

# Plasma enhanced catalytic reforming of biomass tar model compound to syngas

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## ABSTRACT

Direct thermal decomposition, plasma-assisted decomposition, catalytic steam reforming and plasma enhanced catalytic steam reforming of biomass tar using toluene as a model compound were comparatively studied. Plasma enhanced catalytic steam reforming showed the best performance. The introduction of a plasma to the catalytic reforming reaction accelerated the decomposition of toluene, while the co-existing Ni/SiO<sub>2</sub> reforming catalyst, on the other hand, guided the reaction towards formation of CO and H<sub>2</sub>, realizing the highest toluene conversion, and the highest CO and H<sub>2</sub> formation rates simultaneously.

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## 1. Introduction

As a source of renewable energy, biomass has the advantage of neutral emission of greenhouse gas such as CO<sub>2</sub>, compared to fossil fuel. With the depletion of fossil fuel resources as well as global warming issues, the utilization of biomass is getting increased attention as a potential source of renewable energy. Biomass can be utilized effectively via a thermal, biological or physical process. Thermochemical conversion technologies are especially useful to produce fuels, chemicals, combined heat and power with high-energy efficiencies [1]. Among them, biomass gasification has attracted a lot of interest by producing a gas rich in CO and H<sub>2</sub>, which can be used as feed gas for Fischer–Tropsch and methanol synthesis [2]. Various types of gasifiers have been explored for biomass. A fluidized-bed (FB) gasifier with steam as the oxidant represents a balance for potential large-scale applications, high thermal efficiency, low impurity formation and ability to handle wet biomass, compared to updraft and downdraft gasifiers [3]. H<sub>2</sub>, CO, CO<sub>2</sub>, H<sub>2</sub>O, CH<sub>4</sub>, and various light hydrocarbons are the main products of biomass gasification. Impurities such as ash, volatile alkali metals and tar are also generated during biomass gasification. The concentration of tar, which ranges from 5 to 75 g/N m<sup>3</sup> in fluidized-bed gasifiers, is remarkably above the maximum allowed for gas turbines and diesel engines [4,5]. Moreover, tar is also acting as poison for C1 chemistry catalysts. Tar is a complex mixture of condensable aromatics compounds [6]. Tar can condense or polymerize into more complex structures in engines, heat

exchangers and filters, leading to increasing maintenance cost and decreasing process efficiency. The commercialization of biomass gasification will be possible if tar can be eliminated from the gasification products efficiently. Mechanical separation, thermal cracking and steam reforming are the most widely used technologies for tar removal. The mechanical method is efficient, but has a significant environmental impact. Of all these tar removal technologies, steam reforming of tar is very attractive. Steam reforming of tar is an endothermic reaction and, on a thermodynamic basis, it is favored at temperatures above 923 K. Ni catalysts have been proven to be very active in steam reforming of biomass gasification tar and therefore, widely employed for tar conversion [7–9]. Supported Ni catalysts also show methane reforming and water gas shift reaction activity, allowing availability of the desired H<sub>2</sub>/CO ratio in the formed syngas.

Recently, plasma, which consists of highly excited atoms and molecules, ions, electrons, radicals, neutral particles and so on, is widely utilized [10]. It can be divided into thermal and non-thermal plasmas (or non-equilibrium plasma). For thermal plasma, such as arc discharge and gliding arc discharge, the typical gas temperature is higher than 2000 K and all charged and neutral species are in thermal equilibrium. But, for non-thermal plasma, like dielectric barrier discharge (DBD), corona discharge or pulsed discharge, the temperature of the electrons can reach 10<sup>4</sup>–10<sup>5</sup> K, while the gas temperature can remain in the range of room temperature [11]. As a novel molecule activation technology, non-thermal plasma is widely used for the modification of surface oxides, the preparation and regeneration of catalysts as well as for the catalytic synthesis and decomposition. A synergistic effect may be obtained through combination of non-thermal plasma with a

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desirable catalyst. This catalysis-plasma process has simultaneously the advantage of high product's selectivity from thermal catalysis and the fast startup from the plasma technique [12]. As a new technology, the plasma-catalytic process has been widely applied for volatile organic compounds (VOCs) removal [13] and hydrocarbon reforming for hydrogen production [14]. In the present work, toluene was used as the tar model compound, because, firstly, toluene is relatively stable [15]; secondly, toluene is less harmful and its high-temperature chemistry is fairly well known [16] and finally, toluene can be used to get a realistic information on the tar-decomposition activity of catalysts [17]. Plasma enhanced catalytic reforming (PCR) of toluene was studied. For comparison, direct thermal decomposition (DD), plasma-assisted decomposition (PD) and catalytic reforming (CR) of toluene were also studied. It was found that introduction of plasma prior to catalyst bed remarkably enhanced the conversion rate of toluene as plasma activated hydrocarbons to radical state, resulting in accelerated decomposition of toluene to form CO and H<sub>2</sub>.

## 2. Experimental

### 2.1. Catalyst preparation and characterization

The 5 wt% Ni/SiO<sub>2</sub> catalyst was prepared by incipient-wetness impregnation of commercially available silica gel (Carriact Q-50, Fuji Silysia Co., Inc.) with Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (KANTO Chemical. Co., Inc.). The catalyst precursor was dried in air at 393 K for 12 h, then calcined in air from room temperature to 673 K with a ramping rate of 2 K min<sup>-1</sup> and kept at 673 K for 2 h. After calcination, the catalyst was reduced in flowing pure hydrogen at 673 K for 10 h, and finally, passivated by 1% oxygen in nitrogen at room temperature for 5 h.

The BET surface area, pore size diameter and pore volume were determined by nitrogen adsorption/desorption isotherms carried out on a Quantachrome Autosorb-1 (Yuasa Ionics) instrument. The BJH method was employed to evaluate the pore diameter. The measured catalyst textural properties are summarized in Table 1.

### 2.2. Experimental setup

The configuration of the plasma-catalyst reactor and the experimental setup are shown in Figs. 1 and 2, respectively. A quartz tube with 17.5 mm internal diameter and 30 cm length was used as a reactor for the experiment. Toluene and H<sub>2</sub>O were vaporized and premixed in the upper part of the reactor. The reaction was carried out at the lower end of the reactor. Two stainless steel rods were inserted in parallel from the opposite direction as electrodes. The gap between the two rods was 2 mm. The non-thermal pulsed plasma was generated by applying a negative high voltage with a direct current (DC) power supply (MATSUDA Precision Inc.). The output current and voltage of the DC power supply were measured by a digital oscilloscope (TDS3012, Tektronix Inc.). The average output current and voltage were 3.6 mA and 4.8 kV, respectively. The pulse width was about 120 ns.

In the present study, DD, PD, CR and PCR were studied. For catalytic steam reforming processes, 0.5 g of the Ni/SiO<sub>2</sub> catalyst was

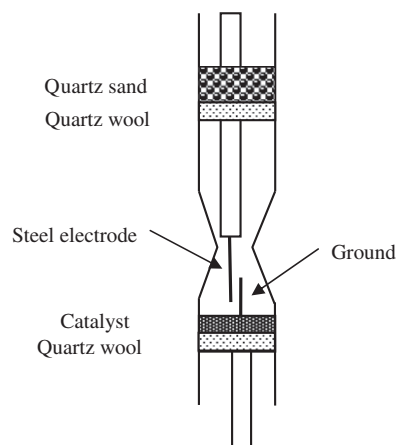


Fig. 1. Schematic diagram of reactor.

used. Before reaction, the catalyst was reduced in situ at 773 K for 1 h in H<sub>2</sub> flowing at 40 ml/min. Then, liquid toluene and H<sub>2</sub>O were pumped into the reactor by two syringe pumps. The flow rates of toluene and H<sub>2</sub>O were fixed at 0.024 ml/min and 0.027 ml/min to achieve an S/C ratio (steam/carbon carbon-molar ratio) of 1 throughout the experiment unless otherwise stated. Helium was used as carrier gas and its flow rate was kept at 40 ml/min unless otherwise mentioned. The reaction was mainly carried out at 773 K. During the reaction, effluent gases released from the reactor were analyzed by on-line gas chromatography. CO was analyzed by GC-14B (Shimadzu Corporation) equipped with a thermal conductivity detector (TCD) and a Carbosphere column. H<sub>2</sub> was analyzed by another on-line gas chromatograph (Shimadzu GC-8A) equipped with a TCD and a Carbosphere column. The liquid products were collected in an ice trap and analyzed by GC using a GC-8A (Shimadzu Corporation) equipped with a flame ionization detector (FID). A Porapak S packed column was used to separate the liquid products.

## 3. Results and discussion

### 3.1. Reaction studies

In the present work, four kinds of biomass tar removal reactions using toluene as model compound were conducted. The toluene conversions of the four different types of reactions performed at 773 K are compared in Fig. 3. It can be seen that toluene conversions increased in the following sequence: DD < CR < PD < PCR. In the case of direct decomposition of toluene, the toluene conversion is very low (5.4%). It indicated that at low temperature, toluene can not be decomposed efficiently to produce CO and H<sub>2</sub>. It is known that hot gas conditioning following the gasifier can also be used to remove biomass tar [18]. But, tar can only be extensively removed by thermal cracking at temperature higher than 1373 K. Considering the required temperature, which is higher than those used during gasification, this process is not desirable. Catalytic steam reforming of tar is a very attractive technique for tar destruction. Toluene is extensively used as a model compound of tar because it is largely formed and is very stable. Steam reforming of toluene involves many reactions. The main reaction of this process involves the reaction of toluene with water to generate hydrogen and carbon monoxide, as shown in Eq. (1), coupled with the water gas shift reaction (WGSR) (Eq. (2)).

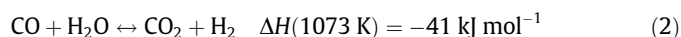
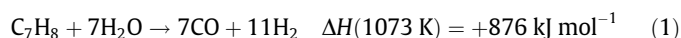


Table 1  
Catalyst and support characterization.

Catalyst	S <sub>BET</sub> (m <sup>2</sup> g <sup>-1</sup> )	Average pore diameter (nm)	Pore volume (ml g <sup>-1</sup> )
SiO <sub>2</sub> (Q-50)	94	59	1.35
Ni/SiO <sub>2</sub>	80.8	57	1.15

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