Selective control of reformed products of n-pentane by plasma chemistry

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Abstract: In this paper, we studied the reforming of n-pentane (n-pentane) using a temperature-controlled dielectric barrier discharge reactor. We found that the products of n-pentane reformation can be controlled by the blending of feed gases, thereby selectively increasing the valuable chemicals (such as H2, short chain alkanes and oxygenates) in the product. The discharge characteristics as well as reforming performance during the reforming process, such as product selectivity, yield and energy efficiency, will be described in detail.

Keywords: dielectric barrier discharge, plasma chemistry, reforming, n-pentane, oxygenates, hydrogen

1 Introduction

In recent decades, fossil fuels have been widely used in daily life. Used in power generation, industry and transportation, it also generates huge pollution while promoting people's lives, especially as the combustion of motor fuel (diesel, gasoline) leads to the inevitable emission of PM, CO₂ and NO_x [1]. Despite the presence of catalytic and non-catalytic after-treatment systems to mitigate nitrogen oxide emissions, the accumulation of CO₂ in the atmosphere often results in a "greenhouse effect". In addition, emissions of PM, NOx have also greatly increased the probability of extreme weathering such as haze and photochemical smog [2]. In order to protect the environment, clean fuels with low pollution emissions have attracted great interest. In this respect, the hydrogen energy which can produce water as its sole by-product is particularly attractive to relevant scholars to explore [3]. The addition of clean fuels during the combustion process is an important means of reducing vehicle emissions. For example, when a short-chain alkane, hydrogen or oxygen-containing hydrocarbon fuel is added to a diesel engine, the fine particle concentration is reduced by 40%, and the combustion efficiency can be increased by 10-15% [4-5]. Similar results have also been reported in the testing of gasoline engines. Alcohol fuels and their blends with gasoline can reduce HC and CO emissions from ignited engines, improve engine power and economy; dimethyl ether (DME) fuel, diesel and dimethyl carbonate (DMC) or two mixed fuels such as dimethoxymethane (ADMM) have a significant effect on reducing particulate emissions from compression-ignition engines [6-7].

Promising methods are to reform the liquid alkanes such as diesel or gasoline in a vehicle to produce hydrogen and oxygenated fuel in situ. Therefore, the development of hydrogen based on liquid alkanes and the production of oxygen-containing hydrocarbon fuels are developed. The whole instrument is a common research goal of scholars at home and abroad.

The main methods for the preparation of hydrogen or other clean fuels for alkane reforming are thermal catalysis (steam reforming, partial oxidation, dry reforming and autothermal reforming) and plasma methods [7]. The hydrogen-rich syngas produced in the process is also of interest as a feedstock for the gasliquid process for Fischer-Tropsch synthesis. However, the thermo-catalytic reforming of hydrocarbons is usually carried out in synergy with a catalyst at a high temperature (800-1100 °C) and a high pressure (2-3 MPa). Heat loss and carbon deposition on the catalyst are major problems in thermo-catalytic reforming [8,9]. Fortunately, the plasma method is relatively insensitive to the coking problem of conventional thermo-catalytic alkane reforming, and can be quickly started and stopped, normal temperature and atmospheric pressure operation, and has unique advantages as a vehiclemounted reformer [10-11].

Non-thermal plasma (NTP) has been extensively studied as an alternative fuel reforming method [12, 13]. The NTP process is accompanied by the electron impact reaction of high-energy electrons, so even at very low temperatures, electron collision dissociation can initiate plasma chemical reactions [14]. In plasma alkane reforming, active substances such as electrons or radicals attack hydrogen radicals generated by alkane molecules to form hydrogen or water; and the generated hydrocarbon radicals mainly have the following orientations: (1) mutual combination to form short chains Alkane or other hydrocarbons; (2) further by electron bombardment or pyrolysis to produce carbon black; (3) if the reaction contains oxygen, partial oxidation to obtain oxygenated hydrocarbons and carbon monoxide; (4) deep oxidation to obtain carbon dioxide. The ideal alkane reforming process utilizes carbon at the same time as efficient hydrogen production to produce oxygenated hydrocarbon fuels or high valueadded chemicals. Tu et al [15] used a plasma-bonded catalyst to increase the selectivity of the synthesis gas. However, long-term stable operation of the catalyst is an unsolved practical problem. Another possible method is to control the plasma action time and quench the chemical reaction to obtain a useful intermediate before reaching the chemical equilibrium state. Grandy et al [16] designed a reactor that can rapidly quench plasma chemical reactions within 1 ms, yielding 100% methane conversion and 98% acetylene yield while efficiently producing hydrogen.

The team has used a temperature-controlled dielectric barrier reactor to study the reaction pathways of methane CO_2 reforming and partial oxidation reforming. The results show that the conversion of methane is mainly dominated by electron bombardment reaction, while the product distribution is mainly composed of thermo-chemical (free radical). Reaction control [17, 18]. Agiral et al [14]. also found a similar reaction mechanism in the study of n-hexane reforming.

In this study, we used a self-developed temperature-pressure dual-control dielectric barrier discharge (DBD) reactor to achieve independent control of the internal pressure of the reaction system and the temperature of the background gas. N-pentane was chosen as the model liquid hydrocarbon because it represents a substantially saturated liquid hydrocarbon fuel with well-developed chemical Kinetic data. This paper discusses the effects of energy density, temperature, and pressure on n-pentane conversion and product selectivity during n-pentane reforming, and evaluates the effects of electron-induced reaction and thermo-chemical reactions on fuel reforming. More importantly, we studied the effects of various carrier gases (Ar, CH₄ and CO₂) on the detailed components of the gas phase products and liquid phase products during

the n-pentane reforming process, and controlled the reaction pathway by controlling the types and concentrations of free radicals. And in-depth analysis of the production formation mechanism of H_2 , oxygenated products and short-chain alkanes.

2 Experimental Setup

The experimental setup consists of four modules, a temperature-pressure dual-control dielectric barrier discharge (DBD) reactor, a power supply system, a reactant supply system and a measurement system, as shown in Figure 1. The configuration of the experimental setup is similar to that used in our previous methane research work [17-18]. The temperature controlled DBD reactor includes a coaxial DBD reactor and an electric oven. We used a quartz tube with an inner diameter of 14.4 mm as a dielectric barrier to construct a coaxial DBD reactor. A 50 mm wide stainless steel mesh was tightly wound around the outer wall of the quartz tube to serve as a grounding electrode. A high voltage electrode made of a stainless steel rod having a diameter of 12 mm was inserted into a quartz tube to form a discharge gap of 1.2 mm.

The coaxial DBD reactor was powered by an AC high voltage power supply (CTP-2000K, Suman) that can deliver voltages up to 20 kV with a frequency range of 4-10 kHz. The applied voltage and current were measured using a digital oscilloscope (DPO 3034, Tektronix) and a high voltage probe (P6015A, Tektronix) and a current sensor (TCP 0030, Tektronix). The *V-Q* Lissajous diagram was used to calculate the discharge power of the DBD reactor. A capacitance measuring 32 nF was added to the circuit to create a *V-Q* Lissajous diagram. The area of the plot was averaged over 216 scans and multiplied by the corresponding frequency to obtain the discharge power. A digital camera (70D, Canon) equipped with a lens (EF-S18-135mm f/3.5-5.6 ISAPS, Canon) was used to capture the discharge image.

The composition of the reactants was controlled by the reactant supply system. The concentration of 10% npentane in the experiment was always the same. The test conditions included different energy densities, different temperatures, different pressures, types and ratios of different feed gases, and carrier gas (Ar, purity 99.999%, Jingong). To control the concentration of n-pentane in the reaction, the designated portion of the carrier gas was bypassed with a bubbler containing n-pentane solution (purity > 99%, Aladdin), with the bubbler placed in a 303 K water bath, total The flow rate was fixed at Q_{flow} =200 ml / min, and the mass flow controller (MFC, DO7-19C, Beijing Seven Star) controlled the flow of the carrier gas. The electric furnace (T1000-D200, Senko) heated the DBD reactor to the target temperature. The reactor pressure was adjusted using a dry vacuum pump (LC-85, Lichen) installed downstream of the reactor. The gas pressure in the reactor was monitored with a digital pressure gauge (MIK-Y190, Meacon).



Figure 1. Schematic diagram of the experimental setup.

In order to determine the composition of the reformate, the reformed gas was dried by a self-made ice water cooling trap and an on-line gas chromatograph equipped with a flame ionization detector (FID) (GC, SP-3420, Beijing North). Configuring the FID channel to analyze hydrocarbons from C1 to C5. A hydrogen detector (PDA600-H2, Wandi) was used to detect H₂. The liquid product collected from the ice water cooled collector was analyzed using a gas chromatography mass spectrometer (GC-MS, 7890A-5975C, Agilent) equipped with a DB-5MS column.

To characterize the reforming process, the C_5H_{12} conversions are defined as

 $C_{5}H_{12} \text{ conversion (\%)} = \frac{\text{moles of } C_{5}H_{12} \text{ converted}}{\text{moles of } C_{5}H_{12} \text{ input}} \times 100$

the selectivities of the products are calculated as

$$C_X H_Y \text{ selectivity (\%)} = \frac{X \times \text{moles of } C_X H_Y \text{ produced}}{5 \times \text{moles of } C_5 H_{12} \text{ converted}} \times 100$$

H₂ selectivity (%)=
$$\frac{\text{moles of H}_2 \text{ produced}}{6 \times \text{moles of C}_5 \text{H}_{12} \text{ converted}} \times 100$$

and the energy density (ED) is defined as

$$ED (kJ/L) = \frac{P_{dis}}{Q_{flow}}$$

where P_{dis} is the discharge power and Q_{flow} is the total gas flow rate.

When evaluating the energy efficiency, the heat energy from the furnace was also considered to make the evaluation practically meaningful. Thus, the energy efficiency of C_5H_{12} conversion is defined as

$$\eta_c$$
(mol/kWh)= $\frac{\text{moles of C}_5 \text{H}_{12} \text{ converted}}{E_P + E_T}$

where E_T is the thermal energy required to raise the background temperature to the target temperature and E_P is the plasma discharge energy from the DBD.

In addition, the fuel production efficiency is defined as

$$\eta_{FP}(\%) = \frac{\text{(moles of products × LHV of products)}}{\text{(moles of converted } C_5 H_{12} × LHV of } C_5 H_{12} + E_P + E_T$$

where LHV is the low heating value in J/mole.

3. Conclusions

Plasma-induced reforming of n-pentane was dualinvestigated using a temperature-pressure controlled DBD reactor. The gaseous plasma chemical discharge conditions are simulated by the formation of n-pentane in the form of bubbling. The gas phase product and the liquid phase product were analyzed in a pure Ar atmosphere. It was found that H₂ and a series of alkane having a broad carbon number were formed, especially in the liquid phase product, and the selectivity of long chain alkane was high. In order to avoid the generation of long chain HC, CH4 was selected. The methyl group (CH3) from the CH4 dissociation enrichment and the intermediate alkyl group derived from the collision of n-pentane with high energy electrons and an excited species undergo a radical reaction stabilization to form a short chain HC. By selecting CO₂ feed, the alkyl stabilized oxidation form was realized, and the CO₂ provided by electron-induced and free radical reaction produced O and OH free radicals to promote the formation of ketones and alcohols. In addition, it is expected that this heavy HC reforming method can selectively add a short-chain HC, long-chain HC or oxygen-containing compound, which can provide a new method for advanced internal combustion engines, such as homogeneous charge compression ignition and reactivity controlled compression ignition. It can be used as an alternative to the dual fuel concept, although there are many technical obstacles, such as high pressure, addition of water and bubbles, the ignition delay characteristics can be actively controlled by plasma reforming.

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