International Conference on Applied Energy 2020
Dec. 1 - Dec. 10, 2020, Bangkok / Virtual
Paper ID: 524

H_2-rich Syngas Induced from a Waste by Corona Plasma Discharge with Water as Free Radical Source

Ying Kang[1,2], Xu Yang[2], Zucheng Wu[2*]

1 Zhejiang Ecological and Environmental Monitoring Center, Hangzhou 310012, China

2 Department of Environmental Engineering, Zhejiang University, Hangzhou 310058, China

*Corresponding Author: wuzc@zju.edu.cn

ABSTRACT

Cleaner processes to retrieve energy from a waste are urgently needed. To improve the efficiency and hydrogen enrichment, water was used as free radical source in corona plasma discharge for syngas conversion and tar reduction. In oxygen-free environment, anthracene, as a representative in tar, was effectively converted to H_2. The anthracene conversion rate is 78.6% in 100 s reaction and 3.5% H_2 product was detected. This highly advantageous technology demonstrates that it is feasible to convert macromolecular substances into small molecular gases like H_2, a syngas composition, without the by-products of tar produced in the municipal solid waste gasification process at much low temperature.

Keywords: hydroxyl radical, corona plasma discharge, syngas production, oxidation

1. INTRODUCTION

Waste-to-energy as example of energy retrieval from a municipal solid waste (MSW) is a challenge task receiving more attention recently. Producing syngas by gasification [1, 2] is a greener process, however, its by-products of char and tar will often decrease the efficiency. [3] In addition, tar is a secondary pollutant, and the cracking of tar is necessary. Of most promising technologies, plasma discharge technique will be an alternative option due to their syngas produced in rich of H_2 with water as free radical source. [4, 5]

Hydroxyl radical (·OH) plays an important role in the plasma processes with its super oxidation ability to deeply decompose almost all of organic molecules [6]. The generation and application of ·OH under artificial environment were surveyed. [7] In our previous work, we employed the technique to eliminate sulphides utilizing the radicals. [8] Originally, it was focusing on developing clean and safe strong oxidizing free radical to oxidize some unwanted components. Regarding the technique's advantages, more attentions were paid to energy conversion of non-thermal plasma in the hybrid catalytic dehydrogenation of alkyls to a gaseous fuel, or directly utilizing non-thermal plasma activation for low temperature water–gas shift catalysis. [4, 5]

It is extremely interesting how to activate H_2O to produce gas phase free radical as oxidant for tar cracking and H_2 formation simultaneously. Actually, in corona plasma discharge it is a typical dehydrogenation process. We found that organic compounds could degrade in plasma at low temperature and produce rich H_2. In addition, it can be noticed that the generation of free radicals was influenced by dielectric gases of H_2O vapor. Therefore, this study attempts to directly use water as a free radical source to generate ·OH for tar cracking and to form hydrogen for syngas production in rich of H_2, and thus to characterize the cleaner chemical reaction medium for its applicability in energy conversion.

2. MATERIALS AND METHODS

High voltage DC power (HVDC) supply was adopted for operations. The reactor was designed for coaxial structure, different from conventional devices. Corona polar is extremely hollow rotating nozzle type, hollow metal tube nozzle uniformly distributed on the surface

Selection and peer-review under responsibility of the scientific committee of the 12th Int. Conf. on Applied Energy (ICAE2020).

of bigger diameter metal mother pipe. The mother pipe was also hollow and connected to the nozzle inside. Corona polar was installed on the tubular insulation shell (Φ 7.8 cm by 10 cm length) coaxial center. A layer of mesh shell inner wall installation grounding electrodes. The upper and lower parts of the shell were provided with inlet and outlet valves, respectively. Positive corona discharge was used throughout the experiment. High-purity nitrogen pumped into a humidifier with a certain amount of distilled water to obtain the relatively saturated water vapor. The above water vapor was divided into two channels before entering the inlet, one of which passes through anthracene diffusion bottles and then converges and enters the reactor inlet. Controlling the flow of the two channels of gas can produce medium gas containing anthracene of different concentrations. The experimental conditions were as follows: power output voltage: 20 kV; output current: 0.1 mA; the reaction time: 10~120 s.

Bruker EMX-8 (Germany) paramagnetic electron spin resonator (ESR, center field: 3490.00 G, microwave frequency: 9.800~9.850 GHz, power: 19.500~20.500 mW, sweep width: 100.00 G, center field resolution: 1024 points, receiver frequency: 100.00 kHz) was used for free radical detection. In the sample pool, quartz flat tubes were used, which were rinsed with ethanol before use and then dried with high-purity nitrogen.

DMPO (5, 5-Dimethyl-1-pyrrolin-n-Oxide, Sigma) was used as a spin trapping reagent to detect free radicals in electron spin resonance based reactions.

Gas phase composition was tested with Varian CP3800 gas chromatography (Varian, USA, hydrogen flame detector, DB-624 capillary column (J&W Scientific, USA), 30m×0.54mm ID). Liquid phase composition was measured with high performance liquid chromatography (HPLC GILSON MODEL 302, France, REVERSED phase ODS-18 column, UV detector).

3. RESULTS AND DISCUSSION

3.1 Performance of corona plasma

In corona discharge, a typical non-thermal-plasma, the reaction temperature is usually kept at 25-100 °C. In order to avoid possible condensation of tar and water vapor, we set up the experimental temperature at over 300 ° C that agrees with other studies, in which at reaction temperature of 300-600 ° C poly-aromatic hydrocarbons (PAHs) in tar get the highest conversion efficiency in non-thermal-plasma (in a rotating gliding arc discharge reactor) [9]. Compared with conventional syngas making (Table 1), the energy utilization rate of corona discharge is greatly reduced and demonstrates an obvious advantage.

Table 1. Comparison of conventional gasification, catalytic pyrolysis and plasma of this work

	Gasification [10]	Catalytic pyrolysis [11]	Plasma [9], this work
Reactant	Air, O_2	None	H_2O
Temperature	1000-1600°C 550-900°C(O_2)	500-800°C	300-600°C
Products	CO, H_2, CO_2, H_2O, CH_4	CO, H_2, CH_4, C_nH_m	H_2, CH_4, CO, CO_2

We use anthracene as the representative of PAHs in tar, the conversion and its efficiency were tested. The experimental results (Table 2) show that, at actual reaction temperature of 300 ° C, an optimistic 78.6% conversion efficiency can be achieved for anthracene with initial concentration of 1g/Nm^3 treated by corona discharge point plasma, while H_2 and CO_2 with volume concentration of 3.4% and 0.6% respectively can be obtained.

A parallel experimental testing was also conducted. In a tubular quartz furnace, a certain amount of domestic garbage (about 5g household waste) was digested and downstream of nitrogen carrier gas was collected. Similar results of same H_2 portion were gained. Except for H_2 and CO_2 small amount of CH_4 and CO was also detected. Meanwhile, the downstream of digestion gas was bubbled and scrubbed into a vial, in which we can cleanly observe that the color of solution was obviously turned black indicating that the tar was formed and dissolved, while under corona plasma the solution was kept clean.

Table 2. Anthracene conversion (E %) and H_2 formation by different initial concentrations of anthracene

	100mg/Nm^3		500mg/Nm^3		1000mg/Nm^3	
Time	E (%)	H_2(%)	E (%)	H_2(%)	E (%)	H_2(%)
10 s	42.1	0.13	9.8	0.2	3	0.1
30 s	61.5	0.26	36.5	0.8	21.2	0.9
60 s	84.7	0.36	65.3	1.5	44.4	1.8
90 s	93.6	0.41	81.9	1.9	63.6	2.7
100 s	99.0	0.44	90.6	2.2	78.6	3.4

3.2 Cracking of tar

Conventionally, pyrolysis and gasification is a reaction process of organic carbon and hot water steam. H_2O participates in the reaction of C to produce

H_2 and CO (formula 1), and CO can further react with H_2O to produce one mole of H_2 and CO_2 (formula 2). If CO_2 is removed by absorption in the product, H_2-rich combustible gas can be formed. In solid waste, it mainly exists in form of hydrocarbons, which is the reforming reaction process of C_nH_m and CO_2 (formula 4) to generate H_2 and CO. The potential of H_2 or CO can be used as fuel (chemical energy) or further synthesis of other downstream chemicals, and/or directly burned for power generation. The disadvantage of this process is that unwanted tar will be generated simultaneously. In fact, in the plasma atmosphere, H_2O is activated to form hydroxyl radicals (2.8 V) and hydrogen atoms (·H) participate in the reaction (plasma catalytic reaction). The strong oxidizing hydroxyl radicals strengthen the reaction process and accelerate the reaction rate. [12]

$C + H_2O \leftrightarrow CO + H_2$, $\Delta H = -131$ kJ/mol (1)

$C + 2H_2O \leftrightarrow CO_2 + 2H_2$, $\Delta H = -90$ kJ/mol (2)

$H_2 + 1/2O_2 \leftrightarrow H_2O$, $\Delta H = -242$ kJ/mol (3)

Reforming reaction:

$C_nH_m + nCO_2 \leftrightarrow 2nCO + 1/2mH_2$ (4)

Water as oxidant and free radicals source under corona plasma discharge can form H_2 (the combination of hydrogen atoms H forms H_2):

$H_2O \leftrightarrow HO\cdot + H\cdot$; i.e., $2H_2O \leftrightarrow 2HO\cdot + H_2$ (5)

Therefore, hydroxyl radical reaction will be:

$HO\cdot + CO \leftrightarrow 1/2H_2 + CO_2$ (6)

In the process of MSW gasification, tar generation will blocks facilities and decreases efficiencies. PAHs were main components of the formed tar. Under plasma discharge, H_2O is activated as to form a ·OH, which will attacks the PAHs for their cracking and produces H_2. The whole process is a dehydrogenation to form H_2-rich syngas and decrease the tar content, the reaction will be as Fig 1.

3.3 Detection of free radicals and mechanism

0.01 mol/L DMPO aqueous solution was prepared before reaction. Took 5 mL DMPO aqueous solution within Φ30 mm petri dishes and placed the petri dishes at the bottom of the corona discharge reactor. The position of the petri dishes is below the two electrodes and avoid contact with them, the same goes for the rest of the operating conditions.

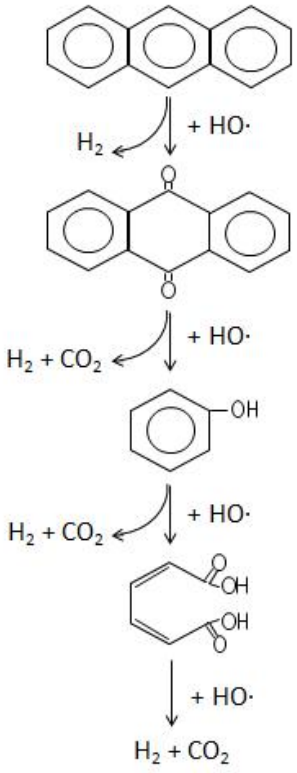

Fig 1. Schematic diagram of tar dehydrogenation in a free radical environment

Unsaturated diamagnetic substance (spin trap) DMPO can react with ·OH to form a long-lived spin adder that can be easily captured by ESR spectrometers. With the conditions of 20 kV power supply output voltage, 0.1 mA output current, 120 s electricity reaction time, obvious 1:2:2:1 quad peak spectral lines can be got after putting DMPO solution in corona discharge in the reaction system. The ESR spectrum of ·OH and DMPO formation is close to the DMPO-·OH characteristic spectrum. The ESR spectrum simulated according to ·OH hyperfine coupling constant (H= N= 14.9g) is consistent with the experimental results. When isopropanol, an ·OH scavenging agent, was added to the absorption solution in advance and the above process was repeated, the obtained ESR signal strength was significantly reduced. When the reactor was not energized, no ESR signal was detected in the DMPO absorption solution, which is consistent with the fact that ·OH does not exist in the system when no physical or chemical changes occur. The above results show that ·OH is indeed produced in the chemical process of corona discharge.

In our previous work, we have confirmed that the source of ·OH can be generated either in air or in nitrogen. When we replaced the medium gas air with

high-purity nitrogen, both the air and the high-purity nitrogen carried saturated steam into the corona discharge reactor to create an oxygen-free reaction environment, we can gain same measurement results of above ·OH detection experiment. In the ESR test after the reaction, the ESR characteristic quadrangle of the DMPO-·OH adduct can still be obtained, and the intensity was slightly lower than that under the air medium. Therefore, it can be judged that the generation source of ·OH in the corona discharge reaction system is H_2O molecule. We noticed that in the presence of O_2, H_2 will be no longer produced because O_2 can increase the yield of excess ·OH, which oxidizes the H_2. That is the corona discharge system with air as medium gas has stronger practical value for degrade unwanted pollutants [13].

·OH is obtained mainly from the collision reaction (7)~(8) between high-energy electrons (5-15 eV) and water molecules (H-OH bond energy 4.96 eV) and the charge transfer reaction (9)~(10) between excited oxygen and water molecules under the action of strong electric field of corona discharge if oxygen coexists.

$$e + H_2O \rightarrow \cdot OH + \cdot H + e \quad (7)$$

$$e + O_2 \rightarrow O + O(^1D) + e \quad (8)$$

$$O_2 + \cdot H \rightarrow HO_2 \quad (9)$$

$$O(^1D) + H_2O \rightarrow \cdot OH + \cdot OH \quad (10)$$

4. CONCLUSIONS

Corona plasma discharge activation of water as free radical source enables the cracking of macromolecular substances without the formation of unwanted tar and it operates at a low-temperature. The protocol testified in this work showed it is potential to convert organics in solid waste due to highly effective formation of free radicals that decompose PAHs into small molecules such as H_2, CO_2, etc. Instead of air or oxygen the addition of water vapor causes the minimal dilution of gasification since one mol H_2O produces one mol H_2 itself, so as to make it rich in H_2 synthesis gas.

ACKNOWLEDGEMENT

This work is supported by the National Natural Science Foundation of China (No. 21473158) and the National High Technology Research and Development Program ("863" Program) of China (No. 2013AA065901).

REFERENCE

[1] Scarlat N, Fahl F, Dallemand JF. Status and opportunities for energy recovery from municipal solid waste in Europe. Waste Biomass Valori 2019;10:2425-44.

[2] Mukherjee C, Denney J, Mbonimpa EG, Slagley J, Bhowmik R. A review on municipal solid waste-to-energy trends in the USA. Renew Sust Energ Rev 2020;119:109512.

[3] Munir MT, Mardon I, Al-Zuhair S, Shawabkeh A, Saqib NU. Plasma gasification of municipal solid waste for waste-to-value processing. Renew Sust Energ Rev 2019;116:109461.

[4] Gibson EK, Stere CE, Curran-McAteer B, Jones W, Cibin G, Gianolio D, Goguet A, Wells PP, Catlow CRA, Collier P, Hinde P, Hardacre C. Probing the role of a non-thermal plasma (NTP) in the hybrid ntp catalytic oxidation of methane. Angew Chem Int Edit 2017;56:9351-5.

[5] Stere CE, Anderson JA, Chansai S, Delgado JJ, Goguet A, Graham WG, Hardacre C, Taylor SFR, Tu X, Wang ZY, Yang H. Non-thermal plasma activation of gold-based catalysts for low-temperature water-gas shift catalysis. Angew Chem Int Edit 2017;56:5579-83.

[6] Yuan B, Mao XZ, Wang Z, Hao RL, Zhao Y. Radical-induced oxidation removal of multi-air-pollutant: A critical review. J Hazard Mater 2020;383:121162.

[7] Liu X, Zhang HM, Qin DD, Yang Y, Kang Y, Zou F, Wu ZC. Radical-initiated decoloration of methylene blue in a gas-liquid multiphase system via DC corona plasma. Plasma Chem Plasma Process 2015;35:321-37.

[8] Xia FF, Liu X, Kang Y, He R, Wu ZC. Elimination of sulphur odours at landfills by bioconversion and the corona discharge plasma technique. Environ Technol 2015;36:2959-66.

[9] Xu RY, Zhu FS, Zhang H, Ruya PM, Kong XZ, Li L, Li XD. Simultaneous removal of toluene, naphthalene, and phenol as tar surrogates in a rotating gliding arc discharge reactor. Energy Fuels 2020;34:2045-54.

[10] Arena U. Process and technological aspects of municipal solid waste gasification. A review. Waste Manag 2012;32:625-39.

[11] Liu JJ, Hou QD, Ju MT, Ji P, Sun QM, Li WZ. Biomass pyrolysis technology by catalytic fast pyrolysis, catalytic co-pyrolysis and microwave-assisted pyrolysis: A Review. Catalysts 2020;10:742.

[12] Tavares R, Ramos A, Rouboa A. A theoretical study on municipal solid waste plasma gasification. Waste Manag 2019;90:37-45.

[13] Kang Y, Wu ZC. Formation of hydroxyl radicals and oxidation of toluene under corona discharge with water vapor as radical source. Chin Sci Bull 2008;53:2248-52.