

Article

# Removal of Tar Contents Derived from Lignocellulosic Biomass Gasification Facilities Using MgAl-LDH@clinoptilolite

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**Abstract:** Gasification of lignocellulosic biomass requires the effective removal method of tar. This study focused on the application of specially designed Mg/Al-layered double hydroxides clinoptilolite (Mg/Al-LDH@clinoptilolite) to improve the removal efficiency of tar, which would eventually lead to enhancing the power efficiency of gasification, preventing damage to facilities, and deducing durability improvement plans. Zeolite-layered double hydroxides impregnated with clinoptilolite, a natural zeolite, and Mg/Al-layered double hydroxide incorporated into conventional water scrubbers were prepared to enhance the removal efficiency of the tar and improve the quality of the syngas produced during the gasification process. The simultaneous removal of moisture and CO<sub>2</sub> in the syngas was also investigated during the removal of the tar. The drastic decrease in tar and CO<sub>2</sub> concentration was confirmed, which triggered a relative increase in the effective content of inflammable gas. The findings of the present study provide a practical approach to increasing power efficiency and durability during the gasification of lignocellulosic biomass.

**Keywords:** lignocellulosic biomass; gasification; syngas; tar; CO<sub>2</sub>; clinoptilolite; Mg/Al-LDH@clinoptilolite



**Citation:** Kim, I.-T.; Ahn, K.-H.; Jung, J.; Jeong, Y.; Shin, D.-C.; Lee, Y.-E. Removal of Tar Contents Derived from Lignocellulosic Biomass Gasification Facilities Using MgAl-LDH@clinoptilolite. *Catalysts* **2021**, *11*, 1111. <https://doi.org/10.3390/catal11091111>

Academic Editors: Ákos Kukovecz and Violeta Niculescu

Received: 23 August 2021

Accepted: 13 September 2021

Published: 16 September 2021

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## 1. Introduction

The South Korean Government announced its “2050 Carbon Neutrality Development Strategy of the Republic of Korea” on 7 December 2020. According to this strategy, fossil fuels should be replaced as major energy sources with renewable energy sources that are both safe to use and have low carbon emissions to accelerate energy conversion and thus facilitate carbon neutralization [1]. Currently, in Korea, approximately 40.4% of the electricity produced uses coal as the energy source, which is higher than that in other major countries such as the United States (24%), Japan (32%), and Germany (30%), implying that the movement toward carbon neutralization needs to be emphasized [2,3]. Small-scale dispersive gasification power generators that use thinning-out trees or waste wood as raw materials instead of fossil fuels are more likely to aid in achieving carbon neutrality than fossil fuels such as coal. Tar is composed of organic polymers with varying and complex structures. The tar generated during the gasification of lignocellulosic biomass comprises condensed hydrocarbons containing 1–5 benzene rings [4,5]. The main components of the tar generated in this process are mixed oxygenates, heterocyclic ethers, alkyl phenolics, polycyclic aromatic hydrocarbons (PAHs), and phenolic ethers. As the reaction proceeds in the gasification reactor, the components of the tar change from high molecular-weight PAHs to low-molecular-weight mixed oxygenates [6–10].

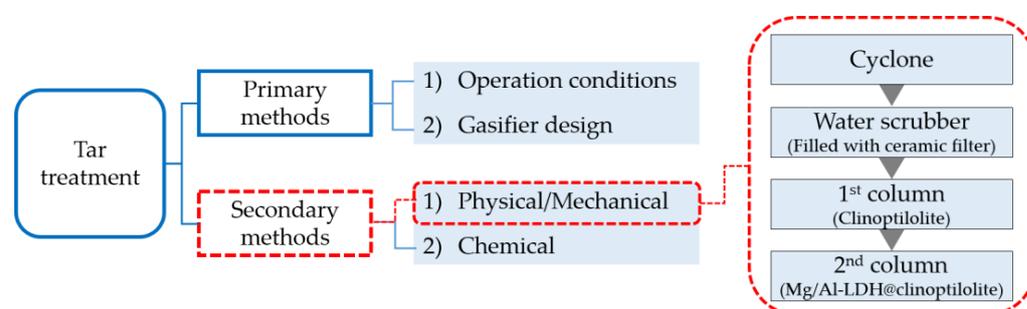
The tar produced by the gasifier reduces the gasification efficiency and quality of the syngas, which is responsible for corrosion and blockage in the reactor, pipes, gas engine, and turbines, leading to high maintenance costs for subsequent filtration systems and generators [11].

Existing methods for tar removal can be classified as primary and secondary [12]. Primary methods are based on the primary reduction of tar formation within the gasifier by changing the catalyst or design of the reactor. However, even when primary methods are adopted, the application of the secondary is required for better removal of tar downstream of the gasifier [13,14].

Dolomite, which is inexpensive and excellent for tar removal, is typically used as a catalyst [15–21]. However, it is difficult to apply in circulating fluidized bed reactors owing to its weak mechanical strength and vulnerability to abrasion. Active alumina and silica-alumina are also effective in removing tar. However, rapid loss of activity is observed due to coke deposition on the catalyst surface. Tar removal methods using olivine have also been extensively studied [22–26]. While the tar removal efficiency of olivine is relatively lower than that of dolomite, it is highly resistant to mechanical abrasion. Nitrogen-based catalysts exhibit the highest activity but have the disadvantages of high manufacturing costs and vulnerability to deactivation by sulfur [14]. Sutton et al. [27] proposed five conditions that need to be satisfied if a catalyst is to be used to remove tar generated during the gasification process: (1) The catalyst should be effective in tar removal, (2) it should be resistant to deactivation, (3) it should be readily regenerated, (4) it should be strong, and (5) it should be a reasonable price.

Zeolites have been used as catalysts in various hydrocarbon conversion reactions such as alkylation, cracking, hydrocracking, isomerization, dehydration, Fischer–Tropsch reactions, methanation, and methanol synthesis [28]. However, research on the utilization of zeolite for tar removal from biomass has been limited to the removal of phenol through gasification methods involving the combination of the commercially available zeolite, HZSM-5 catalyst, and palm shell [29], and zeolites have never been researched as catalysts to remove tar and CO<sub>2</sub> from gasification power generators. The advantages of zeolites over amorphous catalysts are their acidity, resistance to nitrogen and sulfur compounds, low rate of coke formation, greater thermal/hydrothermal stability, and easy regeneration [30].

This study aimed to enhance tar removal efficiency by supplementing conventional gasification power generation processes with catalysts that satisfy the aforementioned conditions. Simultaneously, we aimed to enhance the quality of syngas by increasing the CO<sub>2</sub> removal rate from the syngas compared to conventional methods and deduce methods for reducing carbon emissions. To meet our aims, we produced Mg/Al-LDH@clinoptilolite by impregnating clinoptilolite, a type of zeolite that is easy and inexpensive to excavate, as it is naturally prevalent in Korea, with Mg/Al-layered double hydroxide, and applied these catalysts to the wet scrubber processes marked in red in Figure 1. The overall goal was to enhance the efficiency of power generation by improving the durability of the process and the quality of the syngas.



**Figure 1.** Schematic illustration of the different methods used for tar treatment. The processes marked in red are applicable to this study and have been targeted for improvement.

## 2. Results and Discussion

### 2.1. Characteristics of Tar Production and Removal in Syngas

Through the analysis, it was confirmed that the tar in the syngas contained 19 compounds. These compounds largely consisted of carbohydrates, furans, phenols, and guaia-

cols, as shown in Table 1. The most prevalent compounds were guaiacols, comprising 41.5% of the total compounds, followed by phenols (35.6%). The combustion of lignocellulosic biomass, such as wood, generates various tar compounds, such as phenols and cresols. If the combustion temperature reaches 900 °C, high-molecular-weight PAHs can also be generated [31].

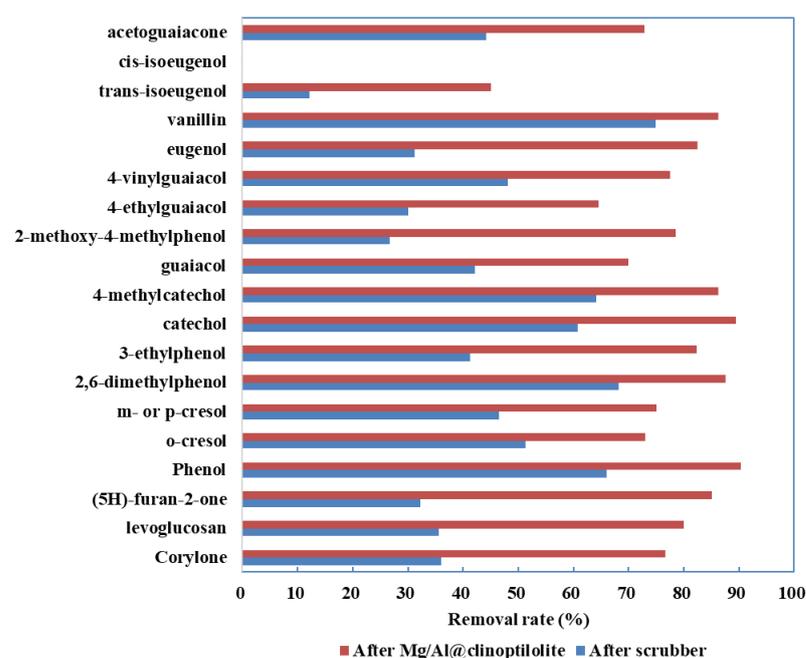
**Table 1.** The chemical composition of tar in syngas.

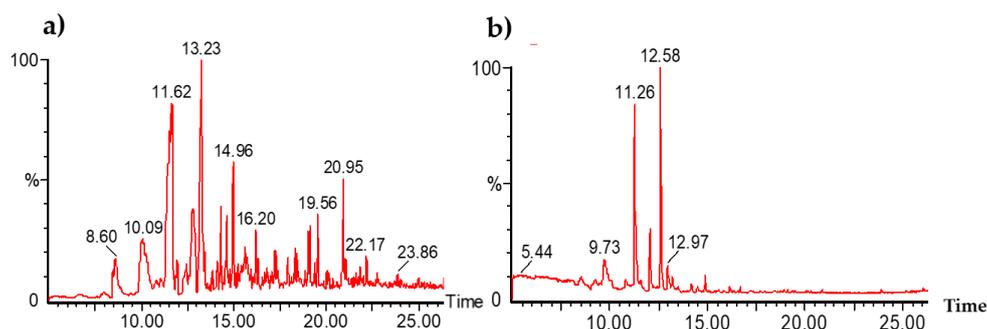
Compounds	CAS No	Detected Mass-to-Charge Ratio ( <i>m/z</i> )	%
<b>Carbohydrates</b>			<b>7.3</b>
Corylone	80-71-7	112, 69, 55	5.4
levoglucosan	498-07-7	60, 57, 73	1.9
<b>Furans</b>			<b>1.2</b>
(5H)-furan-2-one	497-23-4	55, 84, 27	1.20
<b>Phenols</b>			<b>35.6</b>
Phenol	108-95-2	94, 66, 65	9.1
o-cresol	95-48-7	108, 107, 79	4.8
m- or p-cresol	108-39-4	108, 107, 79	8.6
2,6-dimethylphenol	576-26-1	122, 107, 77	3.4
3-ethylphenol	620-17-7	107, 122, 77	5.2
catechol	120-80-9	110, 64, 63	2.2
4-methylcatechol	452-86-8	124, 123, 78	2.3
<b>Guaiacols</b>			<b>41.5</b>
guaiacol	90-05-1	109, 124, 81	11.2
2-methoxy-4-methylphenol	93-51-6	138, 123, 95	1.9
4-ethylguaiacol	2785-89-9	137, 152, 15	9.8
4-vinylguaiacol	7786-61-0	135, 150, 107	2.7
eugenol	97-53-0	164, 103, 77	3.8
vanillin	121-33-5	152, 151, 81	4.4
trans-isoeugenol	97-54-1	164, 149, 103	1.5
cis-isoeugenol		164, 77, 149	
acetoguaiacone	498-02-2	151, 166, 123	6.2

Table 2 lists the concentrations of the generated tar compounds in the water scrubber column and the final discharged gas. With this, the changes of the tar in the syngas after each removal process can be monitored. In this study, syngas consecutively passed through the water scrubber filled with a ceramic filter; a column filled with clinoptilolite and a column filled with Mg/Al-LDH@clinoptilolite at an SV of 0.3 m·s<sup>-1</sup>. The removal rate for each compound is shown in Figure 2, while Figure 3 depicts the subsequent changes in the total ion chromatogram pattern.

**Table 2.** Concentrations of generated tar compounds and the tar compound content in the syngas for each removal process.

No.	Chemical Species	Syngas from Cyclone	After Scrubber	After Mg/Al-LDH@Clinoptilolite		
		mg/Nm <sup>3</sup>	mg/Nm <sup>3</sup>	mg/Nm <sup>3</sup>		
1	Carbohydrates	Corylone	101.20	64.7	23.6	
2		levoglucosan	12.34	7.9	2.1	
3	Furans	(5H)-furan-2-one	23.50	15.2	3.4	
4	Phenols	Phenol	359.90	122.4	34.6	
5		o-cresol	67.40	32.8	18.2	
6		m- or p-cresol	181.20	96.8	45.2	
7		2,6-dimethylphenol	11.3	4.8	1.3	
8		3-ethylphenol	76.90	45.2	13.6	
9		catechol	18.21	11.2	2.5	
10		4-methylcatechol	21.38	8.9	1.8	
11		Guaiacols	guaiacol	31.30	18.1	9.4
12			2-methoxy-4-methylphenol	58.90	43.2	12.6
13	4-ethylguaiacol		26.30	18.4	9.3	
14	4-vinylguaiacol		152.10	78.9	34.2	
15	eugenol		38.20	26.28	6.7	
16	vanillin		61.40	15.4	8.4	
17	trans-iso Eugenol		21.30	18.7	11.7	
18	cis-iso Eugenol					
19	acetoguaiacone		87.60	48.9	23.8	
Total	-	-	1263.7	629.8	251.3	

**Figure 2.** Comparison of removal rates for each tar compound in the syngas that passed through the water scrubber and Mg/Al-LDH@clinoptilolite.

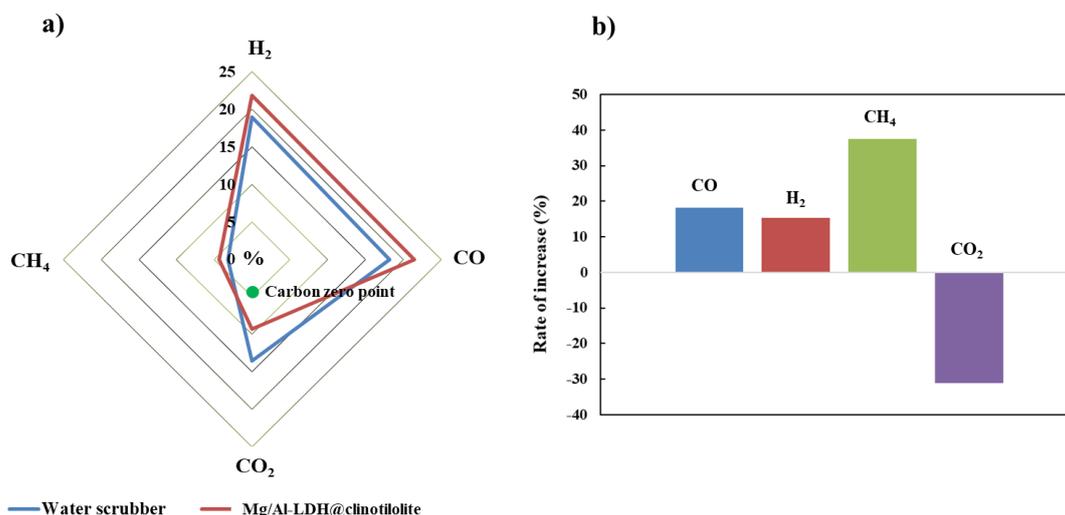


**Figure 3.** TIC (Total Ion Chromatogram) of quantified compounds in wood tar wastewater with internal standards from SPA sampling (Y-axis: Relative intensity). Tar species and content ratios in syngas: after passing through (a) water scrubber column and (b) Mg/Al-LDH@clinoptilolite.

The total tar removal rates after passage through the water scrubber and clinoptilolite and Mg/Al-LDH@clinoptilolite columns were 50.2 and 80.1%, respectively, indicating that the removal rate increased by 29.9% due to catalyst contact.

### 2.2. Reformation Characteristics of Inflammable Gas in Syngas

Figure 4 illustrates the changes in the contents of  $H_2$ , CO,  $CH_4$ , and  $CO_2$  in the syngas after tar removal by passing through the water scrubber and Mg/Al-LDH@clinoptilolite columns. After consecutive passage through the water scrubber and Mg/Al-LDH@clinoptilolite columns, the proportion of  $H_2$  increased from 18.9% to 21.8%, that of CO increased from 18.2% to 21.5%, and that of  $CH_4$  increased from 3.2% to 4.4%, while the proportion of  $CO_2$  decreased from 13.5% to 9.3%. A comparison with the corresponding values obtained from the conventional method, where only the water scrubber was used, showed that the proportion of inflammable gaseous components  $H_2$ , CO, and  $CH_4$  increased by 15.3%, 18.1%, and 4.7%, respectively, while that of  $CO_2$ , which is a key contributor to carbon emissions, decreased by 31.1%.



**Figure 4.** Change in content of  $H_2$ , CO,  $CH_4$ , and  $CO_2$  in syngas for which tar removal was performed by passing through the water scrubber and Mg/Al-LDH@clinoptilolite column (a): composition ratio %, (b): rate of change %.

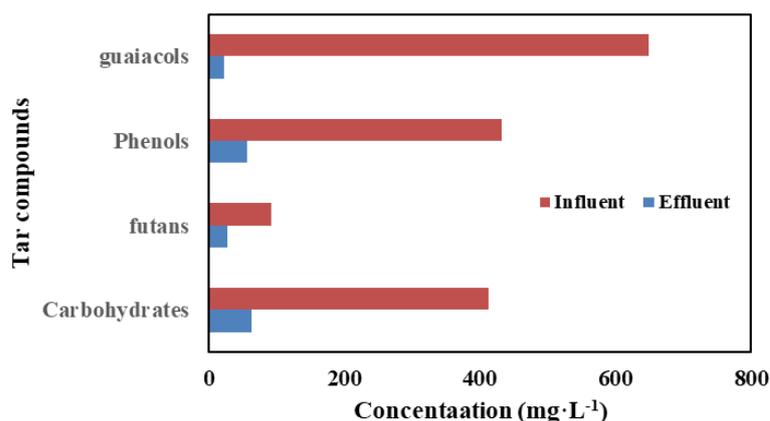
### 2.3. Processing and Recirculation of Tar Wastewater

To recirculate the treated water, we referred to the literature method [32] to control the pH using NaOH and optimally designed the treatment unit using the jar test to determine the amount of  $Ca(OH)_2$  and powdered activated carbon (PAC) to be added, which act as a coagulant aid and coagulant, respectively. Table 3 lists the pH, turbidity, and suspended solid (SS) contents of the tar after each process of cohesion and precipitation. NaOH was

added to the raw water of low pH to increase the pH to 8.7, and the addition of PAC caused the turbidity and SS content to be reduced to 12.7 nephelometric turbidity units (NTU) and 15 mg/L, respectively, due to cohesion. The chemical oxygen demand (COD) and ammonium-nitrogen ( $\text{NH}_4^+\text{-N}$ ) components of the treated water that passed through the clinoptilolite decreased drastically. As illustrated in Figure 5, the final treated water had low concentrations of tar components, while its pH was approximately 6, indicating that it could be reused as circulating water in the water scrubber of the integrated gasification combined cycle power plant. This implies that the treated water released along with the aggregated sludge can be recirculated as tap water.

**Table 3.** Change in pH, turbidity, and SS contents at each processing step.

Analysis Items	Raw Wastewater	NaOH + Ca(OH) <sub>2</sub> Injection	PAC Injection	Zeolite (Clinoptilolite)
pH	4.9	8.7	5.9	5.9
Turbidity (NTU)	41.7	129.0	12.7	8.8
SS (mg·L <sup>-1</sup> )	75.0	155.0	15.0	11.2
COD <sub>cr</sub> (mg·L <sup>-1</sup> )	2249.6	2136.8	1140.3	326.8
NH <sub>4</sub> <sup>+</sup> -N(mg·L <sup>-1</sup> )	31.2	22.4	15.8	2.6



**Figure 5.** Change in the concentration of tar components in treated water upon tar wastewater treatment.

The utilization efficiency of purified syngas was estimated by calculating the cold gas efficiency (CGE), as shown in Equation (1). The CGE is calculated by the ratio of the total heat input to the total heat output of the syngas [33,34].

$$\text{CGE} = \frac{\text{LHV}(\text{H}_2 + \text{CO} + \text{CH}_4)_{\text{gas}} \times V_{\text{gas}}}{\text{LHV}_{\text{fuel}} \times m_{\text{fuel}}} \times 100 (\%) \quad (1)$$

Syngas low heating value (LHV):  $\text{LHV}_{\text{synG}} : \text{HHV}_{\text{synG}} - 2.0\text{MJ}/\text{m}^3(\text{H}_2_{\text{vol}} + 2\text{CH}_4_{\text{vol}})$

Syngas high heating value (HHV):  $\text{HHV}_{\text{synG}} : 12.7\text{MJ}/\text{m}^3\text{CO}_{\text{vol}} + 12.8\text{MJ}/\text{m}^3\text{H}_2_{\text{vol}} + 39.9\text{MJ}/\text{m}^3\text{CH}_4_{\text{vol}}$  where  $\text{LHV}_{\text{gas}}$  is the LHV of syngas ( $\text{MJ}/\text{Nm}^3$ );  $\text{LHV}_{\text{fuel}}$  is the LHV of waste ( $\text{MJ}/\text{kg}$ );  $V_{\text{gas}}$  is the flowrate of syngas ( $\text{Nm}^3/\text{h}$ );  $m_{\text{fuel}}$  is the feeding rate of waste ( $\text{kg}/\text{h}$ ).

The total heat produced by the syngas was calculated using the percent concentrations of  $\text{H}_2$ ,  $\text{CO}$ ,  $\text{CH}_4$ , and the flow of the syngas. As a result, the energy utilization efficiency calculated from the CGE value increased by 11.14%, from 74.32% when the gas passed through the water scrubber to 85.46% when the gas passed through the Mg/Al-LDH@clinoptilolite column.

Studies not relevant to tar removal, such as those related to CO<sub>2</sub> capture [35–37], have confirmed that the efficient removal of CO<sub>2</sub> from syngas demonstrated in this study was mostly caused by clinoptilolite and Mg/Al-LDH@clinoptilolite. Davarpanah et al. [35] conducted a study on the adsorption capacity of clinoptilolite toward CO<sub>2</sub> emitted from industrial processes at moderate temperatures. According to their findings, clinoptilolite is a promising adsorbent that can be used to directly remove CO<sub>2</sub> from different flue gas sources at working temperatures. Furthermore, according to Megias-Savago et al. [36], the ability of zeolites and LDH zeolites to capture CO<sub>2</sub> is highly dependent on the aluminum concentration in the zeolite framework and its cationic nature. For LDHs, the combination of a high specific surface area combined with a high pore volume appears to be a decisive factor in obtaining high adsorption [36]. Murge et al. [37] also evaluated the CO<sub>2</sub> capture characteristics of various zeolite-based sorbents and reported adsorption values of 114 and 190 mg CO<sub>2</sub>·g<sup>-1</sup> under atmospheric and 5 bar pressures, respectively. They also observed that the adsorption capacity of the zeolites was affected by the presence of alkali metal ions. Biomass gasification plants need to be equipped with wet scrubber gas cleaning to produce syngas that meets the specifications for use in various applications. To be used in internal combustion engines for power generation, the particulate and tar contents of syngas are required to be approximately 30 mg·Nm<sup>-3</sup> and less than 100 mg·Nm<sup>-3</sup>, respectively [5,38]. The scrubber is operated in the co-current mode to remove tar and prevent backfire. The dehydration section is utilized to separate microdrops of water included in the syngas during its purification by passing through the water scrubber tower. This step is necessitated by the reduction in efficiency, corrosion, condensation, and hydrate formation, which occur in the presence of moisture. The heavy insoluble tar (C20–C40 or higher) is typically collected in the conical base of the scrubber along with the inert substances and unreacted dust separated from the syngas and removed through the screw pump. The relatively lighter water-soluble substances are discharged along with water as tar wastewater [39]. As shown in previous studies, the wet scrubber method is the most commonly used of the various tar removal methods (Figure 1). Therefore, the present study is the first attempt to enhance the removal efficiency of the tar and CO<sub>2</sub> by improving refining parts in syngas while also taking advantage of the wet scrubber method.

High temperatures above 700 °C are required for repeated regeneration when activated carbon is used for water and CO<sub>2</sub> adsorption in tar mist, aerosols, and syngas. Furthermore, activated carbon is difficult to apply in purification processes because of the risk of explosion caused by spontaneous reaction with moisture upon exposure to the external environment [40,41]. However, when the zeolite is used as an alternative to activated carbon, its regeneration temperature is relatively lower (below 300 °C). In addition, zeolite, being an inorganic adsorbent, can be safely exposed to the external environment. The porous structures of zeolite adsorbents enable the removal of internal impurities in addition to moisture through the micropores, indicating that zeolites are suitable for use in purification processes [42,43]. Therefore, it is plausible that the zeolite played a significant role in removing moisture from the tar mist, aerosol, and syngas that passed through the water scrubber, although we did not conduct experiments for the quantitative evaluation of moisture removal in this study. Favvas et al. [44] also utilized clinoptilolite in their study on the dehydration of hydrocarbon-based fuels. The maximum water/vapor adsorption was measured to be 8 mmol/g at 22 °C, which proves the efficiency of zeolite at removing moisture from syngas.

Therefore, in this study, clinoptilolite, a natural zeolite that is inexpensive and easily excavated from open-air mines in Korea, and the corresponding Mg/Al-LDH@clinoptilolite have been utilized for the efficient removal of tar components that cannot be removed using conventional water scrubbers. Enhanced removal of CO<sub>2</sub> and dehydration of syngas have also been achieved. The effectiveness of clinoptilolite was thoroughly demonstrated by the results obtained in this study.

### 3. Materials and Methods

#### 3.1. Materials

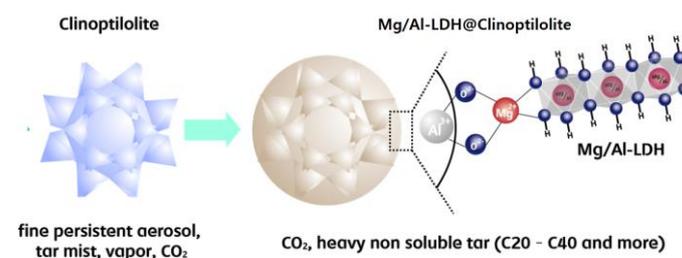
The natural zeolite clinoptilolite ( $\text{Ca, Na}_2(\text{Al}_2\text{Si}_7\text{O}_{18})6\text{H}_2\text{O}$ ) was procured from a mining and processing manufacturer (H Trade). The zeolite was crushed and screened for particles smaller than 100 mesh (254  $\mu\text{m}$ ). The particles were then washed with distilled water (clinoptilolite:distilled water ratio (wt), 1:3) that had been subjected to reverse osmosis filtration and deionization (RO/DI), followed by drying at 105 °C. The selectivity affinity order of the cation exchanger (SIR-600) was  $\text{Cs}^+ > \text{Rb}^+ > \text{K}^+ > \text{NH}_4^+ > \text{Ba}^{2+} > \text{Sr}^{2+} > \text{Na}^+ > \text{Ca}^{2+}$  with a micropore size of 4 Å. The chemical composition of clinoptilolite is listed in Table 4 [45].

**Table 4.** The chemical composition of clinoptilolite used in this study.

Chemical Component	Percent (%)	Chemical Component	Percent (%)
$\text{SiO}_2$	66.50	$\text{Na}_2\text{O}$	1.90
$\text{Al}_2\text{O}_3$	14.70	$\text{K}_2\text{O}$	3.25
$\text{Fe}_2\text{O}_3$	1.68	$\text{P}_2\text{O}_5$	0.04
$\text{MgO}$	1.25	$\text{H}_2\text{O}$	8.04
$\text{CaO}$	1.82		

#### 3.2. Mg/Al-LDH@Clinoptilolite Preparation

The layered double hydroxides (LDHs) were synthesized by adding 30 g of the natural clinoptilolite prepared in Section 3.1 to distilled water, followed by the addition of 0.024 mol  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and 0.008 mol  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ . The mixed solution was then stirred at a speed of 150 rpm while adding 2 mol  $\text{Na}_2\text{CO}_3$  solution to achieve a pH of 9–10. Subsequently,  $\text{N}_2$  gas was injected as fine bubbles using a woodstone while stirring for 30 min. After 2 h of stirring, the precipitate was dried for 24 h at 105 °C, followed by calcination in a muffle furnace for 2 h at 400 °C [46,47]. Microstructure scheme of Mg/Al-LDH@clinoptilolite was shown in Figure 6.



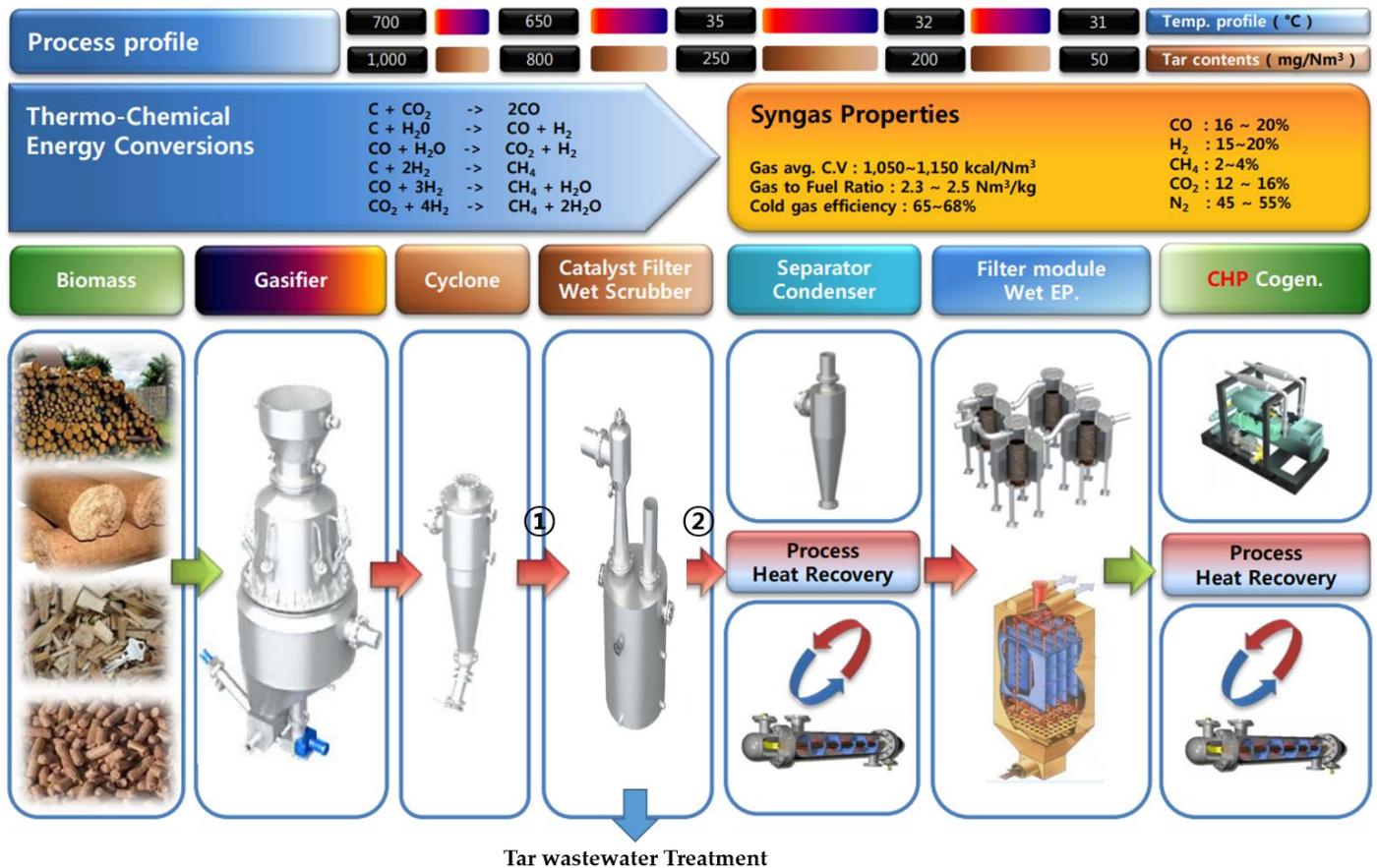
**Figure 6.** Microstructure scheme of Mg/Al-LDH@clinoptilolite.

#### 3.3. Syngas Source and Tar Removal Process

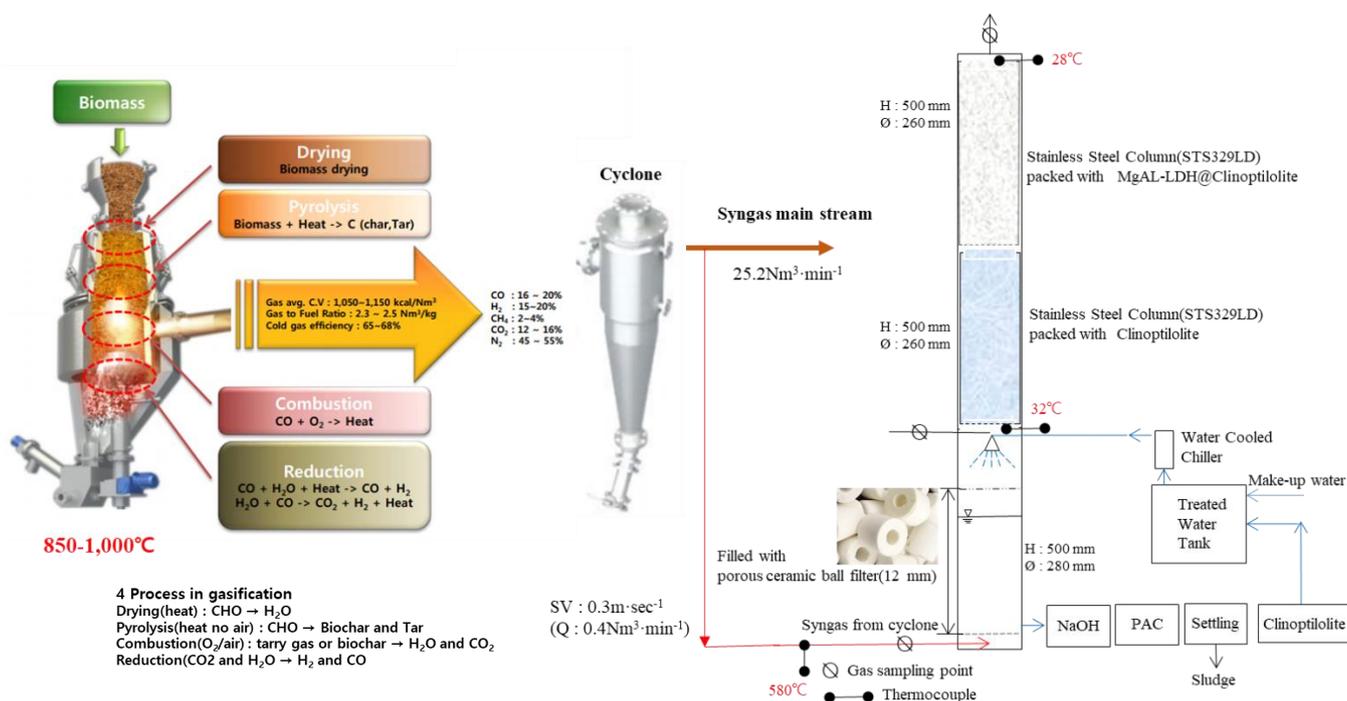
Wood chips obtained by crushing thinning-out trees were used as raw materials in the experimental apparatus, and their characteristics are presented in Table 5. The syngas was produced as in Figure 7 at a site adjacent to the gasification power generation demonstration plant with a generation capacity of 500 kWe (raw material input: 20 ton/d) in Goseong, Gangwon-do, South Korea. A portion of the 25.176  $\text{Nm}^3/\text{min}$  of synthetic gas generated by the gasification demonstration facility was fed into the experimental apparatus, and the bench-scale syngas refining reactor used in this experiment is shown in Figure 8.

**Table 5.** Characteristics of the raw materials (wood chips) used to produce syngas.

	Value	Unit
C	46.2	w/w (%)
H	6.1	
O	31.2	
S	0.01<	
N	0.07	
Cl	0.03	
Water	17.2	
Volatile Matter	67.8	
Fixed Carbon	13.7	
Non-volatile Matter	1.3	
Low Heating Value	13.9	MJ·kg <sup>-1</sup>



**Figure 7.** Process diagram demonstrating power generation facilities and characteristics of tar and syngas generation in operation: ①, ② Syngas sampling point (Original source of diagram: Samyang Econergy Inc. in Korea).

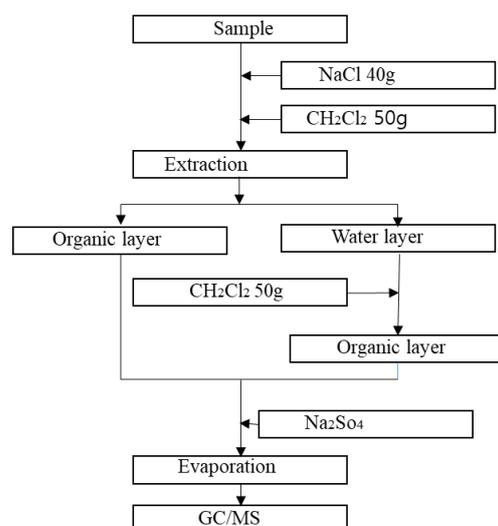


**Figure 8.** Schematic diagram of bench scale syngas refining reactor. 1st column: water scrubber with water spray volume 5 L·min<sup>-1</sup>, diameter 280 mm, height 500 mm, filled with ceramic ring filter (height 300 mm), spray water temperature below 20°C, 2nd column: reactor filled with prepared clinoptilolite, diameter 260 mm and height 500 m, 3rd column: reactor filled with prepared Mg/Al-LDH@clinoptilolite, diameter 260 mm and height 500 m (Gasifier structure and operation parameters source: Samyang Econergy Inc. in Korea).

The gas was injected from the lower end of the first column with the inflow rate set to 0.4 Nm<sup>3</sup>·min<sup>-1</sup>. The gas was then consecutively passed through the second and third columns, which can be replaced with cartridges, with a superficial velocity (SV) of 0.3 m·s<sup>-1</sup>. The reactor was constructed considering the main target substances for removal in each column: (1) water scrubber column: water-soluble light tar (C10–C20); (2) clinoptilolite column: fine persistent aerosol (tar mist, vapor, CO<sub>2</sub>) and heavy non-soluble tar (C20–C40 and higher); (3) Mg/Al-LDH@clinoptilolite column: heavy non-soluble tar (C20–C40 and higher) and CO<sub>2</sub>.

### 3.4. Tar Sampling and Analysis Method

The tar sampling protocol proposed by van de Kamp, W. L., et al. [48] was used. Briefly, this method consists of a series of six impingement bottles passing through syngas. The first bottle acts as a moisture collector. Then the gas passes through four impingement bottles filled with acetone to dissolve the tar. The last bottle is left empty for the collection of the final condensate. We analyzed the chemical composition of the tar by the two methods proposed by Dufour et al. [49] on using wood pyrolysis tar to improve the accuracy of the lignocellulosic tar analysis. First, the sampled tar was pretreated using the procedures listed in Figure 9, and the tar composition was analyzed using the following two methods. The first method employed a typical cold-trapping technique in solvent-filled impingers, followed by liquid injection. The second involved the application of multibed solid-phase adsorbent (SPA) tubes and thermal desorption (TD). Both methods are based on gas chromatography (GC) and mass spectrometry (MS). The GC-MS analysis conditions are listed in Table 6.



**Figure 9.** Pre-treatment method for tar (liquid-liquid extraction (LLE)).

**Table 6.** GC/MS analysis conditions for tar generated from biomass gasification plants.

	First Method (GC/MS)	Second Method (TD–GC/MS)
Instrument	Perkin Elmer Clarus 600 GC/MS (Waltham, MA, USA)/(Detector: Clarus 600T)	GC/MS(TD–GC/MS), using a TurboMatrix thermal desorber (Perkin-Elmer) and a Clarus 600 GC/MS (Perkin-Elmer). (Detector: Clarus 600T)
Column	HP-5MS-UI, (5%-Phenyl)-methylpolysiloxane (Agilent J&W, Folsom, CA, USA)	
Carrier gas	Helium (Alphagaz 2, Air Liquide, Nancy, France), 1.2 mL/min	
GC oven	40 °C, 5 min, 10 °C/min, 320 °C	
Inlets	Split less, Heater 250 °C	

### 3.5. Analysis of Syngas

The gas samples were collected in 2 L polyvinyl fluoride gas sampling bags and analyzed using a gas chromatograph (SRI 8610, SRI Instruments, Torrance, CA, USA) equipped with a thermal conductivity detector (GC-TCD). The gases, H<sub>2</sub>, CO, CH<sub>4</sub>, CO<sub>2</sub>, and N<sub>2</sub>, were separated and quantified using a Carbosphere 80/100 (6 ft × 1/8 in stainless steel column (Alltech Associates Inc., Deerfield, IL, USA). The method involved injecting 500 µL of the gas sample into the gas chromatograph. The temperature of the column was maintained at 100 °C, and the run time was set to 6 min. The detector and injector temperatures were set to 150 °C and 120 °C, respectively. The TCD cell was maintained at 140 °C, and the GC was maintained at a pressure of 25 psi. Argon (Nexair, Memphis, TN, USA) was used as the carrier gas.

## 4. Conclusions

A natural zeolite (clinoptilolite) catalyst impregnated with Mg/Al LDH was incorporated into a water scrubber, which purified the generated wastewater, enabling its reuse. The syngas from the lignocellulosic biomass gasification system was found to contain 19 tar compounds, including carbohydrates, furans, phenols, and guaiacols. Guaiacols were the most prevalent, accounting for 41.5% of the compounds, followed by phenols (35.6%). The tar removal rate after passing through the water scrubber was 50.2%. However, the total tar removal rate after passing through the clinoptilolite and Mg/Al-LDH@clinoptilolite columns was 80.1%, indicating that catalyst contact enhanced the tar removal rate by 29.9%. Compared to the conventional method of only passing the syngas through the water scrubber, the proportions of inflammable gaseous components, such as H<sub>2</sub>, CO, and CH<sub>4</sub>, increased by 15.3%, 18.1%, and 4.7%, respectively, while that of CO<sub>2</sub>, which is a key contributor to carbon emissions, decreased by 31.1%.

**Author Contributions:** Conceptualization, methodology, investigation, and writing—original draft preparation, I.-T.K.; visualization and writing—review and editing, Y.-E.L. and Y.J.; formal analysis, K.-H.A. and J.J.; investigation, D.-C.S.; supervision, project administration, I.-T.K. All authors have read and agreed to the published version of the manuscript.

**Funding:** This research was funded by the Korea Institute of Civil Engineering and Building Technology (KICT) (grant number 20210105-001).

**Conflicts of Interest:** The authors declare no conflict of interest.

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