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Complete gasification of cellulose in glow-discharge plasma

AUTHOR(S):

Minami, Eiji; Fujimoto, Syunpei; Saka, Shiro

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Title page

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Authors' names, affiliation and address:

Eiji Minami*, Syunpei Fujimoto, Shiro Saka

Department of Socio-Environmental Energy Science, Graduate School of Energy Science,
Kyoto University

Yoshida-honmachi, Sakyo-ku, Kyoto 606-8501, Japan

Corresponding author:

Eiji Minami

minami@energy.kyoto-u.ac.jp

Tel: +81-(0) 75-753-5713, Fax: +81-(0) 75-753-4736

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Abstract

The behaviors of cellulose (commercially available filter paper) were investigated in glow-discharge plasma, where pyrolysis does not occur because of low temperatures. Cellulose filter papers were decomposed in a glow-discharge plasma with nitrogen flow even at low temperatures of around 50 °C and disappeared completely after a treatment of approximately 90 h without char formation. Tar formation was not observed on any surfaces inside the plasma chamber and vacuum lines. Hence, it was concluded that all cellulose was decomposed into gaseous products. An in-situ analysis of gaseous products by quadrupole mass spectrometry suggested the formation of H₂, H₂O, CO and CO₂ from cellulose. These findings indicate that a clean and complete gasification of cellulose can be achieved with glow-discharge plasma.

Introduction

Lignocellulosics are the most abundant organic resources on Earth and have received attention as a source of energy and chemicals instead of fossil resources from an environmental perspective. Cell walls of lignocellulosics are complex natural composite materials that are composed mainly of cellulose, hemicelluloses and lignin. Although a variety of thermochemical and biochemical processes have been studied for lignocellulosics conversion over many years [1,2], many challenges remain to improve the product selectivity, yield and production cost.

We are studying plasma technology as a candidate for the conversion of lignocellulosics. Plasma is a partly or fully ionized gas, and consists of electrons, ions and neutral particles, such as radicals and excited species, but that are electrically quasi-neutral [3]. Plasma is often termed the fourth state of matter owing to its unique properties, unlike solid, liquid and gas phases [4]. An electric discharge is the simplest method to generate plasma for practical applications and is used widely in illumination, surface cleaning and reforming, arc welding and various material processes.

Plasma provides a promising reaction field where various reactions will occur without a catalyst because of the presence of ions, electrons, radicals and excited species. A number of studies have been conducted for the decomposition of lignocellulosics in high-temperature plasmas generated by arc, radio-frequency (13.56 MHz) and microwave (2.45 GHz) discharges. Du et al. carried out the gasification of corn cob in arc-discharge plasma under atmospheric pressure [5] and reported that the gas yield reached about 80% of the biomass feed with a good selectivity of H₂ and CO. They did not mention the reaction temperature, but in general, an arc discharge has a gas temperature that is sufficiently high to gasify lignocellulosics. The electrode lifetime is of concern in the usage of arc discharge. Tang and

Huang studied the pyrolysis of fir sawdust with an unspecified scientific name, in radio-frequency discharge plasma, which is an electrodeless plasma. They achieved excellent conversion rates of biomass into gases from 900 to 1500 °C [6]. Kobayashi et al. studied the gasification of microcrystalline cellulose in microwave discharge plasma between 300 and 800 °C and achieved high yields of gaseous products [7].

Most efforts for the gasification of lignocellulosics in plasmas have been carried out by using high-temperature plasmas, in which the formation of char and tar tend to be suppressed to some extent. In these high-temperature plasmas, however, lignocellulosics pyrolysis may dominate, and involves complicated reactions in the solid, liquid and gas phases, to yield various products, such as char, tar and gases [8,9]. The effect of the plasma itself on lignocellulosics decomposition remains unclear.

Glow discharge is a form of electric discharge that occurs at a low pressure [3]. In an electric field, electrons are accelerated easily but other heavy particles (ions and neutrals) are not. Under low-pressure conditions, collisions between electrons and other particles do not occur frequently, so the system does not reach thermal equilibrium. This means that the electron temperature is high, whereas the gas temperature remains low. Therefore, glow-discharge plasma is referred to as a low-temperature plasma, in which the pyrolysis of lignocellulosics does not occur. A typical application of the glow-discharge plasma is the surface modification of materials, such as hydrophilization and hydrophobization [10]. Surface modifications of cellulosic fibers in glow-discharge plasma have also been reported [11,12], but limited studies exist on lignocellulosics decomposition. Hence, this study deals with glow-discharge plasma to elucidate the decomposition behaviors of cellulose without the effect of pyrolysis reactions.

Materials and methods

Treatment of cellulose in glow-discharge plasma

Figure 1 shows the glow-discharge plasma reactor (SAKIGAKE-Semiconductor Co., Ltd, Japan) that was developed in this study. A pair of parallel plate electrodes (100-mm diameter, 50-mm distance between electrodes) is located in the reaction chamber. Three sheets of vacuum-dried ashless filter paper (~0.6 g total, Whatman No.42, α -cellulose content > 98%, 55 mm in diameter, GE Healthcare UK Ltd., England) were stacked and placed on the bottom electrode as a cellulose sample. Nitrogen (N₂, 99.99%, Imamura Sanso KK., Japan) or argon (Ar, 99.99%, Imamura Sanso KK.) was introduced into the chamber by using a mass flow controller at 100 mL/min and the chamber was vacuumed with a rotary pump. The pressure inside the chamber was controlled at 20 Pa or 100 Pa by adjusting a diaphragm valve and the gas flow rate.

After the pressure had stabilized, a high voltage was applied across the electrodes to ignite the glow discharge and the cellulose treatment started. A high voltage was generated from a commercial power source (AC100 V, 60 Hz) through a stray-field transformer (G7023-ZC, LECIP SLP Corp., Japan). The transformer can boost the voltage to 7 kV in output, but once a discharge occurs, the output voltage decreases autonomously owing to the character of the stray-field transformer, and reaches an appropriate value to maintain a steady-state glow discharge. Although the power source was an alternating current (AC), this glow discharge can be regarded as a direct-current (DC) plasma, because a half-cycle of 60 Hz is sufficiently long to allow the glow discharge to be stable. The thermocouple tip was located inside the bottom electrode to measure the temperature during plasma treatment.

After a certain treatment time, the voltage supply was turned off and the

chamber was opened to the atmosphere. The remaining filter paper was removed from the chamber and weighed (AUW220D, Shimadzu Corp., Japan). If the plasma treatment was continued, the filter paper was returned to the original position on the bottom electrode, and the glow-discharge plasma was turned on again in the same way mentioned above. The total treatment time was defined as the treatment time.

Analytical methods

The molecular-weight distribution of the remaining filter paper was evaluated by gel permeation chromatography (GPC). According to reference [13], 5 mg of sample (part of the filter paper) was added into 2 mL of pyridine (Specially prepared reagent, SP, Nacalai Tesque, Inc., Japan) with 0.2 mL of phenyl isocyanate (Guaranteed reagent, GR, Nacalai Tesque, Inc.). The mixture was stirred at 80 °C for 24 h and 0.5 mL of methanol (GR, Nacalai Tesque, Inc.) was added to terminate the reaction. After the solvent had been removed by using a rotary evaporator, the obtained phenyl carbamate derivatives were dissolved in tetrahydrofuran (THF, SP, Nacalai Tesque, Inc.) and analyzed by GPC with LC-10A (Shimadzu Corp.) under the following conditions: column, Shodex LF-804 (Showa Denko, Japan); column temperature, 40 °C; eluent, THF; flow rate, 1.0 mL/min; detector, refractive index detector (RID-10A, Shimadzu Corp.). Polystyrene standards (Agilent Technologies Inc., California, United States) were used for the mass calibration.

A quadrupole mass spectrometer (QMS, BGM-102, ULVAC, Inc., Japan) was connected to the vacuum line of the reaction chamber for the in-situ analysis of gaseous products from cellulose. Gas from the chamber was collected into the QMS through an orifice plate with a 0.1-mm hole. The collected gas was ionized by electron impact with a 50-eV ionizing energy and detected from 1 to 100 Da. A liquid-nitrogen trap was inserted between

the chamber and the vacuum pump to collect other products, if they were present.

A digital oscilloscope (GDS-2202A, Good Will Instrument Co., Ltd., Taiwan) was used to monitor the voltage and current waveforms across the electrodes. The voltage was detected by using a high-voltage probe (P6015A, Tektronix, Inc., Oregon, United States). The current was measured as a voltage drop across a 100- Ω resistance between the bottom electrode and the ground point by a voltage probe (GTP-250A-2, Good Will Instrument Co., Ltd.). The electric power supplied to the plasma was estimated by multiplying the voltage and current waveforms on the oscilloscope.

Results and discussion

Plasma-treatment conditions

Figure 2 shows a typical photograph taken in a dark room during the plasma treatment of filter papers under N₂ flow. The plasma had a weak luminescence in purple light. Three sheets of filter paper stacked on the bottom electrode are termed the upper, middle and lower papers. The voltage and current across the electrodes at 100 Pa were 356 V and 1.83 mA, respectively, in root mean square value, and the electric power supplied to the plasma was estimated to be 0.59 W (power factor, PF = 0.90). At 20 Pa, these were 682 V, 1.75 mA and 1.16 W (PF = 0.97). The higher electric power at 20 Pa is associated with a higher impedance because a lower pressure tends to yield a lower ion density. The impedance can be estimated to be 195 k Ω (= 356 V/1.83 mA) at 100 Pa and 390 k Ω (= 682 V/1.83 mA) at 20 Pa.

The temperature in the chamber increased gradually when the glow discharge was running, and after a few hours, it plateaued at 50 °C and 70 °C at 100 Pa and 20 Pa,

respectively. Cellulose pyrolysis does not occur under such low temperatures [8].

Cellulose decomposition behavior

Within minutes, the visual appearance of the filter paper did not change, but when the treatment was extended for several hours, filter-paper decomposition was clearly visible. Figure 3 shows the weight percentage of all three filter papers that remained after plasma treatment under N_2 flow. The filter-paper mass decreased steadily from cellulose decomposition in the glow-discharge plasma and disappeared completely after 92 h at 100 Pa without char formation. The decomposition rate slowed when the pressure decreased to 20 Pa. Under this condition, it took time to complete the decomposition so that the treatment was interrupted at 51 h. Fig. 3 shows that the decomposition behavior of cellulose depends on the plasma conditions.

Figure 4 (a) shows the filter papers as treated at 100 Pa under N_2 flow. Of the three filter papers, the upper filter paper was decomposed most rapidly. The decomposition proceeded mainly on the edge of the upper paper but also around on the center. Two filter papers in the middle and lower positions were also decomposed on the edge and center even though they were hidden behind the upper paper. The filter-paper color remained almost white until the paper disappeared.

Figure 4 (b) shows the case at 20 Pa. The visual appearance differed significantly from that at 100 Pa. First, the decomposition appears to proceed mainly at the center of the filter paper and a large hole was visible in the upper paper at 51 h. This trend is opposite to that in Fig. 4 (a). Second, all three papers changed from white to light-cream during the early treatment stage. The upper paper, which was exposed to the glow discharge, was most discolored, whereas the other two papers behind the upper paper were discolored slightly. The

strongly discolored area around the center of the middle paper at 51 h results from the hole on the upper paper.

Figure 5 represents the GPC chromatograms of THF-soluble fractions from the derivatized filter papers treated in glow-discharge plasma at 100 Pa along with an untreated filter paper. This analysis provides a measure of the molecular-weight distribution of the cellulose. A small amount of sample (5 mg) for this analysis was collected from around the edge of the upper paper, which appeared to be most decomposed. The molecular-weight distribution did not change drastically and it was almost the same as that of the untreated paper even though it was slightly shifted to lower molecular weight with plasma treatment time. It can be assumed that decomposition occurred only on the sample surface, and cellulose inside the sample was unaffected from the glow-discharge plasma. That may be the reason why cellulose decomposition takes such a long time in glow-discharge plasma.

Although the behaviors and roles of ions, electrons and other neutral species in the plasma may be complicated, we provide a simple explanation for the above-mentioned phenomena. Figure 6 (a) illustrates a simplified model inside the plasma chamber. The discharging current will flow along the electrical pathway shown in gray because the filter paper is an electrical insulator. As a result, a no-plasma region will appear above the filter papers. Although ions and electrons exist in the electrical pathway (plasma region), these charged particles cannot enter the no-plasma region because they are influenced by electric field. However, radicals and excited species can move into the no-plasma region because they are electrically neutral and free against the electric field. In these situations, if ions or electrons play an important role in the degradation of cellulose, filter papers will be decomposed only on the outer edge because the charged particles can move along the electric pathway, which is in contact only at the outer edge of the filter papers. The decomposition occurred on the edge and around the center of the filter papers as observed in Fig. 4 (a) and

(b). Hence, the cellulose reaction may be caused mainly by radicals and/or excited species. In the case of the N_2 gas, many excited states and dissociation modes of N_2 are known [14], but the current study could not specify which most affects the cellulose degradation.

Figure 6 (b) shows an expanded drawing. Part of the reactive neutral species (radicals and/or excited species) could be introduced into the slight gap between the filter papers. The middle and lower papers can be decomposed by these species as observed, even though these papers do not face the plasma directly.

Figures 6 (c) and (d) provide an explanation on the effect of pressure difference. First, we found that the decomposition rate of cellulose at 100 Pa was higher than that at 20 Pa as mentioned in Fig. 3. This result is reasonable because a higher pressure will result in a higher density of reactive species in the plasma. Second, the mean free paths of the reactive species become shorter at a higher pressure because the frequency of collision with other species increases. At 100 Pa, it is difficult for the reactive species to fly over long distances because of short mean free paths, and the edge of the paper is prone to attack by the reactive species from short distances as depicted in Fig. 6 (c) and as observed in Fig. 4 (a). At 20 Pa, the reactive species are able to move long distances and to reach to the center of the filter paper as shown in Fig. 6 (d) and Fig. 4 (b). These reasons could explain the difference in decomposition behaviors between Fig. 4 (a) and (b).

Products from the plasma treatment of cellulose

Although filter-paper plasma treatment was carried out repeatedly during this study, no substances, such as tar, were observed on any surfaces of the reaction chamber and vacuum lines. After treatment, no substance existed in the liquid-nitrogen trap by visual inspection. The inside of the trap was washed carefully with a small amount of ion-exchange

water, whereafter the water was analyzed by high-performance anion-exchange chromatography with a high-sensitivity electrochemical detector according to the literature [15], but no meaningful peak was obtained in the chromatogram. This evidence indicates that the filter papers were decomposed into gaseous products, or at least, volatile compounds around room temperature under reduced pressures of less than 100 Pa.

The gaseous products were analyzed by in-situ QMS connected to a vacuum line. Figure 7 shows the result at 100 Pa with N₂ flow. The mass spectrum was measured when the plasma was on, and I_{blank} is the spectrum measured without filter paper, whereas I_p is that with filter papers. The value of $I_p - I_{\text{blank}}$ is expected to represent the amount of gaseous products from cellulose. It should be noted that no meaningful peak was found in the range higher than 50 Da. In the blank measurement (I_{blank}) in Fig. 7 (a), the maximum peak exists at 28 Da as N₂, and peaks at 2, 18, 32 and 40 Da are thought to be H₂, H₂O, O₂ and Ar, respectively, as impurity gases. The other peaks are fragments from the following gases: 1 Da is H from H₂ and H₂O; 12 Da is C from CO₂; 14 Da is N from N₂ and 16 Da is O from H₂O, O₂ and CO₂ [16].

In the data measured with filter papers (I_p), some increased peaks are thought to be products from cellulose, and Fig. 7 (b) shows the subtraction result ($I_p - I_{\text{blank}}$). This graph indicates the production of H₂, H₂O, CO and CO₂ from cellulose by glow-discharge plasma treatment. However, the evidence is weak for CO production (28 Da) because this atomic mass overlaps with N₂ and a fragment from CO₂. The effect of the fragment may be negligible because the ion current of the CO that originated from CO₂ has been reported to be only ~20% of the CO₂ [16]. To eliminate the effect of overlapping with N₂, the flowing gas was changed from N₂ to Ar and the result is shown in Fig. 8. A maximum peak exists at 40 Da (Ar), and the peak at 28 Da (N₂) decreases in the blank measurement. Thus, the difference between I_p and I_{blank} at 28 Da increases compared with the case of Fig. 7 and indicates the

production of CO from cellulose with a good reliability.

Concluding remarks

Cellulose filter papers were decomposed completely in glow-discharge plasma into gaseous products without char and tar formation even at low temperature where cellulose pyrolysis does not occur. The production of H₂, H₂O, CO and CO₂ was suggested from cellulose by in-situ QMS analysis. The molecular-weight distribution of cellulose in filter paper did not change drastically by the glow-discharge plasma treatment. This implies that the filter-paper decomposition proceeds only at the sample surface.

This study indicates that a clean and complete gasification of cellulose can be achieved by glow-discharge plasma treatment even though the decomposition rate is low. We believe that the plasma technology will contribute to a clean gasification of lignocellulosics. In the future work, therefore, decomposition mechanisms not only of cellulose but also of other cell wall components (i.e. hemicelluloses and lignin) in plasma should be determined.

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Fig. 6 Explanation for decomposition behavior of cellulose in glow-discharge plasma.

Fig. 7 Quadrupole mass spectrometry for gaseous products from filter papers treated by glow-discharge plasma with N₂ at 100 Pa/0.59 W.

Fig. 8 Quadrupole mass spectrometry for gaseous products from filter papers treated by glow-discharge plasma with Ar at 100Pa.

Figure 1

Figure 2

Figure 3

(a) 100 Pa/0.59 W

(b) 20 Pa/1.16 W

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8