

Solid degradation and its kinetics on phenol-rich bio-oil production from pyrolysis of coconut shell and Lamtoro wood residue

Apip Amrullah^{*,†}, Obie Farobie^{**,***,†}, and Gatut Pujo Pramono^{****}

*Department of Mechanical Engineering, Lambung Mangkurat University, Banjarmasin, South Kalimantan, Indonesia

**Department of Mechanical and Biosystem Engineering, Faculty of Agricultural Engineering and Technology, IPB University (Bogor Agricultural University), IPB Darmaga Campus, PO BOX 220, Bogor, West Java 16680, Indonesia

***Surfactant and Bioenergy Research Center (SBRC), IPB University (Bogor Agricultural University), Jl. Pajajaran No. 1, IPB Baranangsiang Campus, Bogor, West Java 16144, Indonesia

****PLN UPDK Gorontalo, Jl. Prof. DR. Jhon Aryo Katili, Tanggikiki, Gorontalo, Indonesia

(Received 20 May 2021 • Revised 9 August 2021 • Accepted 11 August 2021)

Abstract—The pyrolysis of coconut shell (CS) only, lamtoro (*Leucaena leucocephala*) wood residues (LWR) only, and a CS/LWR mixture was experimentally studied herein for the first time. Additionally, the reaction kinetics of solid destruction during the pyrolysis process of CS and LWR was deduced. An experimental investigation was carried out in a batch reactor at the different pyrolysis temperatures (300–500 °C). The highest phenol yield (30.97%) was observed at 500 °C for the pyrolysis of CS. The activation energy and pre-exponential factor and for degradation of solid were successfully determined for the first time using the Arrhenius equation. The activation energy was determined in the range of 121–153 kJ mol⁻¹ for the temperature range of 300–500 °C. Meanwhile, the pre-exponential factors of 3.51 × 10¹⁰ s⁻¹, 4.77 × 10¹⁰ s⁻¹, and 5.38 × 10¹⁰ s⁻¹ were calculated for the pyrolysis of CS only, LWR only, and a CS/LWR mixture, respectively. This research presents the mitigation for the alleviation of the energy crisis and to convert underutilized biomass to high-value products.

Keywords: Pyrolysis, Coconut Shell, *Leucaena leucocephala*, Phenol, Reaction Kinetics

INTRODUCTION

World energy demand is increasing due to rapid population growth and industrialization. Current energy demand mostly depends on non-renewable fossil-based fuels such as coal, petroleum, and natural gas. Therefore, the utilization of biomass, which mainly consists of hemicelluloses (20–40%), cellulose (30–60%), and lignin (15–25%), as energy sources is believed to be one of the best choices to accommodate the high demand for energy [1]. Biomass is considered as one of the most significant fossil-fuel substitutes for the production of chemicals and energy owing to its renewability, abundance, and environmental friendliness due to its low ash, nitrogen, and sulfur content [2,3]. Hence, the production of renewable energy and chemicals from biomass has attracted many researchers all over the world to maintain energy security and sustainability [4–6].

There are several ways to convert biomass into fuels and high-value chemicals: chemical, biological, and thermochemical treatments. The thermochemical conversion of lignocellulosic biomass has received considerable attention since it is an inexpensive carbon source and abundantly available [7]. The annual production of lignocellulosic biomass across the world is 181.5 billion tons [8].

Of these, about 7 billion tons from agricultural, grass or forest land is currently used as fodder or for energetic and material purposes. Additionally, about 4.6 billion tons of lignocellulosic biomass residues is produced as agricultural residues, of which only about 25% is used intensively [9]. To convert biomass into fuels and energy, several thermochemical processes such as direct combustion, liquefaction, pyrolysis, and gasification, are being employed presently [10–12]. Pyrolysis is one of the most promising pathways for biomass conversion to generate useful products such as bio-oil, bio-char, and gases due to its several socio-economic advantages as well as the fact it is an efficient conversion method compared to other thermo-chemical conversion technologies [13–15]. Concerning biomass pyrolysis, bio-oil can be utilized as a renewable replacement for petroleum-based fuels or the production of chemicals by upgrading and hydrodeoxygenation approaches [16,17]. Moreover, the potential sustainable chemicals from bio-oil such as cyclic ketones and phenolic compounds for solvents and resins, aromatic hydrocarbon for solvents and fuels, as well as levoglucosan for polymers are also generated. Phenol and its derivative compounds are important chemicals found in myriad industrial products mostly produced from fossil-fuel-derived benzene and propane as feedstocks. Recently, phenol is mainly used in a variety of industries such as resin and synthetic products [18,19]. Since the availability of phenol is determined by petroleum, the products of the industry using phenol as raw material such as phenolic resins and phenol-formaldehyde are relatively expensive. Therefore, thorough research regard-

[†]To whom correspondence should be addressed.

E-mail: apip.amrullah@ulm.ac.id, obiefarobie@apps.ipb.ac.id

Copyright by The Korean Institute of Chemical Engineers.

Table 1. Proximate and ultimate analysis of feedstock

Properties	Coconut shell	Lamtoro wood residue
	Value	Value
Ultimate analysis [wt%]		
Carbon	46.54	49.03
Hydrogen	6.88	6.03
Nitrogen	0.36	0.22
Sulfur	0.19	0.11
Oxygen	43.13	44.12
Ash content	2.9	0.49
Proximate analysis [wt%]		
Volatile matter	79.61	83.16
Ash content	2.9	2.9
Fixed carbon	17.5	17.5
Heating value [Kcal/Kg, db]	3.8	3.8

ing mitigation of the challenges to reduce resin costs is sought to achieve competitive renewable and sustainable phenolic resins. One alternative option to substitute the petroleum-based phenol is by employing pyrolysis of lignocellulosic biomass. As reported by Choi et al. [20], palm-based biomass was a good feedstock for phenolic compound production. Furthermore, Fan et al. [21] investigated that 16–47 wt% of phenolic compounds were produced during fast pyrolysis of lignin at 300–800 °C. Recently, Idris et al. [22] reported that the total of phenol compound up to 42.95% was produced via microwave-induced fast pyrolysis of oil palm empty fruit bunch with activated carbon.

All aforementioned studies provide insights that phenol can be generated via pyrolysis of lignocellulosic biomass, which is mainly from the decomposition of lignin. However, a thorough study about phenolic-rich bio-oil production from coconut shell and Lamtoro wood residue has yet to be reported. Coconut is being planted in many countries around the world mainly Indonesia, Philippines and India that produce nearly 75% of world coconut production nearly. Coconut shell waste (30–40%) is one of the widely available lignocellulosic biomasses found in tropical regions all over the world. Meanwhile, Lamtoro (*Leucaena leucocephala*) is abundantly (more than 50 ton ha⁻¹ yr⁻¹) found in most tropical and subtropical countries in southeast Asia, the Caribbean, the Pacific islands, South Asia, including Hawaii, Australia, and New Guinea [23]. Both feedstocks are widely available in Indonesia, especially in South Kalimantan. Utilizing these biomasses can support government programs to reduce the use of fossil fuels, energy consumption, and environmental pollution problems. The characteristics of pyrolysis of single coconut shell (CS) only, Lamtoro wood residue (LWS) only, as well as a CS/LWR mixture are possibly interesting. Therefore, this study investigated the effect of temperature on phenolic compound production during pyrolysis of CS only, LWR only, and a CS/LWR mixture, because the temperature plays a primary role in endothermic chemical processes, as temperature allows the heat needed to decompose the biomass. Moreover, a detailed destruction rate of the solid biomass and corresponding reaction rates was also studied to provide a better understanding of the conversion behavior of lignocellulosic biomass under pyrolysis conditions.

MATERIALS AND METHODS

1. Feedstock Preparation and Analysis

The feedstocks of LWR and CS were collected from the Banjarbaru area in South Kalimantan, Indonesia. Prior to treatment, the feedstocks were washed with deionized water to remove the impurities. To reduce the moisture content, the feed materials were dried in an air circulating oven for 24 h at 105 °C. After that, the feedstocks were vigorously ground using a grinder and subsequently sieved with a vibration sieve to achieve 0.8 µm of particle size. The characteristic of feedstock is presented in Table 1.

ASTM D3172 method was used to analyze the proximate analysis. This covered the determination of moisture, volatile matter, ash, and calculation of fixed carbon [24]. It reveals that the feedstocks were mainly composed of volatile matter (approximately 79.61 and 83.16 wt% for CS and LWR, respectively) and fixed carbon (approximately 17.5 and 16.35 wt% for CS and LWR, respectively). An elemental analyzer (Flash 2000 series, Thermo Scientific) was used to analyze the ultimate. It shows that both CS and LWR primarily consisted of carbon and oxygen.

2. Experimental

Pyrolysis of CS and LWR was conducted in a batch reactor made of stainless steel as that employed in previous studies by our research group [25]. Please note that three types of feedstocks, CS only, LWR only, and a CS/LWR mixture (a mass ratio of 1 : 1), were employed in this study. The experimental apparatus consists of a PID temperature controller, an electrically heated furnace, and a condenser. To measure the temperature inside the reactor, κ -type thermocouple (L-2001E) was used. Initially, the feedstock was introduced in the reactor. For each experimental run, 250 g of feedstock was used. Subsequently, the reactor was purged with N₂ using a pressure gauge to ensure the pyrolysis process was under inert condition. The temperatures reported during the experiments are the actual temperature values inside the reactor. Experiments were conducted at 300, 400, and 500 °C. A water-cooled condenser made of a copper tube was used to condense the vapors generated after pyrolysis. The obtained liquid phase was collected. Subsequently, diethyl ether (1 : 1 mass fraction) was added to the condensed liq-

uid to separate the bio-oil from the aqueous fraction. The bio-oil was dried over 1 wt% of anhydrous sodium sulfate. The mixture was then filtered. To remove the diethyl ether, the solution was evaporated using a rotary evaporator at 25 °C. The obtained bio-oil was weighted. Furthermore, after cooling the reactor the char was collected. The char was then dried at 105 °C using an oven to achieve a constant weight to calculate the yield of the char. The details of product yield calculation are presented in the previous work of Amrullah et al. [25].

3. Characterization of Bio-oil

Bio-oil product was analyzed by gas chromatography-mass spec-

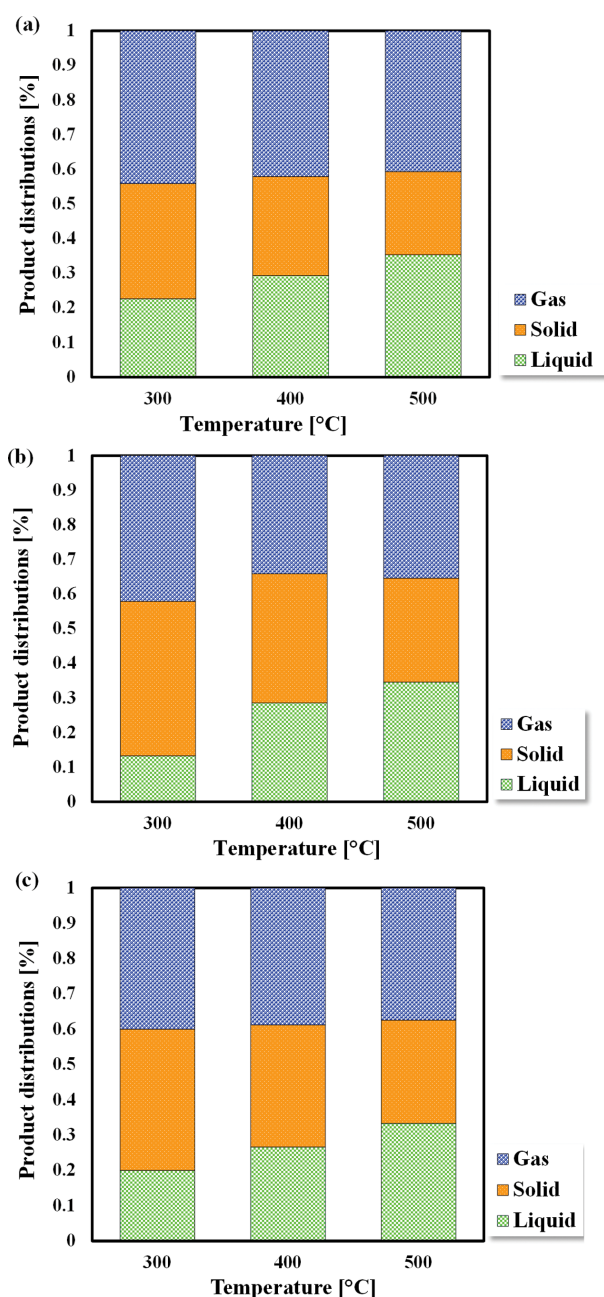


Fig. 1. Product distribution of (a) CS only, (b) LWR only, and (c) a CS/LWR mixture at various temperatures (300, 400, and 500 °C).

trophotometry (GC-MS, QP-2010). A capillary column, as well as the temperature program employed herein, have been reported in the previous study [25]. The GC-MS peaks were identified based on the NIST mass spectra library. The dilution solvent used was methanol with a dilution rate of 1 : 5. All chemicals used were of analytical grades. For consistency, all experimental setup and analyses were carried out in duplicate.

RESULTS AND DISCUSSION

1. Effect of Temperature on Product Distributions

Temperature plays a primary role in endothermic chemical processes such as pyrolysis since temperature allows the heat needed to decompose the biomass. In this study, the pyrolysis of CS only, LWR only, and a CS/LWR mixture was conducted comparatively at temperatures range of 300-500 °C. The product distributions from thermal pyrolysis of CS only, LWR only, and a CS/LWR mixture obtained at various temperatures of 300, 400, and 500 °C are presented in Fig. 1.

As observed, the temperature of pyrolysis considerably affected the product distribution. Notably, by increasing the pyrolysis temperature from 300 °C to 500 °C, bio-oil yield increased from 22.6% to 35.3% for CS only, from 13.3% to 34.6% for LWR only, and from 20.0% to 33.3% for a CS/LWR mixture, which is considered to be due to reinforced primary cracking of the lignin molecules during pyrolysis at higher temperatures to generate liquid hydrocarbons [7]. Meanwhile, solid or char yield decreased from 33.3% to 24.0% for CS only, from 44.6% to 30.0% for LWR only, and from 40.0% to 29.3% for a CS/LWR mixture confirming that the solid materials decompose at higher temperature. The maximum bio-oil yield of 35.3% was obtained from the pyrolysis of CS only at 500 °C. This finding is in line with the previous work of [26] who obtained a maximum bio-oil yield of 38.7% at 500 °C for the pyrolysis of babool seeds. It can be said that the yield of bio-oil can be promising and comparable for alternative fuel production.

As mentioned that the most critical parameter affecting the yield of the products during the pyrolysis of biomass is temperature of which it is correlated with heating value. Pyrolysis characteristic of large-scale of coal was evaluated by Wang et al. [27]. The increasing in scale leads to the decrease of heat transfer efficiency and the

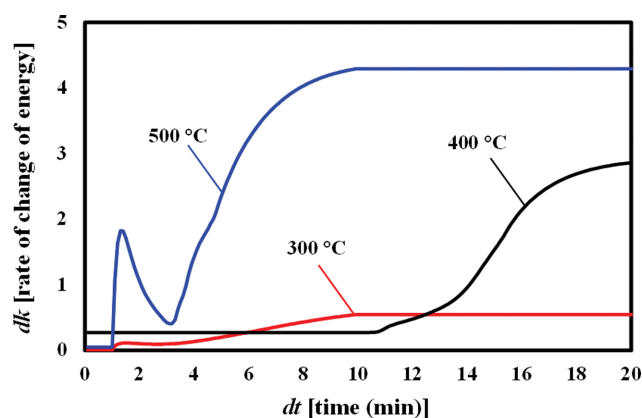


Fig. 2. Rate of change of energy during the pyrolysis process.

increase of pyrolysis retention time, which can improve the pyrolysis efficiency for large-scale coal. It demonstrates that by optimizing existing pyrolysis systems, it is possible to achieve adequate flexibility in the co-pyrolysis of biomass, coal, and plastic waste while also generating promising economic and socio-environmental benefits.

The rate of change of energy during the thermochemical conversion of biomass can be expressed as:

$$\frac{\partial k}{\partial t} + C = -\phi - T - P - D_{\mu} - \varepsilon \quad (1)$$

where C is the energy convection due to particle movement; ϕ is

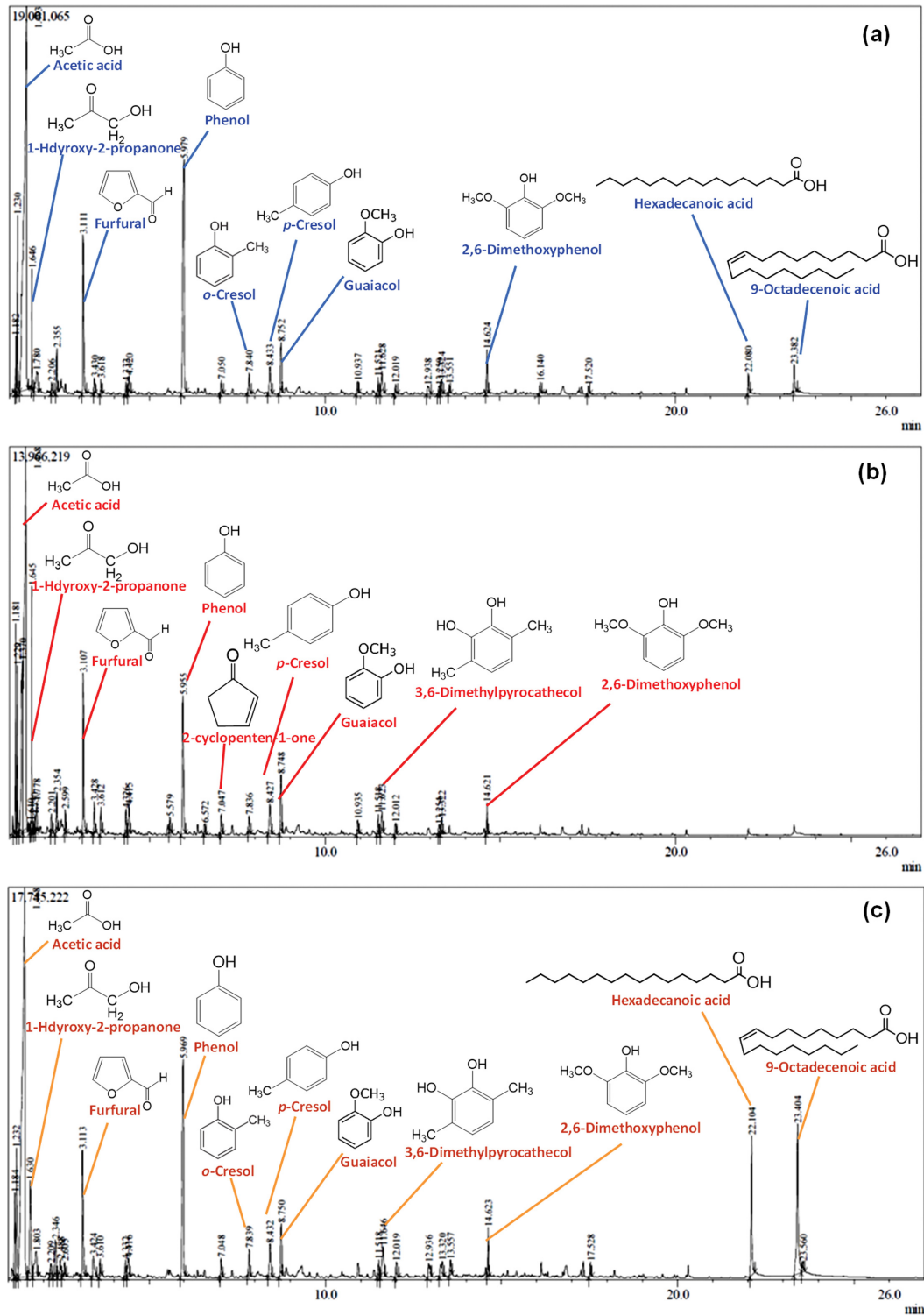


Fig. 3. GC/MS chromatogram from pyrolysis of (a) CS only, (b) LWR only, and (c) a CS/LWR mixture at 500 °C.

the energy transport due to pressure effect); T is energy transport due to the vortices movement; P is the energy production; D_μ is the viscous diffusion, and ε is the viscous dissipation.

By employing Eq. (1), the rate of change of energy during the pyrolysis at different temperatures is presented in Fig. 2. As expected, the higher temperature (500 °C) showed a higher rate of change of energy during the pyrolysis process and contributed to rises in bio-oil yield. This rise in the yield of bio-oil is attributed to the fact that a higher heating rate reduces mass and heat transfer limitations, while also avoiding secondary decomposition reactions (Varma et al. [28]).

2. GC-MS Analysis of CS Only, LWR Only, and CS:LWR bio-Oil Fraction

Due to the complexity of the chemical composition of bio-oil and the limitation of the GC method, the chemical composition of the bio-oils from pyrolysis of CS only, LWR only, and a CS/LWR mixture was analyzed using a GC-MS. The representative GC-MS chromatograms from sample pyrolysis oils of CS only, LWR only, and a CS/LWR mixture are presented in Fig. 3. The main bio-oil products identified from the pyrolysis of LWR only include acetic acid, 1-hydroxy-2-propanone, furfural, phenol, o-cresol, p-cresol, guaiacol, 2,6-dimethoxyphenol. Meanwhile, for the case of pyrolysis of CS only and a CS/LWR mixture, free fatty acid peaks such as hexadecanoic acid and 9-octadecanoic acid were also identified, which are expected to be due to degradation products of triglycerides.

The detailed main components identified from the pyrolysis of CS only, LWR only, and a CS/LWR mixture at various temperatures (300, 400, and 500 °C) are presented in Table 2. The different feedstocks and the pyrolysis temperature have a crucial impact on the chemical composition of bio-oil products. Bio-oils produced through the standard pyrolysis process are typically multi-component combinations of carbohydrate and lignin thermal degradation products with low pH, high viscosity, and high-water content, limiting its use as a fuel on a large scale. By increasing the temperature from 300 °C to 500 °C, the organic acid and phenol content increased for all feedstocks. Overall, the major peaks of bio-oil products identified from pyrolysis are acetic acid (34-49%), phenol (14-30.97%), and 2-propanone (6-19.8%). This result is in accordance with the previous works which reported that aldehydes, ketones, phenols, organic acid, and alcohol groups were among the highly oxygenated organics in the bio-oil (Junming et al. [29]). These chemicals originate from the degradation of hemicellulose, cellulose, and lignin.

3. Temperature Effect on Phenol Production

Phenol is one of the most promising chemicals from the pyrolysis of biomass. The yields of phenolic compounds obtained from the pyrolysis of CS only, LWR only, and a CS/LWR mixture at different pyrolysis temperatures of 300, 400, and 500 °C are shown in Fig. 4. The different biomass feedstock as well as the pyrolysis temperature influence phenol yields. It is interesting that the phenol

Table 2. (a) The chemicals detected from pyrolysis of CS only using GC-MS

Compounds	Molecular weight [g/mol]	Relative content (%)		
		Temperature [°C]		
		300	400	500
Organic acids				
Acetic acid	60.05	49.5	49.0	45.76
Hexadecanoic acid	256.42	1.98	0.9	-
2-Propanoic acid	72.06	0.19	1.37	0.34
9-Octadecanoic acid	282.5	0.04	-	0.46
Ketones				
2-Propanone	58.08	4.76	7.71	7.22
2-Butanone	72.11	0.15	-	-
1-Hydroxy-2-butanone	88.11	2.03	2.53	2.70
Ethanone	44.05	0.34	0.49	0.53
Cyclopentanone	84.12	0.32	0.39	-
2-Cyclopenten-1-one	82.1	0.52	0.96	1.00
Phenols				
Phenol	94.11	26.64	27.98	30.97
2-Methoxy-4-methylphenol	138.16	0.54	0.56	0.64
Hydrocarbons				
1,2,4-Trimethoxybenzene	168.19	0.29	-	0.41
1,2-Benzenediol	110.11	0.82	1.98	2.22
1,4-Benzenediol	110.11	0.34	0.35	0.61
Heptadecene	238.5	2.30	1.26	-
Aldehydes				
Benzaldehyde	106.12	0.19	-	-
2-Furancarboxaldehyde	96.08	5.09	4.49	5.46

Table 2. (b) The chemicals detected from pyrolysis of LWR only using GC-MS

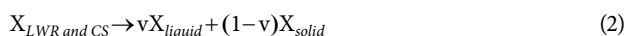
Compounds	Molecular weight [g/mol]	Relative content (%)		
		Temperature [°C]		
		300	400	500
Organic acids				
Acetic acid	60.05	34.24	48.79	34.86
Hexadecanoic acid	256.42	0.58	0.41	-
2-Propenoic acid	72.06	0.39	-	0.33
Ketones				
2-Propanone	58.08	9.95	19.82	0.61
2-Butanone	72.11	0.17	-	5.58
1-Hydroxy-2-butanone	88.11	2.01	-	2.32
Ethanone	44.05	1.03	-	0.83
Cyclopentanone	84.12	1.11	0.64	0.76
2-Cyclopenten-1-one	82.1	1.44	2.58	1.98
Phenols				
Phenol	94.11	14.12	16.16	22.85
Alcohol				
2-Furanmethanol	98.1	1.15	0.42	1.32
Hydrocarbons				
2-Furancarboxaldehyde	96.08	2.88	3.71	3.75
1,2-Benzenediol	110.11	1.22	1.83	1.36
Pyrazine	80.09	1.06	-	-
Pyridine	79.1	0.89	0.51	0.48

yield obtained from the pyrolysis of CS is greater than that of LWR. It could be attributed to the fact that CS composition has higher lignin content than LWR.

Overall, the phenol yield increased from 26.6 to 30.97% (CS only), from 14.12 to 23% (LWR only), and from 22.6 to 25.9% (a CS/LWR mixture) by increasing the temperature from 300 °C to 500 °C. This could be attributed to the enhanced degradation reaction of LWR and CS due to temperature changes from 300 to 500 °C, leading to the devolatilization of biomass. Accordingly, it could increase the phenol yield. This result is slightly higher than the pyrolysis of woody biomass resulting in a phenol yield of 16% (Guzelciftci et al. [30]). Furthermore, Luo et al. [31] reported that phenolic compounds up to 20% were obtained in a fluidized bed reactor from the pyrolysis of wood and rice straw. It can be confirmed that the concentration of phenolic compounds in bio-oil generated by pyrolysis of biomass is highly influenced by the lignin content of biomass, types of biomass feedstock, pyrolysis reaction, and pyrolysis activity conditions [32,33].

4. Determination of Reaction Rate of Solid Destruction

The reaction rate constant is important for understanding the behavior of solid biomass during thermochemical treatment. The reaction rate constant of solid destruction during hydrothermal treatment can be calculated by considering the equation of a first-order rate order. The model of solid destruction during pyrolysis can be expressed as:



The subscripts LWR and CS, liquid, and solid indicate the original

feedstock of LWR and CS, liquid phase, and remaining solid, respectively. Meanwhile, v represents the fraction of solid converted to liquid. All of the solid is destructed at 300 °C, as depicted in Fig. 5(a). The yield of liquid at this temperature should correlate to the value of v , which is 0.114-0.118 mol/mol. The following differential rate equation can be expressed by assuming the first-order reaction:

$$\frac{d[X_{LWR \text{ and } CS}]}{dt} = -k[X_{LWR \text{ and } CS}] \quad (3)$$

Note that $[X_{LWR \text{ and } CS}]$ is the concentration of $X_{LWR \text{ and } CS}$.

The equation mass of mass balance gives:

$$\begin{aligned} [X_{LWR \text{ and } CS}] + [X_{liquid}] + [X_{solid}] &= \text{const} \\ &= [X_{LWR \text{ and } CS}]_i + [X_{liquid}]_i + [X_{solid}]_i = [X_{LWR \text{ and } CS}]_t \end{aligned} \quad (4)$$

where the subscript i is the initial condition and the subscript t is the total amount of LWS and CS. Noting that the concentration of $X_{LWR \text{ and } CS}$ is expressed as:

$$[X_{LWR \text{ and } CS}] = \frac{1-v}{v}[X_{liquid}] \quad (5)$$

Thus,

$$\begin{aligned} [X_{LWR \text{ and } CS}] &= [X_{LWR \text{ and } CS}]_t - [X_{liquid}] - [X_{solid}] \\ [X_{LWR \text{ and } CS}]_t - [X_{liquid}] - \frac{1-v}{v}[X_{liquid}] \\ &= [X_{LWR \text{ and } CS}]_t - \left(1 + \frac{1-v}{v}\right)[X_{liquid}] = [X_{LWR \text{ and } CS}]_t - \frac{1}{v}[X_{liquid}] \end{aligned} \quad (6)$$

Substitution of Eq. (6) into Eq. (3) gives:

Table 2. (c) The chemicals detected from pyrolysis of a CS/LWR mixture using GC-MS

Compounds	Molecular weight [g/mol]	Relative content (%)		
		Temperature [°C]		
		300	400	500
Organic acids				
Acetic acid	60.05	46.23	43.78	37.14
Hexadecanoic acid	256.42	1.17	0.45	1.78
2-Propenoic acid	72.06	1.31	2.41	4.39
Ketones				
2-Propanone	58.08	8.91	14.75	17.56
1-Hydroxy-2-butanone	88.11	2.84	1.35	1.32
Ethanone	44.05	-	0.83	0.69
Cyclopentanone	84.12	0.38	-	0.69
2-Cyclopenten-1-one	82.1	0.98	1.32	1.28
Phenols				
Phenol	94.11	22.61	25.74	25.91
2-Methoxy-4-methylphenol	138.16	-	0.651	0.56
Alcohols				
2-Furanmethanol	98.1	0.28	0.63	0.65
Pentanol	88.15	0.68	-	0.65
Hydrocarbons				
2-Furancarboxaldehyde	96.08	3.91	4.92	4.29
1,2-Benzenediol	110.11	1.92	1.35	3.07
Furan				
Furan	68.07	0.58	0.57	0.56
2(3H)-Furanone	84.07	0.38	-	0.32
Benzene				
1,2,4-Trimethoxybenzene	168.19	0.25	0.33	0.29

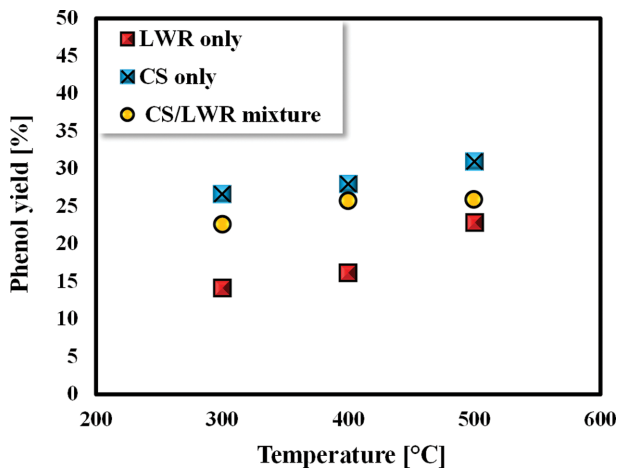


Fig. 4. Temperature effect on phenol yield (Temperature: 300, 400, and 500 °C).

$$\frac{d}{dt}([X_{LWR \text{ and } CS}]_t - \frac{1}{v}[X_{liquid}]) = -k([X_{LWR \text{ and } CS}]_t - \frac{1}{v}[X_{liquid}]) \quad (7)$$

Eq. (7) can be simplified as follows:

$$\frac{d}{dt}([X_{liquid}]) = vk([X_{LWR \text{ and } CS}]_t - \frac{1}{v}[X_{liquid}]) \quad (8)$$

$$\frac{d}{dt} \left(\frac{[X_{liquid}]}{[X_{LWR \text{ and } CS}]_t} \right) = vk - k \frac{[X_{liquid}]}{[X_{LWR \text{ and } CS}]_t} \quad (9)$$

The liquid yield is expressed as:

$$Y_{liquid} = \frac{[X_{liquid}]}{[X_{LWR \text{ and } CS}]_t} \quad (10)$$

Then Eq. (9) can be expressed as:

$$\frac{d}{dt} Y_{liquid} = vk - kY_{liquid} \quad (11)$$

This equation can be solved as follows:

$$\frac{dY_{liquid}}{vk - kY_{liquid}} = dt \quad (12)$$

$$\ln(v - Y_{liquid}) = -kt + C \quad (13)$$

$$Y_{liquid} = v - A \exp(-kt) \quad (14)$$

At $t=0$, the liquid yield is $Y_{liquid, i}$:

$$Y_{liquid} = v - (v - Y_{liquid, i}) \exp(-kt) \quad (15)$$

By assuming Arrhenius behavior, the reaction rate constant can be expressed as:

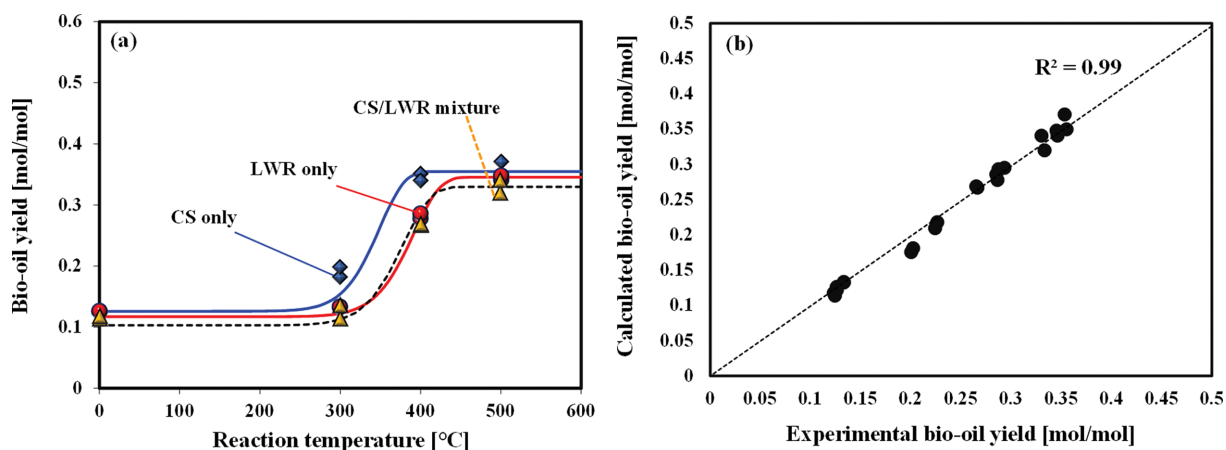


Fig. 5. (a) Temperature effect on liquid bio-oil yield and (b) comparison of experimental and calculated liquid bio-oil yield.

$$k = k_0 \exp\left(\frac{-E_a}{RT}\right) \quad (16)$$

where k_0 is the pre-exponential factor, E_a is the activation energy, R is gas constant and T is temperature.

Finally, by solving the equation above, the yield of liquid can be expressed as follows:

$$Y_{liquid} = v - (v - Y_{liquid,i}) \exp\left(-k_0 \exp\left(\frac{-E_a}{RT}\right)t\right) \quad (17)$$

To reproduce the experimental results, the values of activation energy and the pre-exponential factor were calculated using the least-squares approach. In this study, the pre-exponential factors of $3.51 \times 10^{10} \text{ s}^{-1}$, $4.77 \times 10^{10} \text{ s}^{-1}$, and $5.38 \times 10^{10} \text{ s}^{-1}$ were determined for the pyrolysis of CS only, LWR only, and a CS/LWR mixture, respectively. Meanwhile, the activation energy was determined at the range of 121–153 kJ mol^{-1} . Fig. 5(a) displays the calculated liquid bio-oil yield. As can be seen, the calculated and experimental values are in strong agreement. A parity plot using the least square error (LSE) method to compare the experimental and calculated results is shown in Fig. 5(b). The model shows the high coefficient of determination (R^2) indicates that it represents the experimental data well.

Genieva et al. [34] calculated the activation energies of raw and impregnated almond shells during the pyrolysis process. Their calculation value was 125.3 kJ mol^{-1} , which is lower than that for energy activation determined from this study, namely 153 kJ mol^{-1} . The high value of energy activation from this study indicates that the high energy needs to decompose strong bond molecules contained in LWR and CS. The mixture of CS/LWR biomass allows the formation of complex molecules.

CONCLUSION

Pyrolysis of CS only, LWR only, and a CS/LWR mixture was carried out to produce phenol-rich bio-oil at different temperatures (300, 400, 500 °C). The phenol yield (30.97%) was observed at 500 °C for the pyrolysis of CS. The reaction rate constant for solid destruction of the raw materials was deduced for the first time. The kinetic model was observed in strong agreement with the experimental

data. The generated kinetics model can provide essential pyrolysis data and can be applied to other thermal corresponding models to determine kinetic parameters and the most possible reaction mechanism. The pre-exponential factors were determined for the pyrolysis of CS only, LWR only, and a CS/LWR mixture, respectively. Meanwhile, the activation energy was determined in the range of 121–153 kJ mol^{-1} . Of note is that the optimized reaction temperature obtained at 500 °C yielded higher phenolic compounds in the bio-oil. Therefore, substantial energy savings can be expected using the pyrolysis method and route of comprehensive utilization of CS, LWR, and CS/LWR mix to produce phenols.

ACKNOWLEDGEMENTS

This research was supported by Lambung Mangkurat University, South Kalimantan, Indonesia.

REFERENCES

1. S. Dahadha, Z. Amin, A. A. Baziyar Lakeh and E. Elbeshbishy, *Energy Fuels*, **31**, 10347 (2017).
2. A. Ahmed, M. S. Abu Bakar, R. S. Sukri, M. Hussain, A. Farooq, S. Moogi and Y. K. Park, *Energy Convers. Manag.*, **226**, 113502 (2020).
3. H. Huang, J. Liu, H. Liu, F. Evrendilek and M. Buyukada, *Energy Convers. Manag.*, **207**, 112552 (2020).
4. S. Feng, Z. Yuan, M. Leitch and C. C. Xu, *Fuel*, **116**, 214 (2014).
5. Y. Huang, L. Wei, Z. Crandall, J. Julson and Z. Gu, *Fuel*, **150**, 663 (2015).
6. L. Nazari, Z. Yuan, S. Souzanchi, M. B. Ray and C. Xu, *Fuel*, **162**, 83 (2015).
7. H. Paysepar, K. T. Venkateswara Rao, Z. Yuan, H. Shui and C. Xu, *J. Anal. Appl. Pyrolysis*, **149**, 104842 (2020).
8. N. Dahmen, I. Lewandowski, S. Zibek and A. Weidtmann, *GCB Bioenergy*, **11**, 12586 (2019).
9. S. Piotrowski, M. Carus and R. Essel, *Biotechnol.*, **11**, 29021 (2015).
10. R. A. Garrido, J. M. Reckamp and J. A. Satrio, *Environ. - MDPI*, **4**, 4040096 (2017).
11. O. Farobie, P. Changkiendee, S. Inoue, T. Inoue, Y. Kawai, T. Noguchi, H. Tanigawa and Y. Matsumura, *Ind. Eng. Chem. Res.*, **56**,

- 6407 (2017).
12. T. Samanmulya, O. Farobie and Y. Matsumura, *J. Japan Pet. Inst.*, **60**, 34 (2017).
 13. S. Zhong, B. Zhang, C. Liu and A. Shujaa aldeen, *Energy Convers. Manag.*, **228**, 113717 (2021).
 14. P. Zong, Y. Jiang, Y. Tian, J. Li, M. Yuan, Y. Ji, M. Chen, D. Li and Y. Qiao, *Energy Convers. Manag.*, **216**, 112777 (2020).
 15. X. Lv, H. Liu, Y. Huang, J. Yao, H. Yuan, X. Yin and C. Wu, *Energy Convers. Manag.*, **229**, 113772 (2021).
 16. Y. Fan, M. Zhu, L. Jin, E. Cui, L. Zhu, Y. Cai and W. Zhao, *Renew. Energy*, **157**, 115 (2020).
 17. M. Razavian and S. Fatemi, *J. Anal. Appl. Pyrol.*, **156**, 105093 (2021).
 18. Q. Bu, H. Lei, S. Ren, L. Wang, J. Holladay, Q. Zhang, J. Tang and R. Ruan, *Bioresour. Technol.*, **102**, 7007 (2011).
 19. M. Del Olmo, A. Zafra, A. B. Jurado and J. L. Vilchez, *Talanta*, **50**, 9140 (2000).
 20. G. G. Choi, S. J. Oh, S. J. Lee and J. S. Kim, *Bioresour. Technol.*, **178**, 107 (2015).
 21. L. Fan, Y. Zhang, S. Liu, N. Zhou, P. Chen, Y. Cheng, M. Addy, Q. Lu, M. M. Omar, Y. Liu, Y. Wang, L. Dai, E. Anderson, P. Peng, H. Lei and R. Ruan, *Bioresour. Technol.*, **241**, 129 (2017).
 22. R. Idris, W. W. F. Chong, A. Ali, S. Idris, M. F. Hasan, F. N. Ani and C. T. Chong, *Environ. Technol. Innov.*, **21**, 101291 (2021).
 23. M. J. Feria, F. López, J. C. García, A. Pérez, M. A. M. Zamudio and A. Alfaro, *Biomass Bioenergy*, **35**, 2233 (2011).
 24. ASTM D3172-13, ASTM International, West Conshohocken, PA, **13**, 3172 (2013).
 25. A. Amrullah, O. Farobie and R. Widyanto, *Bioresour. Technol. Rep.*, **13**, 100642 (2021).
 26. R. Garg, N. Anand and D. Kumar, *Renew. Energy*, **96**, 171 (2016).
 27. Z. Wang, D. Liang, Y. Li, H. Tian and J. Liang, *J. Anal. Appl. Pyrol.*, **158**, 105060 (2021).
 28. A. K. Varma, L. S. Thakur, R. Shankar and P. Mondal, *Waste Manag.*, **89**, 235 (2019).
 29. X. Junming, J. Jianchun, S. Yunjuan and L. Yanju, *Biomass Bioenergy*, **32**, 1061 (2008).
 30. B. Guzelciftci, K. B. Park and J. S. Kim, *Energy*, **200**, 117536 (2020).
 31. Z. Luo, S. Wang, Y. Liao, J. Zhou, Y. Gu and K. Cen, *Biomass Bioenergy*, **26**, 462 (2004).
 32. J. S. Kim, *Bioresour. Technol.*, **178**, 121 (2015).
 33. A. Amrullah, N. Paksung and Y. Matsumura, *Korean J. Chem. Eng.*, **36**, 11814 (2019).
 34. S. Genieva, L. Gonsalvesh, V. Georgieva, M. Tavlieva and L. Vlaev, *Thermochim. Acta*, **698**, 178877 (2021).