheless, the lignin decomposition, represented in Phase 3, followed a decreasing trend, giving mass loss percentage from 5.37 wt% at 10 K min⁻¹ to 2.83 wt% at 50 K min⁻¹. The mass loss percentages in Phase 3 for leached biomass was 2.3–6.7% lower than the percentages for un-leached biomass. It is assumed that the lignin was mostly decomposed in Phase 2 for leached biomass. Furthermore, the residual solid in Phase 4 decreased from 8.54 wt% at 10 K min⁻¹ to 6.42 wt% at 50 K min⁻¹.

The findings above is consistent with the result of Gomez, et al. [85]. They investigated the thermal characteristics of beech wood chips and found that the water-washed sample had a 3% less solid residual compared to un-treated samples. The water-washed sample gave a 11 wt% of solid residual, while the un-leached sample obtained 14 wt% [85]. Varhegyi, et al. [86] also observed that the effect of water-washing pre-treatment had smaller effects for beech wood. There was only small increases by 9 K for T-peak, even though there was a significant decrease of the solid residual by 7% when using hot water washing [86].

3.4. Influence of catalyst ratio

Considering the potential mixture H-ZSM-5:Al-MCM-41 ratio of 3:1 with respect to favourable compounds [21] as well as Benzene, Toluene, and Xylene (BTX) [51] contents in bio-oil, the influence of this catalyst mixture was studied in the pyrolysis of leached lignocellulose biomass. Other variation of H-ZSM-5:Al-MCM-41 ratios: H (1:0), HA-71 (7:1), HA-31 (3:1), HA-11 (1:1), and A (0:1) were also investigated and the complete results of them were provided in the supplement pages.

TG and DTG curves from the un-leached and leached lignocellulose pyrolysis process with H-ZSM-5:Al-MCM-41 ratio of 3:1 are shown in Fig. 4. Fig. 4(a) and (b) can be compared with Fig. 2(a) and (b), respectively. This comparison shows that all test runs showed similar trends of mass loss as a function of temperature. Fig. 4 also illustrates four stages, Phase 1, 2, 3, and 4, of the biomass decomposition. In general, the trend was close to the experiments without using a catalyst. Phase 1 represents a drying stage, Phase 2 started around 160 °C, followed by Phase 3 at 360 °C and Phase 4 up to 900 °C. The difference was

Table 5

Mass losses (wt%) of un-leached (L1) and leached (L2) lignocellulose biomass without catalyst and with H-ZSM-5:Al-MCM-41 ratio of 3:1 (HA-31) at various heating rates.

Sample	Heating Rate (K/min)	Mass losses (wt.%), without catalyst				Mass losses (wt.%), with HA-31 catalyst			
		Phase 1	Phase 2	Phase 3	Phase 4	Phase 1	Phase 2	Phase 3	Phase 4
L1	10	1.52	68.62	12.05	17.81	3.26	64.95	4.31	27.48
	20	3.14	68.34	8.64	19.88	2.49	65.12	3.38	29.01
	30	2.59	70.91	8.03	18.47	0.95	67.40	2.51	29.13
	50	2.83	75.54	5.20	16.43	1.11	68.33	1.46	29.10
L2	10	1.36	84.72	5.37	8.54	2.05	65.71	4.51	27.74
	20	1.10	86.29	4.89	7.72	3.52	66.24	4.01	26.22
	30	0.48	89.11	4.00	6.42	5.38	66.73	4.11	23.78
	50	1.95	87.97	2.83	7.25	2.84	62.44	5.88	28.84

Phase 1 (room temperature – T-onset); Phase 2 (T-onset – T-offset); Phase 3 (T-offset – 900 °C); Phase 4 (> 900 °C).

Fig. 4. TG and DTG curves of (a) un-leached (L1 H-31) and (b) leached (L2 H-31) lignocellulose biomass with the addition of H-ZSM-5:Al-MCM-41 ratio of 3:1 at various heating rates.

found with respect to the range of temperature corresponding to Phase 2. For the experiments with catalyst, Phase 2 indicated a range of temperature from 160 to 486 °C, while the experiments without using a catalyst showed a range of 160–447 °C. The process operated using a catalyst run to a 39 °C higher temperature compared to that without catalyst.

The thermal properties of lignocellulose biomass, un-leached and leached, with the addition of H-ZSM-5:Al-MCM-41 ratio of 3:1 for different heating rates are summarized in Table 4. The T-onset, which represents the start of the devolatilization, decreased as the heating rates increased from 221 °C at 10 K min⁻¹ to 166 °C at 50 K min⁻¹. The hemicellulose devolatilization was only noticed at 10 K min⁻¹ with a temperature of 278 °C. The decreased values were also observed for the T-peak from 323 °C at 10 and 20 K min⁻¹ to 290 °C at 50 K min⁻¹. Additionally, the T-offset showed an increase from 363 °C at 10 K min⁻¹ to 447 °C at 50 K min⁻¹.

Comparably, a decrease of T-onset value was also observed in the case of leached biomass using a H-ZSM-5:Al-MCM-41 ratio of 3:1. As the heating rates increased from 10 to 50 K min⁻¹, the T-onset values decreased from 237 to 166 °C. There was no significant shifting in temperature between un-leached and leached biomass experiments, even though a 7 °C increase in temperature for leached biomass was observed at 10 K min⁻¹. The temperature corresponding to hemicellulose devolatilization was only indicated at heating rate of 10 K min⁻¹. For the T-peak value, a decrease from 332 °C at 10 K min⁻¹ to 296 °C at 50 K min⁻¹ was detected, whereas for T-offset, there was an increase from 368 °C at 10 K min⁻¹ to 371 °C at 50 K min⁻¹. The finding of the present study suggest that the rate of degradation is delayed for leached lignocellulose compared to the un-leached lignocellulose with 3:1 ratio of H-ZSM-5/Al-MCM-41.

The thermal properties from lignocellulose biomass with the H-ZSM-5:Al-MCM-41 ratio of 3:1 can be compared to the thermal properties of it without catalyst, presented in Table 4, which shows the degradation peak temperatures (T-peak). For both cases of un-leached lignocellulose and leached lignocellulose, mostly shifted to higher values when using H-ZSM-5/Al-MCM-31 ratio of 3:1. Wang, et al. [87] found differences suggesting that H-ZSM-5 catalyst led to a lowering of the values of the degradation peak temperatures for the blended mixture of corn stove and HDPE. The negation effect of catalyst mixture in the present study may be explained by the correlation between the

degradation rate and coke formation rate, which will be presented later as mass losses during the thermal degradation.

Table 5 shows the mass losses from un-leached and leached biomass with H-ZSM-5:Al-MCM-41 ratio of 3:1. During the Phase 1, the moisture removal was at the level below 5.5% for all test runs. For Phase 2, the mass loss percentages increased with increased heating rates for both un-leached and leached biomasses. From the un-leached biomass experiments, the percentage of mass loss increased from 64.95 wt% at 10 K min⁻¹ to 68.33 wt% at 50 K min⁻¹, while for the leached biomass, it rose from 65.71 wt% at 10 K min⁻¹ to 66.73 wt% at 30 K min⁻¹, before decreasing to 62.44 wt% at 50 K min⁻¹.

A similar trend was observed during Phase 3. The experiments with un-leached biomass obtained a decrease of the mass loss percentages from 4.31 wt% at 10 K min⁻¹ to 1.46 wt% at 50 K min⁻¹, whereas for leached biomass experiments, the percentages decreased from 4.51 wt% at 10 K min⁻¹ to 4.11 wt% at 30 K min⁻¹ and increased to 5.88 wt% at 50 K min⁻¹. The decreasing of mass loss percentage during Phase 3 is assumed to reflect the decay in the reaction intensity. Within Phase 4, coke, catalyst, and ash left from the process as the final residual.

A decrease of mass losses during Phase 2 was observed for the measurements using a catalyst mixture compared to measurements without a catalyst, Table 5. In the case of un-leached biomass, Phase 2 from the measurement with catalyst mixture gave mass losses that were 3.2–7.2 wt% lower compared to when no catalyst mixture was used. The decrease of mass losses was more significant for leached biomass cases. Specifically, the measurement with catalyst mixture obtained 19–26 wt% lower than without catalyst.

Furthermore, an increase of solid residual was observed in Phase 4. The mass losses of 9.1–12.7 wt% more was observed from the measurement with catalyst mixture for the un-leached biomass and 18.5–21.6 wt% more for the leached biomass, in comparison to the measurements without catalyst. These results clarify that using the catalyst mixture lowers the rate of degradation due to a coke deposition in the catalyst pores. The formation of coke was up to two times more severe in the case of leached biomass compared to un-leached biomass, even though the leaching affected positively on the devolatilization of biomass with a value of 3.5–6.4 times higher than without an acid leaching pre-treatment.

Table 6

TGA kinetic calculations of un-leached and leached lignocellulose biomass with second-order reaction model (F2) as the selected mechanism at various heating rates.

Samples	Heating rates (K min ⁻¹)			
	10	20	30	50
<i>Un-leached lignocellulose</i>				
	Ea (kJ mol ⁻¹)	Ea (kJ mol ⁻¹)	Ea (kJ mol ⁻¹)	Ea (kJ mol ⁻¹)
L1	26.94	19.93	16.38	15.35
L1 HA-31	25.56	19.05	18.92	18.29
<i>Leached lignocellulose</i>				
	Ea (kJ mol ⁻¹)	Ea (kJ mol ⁻¹)	Ea (kJ mol ⁻¹)	Ea (kJ mol ⁻¹)
L2	24.05	20.40	11.91	15.91
L2 HA-31	21.80	19.29	17.62	16.88

3.5. Kinetics and reaction mechanisms parameters

Several forms of mechanism functions, Supplement S1, were used to find a better approximation for the activation energy. The activation energies obtained from calculations with those mechanisms are given in the supplement pages. Jankovic and Jankovic [88] found that a three-dimensional (D4) diffusion could be used to describe the thermal degradation of beech wood with Ea value of 155.5 kJ mol⁻¹. This value is in agreement with the result for un-leached biomass at 20 K min⁻¹ (Ea = 156.5 kJ mol⁻¹) when using the same reaction model (D4). This value of 156.5 kJ mol⁻¹ is also comparable with the value of Ea reported by Blasi and Branca [89] (Ea = 157.0 kJ mol⁻¹). However, the diffusion mechanisms (D1, D2, D3, and D4) in the present study were not statistically satisfactory. The square-R for these mechanisms showed less than 0.99 in most cases.

Another study by Radojevic, et al. [90] resulted in 225.04 and 227.76 kJ mol⁻¹ as Ea values for beech sawdust, calculated by Friedman and Kissinger-Akahira-Sunose (KAS) methods, respectively. By using a first order mechanism (F1), Grønli, et al. [91] found an Ea value of 127 kJ mol⁻¹ for beech wood. Ding, et al. [92] estimated that the activation energies of beech wood were 148.63–174.44 kJ mol⁻¹ by using the Flynn-Wall-Ozawa method (FWO) and 146.84–172.21 kJ mol⁻¹ by KAS. The findings of the present study also suggest that different values of activation energies were obtained from different kinetic mechanism. It can be concluded that the apparent activation energy (Ea) depends on the considered kinetic functions [88].

This study indicates that the F2 mechanism was able to illustrate the catalytic pyrolysis process, proven by that the coefficient of determination (R²) was more than 0.99 compared to other mechanism and it applied to every heating rates. Results of the kinetic calculation of lignocellulose biomass with second-order reaction model (F2) under different heating rates, either without catalyst or with the catalyst addition, are shown in Table 6.

As observed from Table 6, as the heating rates increased, the activation energies decreased for the process without using catalysts (L1 and L2), either for un-leached or leached lignocellulose. Similar case occurred in the processes using catalysts (L1 H-31 and L2 H-31). However, for the un-leached lignocellulose, the activation energies from the catalytic process (L1 HA-31) at heating rate 30 and 50 K min⁻¹ were 15–20% higher compared to the process without using a catalyst (L1). However, for the leached lignocellulose, the activation energies for the catalytic process (L2 HA-31) were 6–48% higher than un-catalysed process (L2). In most of cases, leaching resulted in a reduction of the activation energies, which implied an increase in the reaction rate [74]. The results of the present study suggest that it is advantageous to use acid leaching as a treatment prior to the catalytic pyrolysis to reach high devolatilization and reaction rates.

4. Conclusion

The study was designed to determine the effect of acid leaching on thermal degradation of lignocellulose biomass without or with the use of H-ZSM-5/Al-MCM-41 catalyst mixtures. The acid leaching processes were carried out using different concentrations of acetic acid (0.3, 1.0, 5.0, and 10.0 wt%), temperatures (30, 60, and 90 °C), and residence times (30 and 120 min). In addition, the activation energies were calculated based on solid-state reaction mechanism.

The leaching parameters to produce leached biomass for the TGA experiments were set to 30 min, 30 °C and 5 wt% acetic acid in the leaching liquid, with respect to economic aspects. At these parameters a significant reduction of AAEM in the leached biomass can be achieved (Ca: 59%, Mg: 95%, K: 99%, and Na: 96%).

The HHV value is not significantly influenced by the acid-leaching pre-treatment, even though it should be noted that the mineral content in leached biomass is clearly decreased. The HHV values for un-leached and leached biomass were 19.42 and 19.14 MJ/kg, respectively, calculated by using the Milne formula.

The removal of AAEM significantly affected the degradation of hemicellulose, cellulose, and lignin. There were an 12.4–18.2% increase of mass losses in Phase 2 and a lower mass loss in Phase 4 for leached biomass, compared to un-leached biomass, even though there was no significant shift in the temperature profiles between un-leached and leached biomass degradation.

Furthermore, it is advantageous to use acid leaching process as a treatment prior to catalytic pyrolysis to reach high devolatilization and reaction rate. The second order (F2) mechanism was able to illustrate the catalytic pyrolysis process, proven by that the coefficient of determination (R²) reached a value higher than 0.99 compared to the other studied mechanism.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.fuel.2019.116086>.

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Corrigendum to “The thermal degradation of lignocellulose biomass with an acid leaching pre-treatment using a H-ZSM-5/Al-MCM-41 catalyst mixture” [Fuel 257 (2019) 116086]

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The authors regret that an error appears in page no. 4 in the ‘Results and Discussion’ section [sub section 3.1. *Leaching of Alkali and Alkaline Earth Metallic (AAEM) Species*].

The first line:

Kesalahan! Sumber referensi tidak ditemukan. show the results of the leaching tests at different acetic acid concentrations at a liquid to solid (l/s)-ratio of 10:1, a temperature of 90 °C, and a residence time of

120 min.

Should be read as:

Table 2 shows the results of the leaching test at different acetic acid concentrations at a liquid to solid (l/s)-ratio of 10:1, a temperature of 90 °C, and a residence time of 120 min.

The authors would like to apologise for any inconvenience caused.

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Mathematical models for the solid-state reaction mechanism

Function name	Reaction model	$g(\alpha)$	Ref.
Nucleation models			
P0.7	Power law	$\alpha^{3/2}$	[58]
P2	Power law	$\alpha^{1/2}$	[58–60]
P3	Power law	$\alpha^{1/3}$	[58–60]
P4	Power law	$\alpha^{1/4}$	[58–60]
A1.5	Avrami-Erofeev	$[-\ln(1-\alpha)]^{2/3}$	[61,62]
A2	Avrami-Erofeev	$[-\ln(1-\alpha)]^{1/2}$	[58–60]
A3	Avrami-Erofeev	$[-\ln(1-\alpha)]^{1/3}$	[58–60]
A4	Avrami-Erofeev	$[-\ln(1-\alpha)]^{1/4}$	[58–60]
Geometrical contraction models			
R2	Contracting cylinder (contracting surface)	$1 - (1 - \alpha)^{1/2}$	[58–61]
R3	Contracting sphere (contracting volume, three dimension)	$1 - (1 - \alpha)^{1/3}$	[42,58–61]
Diffusion models			
D1	One-way transport (1-D diffusion, parabola law)	α^2	[42,58–61]
D2	Two-way transport (2-D diffusion, valensi equation)	$\alpha + ((1 - \alpha) \ln(1 - \alpha))$	[59,63]
D3	Three-way transport (3-D diffusion, Jander equation)	$(1 - (1 - \alpha)^{1/3})^2$	[42,58–61]
D4	Ginstling-Brounshtein equation	$1 - \frac{2}{3}\alpha - (1 - \alpha)^{2/3}$	[42,59,60,62]
Reaction-order models			
F0/R1	Zero-order	α	[59,60]
F1	Mampel (first order, Chemical reaction n = 1)	$-\ln(1 - \alpha)$	[58,60,62]
F2	Second-order	$\frac{1}{(1 - \alpha)} - 1$	[59,60,62]
F3	Third order	$\frac{1}{2}[(1 - \alpha)^{-2} - 1]$	[59,60,62]

Thermal properties of un-leached lignocellulose biomass

Sample	Heating Rate (K min ⁻¹)	T-onset (°C)	T-hc (°C)	T-peak (°C)	T-offset (°C)
L1	10	228	291	330	364
	20	208	280	326	384
	30	197		307	416
	50	166		287	438
L1 H	10	228	277	330	364
	20	212		332	384
	30	186		304	439
	50	165		296	406
L1 H-71	10	228	272	329	361
	20	213		328	378
	30	191		304	437
	50	163		289	485
L1 H-31	10	230	268	330	362
	20	204		313	386
	30	184		304	435
	50	167		288	486
L1 H-11	10	227	270	362	369
	20	201		311	380
	30	181		301	438
	50	154		281	484
L1 H-13	10	212	260	320	369
	20	193		313	376
	30	170		303	437
	50	152		284	481
L1 A	10	222	273	330	361
	20	196		310	378
	30	172		300	427
	50	155		284	468

Mass losses (wt.%) of un-leached lignocellulose biomass

Sample	Heating Rate (K min ⁻¹)	Phase 1	Phase 2	Phase 3	Phase 4
L1	10	1.52	68.62	12.05	17.81
	20	3.14	68.34	8.64	19.88
	30	2.59	70.91	8.03	18.47
	50	2.83	75.54	5.20	16.43
L1 H	10	2.11	59.85	9.43	28.60
	20	2.19	66.24	3.41	28.17
	30	0.77	67.30	2.46	29.46
	50	1.09	62.08	5.63	31.20
L1 H-71	10	2.00	63.73	4.51	29.76
	20	2.35	64.26	4.08	29.31
	30	0.77	67.02	2.52	29.69
	50	1.19	68.52	1.45	28.84
L1 H-31	10	3.26	64.95	4.31	27.48
	20	2.49	65.12	3.38	29.01
	30	0.95	67.40	2.51	29.13
	50	1.11	68.33	1.46	29.10
L1 H-11	10	0.31	65.20	4.31	30.18
	20	2.22	64.15	3.87	29.76
	30	0.29	68.26	2.61	28.84
	50	2.71	67.07	1.42	28.80
L1 H-13	10	1.48	65.92	4.12	28.48
	20	1.68	60.98	3.52	33.81
	30	3.76	66.72	2.50	27.03
	50	0.90	68.02	1.48	29.59
L1 A	10	0.52	68.31	4.78	26.39
	20	1.98	65.59	4.26	28.17
	30	0.76	72.66	2.70	23.88
	50	0.30	74.69	2.72	22.29

Thermal properties of leached lignocellulose biomass

Sample	Heating Rate (K min ⁻¹)	T-onset (°C)	T-hc (°C)	T-peak (°C)	T-offset (°C)
L2	10	221	278	323	363
	20	209		323	394
	30	196		311	412
	50	166		290	447
L2 H	10	242	284	333	367
	20	201		305	392
	30	196		312	440
	50	165		289	450
L2 H-71	10	232	281	332	368
	20	197		306	394
	30	198		308	408
	50	170		300	475
L2 H-31	10	237	281	332	368
	20	209		324	392
	30	183		304	414
	50	166		296	371
L2 H-11	10	228	282	330	371
	20	187		304	395
	30	184		309	429
	50	168		294	469
L2 H-13	10	229	283	330	370
	20	190		321	400
	30	169		306	453
	50	162		294	468
L2 A	10	221	281	331	373
	20	177		304	415
	30	206		344	449
	50	148		285	458

Mass losses (wt.%) of leached lignocellulose biomass

Sample	Heating Rate (K min ⁻¹)	Phase 1	Phase 2	Phase 3	Phase 4
L2	10	1.36	84.72	5.37	8.54
	20	1.10	86.29	4.89	7.72
	30	0.48	89.11	4.00	6.42
	50	1.95	87.97	2.83	7.25
L2 H	10	2.45	65.69	4.29	27.57
	20	3.70	68.04	3.67	24.58
	30	4.43	66.26	2.60	26.72
	50	0.92	67.71	2.43	28.94
L2 H-71	10	2.03	64.46	4.01	29.51
	20	3.48	65.02	3.42	28.08
	30	0.56	67.57	3.45	28.42
	50	1.35	67.97	1.45	29.22
L2 H-31	10	2.05	65.71	4.51	27.74
	20	3.52	66.24	4.01	26.22
	30	5.38	66.73	4.11	23.78
	50	2.84	62.44	5.88	28.84
L2 H-11	10	1.78	62.07	4.12	32.03
	20	4.49	64.35	3.50	27.66
	30	4.33	66.71	2.70	26.26
	50	0.46	67.61	2.59	29.34
L2 H-13	10	0.92	63.46	4.57	31.05
	20	6.11	63.56	4.93	25.40
	30	13.99	61.49	4.95	19.57
	50	2.44	67.32	2.67	27.56
L2 A	10	0.52	60.58	3.95	34.95
	20	0.01	61.79	2.77	35.43
	30	1.78	63.52	3.18	31.52
	50	2.97	67.95	2.66	26.42

S6

Un-leached biomass

Reaction Model	Heating Rates (K min ⁻¹)							
	10		20		30		50	
	Ea kJ mol ⁻¹	R ²	Ea kJ mol ⁻¹	R ²	Ea kJ mol ⁻¹	R ²	Ea kJ mol ⁻¹	R ²
Nucleation models								
P0.7	8.31E-04	0.9578	4.99E-04	0.9314	4.16E-04	0.9934	3.33E-04	0.9684
P2	3.33E-04	0.9578	1.66E-04	0.9314	1.66E-04	0.9934	8.31E-05	0.9684
P3	2.49E-04	0.9578	8.31E-05	0.9314	8.31E-05	0.9934	6.65E-05	0.9684
P4	1.66E-04	0.9578	8.31E-05	0.9314	6.65E-05	0.9934	4.99E-05	0.9684
A1.5	86.96	0.9898	51.82	0.9918	33.73	0.9502	27.52	0.9971
A2	63.12	0.9890	36.60	0.9904	23.07	0.9425	18.35	0.9958
A3	39.27	0.9871	21.38	0.9864	12.42	0.9193	9.18	0.9907
A4	27.35	0.9847	13.77	0.9801	7.09	0.8758	4.60	0.9746
Geometrical contraction models								
R2	129.31	0.9855	74.61	0.9803	50.44	0.9660	40.89	0.9922
R3	131.03	0.9881	77.00	0.9855	51.91	0.9632	42.50	0.9946
Diffusion models								
D1	257.38	0.9822	145.77	0.9663	101.66	0.9757	82.02	0.9866
D2	263.50	0.9858	153.38	0.9771	106.75	0.9725	87.67	0.9918
D3	270.46	0.9890	163.05	0.9876	112.71	0.9675	94.16	0.9960
D4	265.82	0.9870	156.54	0.9811	108.73	0.9710	89.82	0.9934
Reaction-order models								
F0/R1	124.49	0.9808	68.36	0.9608	46.38	0.9720	36.43	0.9820
F1	134.64	0.9906	82.26	0.9930	55.03	0.9563	45.87	0.9980
F2	26.94	0.9900	19.93	0.9968	16.38	0.9917	15.35	0.9999
F3	160.94	0.9811	126.10	0.9450	78.60	0.8924	70.75	0.9910

Un-leached + H

Reaction Model	Heating Rates (K min ⁻¹)							
	10		20		30		50	
	Ea kJ mol ⁻¹	R ²	Ea kJ mol ⁻¹	R ²	Ea kJ mol ⁻¹	R ²	Ea kJ mol ⁻¹	R ²
Nucleation models								
P0.7	7.48E-04	0.9833	4.99E-04	0.9430	4.99E-04	0.9774	4.16E-04	0.9988
P2	2.49E-04	0.9833	1.66E-04	0.9430	1.66E-04	0.9774	1.66E-04	0.9988
P3	1.66E-04	0.9833	8.31E-05	0.9430	8.31E-05	0.9774	8.31E-05	0.9988
P4	1.66E-04	0.9833	8.31E-05	0.9430	8.31E-05	0.9774	6.65E-05	0.9988
A1.5	74.96	0.9974	52.33	0.9969	40.91	0.9958	37.80	0.9748
A2	54.09	0.9973	36.99	0.9962	28.47	0.9953	26.07	0.9713
A3	33.22	0.9969	21.65	0.9944	16.03	0.9940	14.33	0.9609
A4	22.78	0.9963	13.98	0.9914	9.81	0.9915	8.47	0.9422
Geometrical contraction models								
R2	110.24	0.9985	75.63	0.9887	61.81	0.9957	57.18	0.9842
R3	112.33	0.9985	77.94	0.9926	63.09	0.9961	58.51	0.9821
Diffusion models								
D1	217.34	0.9969	148.21	0.9771	125.24	0.9939	115.95	0.9909
D2	224.75	0.9983	155.55	0.9858	129.83	0.9956	120.79	0.9878
D3	233.18	0.9986	164.89	0.9937	135.04	0.9965	126.16	0.9840
D4	227.55	0.9986	158.61	0.9889	131.55	0.9960	122.57	0.9865
Reaction-order models								
F0/R1	104.41	0.9965	69.59	0.9733	58.20	0.9927	53.40	0.9898
F1	116.70	0.9976	83.01	0.9974	65.79	0.9962	61.27	0.9777
F2	23.84	0.9990	20.06	0.9983	17.92	0.9992	17.47	0.9961
F3	148.67	0.9634	125.23	0.9379	85.45	0.9734	80.71	0.9465

S8

Un-leached + H-71

Reaction Model	Heating Rates (K min ⁻¹)							
	10		20		30		50	
	Ea kJ mol ⁻¹	R ²	Ea kJ mol ⁻¹	R ²	Ea kJ mol ⁻¹	R ²	Ea kJ mol ⁻¹	R ²
Nucleation models								
P0.7	8.31E-04	0.9875	4.99E-04	0.9523	4.99E-04	0.9441	4.16E-04	0.9543
P2	2.49E-04	0.9875	1.66E-04	0.9523	1.66E-04	0.9441	1.66E-04	0.9543
P3	1.66E-04	0.9875	8.31E-05	0.9523	8.31E-05	0.9441	8.31E-05	0.9543
P4	1.66E-04	0.9875	8.31E-05	0.9523	8.31E-05	0.9441	6.65E-05	0.9543
A1.5	75.21	0.9978	51.08	0.9987	45.35	0.9899	38.79	0.9889
A2	54.33	0.9977	36.05	0.9986	31.80	0.9878	26.81	0.9863
A3	33.45	0.9975	21.02	0.9981	18.24	0.9819	14.82	0.9784
A4	23.01	0.9973	13.51	0.9973	11.47	0.9719	8.83	0.9632
Geometrical contraction models								
R2	111.96	0.9997	72.58	0.9946	68.09	0.9831	57.28	0.9812
R3	113.59	0.9994	75.21	0.9975	69.49	0.9862	59.04	0.9848
Diffusion models								
D1	223.13	0.9994	140.70	0.9834	137.17	0.9762	113.86	0.9736
D2	228.94	0.9998	148.77	0.9915	142.15	0.9824	120.09	0.9808
D3	235.49	0.9994	159.47	0.9979	147.85	0.9883	127.24	0.9874
D4	231.12	0.9998	152.25	0.9943	144.04	0.9846	122.46	0.9832
Reaction-order models								
F0/R1	107.41	0.9994	65.83	0.9803	64.16	0.9720	52.35	0.9680
F1	116.98	0.9979	81.15	0.9988	72.46	0.9916	62.77	0.9909
F2	24.17	0.9997	19.65	0.9996	18.83	0.9972	17.47	0.9984
F3	141.44	0.9659	132.77	0.8956	94.33	0.9932	90.29	0.9974

S9

Un-leached + H-31

Reaction Model	Heating Rates (K min ⁻¹)							
	10		20		30		50	
	Ea kJ mol ⁻¹	R ²	Ea kJ mol ⁻¹	R ²	Ea kJ mol ⁻¹	R ²	Ea kJ mol ⁻¹	R ²
Nucleation models								
P0.7	8.31E-04	0.9801	4.99E-04	0.9473	4.99E-04	0.9370	4.16E-04	0.9528
P2	3.33E-04	0.9801	1.66E-04	0.9473	1.66E-04	0.9370	1.66E-04	0.9528
P3	1.66E-04	0.9801	8.31E-05	0.9473	8.31E-05	0.9370	8.31E-05	0.9528
P4	1.66E-04	0.9801	7.48E-05	0.9473	8.31E-05	0.9370	7.48E-05	0.9528
A1.5	81.31	0.9967	48.13	0.9988	45.85	0.9855	42.96	0.9882
A2	58.90	0.9964	33.84	0.9985	32.17	0.9827	29.94	0.9858
A3	36.49	0.9959	19.55	0.9977	18.49	0.9749	16.91	0.9788
A4	25.29	0.9952	12.41	0.9963	11.65	0.9620	10.39	0.9664
Geometrical contraction models								
R2	121.17	0.9972	68.40	0.9925	68.71	0.9976	63.42	0.9805
R3	122.76	0.9973	70.96	0.9961	70.16	0.9813	65.22	0.9841
Diffusion models								
D1	241.63	0.9959	132.62	0.9799	138.25	0.9701	125.93	0.9728
D2	247.38	0.9971	140.54	0.9891	143.33	0.9772	132.28	0.9799
D3	253.85	0.9975	150.96	0.9968	149.19	0.9841	139.58	0.9866
D4	249.53	0.9973	143.94	0.9923	145.27	0.9797	134.70	0.9823
Reaction-order models								
F0/R1	116.65	0.9956	61.79	0.9761	64.69	0.9649	58.39	0.9676
F1	126.12	0.9969	76.71	0.9989	73.21	0.9877	69.02	0.9902
F2	25.56	0.9975	19.05	0.9995	18.92	0.9960	18.29	0.9977
F3	150.20	0.9724	126.19	0.9062	95.77	0.9942	97.12	0.9978

S10

Un-leached + H-11

Reaction Model	Heating Rates (K min ⁻¹)							
	10		20		30		50	
	Ea kJ mol ⁻¹	R ²	Ea kJ mol ⁻¹	R ²	Ea kJ mol ⁻¹	R ²	Ea kJ mol ⁻¹	R ²
Nucleation models								
P0.7	8.31E-04	0.9816	4.16E-04	0.9622	5.82E-04	0.9622	2.49E-04	0.9752
P2	2.49E-04	0.9816	1.66E-04	0.9622	1.66E-04	0.9622	8.31E-05	0.9752
P3	1.66E-04	0.9816	8.31E-05	0.9622	1.66E-04	0.9622	5.82E-05	0.9752
P4	1.66E-04	0.9816	8.31E-05	0.9770	8.31E-05	0.9622	4.16E-05	0.9752
A1.5	86.42	0.9988	48.04	0.9938	52.30	0.9957	15.36	0.9781
A2	62.65	0.9987	33.71	0.9926	37.00	0.9950	9.24	0.9635
A3	38.88	0.9985	19.37	0.9892	21.71	0.9930	3.13	0.8534
A4	26.99	0.9983	12.21	0.9835	14.07	0.9898	0.07	0.0044
Geometrical contraction models								
R2	125.34	0.9976	66.33	0.9798	79.06	0.9933	26.01	0.9816
R3	128.12	0.9984	69.55	0.9863	80.29	0.9945	26.53	0.9831
Diffusion models								
D1	243.85	0.9938	125.28	0.9603	160.03	0.9902	58.07	0.9845
D2	253.66	0.9966	135.33	0.9750	164.45	0.9930	60.06	0.9866
D3	264.90	0.9985	148.40	0.9884	169.45	0.9953	62.16	0.9887
D4	257.39	0.9974	139.60	0.9802	166.11	0.9938	60.76	0.9873
Reaction-order models								
F0/R1	117.59	0.9932	57.99	0.9529	75.58	0.9886	24.48	0.9765
F1	133.96	0.9989	76.70	0.9947	82.88	0.9963	27.59	0.9859
F2	25.74	0.9986	18.93	0.9981	20.49	0.9982	13.45	0.9999
F3	177.03	0.9720	137.56	0.9368	101.55	0.9869	34.53	0.9965

S11

Un-leached + H-13

Reaction Model	Heating Rates (K min ⁻¹)							
	10		20		30		50	
	Ea kJ mol ⁻¹	R ²	Ea kJ mol ⁻¹	R ²	Ea kJ mol ⁻¹	R ²	Ea kJ mol ⁻¹	R ²
Nucleation models								
P0.7	8.31E-04	0.9677	4.99E-04	0.9220	4.16E-04	0.9276	3.33E-04	0.9412
P2	3.33E-04	0.9677	1.66E-04	0.9220	1.66E-04	0.9276	8.31E-05	0.9412
P3	1.66E-04	0.9677	8.31E-05	0.9220	8.31E-05	0.9276	7.48E-05	0.9412
P4	1.66E-04	0.9677	7.48E-05	0.9220	7.48E-05	0.9276	5.82E-05	0.9412
A1.5	81.17	0.9968	48.40	0.9908	39.21	0.9808	34.72	0.9765
A2	58.81	0.9965	34.05	0.9891	27.20	0.9766	23.75	0.9709
A3	36.44	0.9957	19.69	0.9844	15.18	0.9641	12.79	0.9530
A4	25.25	0.9947	12.51	0.9766	9.17	0.9415	7.31	0.9167
Geometrical contraction models								
R2	120.21	0.9936	68.44	0.9766	58.33	0.9704	50.86	0.9660
R3	122.05	0.9950	71.12	0.9832	59.90	0.9754	52.72	0.9714
Diffusion models								
D1	238.44	0.9890	132.13	0.9586	116.80	0.9608	100.55	0.9569
D2	244.96	0.9924	140.39	0.9723	122.27	0.9702	107.03	0.9668
D3	252.39	0.9954	151.26	0.9856	128.66	0.9794	114.58	0.9764
D4	247.42	0.9936	143.94	0.9774	124.39	0.9736	109.54	0.9703
Reaction-order models								
F0/R1	115.07	0.9879	61.55	0.9514	53.97	0.9530	45.70	0.9469
F1	125.91	0.9971	77.12	0.9921	91.21	0.9615	56.65	0.9807
F2	25.32	0.9954	19.06	0.9968	17.43	0.9964	16.61	0.9974
F3	154.19	0.9837	128.96	0.9251	88.46	0.9925	86.16	0.9996

S12

Un-leached + A

Reaction Model	Heating Rates (K min ⁻¹)							
	10		20		30		50	
	Ea kJ mol ⁻¹	R ²	Ea kJ mol ⁻¹	R ²	Ea kJ mol ⁻¹	R ²	Ea kJ mol ⁻¹	R ²
Nucleation models								
P0.7	8.31E-04	0.9681	4.16E-04	0.9226	4.99E-04	0.9203	3.33E-04	0.9847
P2	2.49E-04	0.9681	1.66E-04	0.9226	1.66E-04	0.9203	8.31E-05	0.9847
P3	1.66E-04	0.9681	8.31E-05	0.9226	8.31E-05	0.9203	7.48E-05	0.9847
P4	1.66E-04	0.9681	7.48E-05	0.9226	8.31E-05	0.9203	5.82E-05	0.9847
A1.5	82.29	0.9960	46.19	0.9894	43.36	0.9712	29.45	0.9994
A2	59.58	0.9956	32.38	0.9874	30.30	0.9661	19.80	0.9995
A3	36.87	0.9947	18.57	0.9817	17.25	0.9517	10.15	0.9996
A4	25.52	0.9935	11.67	0.9719	10.72	0.9277	5.32	0.9998
Geometrical contraction models								
R2	120.62	0.9923	65.89	0.9755	64.76	0.9624	44.52	0.9999
R3	122.90	0.9940	68.36	0.9819	66.27	0.9671	45.89	1.0000
Diffusion models								
D1	237.03	0.9868	127.93	0.9590	130.01	0.9541	90.42	0.9987
D2	245.11	0.9910	135.74	0.9721	135.29	0.9631	95.39	0.9997
D3	254.33	0.9945	145.75	0.9846	141.40	0.9717	100.93	1.0000
D4	248.16	0.9923	139.03	0.9768	137.32	0.9662	97.22	0.9999
Reaction-order models								
F0/R1	114.25	0.9856	59.44	0.9516	60.57	0.9463	40.64	0.9981
F1	127.69	0.9963	73.80	0.9911	69.46	0.9753	48.75	0.9994
F2	25.28	0.9955	18.69	0.9968	18.36	0.9929	15.80	0.9998
F3	163.05	0.9793	119.39	0.9451	93.27	0.9868	69.17	0.9816

Leached biomass

Reaction Model	Heating Rates (K min ⁻¹)							
	10		20		30		50	
	Ea kJ mol ⁻¹	R ²	Ea kJ mol ⁻¹	R ²	Ea kJ mol ⁻¹	R ²	Ea kJ mol ⁻¹	R ²
Nucleation models								
P0.7	8.31E-04	0.9882	5.82E-04	0.9259	1.66E-04	0.8052	3.33E-04	0.9730
P2	2.49E-04	0.9624	1.66E-04	0.9259	5.82E-05	0.8052	8.31E-05	0.9730
P3	1.66E-04	0.9624	1.66E-04	0.9259	4.16E-05	0.8052	7.48E-05	0.9730
P4	8.31E-05	0.9624	8.31E-05	0.9259	2.49E-05	0.8052	5.82E-05	0.9730
A1.5	75.97	0.9957	58.16	0.9868	9.88	0.2670	30.62	0.9995
A2	54.80	0.9952	41.36	0.9848	5.19	0.1534	20.68	0.9991
A3	33.63	0.9941	24.55	0.9797	0.50	0.0039	10.74	0.9978
A4	23.05	0.9925	16.14	0.9721	1.84	0.0879	5.77	0.9938
Geometrical contraction models								
R2	110.80	0.9897	84.87	0.9758	15.80	0.3404	45.45	0.9964
R3	113.21	0.9922	87.04	0.9807	16.91	0.3536	47.08	0.9979
Diffusion models								
D1	216.87	0.9821	167.28	0.9635	34.43	0.4294	90.98	0.9918
D2	225.36	0.9878	174.34	0.9733	38.22	0.4462	96.71	0.9957
D3	235.14	0.9929	183.15	0.9830	42.69	0.4622	103.28	0.9985
D4	228.60	0.9897	177.24	0.9769	39.70	0.4519	98.90	0.9968
Reaction-order models								
F0/R1	104.08	0.9804	79.11	0.9585	12.78	0.2964	40.92	0.9892
F1	118.31	0.9962	91.78	0.9884	19.25	0.3777	50.50	0.9997
F2	24.05	0.9958	20.40	0.9936	11.91	0.9367	15.91	1.0000
F3	156.13	0.9861	130.46	0.9591	37.19	0.4667	75.74	0.9857

S14

Leached + H

Reaction Model	Heating Rates (K min ⁻¹)							
	10		20		30		50	
	Ea kJ mol ⁻¹	R ²	Ea kJ mol ⁻¹	R ²	Ea kJ mol ⁻¹	R ²	Ea kJ mol ⁻¹	R ²
Nucleation models								
P0.7	7.48E-04	0.9887	4.99E-04	0.9377	3.33E-04	0.9249	4.16E-04	0.9973
P2	2.49E-04	0.9887	1.66E-04	0.9377	8.31E-05	0.9249	1.66E-04	0.9973
P3	1.66E-04	0.9887	8.31E-05	0.9377	7.48E-05	0.9249	8.31E-05	0.9973
P4	1.66E-04	0.9887	8.31E-05	0.9377	5.82E-05	0.9249	6.65E-05	0.9973
A1.5	81.50	0.9972	51.90	0.9961	28.64	0.7569	38.17	0.9806
A2	58.96	0.9971	36.67	0.9953	19.26	0.7171	26.34	0.9780
A3	36.41	0.9967	21.44	0.9931	9.88	0.6061	14.52	0.9704
A4	25.14	0.9963	13.82	0.9895	5.18	0.4363	8.61	0.9568
Geometrical contraction models								
R2	118.61	0.9995	74.58	0.9864	43.68	0.7852	57.21	0.9893
R3	121.17	0.9992	77.00	0.9908	44.88	0.7868	58.70	0.9872
Diffusion models								
D1	231.59	0.9985	145.54	0.9735	89.48	0.8105	115.14	0.9949
D2	240.63	0.9995	153.19	0.9832	93.77	0.8131	120.51	0.9921
D3	251.01	0.9992	163.03	0.9922	98.65	0.8148	126.54	0.9885
D4	244.07	0.9996	156.41	0.9867	95.39	0.8138	122.52	0.9910
Reaction-order models								
F0/R1	111.46	0.9983	68.26	0.9690	40.29	0.7785	53.01	0.9945
F1	126.58	0.9973	82.37	0.9967	47.41	0.7891	61.82	0.9827
F2	24.93	0.9997	19.92	0.9980	15.48	0.9579	17.46	0.9970
F3	166.60	0.9546	127.62	0.9400	65.81	0.7817	84.17	0.9491

S15

Leached + H-71

Reaction Model	Heating Rates (K min ⁻¹)							
	10		20		30		50	
	Ea kJ mol ⁻¹	R ²	Ea kJ mol ⁻¹	R ²	Ea kJ mol ⁻¹	R ²	Ea kJ mol ⁻¹	R ²
Nucleation models								
P0.7	7.48E-04	0.9936	4.99E-04	0.9520	5.82E-04	0.9476	4.16E-04	0.9637
P2	2.49E-04	0.9936	1.66E-04	0.9520	1.66E-04	0.9476	1.66E-04	0.9637
P3	1.66E-04	0.9936	8.31E-05	0.9520	8.31E-05	0.9476	8.31E-05	0.9637
P4	1.66E-04	0.9936	7.48E-05	0.9520	8.31E-05	0.9476	6.65E-05	0.9637
A1.5	65.97	0.9887	47.50	0.9986	48.36	0.9931	39.80	0.9956
A2	47.40	0.9880	33.37	0.9985	34.05	0.9917	27.56	0.9944
A3	28.82	0.9861	19.24	0.9981	19.74	0.9877	15.33	0.9908
A4	19.54	0.9837	12.17	0.9973	12.59	0.9813	9.21	0.9838
Geometrical contraction models								
R2	98.16	0.9951	67.25	0.9953	72.45	0.9872	58.79	0.9899
R3	99.77	0.9935	69.87	0.9980	73.90	0.9899	60.55	0.9925
Diffusion models								
D1	195.63	0.9982	130.16	0.9842	145.73	0.9807	116.87	0.9836
D2	201.37	0.9967	138.14	0.9923	150.81	0.9863	123.11	0.9891
D3	207.85	0.9939	148.76	0.9984	156.67	0.9914	130.26	0.9938
D4	203.53	0.9958	141.60	0.9950	152.74	0.9882	125.47	0.9909
Reaction-order models								
F0/R1	93.66	0.9981	60.56	0.9809	68.43	0.9774	53.86	0.9800
F1	103.12	0.9894	75.77	0.9987	76.96	0.9942	64.27	0.9964
F2	22.16	0.9986	18.91	0.9997	19.48	0.9974	17.67	0.9993
F3	127.37	0.9403	127.30	0.8920	99.78	0.9871	91.74	0.9932

S16

Leached + H-31

Reaction Model	Heating Rates (K min ⁻¹)							
	10		20		30		50	
	Ea kJ mol ⁻¹	R ²	Ea kJ mol ⁻¹	R ²	Ea kJ mol ⁻¹	R ²	Ea kJ mol ⁻¹	R ²
Nucleation models								
P0.7	7.48E-04	0.9957	4.99E-04	0.9678	4.99E-04	0.9448	3.33E-04	0.9805
P2	2.49E-04	0.9957	1.66E-04	0.9678	1.66E-04	0.9448	8.31E-05	0.9805
P3	1.66E-04	0.9957	8.31E-05	0.9678	8.31E-05	0.9448	8.31E-05	0.9805
P4	8.31E-05	0.9957	8.31E-05	0.9678	7.48E-05	0.9448	5.82E-05	0.9805
A1.5	63.99	0.9845	48.84	0.9950	40.31	0.9940	35.88	0.9997
A2	45.91	0.9834	34.36	0.9946	28.03	0.9924	24.62	0.9997
A3	27.83	0.9807	19.88	0.9936	15.76	0.9878	13.37	0.9998
A4	18.79	0.9771	12.64	0.9919	9.62	0.9790	7.74	0.9999
Geometrical contraction models								
R2	95.45	0.9923	69.99	0.9992	59.97	0.9868	52.87	0.9995
R3	96.97	0.9903	72.41	0.9993	61.53	0.9901	54.64	0.9999
Diffusion models								
D1	190.66	0.9967	136.50	0.9939	120.15	0.9787	104.99	0.9969
D2	196.14	0.9944	144.09	0.9981	125.53	0.9856	111.23	0.9990
D3	202.28	0.9909	153.91	0.9994	131.86	0.9919	118.43	1.0000
D4	198.18	0.9933	147.30	0.9991	127.63	0.9880	113.62	0.9995
Reaction-order models								
F0/R1	91.17	0.9965	63.71	0.9925	55.68	0.9742	47.92	0.9959
F1	100.15	0.9855	77.80	0.9953	64.86	0.9952	58.39	0.9996
F2	21.80	0.9979	19.29	0.9996	17.62	0.9986	16.88	0.9999
F3	122.93	0.9342	123.51	0.8778	90.18	0.9812	86.22	0.9763

Reaction Model	Heating Rates (K min ⁻¹)							
	10		20		30		50	
	Ea kJ mol ⁻¹	R ²	Ea kJ mol ⁻¹	R ²	Ea kJ mol ⁻¹	R ²	Ea kJ mol ⁻¹	R ²
Nucleation models								
P0.7	8.31E-04	0.9685	4.16E-04	0.9397	3.33E-04	0.9956	4.16E-04	0.9737
P2	2.49E-04	0.9685	1.66E-04	0.9397	8.31E-05	0.9956	1.66E-04	0.9737
P3	1.66E-04	0.9685	8.31E-05	0.9397	6.65E-05	0.9956	8.31E-05	0.9737
P4	1.66E-04	0.9685	6.65E-05	0.9397	4.99E-05	0.9956	6.65E-05	0.9737
A1.5	90.46	0.9972	45.84	0.9961	23.45	0.8567	28.50	0.9871
A2	65.65	0.9969	32.05	0.9953	15.38	0.8243	19.08	0.9829
A3	40.85	0.9963	18.27	0.9929	7.30	0.7152	9.66	0.9675
A4	28.44	0.9955	11.38	0.9886	3.27	0.4855	4.95	0.9258
Geometrical contraction models								
R2	129.02	0.9914	63.44	0.9847	36.07	0.8961	45.64	0.9872
R3	132.56	0.9939	66.54	0.9902	37.20	0.8911	46.20	0.9882
Diffusion models								
D1	247.30	0.9829	120.01	0.9677	74.59	0.9261	97.17	0.9874
D2	259.55	0.9891	129.77	0.9805	78.64	0.9182	99.33	0.9891
D3	273.88	0.9944	142.36	0.9918	83.26	0.9087	101.58	0.9908
D4	264.29	0.9911	133.90	0.9850	80.17	0.9151	100.08	0.9897
Reaction-order models								
F0/R1	119.26	0.9814	55.36	0.9612	32.87	0.9098	43.99	0.9838
F1	140.07	0.9974	73.40	0.9967	39.60	0.8807	47.34	0.9901
F2	26.20	0.9963	18.54	0.9989	14.44	0.9828	16.15	0.9992
F3	196.91	0.9774	131.33	0.9398	57.07	0.8141	54.69	0.9977

S18

Leached + H-13

Reaction Model	Heating Rates (K min ⁻¹)							
	10		20		30		50	
	Ea kJ mol ⁻¹	R ²	Ea kJ mol ⁻¹	R ²	Ea kJ mol ⁻¹	R ²	Ea kJ mol ⁻¹	R ²
Nucleation models								
P0.7	8.31E-04	0.9874	4.99E-04	0.9380	4.16E-04	0.9531	3.33E-04	0.9764
P2	2.49E-04	0.9874	1.66E-04	0.9380	1.66E-04	0.9531	8.31E-05	0.9764
P3	1.66E-04	0.9874	8.31E-05	0.9380	8.31E-05	0.9531	8.31E-05	0.9764
P4	1.66E-04	0.9874	8.31E-05	0.9380	6.65E-05	0.9531	5.82E-05	0.9764
A1.5	81.45	0.9984	48.05	0.9939	34.46	0.9962	34.88	1.0000
A2	58.98	0.9984	33.80	0.9928	23.65	0.9950	23.87	1.0000
A3	36.50	0.9982	19.54	0.9897	12.83	0.9907	12.86	0.9998
A4	25.26	0.9980	12.41	0.9846	7.42	0.9814	7.36	0.9992
Geometrical contraction models								
R2	119.77	0.9998	69.31	0.9868	51.76	0.9909	51.24	0.9982
R3	121.92	0.9997	71.57	0.9906	53.15	0.9934	53.05	0.9992
Diffusion models								
D1	242.89	0.9978	135.73	0.9750	104.55	0.9845	101.55	0.9942
D2	248.90	0.9990	142.93	0.9842	109.46	0.9901	107.91	0.9974
D3	255.71	0.9995	152.10	0.9921	115.12	0.9949	115.26	0.9995
D4	251.17	0.9993	145.94	0.9873	111.34	0.9920	110.34	0.9983
Reaction-order models								
F0/R1	113.79	0.9984	63.39	0.9705	47.87	0.9805	46.20	0.9924
F1	126.41	0.9985	76.56	0.9948	56.11	0.9971	56.89	1.0000
F2	25.05	0.9996	19.13	0.9979	17.43	0.9964	16.67	1.0000
F3	159.18	0.9640	118.36	0.9226	78.03	0.9816	85.52	0.9798

Reaction Model	Heating Rates (K min ⁻¹)							
	10		20		30		50	
	Ea kJ mol ⁻¹	R ²	Ea kJ mol ⁻¹	R ²	Ea kJ mol ⁻¹	R ²	Ea kJ mol ⁻¹	R ²
Nucleation models								
P0.7	8.31E-04	0.9624	4.16E-04	0.9266	4.16E-04	0.9861	2.49E-04	0.9984
P2	2.49E-04	0.9624	1.66E-04	0.9266	1.66E-04	0.9861	8.31E-05	0.9984
P3	1.66E-04	0.9624	8.31E-05	0.9266	8.31E-05	0.9861	5.82E-05	0.9984
P4	1.66E-04	0.9624	6.65E-05	0.9266	7.48E-05	0.9861	4.99E-05	0.9984
A1.5	84.06	0.9957	40.44	0.9891	34.86	0.9206	23.02	0.9717
A2	60.89	0.9953	28.07	0.9867	23.90	0.9082	14.98	0.9645
A3	37.71	0.9943	15.70	0.9795	12.94	0.8717	6.95	0.9359
A4	26.12	0.9931	9.52	0.9662	7.46	0.8072	2.93	0.8374
Geometrical contraction models								
R2	121.21	0.9893	58.01	0.9765	53.95	0.9341	35.26	0.9842
R3	124.16	0.9920	60.27	0.9824	54.87	0.9331	36.50	0.9818
Diffusion models								
D1	234.80	0.9806	113.05	0.9617	111.57	0.9448	72.61	0.9921
D2	245.02	0.9870	120.41	0.9740	114.99	0.9432	77.11	0.9888
D3	256.97	0.9927	129.57	0.9853	118.72	0.9411	82.13	0.9847
D4	248.98	0.9891	123.42	0.9783	116.23	0.9426	78.78	0.9874
Reaction-order models								
F0/R1	113.08	0.9789	52.00	0.9537	51.29	0.9365	31.74	0.9906
F1	130.42	0.9961	65.18	0.9909	56.78	0.9306	39.09	0.9767
F2	25.27	0.9952	17.58	0.9977	16.99	0.9852	14.58	0.9966
F3	177.83	0.9786	105.08	0.9590	69.92	0.9067	57.46	0.9441