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Enhanced Biomass Gasification by Catalyzing the Pyrolysis of cedarwood Using Biochar Catalyst

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Abstract: *The pyrolysis process of biomass is a promising track to produce renewable energy, chemicals, and bio-oils. However, biomass pyrolysis systems still have several drawbacks such as the formation of coke, the low conversion of biomass to gas, and the difference in temperature required to increase gas production and chemicals at the same time. Therefore, this study aimed to improve the pyrolysis/gasification process of cedarwood biomass using an effective and cheap catalyst. Accordingly, biochar was used as a catalyst during the gasification of cellulose. Results showed that the biochar catalyst significantly increased gas yield by 5.9, 2.2, and 2.5 times at the pyrolysis temperatures of 500, 600, and 700 ˚C, respectively, compared to the uncatalyzed conditions. The improved biogas production using the catalyst was due to the further conversion of Levoglucosan to biogas, as indicated by GC/MS results.*

Keywords: Pyrolysis; Gasification; Catalyst; Cellulose; Cedarwood

1. INTRODUCTION

The generation of renewable energy sources is an interesting path to protect the environment from the continued use of fossil fuels. There are many resources of renewable energy, including solar energy, wind energy, hydro energy, geothermal energy, and biomass energy. The production of energy from biomass is a promising technology as it provides energy by utilizing different types of environmental waste. The process occurs through the anaerobic digestion of organic matter in the presence of microorganisms and through the pyrolysis/gasification process of different biomasses. Anaerobic digestion of biomass requires a long time and the conversion efficiency of organic matter into methane gas is low, and therefore there are many attempts to improve the process following several techniques [1-3]. Gasification of biomass through the pyrolysis process is a faster and more promising approach as it provides a sustainable source of bioenergy and chemicals, which could be an alternative to petroleum energy [4]. However, there are still many drawbacks that affect the gasification of biomass during the pyrolysis process such as coke and tar formation [5]. In addition, the pyrolytic products generated from this process, either gases or chemicals, require further enhancement and upgrading [6].

The gasification of biomass includes the primary and secondary pyrolysis steps. Volatiles and solid char are produced first in the primary step followed by the formation of coke, which is the secondary reaction of the primary step products [7-10]. The formation of coke is a serious problem facing the operation of gasification systems [11]. Coke is a solid carbonaceous residue and its formation during the pyrolysis process causes clogging in the gasification pipelines. Several studies investigated the formation behavior of coke during the pyrolysis of different woody biomass. Hosoya et al.[12] studied the formation of coke from the pyrolysis process of cellulose at 800 ˚C, which is the major component of wood and lignocellulosic biomasses. They demonstrated that the formation of coke on the Pyrex glass walls occurred after cooling the volatile intermediates which are generated in the primary pyrolysis step. On the other hand, Fukutome et al. [13] compared the formation of coke using various cellulose-derived intermediates in a tubular Pyrex reactor at a pyrolysis temperature of 600 ˚C. They found that all the used cellulose-derived intermediates, including levoglucosan, glycolaldehyde, furfural, and 5-hydroxymethylfurfural were found to generate tar and coke after condensation in the molten phase reactions not during gasification. Therefore, finding solutions for the formation of coke during the pyrolysis process is an important goal.

Another issue that is related to the pyrolysis of cellulose and other woody biomass is the pyrolysis temperature. The pyrolysis of cellulose involves the production of gas and condensable chemicals. All pyrolytic products should be highly produced during the pyrolysis process. However, the problem is that the highest gas production occurs at a high temperature above 700 ˚C. In contrast, the production of condensable chemicals occurs at a lower temperature of less than 600 ˚C. For example, Fukutome et al. [4] found that the maximum production of condensable chemicals was observed at a pyrolysis temperature of 600 ˚C and the maximum production of the non-condensable gases was at a pyrolysis temperature of 800 ˚C. Therefore, it's preferred to maximize gas production at a lower temperature of less than 600 ˚C. In this case, the pyrolysis performance will increase in terms of the produced gas and chemicals. In previous reports, attempts to upgrade gasification reactors through biomass catalytic pyrolysis were conducted using different types of catalysts. For instance, zeolite-based catalysts [14], activated alumina [15], fluid catalytic cracking catalysts [16, 17], and transition metals (Fe/Cr) were extensively used. In these studies, they reported that the catalyst significantly reduced the oxygen content in bio-oils. Biochar is one of the pyrolytic products generated from biomass gasification and pyrolysis. Therefore, this study aimed to utilize biochar as a cheap catalyst produced from the pyrolysis of cedarwood to reduce the gasification temperature to enhance the production of gas at a low temperature. Moreover, the catalyst is expected to increase the production fraction of hydrogen and carbon monoxide gases within the produced biogases along with reducing the formation of coke during the pyrolysis process to avoid any clogging in the gasification pipelines.

2. MATERIAL AND METHODS

2.1. preparation of biochar catalyst

The cedar wood was carbonized/pyrolyzed by the high-frequency induction heating unit at a temperature of 750 ˚C under an inert condition by supplying the N_2 gas at a flow rate of 100 ml/min. Then, the carbonized cedar wood was ground into a fine powder using a mortar and pestle to be used as a catalyst to increase syngas production. The preparation procedures and conditions of this catalyst came out after several optimization experiments conducted to find out the best type of wood to be used for the preparation of the catalyst, the best carbonization temperature, and the best pyrolysis time.

2.2 pyrolysis and gasification process

The pyrolysis/gasification experiment was performed using an electric cylindrical furnace (internal diameter: 35 mm, length: 160 mm, Asahi Rika Seisakusho Co., Ltd.). A quartz glass tube (internal diameter: 4 mm, thickness: 1 mm) was installed inside the cylindrical furnace as described in Figure1. The right end of the quartz glass tube was connected to the nitrogen cylinder. The flow of nitrogen during the pyrolysis process was controlled at 60 ml/min using a mass flow controller (Horiba SEC-400MK3). The left end of the quartz glass tube was attached to a one-liter gas bag used for gas collection. In the operation process, cellulose (40 mg) was used as a feedstock sample and placed on the right end of the quartz glass tube (in the cold zone). The pyrolysis experiments were conducted at different temperatures (400 - 700 ˚C) and when the heating zone temperature reached the target degree, the cellulose sample was pushed from the cold zone to the center of the heating zone. To discover the effect of the catalyst on the gasification process, experiments were conducted with and without using the catalyst. In the case of using the catalyst, 25 mg of the catalyst was placed inside the quartz glass tube on the left side in the heating zone, fixed by the glass wool from both sides and heated before starting the pyrolysis process of cedarwood.

2.3 Gas analysis

The collected gas in the gas bag was analyzed using micro-gas chromatography (micro-GC, Agilent 990, Agilent Technologies Inc., Santa Clara, CA, USA). This micro-GC is designed with four channels. In channel 1: the column temperature is 100 °C and the inlet pressure is 170 kPa. In channel 2: the column temperature is 80 °C and the inlet pressure is 190 kPa. In channel 3: the column temperature is 80 °C and the inlet pressure is 190 kPa. In channel 4: the column temperature is 40 °C and the inlet pressure is 130 kPa. Channel 1 is used for the separation of inorganic gases e.g., H_2, O_2, N_2, and CO. Channels 2 and 3 are used for the separation of low-molecular-weight hydrocarbon gases. For example, in channel 2, CH_4, CO_2, C_2H_2, C_2H_4, C_2H_6, H_2O, C_3H_6, and C3H8 were detected. Whereas, in channel 3, CH_4, C_2H_4, C_2H_6, C_2H_2, C_3H_6, and C_3H_8 were detected. Channel 4 is used for the separation of large molecules. At the operation process, Ar was used as the carrier gas for all channels. Before the analysis of the gas composition, 5 mL of Ne gas (>99.999%, Imamura Sanso Corp.) was injected inside the gas bag as an internal standard. Then, the gas bag was connected to the injection unit of the micro-GC to start the gas analysis process.

The gas yield from the pyrolysis of cellulose was calculated using the following equations.

$$Yield\ (wt.\%) = gas\ wight\ (mg)/cellulose\ wight\ (mg) \times 100 \quad (1)$$

$$Gas\ wight\ (mg) = numbr\ of\ moles\ of\ gas \times gas\ atomic\ wight\ \times 10^3 \quad (2)$$

$$Number\ of\ moles\ of\ gas = produced\ gas\ volume\ (ml)/22400 \quad (3)$$

2.4 GCMS analysis

Gas chromatography-mass spectrometry was used to analyze the condensable products which were produced from the pyrolysis of Japanese cedarwood after trimethylsilyl derivatization. The analysis was conducted using a GCMS-QP2010 Ultra instrument (Shimadzu Corporation) with a CPSil 8CB column (length: 30 m, inner diameter: 0.25 mm, film thickness: 0.25 µm; Agilent Technologies, Inc., Santa Clara, CA, USA),

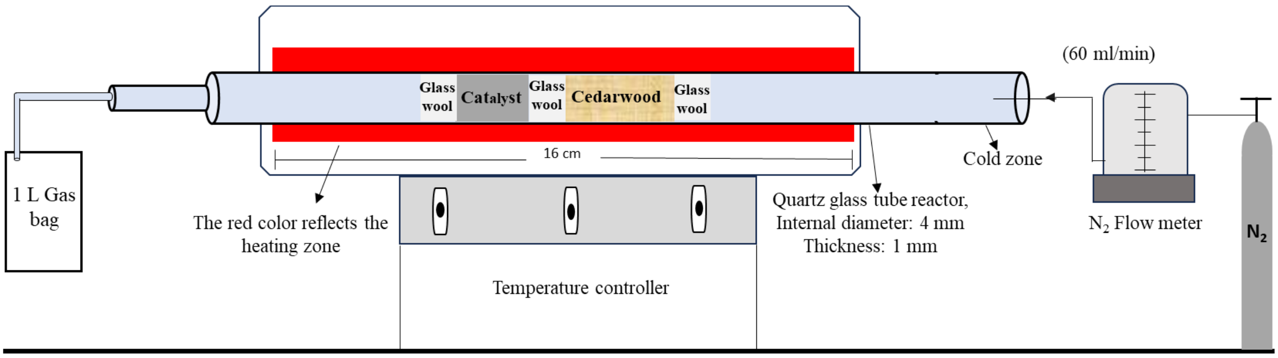

Figure 1. A flow-type tubular reactor used for the pyrolysis/gasification process of cedarwood at different temperatures (400-700 ˚C) with and without biochar catalyst.

H at 2.09 mL min^{-1} as the carrier gas, an injector temperature of 250 °C, and a split ratio of 1/10. The column oven temperature was held at an initial temperature of 70 °C for 2 min, ramped at 4 °C min^{-1} to 150 °C and held for 1 min, and then ramped at 10 °C min^{-1} to 300 °C and held for 1 min. Prior to analysis, 1,3,5-triphenylbenzene (an internal standard) was added to the methanol-soluble portion, and methanol was removed using an evaporator at 30 °C under vacuum. This relatively low temperature was used to avoid the evaporation of some products with relatively low boiling point, e.g., phenol. Trimethylsilylation was performed by addition of pyridine (100 µL), hexamethyldisilazane (150 µL), and trimethylchlorosilane (80 µL), and then heating at 60 °C for 30 min.

3. RESULTS AND DISCUSSION

3.1 Gas production

The pyrolysis of cedarwood biomass generates inorganic gases e.g., H_2, CH_4, CO_2 and CO, and low-molecular-weight hydrocarbon gases e.g., CH_4, C_2H_2, C_2H_4, C_2H_6, H_2O, C_3H_6 [19]. The major component of the produced gases from the pyrolysis of cedarwood were found to be H_2, CO, CO_2, and CH_4. Whereas the yield of hydrocarbon gases was normally low. The composition, volume, and the yield of these gases are shown in Figure 2a and b. The production of gas from the pyrolysis of cellulose started at 500 ˚C and continued to increase by increasing the pyrolysis temperature. These results are consistent with the previous reports in literature [20-24]. Interestingly, the biochar catalyst significantly increased the production of gas. The gas yield has increased 180, 75, and 36 % at the pyrolysis temperatures of 500, 600, and 700 ˚C, respectively, compared to the uncatalyzed conditions. Moreover, biochar catalyst selectively increased hydrogen and carbon monoxide gases within the generated biogas from the pyrolysis of cedarwood especially at temperatures of 600 and 700 ˚C. To understand the reasons behind the improved gas production at high temperatures and at using the catalyst, GC/MS was performed to analyze the main component of the produced bio-oil during the gasification of cedarwood. Figure3 shows the monomer components which were produced from the pyrolysis of cedarwood at different temperatures. It was observed that the lower temperatures of 400 and 500 ˚C showed higher production of monomers. For example, Coniferyl alcohol and Levoglucosan were more produced at 400 and 500 ˚C. In contrast, at the higher temperatures of 600 and 700 ˚C, the production of monomers decreased. For instance, Levoglucosan, an intermediate product generated from the pyrolysis of cellulose and considered as gas generating compound, was less produced at the higher temperatures of 600 and 700 ˚C, explaining that the production of gas was further improved at higher temperatures by the further conversion of Levoglucosan. On the other hand, as shown in Figure 4, the Levoglucosan peak was much lower with using biochar catalyst, especially at temperatures of 500, 600 and 700 ˚C. This means that the catalyst enhanced the conversion

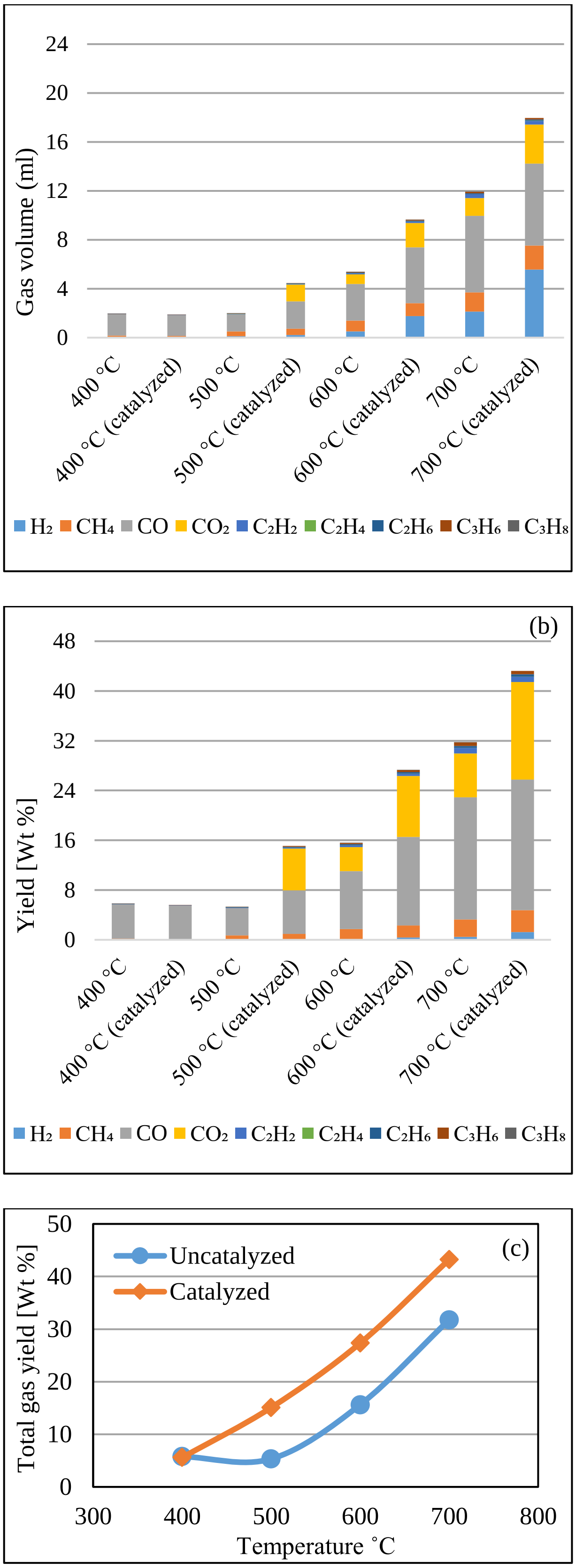

Figure 2. Shows gas production from the pyrolysis of cedarwood (40 mg) at different temperatures (400-700 ˚C) with and without using biochar catalyst a) the produced volume of each gas, b) the corresponding gas yield, and c) the corresponding total gas yield.

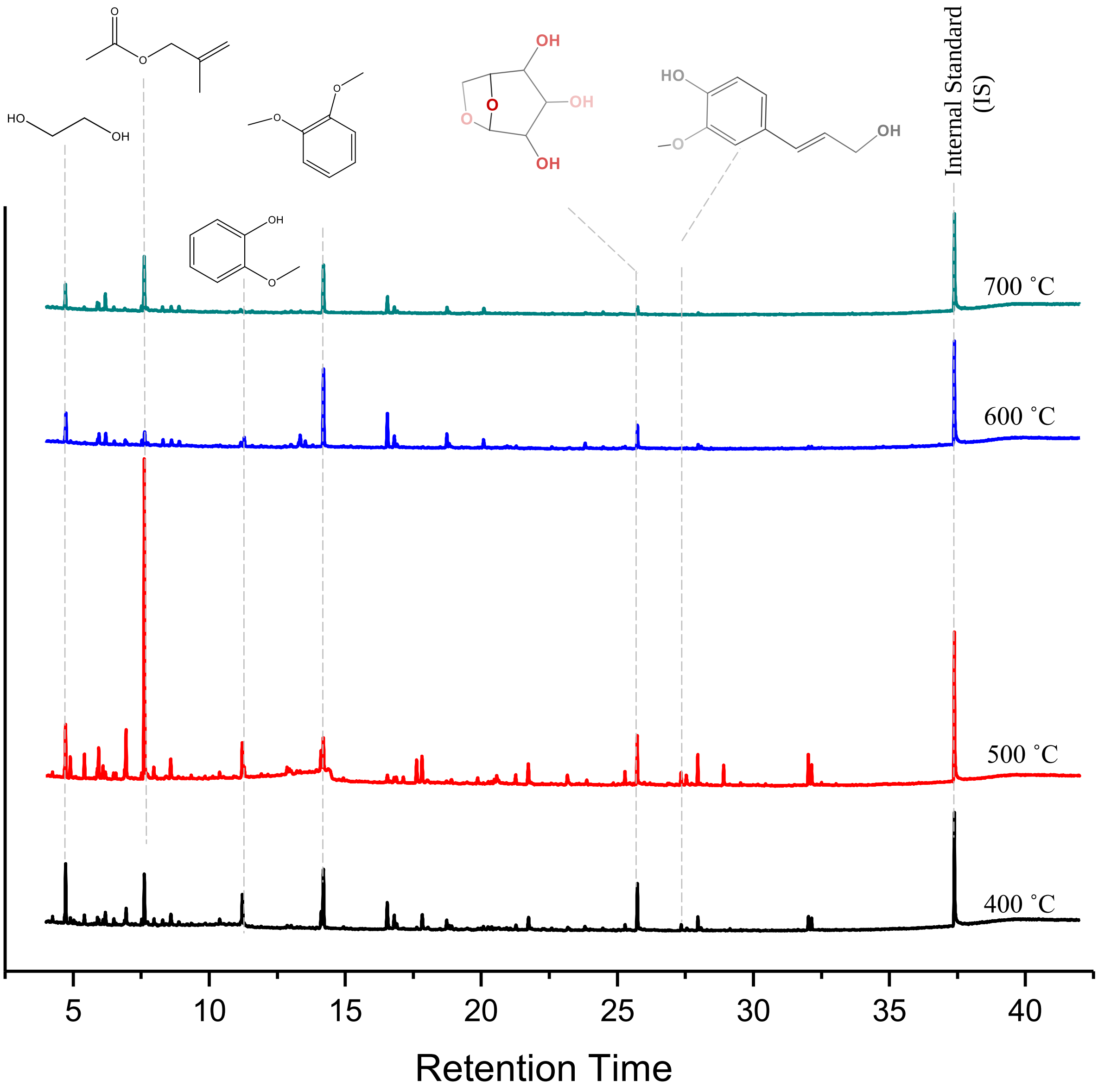

Figure 3. The gas chromatography-mass spectrometry (GC/MS) total ion chromatograms of the TMS reaction mixtures for the generated biooil obtained from the pyrolysis of cedarwood at different temperatures (400 - 700 ˚C).

Levoglucosan to generate biogas. Also, the production of some other monomers such as ethylene glycol, coniferyl alcohol, 2-methylallyl acetate, and Guaiacol were less produced at high temperatures and at using the biochar catalyst. Cellulose, which is the main component of wood, was pyrolyzed alone to understand which component of wood generates biogas (data not shown). The results showed that there was no difference in biogas volume and composition generated from the pyrolysis of cellulose and cedarwood. This implies that the cellulose and its intermediate product of Levoglucosan are the main compounds used for gas production.

4. CONCLUSIONS

In conclusion, the pyrolysis process of biomass is a promising technology for gas generation. In this study, the pyrolysis/gasification of cellulose biomass was performed at different temperatures (400-700 ˚C). Also, biochar catalyst was used to enhance the gasification process of cellulose. Results showed that the gasification of cellulose biomass started at a temperature of 500 ˚C and continued to increase by increasing the temperature. Interestingly, biochar catalyst significantly increased gas yield by 180, 75, and 36 % at the pyrolysis temperatures of 500, 600, and 700 ˚C, respectively, compared to the uncatalyzed conditions.

The GC/MS results showed that the higher temperatures of 600 and 700 ˚C highly improved the conversion of Levoglucosan to generate biogas. Moreover, the use of biochar catalyst further decreased the production of Levoglucosan and some other monomers such as ethylene glycol, coniferyl alcohol, 2-methylallyl acetate, and Guaiacol. The lower production of Levoglucosan at high temperatures and with using the catalyst explains the reason behind the improved biogas production.

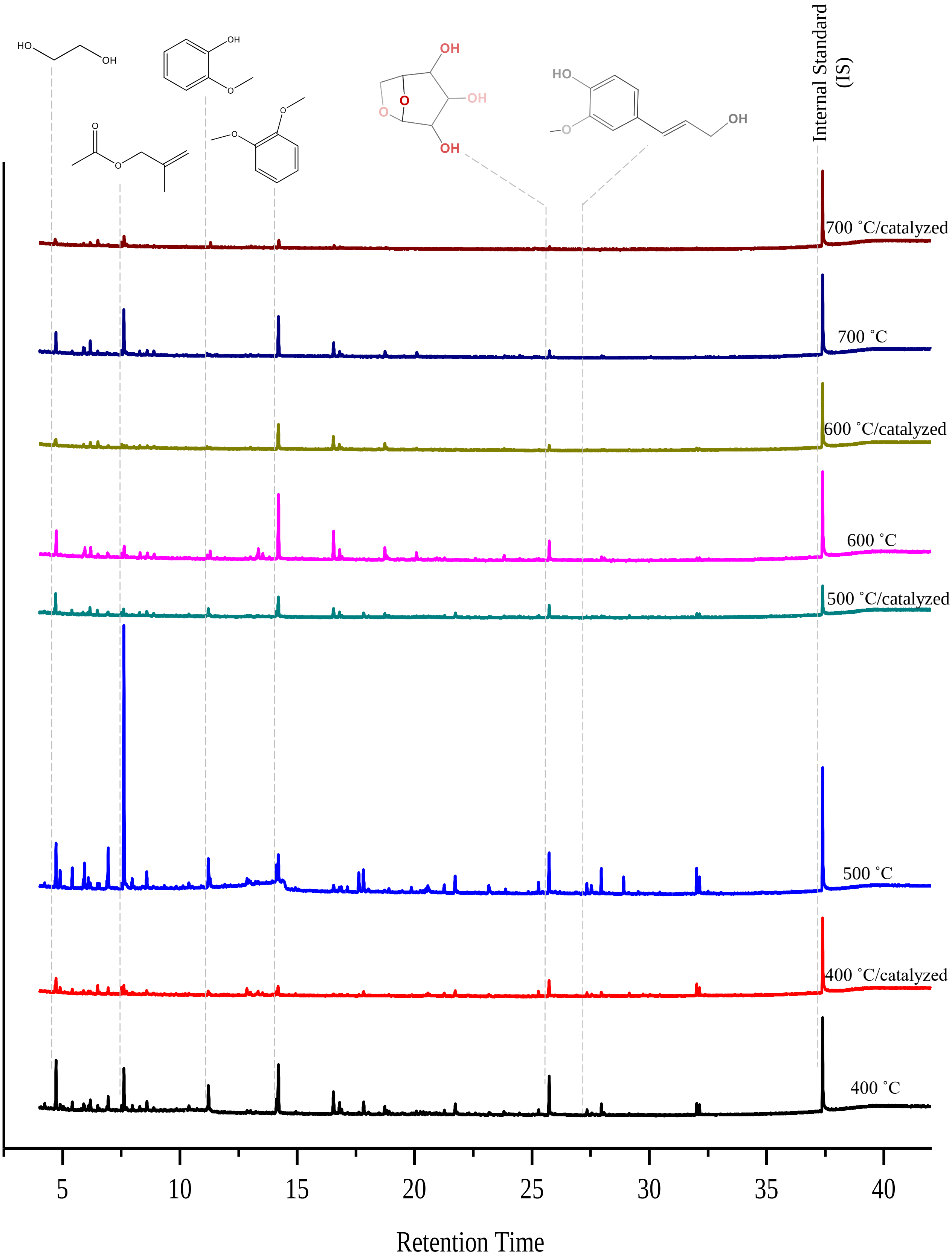

Figure 4. The gas chromatography-mass spectrometry (GC/MS) total ion chromatograms of the TMS reaction mixtures for the generated biooil obtained from the pyrolysis of cedarwood at different temperatures (400 - 700 ˚C) with and without using biochar catalyst.

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