



Article Effect of Nitrogen/Oxygen Substances on the Pyrolysis of Alkane-Rich Gases to Acetylene by Thermal Plasma

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Abstract: It is important to convert alkane-rich gases, such as coke oven gas, to value-added chemicals rather than direct emission or combustion. Abundant nitrogen/oxygen substances are present in the actual alkane-rich gases. However, the research about how they influence the conversion in the pyrolysis process is missing. In this work, a systematic investigation on the effect of various nitrogen/oxygen-containing substances, including N₂, CO, and CO₂, on the pyrolysis of CH₄ to C₂H₂ was performed by a self-made 50 kW rotating arc thermal plasma reactor, and the pyrolysis of a simulated coke oven gas as a model of alkane-rich mixing gas was conducted as well. It was found that the presence of N₂ and CO₂ was not conducive to the main reaction of alkane pyrolysis for C₂H₂, while CO, as a stable equilibrium product, had little effect on the cracking reaction. Consequently, it is suggested that a pretreatment process of removing N₂ and CO₂ should be present before pyrolysis. Both input power and feed rate had considerable effect on the pyrolysis of the simulated coke oven gas, and a C₂H₂ selectivity of 91.2% and a yield of 68.3% could be obtained at an input power of 17.9 kW.

Keywords: thermal plasma; pyrolysis; alkane-rich gas; acetylene; coke oven gas

1. Introduction

As the essential material basis for human survival and development, petroleum, coal, natural gas, and other fossil fuels support the development of human civilization and economy. The utilization process of fossil fuels produce a great deal of alkane-rich gases as their main product or byproduct, such as coke oven gas, refinery gas, natural gas and unconventional natural gas (coalbed methane, shale gas, and tight sandstone gas). For example, the coke-making process produces coke oven gas (COG) as a byproduct, and typically 1.25–1.65 tons of coal produce a single ton of coke, along with approximately 300–360 m³ of COG (6–8 GJ/t coke) [1]. Although there are reports that using those alkane-rich gases as feedstocks of chemicals, most of them are still utilized as fuel by combustion (ca. 70–80%) or directly discharged into the atmosphere without treatment or as a torch, not only causing significant waste of resources, but also producing large amounts of greenhouse gases and hazardous pollutants which jeopardize the environment. Therefore, it is of great importance to develop more ways to convert alkane-rich gases to value-added chemicals through effective reactions.

Acetylene, known as the "mother of organic chemical products", plays a very important role not only in the field of metal processing, welding and cutting [2], but also in the production of poly(vinyl chloride) (PVC), trichloroethylene, vinyl acetate, acrylonitrile, poly-acrylonitrile [3], etc. Its abundant downstream products attract the growing pursuit in the chemical industry for alternative production methods of acetylene, because the two conventional methods—calcium carbide hydrolysis and

partial oxidation of methane—have shown obvious shortcomings in energy cost, water consumption, and pollution [4]. In this context, increasing attention has been paid to studies on thermal plasma pyrolysis of hydrocarbons to acetylene. Acetylene is the main long-lived metastable intermediate product of pyrolysis in a hydrogen atmosphere at high temperatures (T > 1800 K); therefore, it can be obtained as the main hydrocarbon product as long as the product gas is rapidly cooled after pyrolysis to prevent further conversion to carbon black and hydrogen [5]. Due to the ultrahigh reactivity of thermal plasma, this method can effectively convert various hydrocarbons to acetylene-rich gaseous products within milliseconds, along with very little water consumption and CO₂ discharge. In addition to solid and liquid hydrocarbon-rich feedstocks, such as coal, polyethylene, and aromatic compounds [6–10], gaseous alkanes can also be converted to acetylene-rich products with high acetylene yield and selectivity by this method [11,12], which creates a new method for the utilization of alkane-rich gas. However, one significant problem in the current studies on plasma pyrolysis of alkanes or alkane-rich gases is that little attention has been paid to the effect of nitrogen/oxygen-containing substances on the pyrolysis. Actually, there are always various nitrogen/oxygen-containing substances, such as N_2 , CO, CO_2 , and O_2 , in practical alkane-rich gasses, and their concentrations are highly inconstant within a range of approximately 0.1–15%. In addition to the alkanes, these compounds may also be strongly activated by the thermal plasma, leading to different gaseous products from the ideal pure-alkane case, thus, it is imperative to explore how the variety and concentration of nitrogen/oxygen-containing substances would influence the gas conversion and the product composition. It is not only essential to evaluate the intrinsic performance of the pyrolysis process, but also indispensable to establish an optimum separation-pyrolysis-separation integral process. That is, whether a pre-separation of any nitrogen/oxygen-containing compound from alkanes is needed before pyrolysis, and what kinds of purification procedures are needed after pyrolysis, strongly depend on the effect of those compounds on pyrolysis.

In this work, we systematically investigated the effect of various nitrogen/oxygen-containing substances, including N_2 , CO, and CO₂ on the pyrolysis of methane to acetylene by thermal plasma, and conducted the pyrolysis of simulated coke oven gas as a model of alkane-rich mixing gas. A self-made rotating arc plasma reactor was employed to pyrolyze those alkane-rich gases for the first time, because it was proved to have notable advantages in feedstock-plasma mixing and temperature homogenization over conventional thermal plasma reactors. The experimental results indicated that CO₂ and N₂ had palpable and negative effects on the pyrolysis process, thus, it is advisable to remove them from the mixing gas before pyrolysis. CO has little effect on the pyrolysis, thus, it can be removed after pyrolysis for an easier separation. Additionally, the operating conditions, including input power and feed rate, significantly affected not only the yield and selectivity of the products, but also the conversion efficiency of alkanes and the specific energy requirement of acetylene.

2. Materials and Methods

2.1. Materials

CH₄, C₂H₆, H₂, CO, CO₂, N₂, and Ar (all gases had a purity of 99.99%) were purchased from Hangzhou Jingong Special Gas Co, Ltd. (Hangzhou, China). Sodium hydroxide was obtained from Sinopharm Chemical Reagent Co, Ltd. (Shanghai, China). Sodium chloride, potassium chromate, silver nitrate, and rose red reagent were purchased from Aladdin Reagent Co. Ltd. (Shanghai, China). The composition of the simulated coke oven gas is presented in Table 1, which was produced according to the main components of actual coke oven gas [13].

2.2. Reactor Setup

A 50 kW rotating arc plasma reaction device system was used in this experiment, as shown in Figure 1a, mainly consisting of four parts: a constant current power supply, plasma reactor, cooling and quenching system, and a data acquisition and control system. Figure 1b shows the structure of the

50 kW rotating arc plasma reactor, mainly including a cathode, cathode flange, anode, anode upper flange, anode bottom flange, and the excitation coil. The excitation coil is sheathed outside the anode sleeve generating a magnetic field under the action of impressed current, to produce the Lorenz force in the reactor, which results in a high-speed rotation of the arc.

Table 1. The basic composition of practical coke oven gas (a) and simulated coke oven gas (b) in this work.

(a)	Main Component	H ₂	CH_4	$C_m H_n$	СО	CO ₂	O ₂	N ₂
	Vol %	55–60	23–27	2–4	5–8	1.5–3	0.3–0.8	3–7
	Impurity	NH ₃	benzene	HCN	H ₂ S	organic sulfur	naphthalene	Tar
-	g/Nm ³	≤ 0.05	≤2	≤0.3	≤ 0.02	≤ 0.05	≤0.1	≤ 0.05
(b)	Main Component	H ₂	CH ₄	C_2H_6	СО	CO ₂	N ₂	Ar
	Vol %	56.00	27.00	3.01	6.09	2.02	4.88	1.00



Figure 1. The 50 kW rotating arc plasma reactor. (a) Reaction device; and (b) the reactor structure.

2.3. Gas Analysis

The components of pyrolysis gas are complex, possibly including CH₄, C₂H₂, C₂H₄, C₂H₆, CO, CO₂, and N₂, and it is convenient to adopt gas chromatography for analysis with GC 1690 provided by Hangzhou Kexiao Chemical Equipment Co, Ltd. (Hangzhou, China). The chromatographic columns are a PLOT 5A zeolite-packed column provided by Hangzhou Kexiao Chemical Equipment Co, Ltd. (Hangzhou, China) and a PLOT Q capillary column from Agilent Technologies Co, Ltd. (Hangzhou, China). As a possible product in the nitrogen reaction, HCN is highly toxic and must be carefully handled. The relatively safe and simple AgNO₃ titrimetric method was adopted, using a NaCl standard solution (0.0100 mol/L) to calibrate the standard solution of AgNO₃ (0.0100 mol/L), then determining the concentration of cyanide ions in the collection solution with a calibrated AgNO₃ solution. The cyanide ion collecting solution is obtained by slowly accessing the sample bag gas (about 2 L) to 0.1 mol/L NaOH solution to be absorbed.

2.4. Data Processing Method

Carbon yield (*Y*) of acetylene in the product is generally defined as:

$$Y_{C_2H_2} = \frac{2 \times Q_{C_2H_2}}{Q_{CH_4}^0} \times 100\%$$
(1)

Carbon conversion efficiency (CE) of the feed gas is generally defined as:

$$CE_{CH_4} = (1 - \frac{Q_{CH_4}}{Q_{CH_4}^0}) \times 100\%$$
 (2)

Selectivity (*S*) of acetylene is defined as:

$$S_{\rm C_2H_2} = \frac{Y_{\rm C_2H_2}}{CE_{\rm CH_4}} \times 100\%$$
(3)

When pyrolyzed, the siimulated coke oven gas is defined as:

$$Y_{C_2H_2} = \frac{2 \times Q_{C_2H_2}}{Q_{CH_4}^0 + 2 \times Q_{C_2H_6}^0} \times 100\%$$
(4)

$$CE_{CH_4+C_2H_6} = (1 - \frac{Q_{CH_4} + 2 \times Q_{C_2H_6}}{Q_{CH_4}^0 + 2 \times Q_{C_2H_6}^0}) \times 100\%$$
(5)

$$S_{C_2H_2} = \frac{Y_{C_2H_2}}{CE_{CH_4 + C_2H_6}} \times 100\%$$
(6)

Specific energy requirement (SER) of acetylene is defined as:

$$SER(kWh/kg \cdot C_2H_2) = \frac{Input power(kW)}{Mass flow rate of C_2H_2(kW/h)}$$
(7)

where $Q_{CH_4}^0$, $Q_{C_2H_6}^0$ represent the volume flow of CH₄ and C₂H₆ in the feedstock, respectively, and $Q_{C_2H_2}$, Q_{CH_4} , $Q_{C_2H_6}$ are the volume flow of C₂H₂, CH₄, and C₂H₆ in the product.

3. Results and Discussion

3.1. Effect of Nitrogen/Oxygen Substances on Methane Pyrolysis

It has been acknowledged that the thermal energy is the critical point for pyrolysis of hydrocarbons to acetylene by thermal plasma, but the mass and heat transfer mechanism in the reaction system is difficult to describe quantitatively. Up to now, the accredited mechanism and sequence of chemical transformations during the pyrolysis of saturated hydrocarbons is described below [14]:

However, because CO₂, N₂, and CO may also decompose in the atmosphere and react with the intermediate product of alkane pyrolysis in Equation (8), their presence in alkane-rich feed gas is expected to influence the pyrolysis products. To clarify the effect of each of them, CO₂, N₂, and CO were respectively mixed into methane (as a representative alkane) to serve as a binary feed gas for pyrolysis. The experimental conditions are as follows: the molar ratio of input H₂/CH₄ was 1.5/1, the total feed rate of H₂ and CH₄ was 7.5 Nm³/h, the magnetic induction intensity was 0.077 T, and the input power was controlled at 15 ± 0.5 kW.

3.1.1. Effect of CO₂ on Methane Pyrolysis

By adding different amount of CO_2 in methane, the CO_2 volume fraction changed in the range of 2–14%. The plasma-enhanced process of oxidation conversion may be explained as the reaction below in Equation (9) along with reactions in Equation (8):

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2 \qquad \Delta H = +247 \text{ kJ/mol}$$
(9)

Figure 2 shows the effect of CO₂ content on the kinds of products, including mainly hydrocarbons, CO₂, and CO, at an input power of 15 kW. As can be seen from the figure, with the increase in CO₂ content, the mole fraction of C₂H₂ reduced from 8.4% to 6.3% and C₂H₄ concentration reduced slightly from 0.61% to 0.31%. This is mainly ascribed to a competitive relationship between the oxygen-free pyrolysis reactions in Equation (8) and oxidation reaction in Equation (9), and the oxidation reaction hindered the dominant pyrolysis reactions that produce C₂H₂. This is also supported by the result that increasing CO₂ content in the feed gas improved the CO content in the product. On the contrary, CH₄ content in the product ascended from 10.1% to 15.2% although the CH₄ content in the feed gas was slightly reduced when adding CO₂. This is probably because when the CO₂ content increased, the pyrolysis of CO₂ to CO and O· radicals consume a great deal of input energy, which restricted the conversion of CH₄ by either Equation (8) or Equation (9).



Figure 2. The effect of CO₂ concentration on the molar fraction of major products at 15 kW (total gas flow rate of methane and hydrogen: $7.5 \text{ Nm}^3/\text{h}$; magnetic flux intensity: 0.077 T).

Figure 3 illustrates the effect of CO₂ content on the yield (*Y*) of C₂H₂ and CH₄ conversion efficiency (*CE*) at 15 kW. With the increase of CO₂ content, the yield of C₂H₂ and CH₄ conversion efficiency showed a synchronous decreasing trend. This is consistent to the results of Figure 2, suggesting that the increase of CO₂ content was not conducive to the pyrolysis reaction based on the fact that more input energy was taken away by both the pyrolysis of CO₂ and the endothermic reaction Equation (9). The effect of different CO₂ content on the *SER* of C₂H₂ was illustrated in Figure 4. With the increase of CO₂ content, the SER of C₂H₂ was rising. This directly revealed that the higher the proportion of CO₂ in the reaction system, the more energy was consumed by side-reactions. From the viewpoint of product composition and energy utilization, the presence of CO₂ was not conducive to the pyrolysis production of C₂H₂ and it should be removed from alkane-rich feed gas before the reaction.



Figure 3. The effect of CO₂ concentration on the yield of C_2H_2 , conversion efficiency of CH₄ at 15 kW (total gas flow rate of methane and hydrogen: 7.5 Nm³/h; magnetic flux intensity: 0.077 T).



Figure 4. The effect of CO₂ concentration on *SER* of C₂H₂ at 15 kW (total gas flow rate of methane and hydrogen: 7.5 Nm^3 /h; magnetic flux intensity: 0.077 T).

3.1.2. Effect of CO on Methane Pyrolysis

The content of CO in several alkane-rich gases such as coke oven gas cannot be ignored, so it is significant to explore the effect of CO on the pyrolysis of alkanes. Figure 5 showed the effect of CO content on the concentration of major gaseous compounds, with CO volume fraction changing in the range of 2–14%. As seen from the diagram, there was basically no change in the molar fraction of major hydrocarbon products, with CH₄ maintained 13.1–14.1%, C₂H₂ 10.4–11.1%, and C₂H₄ 0.59–0.68%. As for the changes of CO and CO₂ content in the pyrolysis products, only a very small amount of CO₂ was detected with a linear increase of the CO content in the product, and the CO content in the product was very close to that in the feed gas, indicating that CO was almost not involved in the reactions. This is ascribed to the relatively inert character of CO due to the very large energy of carbon-oxygen triple bond in CO molecule (1072 kJ/mol).

Figure 6 shows the effect of CO content on the yield of C_2H_2 and CH_4 conversion efficiency in the pyrolysis products at 15 kW. Agreeing with the above analysis, both the yield of C_2H_2 and CH_4 conversion efficiency changed only slightly with the CO content in the feed gas. This is also the case for the influence of CO content on the *SER* of C_2H_2 (Figure 7). This revealed that within the scope of the experiment, the CO content in the reactant had little influence on the pyrolysis of alkanes. Therefore, the separation of CO from alkane-rich gas is not always necessary before the pyrolysis process, and it can be conducted after pyrolysis because the separation of CO from C_2H_2 will be easier than from alkanes. The C_2H_2 molecule is a notable hydrogen-bond donor due to the weak hydrogen-bonding acidity of its C-H bond, thus, it can be readily dissolved/adsorbed from non-acidic CO and alkanes by dipolar aprotic solvent, ionic liquids, or anion-pillared microporous frameworks [15,16].



Figure 5. The effect of CO concentration on the molar fraction of major products at 15 kW (total gas flow rate of methane and hydrogen: $7.5 \text{ Nm}^3/\text{h}$; magnetic flux intensity: 0.077 T).



Figure 6. The effect of CO concentration on the yield of C_2H_2 , conversion efficiency of CH₄ at 15 kW (total gas flow rate of methane and hydrogen: 7.5 Nm³/h; magnetic flux intensity: 0.077 T).



Figure 7. The effect of CO concentration on *SER* of C_2H_2 at 15 kW (total gas flow rate of methane and hydrogen: 7.5 Nm³/h; magnetic flux intensity: 0.077 T).

3.1.3. Effect of N₂ on Methane Pyrolysis

By adding different volume fractions of N₂ (2–14%) to the alkane-rich gas, its effect was investigated in this part, as shown in Figure 8. Along with the N₂ concentration increasing, the changes of hydrocarbons content in the product are obvious. The molar fraction of CH₄ increased from 9.4% to 14.1%, while the C₂H₂ decreased from 12% to 8.7%, and the C₂H₄ concentration dropped from 0.82% to 0.49%. As for the N₂ and HCN, the content of N₂ in the product ascended significantly while the HCN content increased slightly. The N₂ fraction in the product was notably lower than that in the feed gas, indicating that a part of N₂ was decomposed in the plasma environment and generated HCN, as shown in Equation (10), although the energy to break up the N≡N bond in nitrogen was relatively large (946 KJ/mol). The process of breaking N≡N bonds consumed the input energy that was originally intended to pyrolyze CH₄, thus, both the conversion efficiency of CH₄ and the yield of C₂H₂ decreased (Figure 9), and the CH₄ fraction in the product gas increased, while C₂H₂ and C₂H₄ decreased (Figure 10). Therefore, similar to the case of CO₂, it is advisable to remove N₂ from alkane-rich gas before pyrolysis, because the presence of N₂ not only jeopardizes the production of C₂H₂, but also generates highly-toxic HCN.



Figure 8. The effects of N₂ concentration on the molar fraction of major products at 15 kW (total gas flow rate of methane and hydrogen: $7.5 \text{ Nm}^3/\text{h}$; magnetic flux intensity: 0.077 T).



Figure 9. The effects of N₂ content on yield of C_2H_2 and conversion efficiency of CH₄ at 15 kW (total gas flow rate of methane and hydrogen: 7.5 Nm³/h; magnetic flux intensity: 0.077 T).



Figure 10. The effects of N₂ content on *SER* of C₂H₂ at 15 kW (total gas flow rate of methane and hydrogen: 7.5 Nm³/h; magnetic flux intensity: 0.077 T).

$$\begin{cases} CH_4 + e^* \rightarrow CH_3 + H + e, & CH_3 + e^* \rightarrow CH_2 + H + e \\ CH_2 + e^* \rightarrow CH + H + e, & CH + e^* \rightarrow C + H + e \\ N_2 + e^* \rightarrow N + N + e \\ (a) CH + N \rightarrow HCN, & (b) C + H \rightarrow CH \\ (c) HCN + e^* \rightarrow CN + H + e & (d) CH + CH \rightarrow CH = CH \\ e * (high - energy electron) \end{cases}$$
(10)

3.2. Pyrolysis of Simulated Coke Oven Gas

Coke oven gas is a typical alkane-rich mixed gas containing many nitrogen/oxygen compounds, thus, the simulated coke oven gas shown in Table 1 was used for further investigation on the pyrolysis process of alkane-rich gas by a rotating arc thermal plasma reactor. The influences of input power and feed rate on the pyrolysis process were investigated as they are two important operation parameters in pyrolysis.

3.2.1. Influence of Input Power on the Simulated COG Pyrolysis Process

The investigated experimental conditions were listed as follows: feed rate of 7.5 Nm³/h, magnetic induction intensity of 0.077 T, and input power of 13–26 kW. Figure 11 presents the influence of the input power on the molar fraction of main products. It can be seen that the content of CH₄, CO₂, and N₂ decreased gradually, while CO increased from 6.2% to 7.1% and HCN increased from 0.43% to 0.76% in the whole power range. This is because the increase of input power promoted the transformation of alkanes through not only the desired reactions (toward C_2H_2), but also side reactions. This is also reflected in Figure 12, where the conversion efficiency of alkanes increased with the rise in power. The presence of CO and HCN in the product gas was a result of the pyrolysis of CO₂ and N₂ in the feed gas, as demonstrated by the previous sections. As for the hydrocarbon products, C_2H_6 content did not change obviously, only a small amount, because of its small content in the feed and similar pyrolysis properties to methane. C_2H_4 maintained a low content at first, and then increased from 0.64% to 3.3%. However, the change of C_2H_2 content was complex, showing an increasing trend at first, and then decreasing from 8.0% to 4.4%. Correspondingly, as Figure 13 displays, when the power increased from 12.9 kW to 21.6 kW, the C_2H_2 yield rose from 54.8% to 68.3%, and then it dropped to 42.7% with a continual increase of power. As for the C_2H_2 selectivity, it maintained above 90.3% when the power was between 12.9 kW to 17.9 kW, and then it dropped to 51.0%. The SER of C_2H_2 also exhibited similar change (Figure 12). When the power ascended from 12.9 kW to 21.6 kW, the SER of C₂H₂ increased

slowly from 16.7 kWh/kg C_2H_2 to 18.8 kWh/kg C_2H_2 , but then increased rapidly from 18.8 kWh/kg C_2H_2 to 41 kWh/kg C_2H_2 when the power continued to increase from 21.6 kW to 25.6 kW.



Figure 11. The effect of input power on the molar fraction of major products in the pyrolysis of simulated coke oven gas (total gas flow rate of simulated coke oven gas: 7.5 Nm³/h; magnetic flux intensity: 0.077 T).



Figure 12. The effects of input power on the conversion of alkanes and *SER* of C_2H_2 in the pyrolysis of simulated coke oven gas (total gas flow rate of simulated coke oven gas: 7.5 Nm³/h; magnetic flux intensity: 0.077 T).

This could be attributed to the dual effect of the input power on the pyrolysis. On one hand, increasing input power can provide more energy to convert the components in feed gas and, thus, produce more C_2H_2 . On the other hand, increasing input power will also elevate the temperature in the reactor, and once the temperature is too high, the generated metastable C_2H_2 decomposes into solid carbon and H_2 . Therefore, there should be an optimum input power for the pyrolysis of alkane-rich gases to produce the C_2H_2 -rich product gas. In the current experiment, taking the various factors into consideration, an input power of approximately 17.9 kW was a desired condition for pyrolysis because

it combined high alkane conversion (75.4%), high C_2H_2 yield (68.3%) and selectivity (91.2%), and low *SER* (18.8 kWh/kg C_2H_2).



Figure 13. The effects of input power on the yield and selectivity of C_2H_2 in the pyrolysis of simulated coke oven gas (total gas flow rate of simulated coke oven gas: 7.5 Nm³/h; magnetic flux intensity: 0.077 T).

3.2.2. Influence of Feed Rate on the Simulated COG Pyrolysis Process

Experimental conditions in investigating the influence of feed rate are listed as follows: input power of 15 ± 0.5 kW, magnetic induction intensity of 0.077 T, and feed rate of 3.6-10 Nm³/h. Figure 14 exhibits the effect of the feed rate on the major products' content. With the increase of the feed rate, the CO fraction showed a decreasing trend in the pyrolysis product from 7.5% to 6.2%, and the CO_2 fraction had a sensible growth from 0.042% to 0.79%, implying that the reaction in Equation (9) was weakened to some extent. At the same time, the side reaction of N_2 in Equation (10) also became slightly weakened, as indicated by the results that with the increase of the feeding rate, the N₂ content in the product increased slightly overall, while the content of HCN slightly decreased. The content of C_2H_4 and C_2H_6 hardly changed, as could be seen as the molar fraction of C_2H_4 was between 0.63% and 0.85%, and that of C_2H_6 was below 0.26%. The most obvious and important changes were the levels of CH_4 and C_2H_2 . With the increase of the feed rate, the molar fraction of CH_4 in the product increased sharply from 0.86% to 10.4%, but that of C_2H_2 dropped from 9.5% to 6.2%. This suggested that more CH₄ was not cracked as the feeding rate increased, resulting in an increase in the CH₄ mole fraction and a dilution of C₂H₂. In fact, as shown in Figures 15 and 16, the alkanes' conversion efficiency decreased rapidly from 96.1% to 56%, but the C_2H_2 selectivity remained at a high level, between 88.1% and 90%. This indicated that when the alkane conversion efficiency decreased, the side reactions were not enhanced, and the conversion of alkanes was still dominated by the formation of C_2H_2 . As the conversion of alkanes decreased, and C_2H_2 selectivity remained unchanged, the yield of C_2H_2 decreased with the increase of the feed rate, from 84.7% to 50.3%. Moreover, the SER of C_2H_2 was reduced from 26.4 kWh/kg C_2H_2 to 15.8 kWh/kg C_2H_2 . The phenomenon above was probably the result of the shorter gas residence time and lower temperature in the reactor caused by the increase of the feed rate, which made it difficult to convert the increased alkanes into C_2H_2 in time.

In the entire range of the flow rates investigated, the C_2H_2 selectivity was always maintained at a high level, but the conversion of alkanes and the yield of C_2H_2 decreased with the flow rate. This indicated that the processing capacity of alkanes was limited under this input power, and the feed rate could be appropriately increased to obtain optimum technical and economic performance.



Figure 14. The effects of feeding flow rate on the molar fraction of major products in the pyrolysis of siimulated coke oven gas (input power: 15 ± 0.5 kW; magnetic flux intensity: 0.077 T).



Figure 15. The effects of feed rate on the yield and selectivity of C_2H_2 in the pyrolysis of simulated coke oven gas (input power: 15 ± 0.5 kW; magnetic flux intensity: 0.077 T).



Figure 16. The effects of the feed rate on the conversion efficiency of alkanes and *SER* of C_2H_2 in pyrolysis of simulated coke oven gas (input power: 15 ± 0.5 kW; magnetic flux intensity: 0.077 T).

In this work, the effect of various nitrogen/oxygen-containing substances including N_2 , CO, and CO₂ on the pyrolysis of CH₄ to C_2H_2 was conducted by thermal plasma, as well as pyrolysis of

simulated coke oven gas as a model of alkane-rich gas. The above experimental results indicated that nitrogen/oxygen-containing substances CO_2 and N_2 had palpable and negative effects on the pyrolysis process, whereas CO exhibited little effect. Therefore, the following technical flow is advisable for the pyrolysis process: separate CO_2 and N_2 from the alkane-rich feed gas at first, and then pyrolyze the feed gas with a rotary thermal plasma reactor to produce C_2H_2 -rich pyrolysis gas, and, finally, separate C_2H_2 from the other components, including CO, in the pyrolysis gas.

4. Conclusions

The influence of nitrogen/oxygen substances CO₂, N₂, and CO for the pyrolysis of alkane-rich mixing gases to produce C_2H_2 had been illustrated for the first time, using a 50 kW self-made rotary thermal plasma reactor. In the mole fraction range of 2-14%, N₂ and CO had negative effects on the main reaction that converted CH₄ to C₂H₂, while CO had little effect. Considering this difference, along with the toxicity of byproducts and the level of difficulty in separating different gas mixtures, it is advisable to remove CO_2 and N_2 from the feed gas before pyrolysis, and to separate the product gas from CO after pyrolysis. The pyrolysis of simulated coke oven gas, an important alkane-rich mixing gas containing CO₂, N₂, and CO, was also conducted in this work, and the effect of the input power and feeding rate on pyrolysis were investigated. Considering the non-monotonic change of C_2H_2 selectivity and yield, along with the input power, the selectivity of C_2H_2 up to 91.2% and a C_2H_2 yield of 68.3% were obtained at the input power of 17.9 kW. Higher C_2H_2 selectivity and a lower C₂H₂-specific energy requirement could be obtained when the feed rate was increased, although at the expense of lower alkane conversion and C_2H_2 yield. Overall, the experimental results revealed that it was a promising method to convert alkane-rich gases to value-added chemicals, and provided indispensable information for creating a technical flow for a whole process integrating pretreatment, pyrolysis, and posttreatment.

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References

- 1. Agency, I.E. *Tracking Industrial Energy Efficiency and CO*₂ *Emissions*; Organizations for Economic Co-Operation and Development: Paris, France, 2007.
- 2. Munoz-Escalona, P.; Payares, M.C.; Dorta, M.; Diaz, R. Analysis and influence of acetylene and propane gas during oxyfuel gas cutting of 1045 carbon steel. *J. Mater. Eng. Perform.* **2006**, *15*, 684–692. [CrossRef]
- 3. Schobert, H. Production of acetylene and acetylene-based chemicals from coal. *Chem. Rev.* **2014**, *114*, 1743–1760. [CrossRef] [PubMed]
- 4. Diercks, R.; Arndt, J.D.; Freyer, S.; Geier, R.; Machhammer, O.; Schwartze, J.; Volland, M. Raw material changes in the chemical industry. *Chem. Eng. Technol.* **2008**, *31*, 631–637. [CrossRef]
- 5. Slovetskii, D.I. Plasma-chemical processes in petroleum chemistry (review). *Pet. Chem.* **2006**, *46*, 295–304. [CrossRef]
- 6. Zhang, M.; Ma, J.; Su, B.G.; Wen, G.D.; Yang, Q.W.; Ren, Q.L. Pyrolysis of polyolefins using rotating arc plasma technology for production of acetylene. *Energies* **2017**, *10*, 513. [CrossRef]
- 7. Bond, R.L.; Ladner, W.R.; Mcconnell, G.I.T.; Galbraith, I.F. Production of acetylene from coal, using a plasma jet. *Nature* **1963**, *200*, 1313–1314. [CrossRef]
- 8. Beiers, H.G.; Baumann, H.; Bittner, D.; Klein, J.; Juntgen, H. Pyrolysis of some gaseous and liquid hydrocarbons in hydrogen plasma. *Fuel* **1988**, *67*, 1012–1016. [CrossRef]

- 9. Ma, J.; Zhang, M.; Wu, J.; Yang, Q.; Wen, G.; Su, B.; Ren, Q. Hydropyrolysis of n-Hexane and Toluene to Acetylene in Rotating-Arc Plasma. *Energies* **2017**, *10*, 899. [CrossRef]
- 10. Ma, J.; Su, B.; Wen, G.; Yang, Q.; Ren, Q.; Yang, Y.; Xing, H. Pyrolysis of pulverized coal to acetylene in magnetically rotating hydrogen plasma reactor. *Fuel Process. Technol.* **2017**, *167*, 721–729. [CrossRef]
- 11. Maleki, M.; Parvin, P.; Reyhani, A.; Mortazavi, S.Z.; Moosakhani, A.; Ghorbani, Z.; Kiani, S. Decomposition of ethane molecules at atmospheric pressure using metal assisted laser induced plasma. *J. Opt. Soc. Am. B Opt. Phys.* **2015**, *32*, 493–505. [CrossRef]
- 12. Laktiushin, A.N.; Laktiushina, T.V. Computer synthesis by specified characteristic of the process of acetylene and technical hydrogen production from nature gas in hydrogen plasma. *High Temp. Mater. Process.* **2012**, *16*, 153–177. [CrossRef]
- Qi, J.L.; Kong, F.R. Status and prospect for chemical utilization of coke oven gas in China. *Nat. Gas Chem. Ind.* 2013, 1, 013. [CrossRef]
- 14. Slovetsky, D.I. Modern Problems of Combustion and Its Application. In Proceedings of the IV International School-Seminar, Minsk, Belarus, 2–7 September 2001; p. 97.
- 15. Jin, W.B.; Li, X.N.; Zhang, Y.; Yang, Q.W.; Xing, H.B.; Ren, Q.L. Separation of structurally-related compounds with ionic liquids. *Sci. China Chem.* **2016**, *46*, 1251–1263. [CrossRef]
- Cui, X.; Chen, K.; Xing, H.; Yang, Q.; Krishna, R.; Bao, Z.; Wu, H.; Zhou, W.; Dong, X.; Han, Y.; et al. Pore chemistry and size control in hybrid porous materials for acetylene capture from ethylene. *Science* 2016, 353, 141–144. [CrossRef] [PubMed]



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