

# Autothermal Reforming of Diesel Oil for PdCeCrFeCu/Al<sub>2</sub>O<sub>3</sub>-Catalyzed Hydrogen Production

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Zero-dimensional two-stage SOFC stacks dynamic model was developed to investigate the effect of operating parameters on stacks performance. The model resolves spatially thermal and thermo-electrochemical behaviour for electrochemical reactions, Catalytic Partial Oxidation and Steam Reforming processes. Design variables and thermo-electrochemical properties were obtained from in-house-fabricated SOFCs carried out by project partners. The completed SOFCs based Combined Heat and Power, CHP, system model was validated by data<sup>18</sup> and numerical results obtained at steady-state mode showing its high-fidelity. A parametric study with respect to key operating parameters including changes in fuel utilization, lambda number and current density values was conducted. The global CHP system dynamic response, in term of the current/voltage delivered by two-stage SOFC stacks, under a fixed fuel utilization, has been determined resulting in greater variations in the voltage of a single cell in the first stack in comparison to the corresponding values in the second stack.

**Keywords:** diesel & reform & hydrogen & catalyst.

## INTRODUCTION

The global energy demand is increasing day by day. Waste generated by the unreasonable use of existing energy resources and the debilitating consequences of air pollution and the greenhouse effect has led all countries in the world to introduce relevant policies to actively manage the intricate system comprising mankind, energy, and the environment<sup>1–5</sup>. This will allow the development and utilization of “clean energy” to realize a healthy and sustainable growth of the national economy. Therefore, the rational utilization of the existing energy resources, development and utilization of new energy resources, and expansion of energy-saving fields are highly valued. Hydrogen energy is a renewable green energy source, and hydrogen is an excellent energy carrier<sup>6–12</sup>. If the theoretical potential of hydrogen energy is put to practical use, two key technical problems, hydrogen utilization and hydrogen source development, must be addressed. In this context, fuel cell technology, known as the best way of using hydrogen, together with hydrogen production technologies has attracted worldwide attention. China has also listed it as a subject of advanced energy technology at the forefront of national long-term scientific and technological development planning<sup>13–17</sup>. Hydrogen production technologies based on fuel cells are also called fuel cell hydrogen source technology. At present, hydrogen is mainly produced from methanol, ethanol, natural gas, gasoline, sodium borohydride, etc. In recent years, diesel reforming has emerged as an effective approach for the development of a hydrogen source in fuel cells. Hydrogen production from diesel reforming can be realized through water reforming (SR), oxygen reforming (OX), partial oxidation reforming (POX), or autothermal reforming (ATR)<sup>18–23</sup>. Among these, autothermal reforming of diesel has emerged an effective approach for hydrogen production from diesel reforming due to its more reasonable energy utilization. Because of the long carbon chain and easy carbon evolution in diesel oil, catalysts for hydrogen production through diesel oil

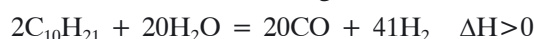
reforming must have high activity, long service life, and carbon evolution resistance. Hydrogen production from autothermal reforming of diesel oil is realized through heat coupling between the exothermic oxygen reforming and endothermic water reforming processes<sup>24–27</sup>. Diesel oil is mainly burned directly, but the thermal efficiency and energy efficiency of this method are low. Also, toxic gases are released as pollutants after burning, which is harmful to the environment. However, by reforming diesel fuel into hydrogen-rich fuel, the energy efficiency of fuel cells can be significantly improved, and then the environmental pressure can be relieved. Steam reforming is the most commonly used hydrogen reforming method because of its high hydrogen content. In this way, the fuel is mixed with steam and then put into the reformer. The main problems of this technology are the service life of adsorbents and catalysts and the complexity of system design. Compared with steam reforming, autothermal reforming has a simple structure. Without large heat exchange equipment, the manufacturing cost is low. Compared with partial reformer, the heat released by oxidation reaction is directly absorbed by steam reformer reaction which absorbs heat, so the efficiency of the system is also improved. However, it is difficult to control the ratio of oxygen, steam and fuel at the same time, and it is easy to produce carbon deposition and damage the catalyst in the reforming process. Thus, in addition to the abovementioned requirements, the catalyst should be thermally stable and have the ability to withstand repeated oxidation and reduction. In this study, straight-run diesel oil is used as a raw material to produce hydrogen by autothermal reforming in the presence of a catalyst. The hydrogen system is described, and state analysis is performed to explore the rules and mechanism of hydrogen production by autothermal reforming of diesel oil. This study will provide a reference for the early application of hydrogen production technology by autothermal reforming of diesel oil<sup>28–31</sup>.

## EXPERIMENTAL SECTION

### Diesel autothermal reforming hydrogen principle

Analyses of the composition of the diesel and product gas were conducted using SP-3420 GC. The autothermal reforming system of diesel containing carbon includes eight independent elements,  $C_{10}H_{21}$ ,  $H_2O$ ,  $O_2$ ,  $C$ ,  $CO$ ,  $CO_2$ ,  $H_2$ , and  $CH_4$ , all of which involve three elements: C, H and O. In this respect, five independent reactions can occur. According to the composition analysis of straight-run diesel oil, the simulated formula of diesel oil is  $C_{10}H_{21}$ . Therefore, the following five independent reactions are used to describe the autothermal reforming process of diesel oil:

R1: Diesel water reforming reaction



R2: diesel oxygen reforming reaction



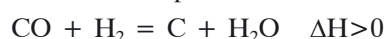
R3: Methane steam reforming reaction



R4: CO conversion



R5: carbon separation reaction



The key to autothermal reforming hydrogen from diesel oil is to use suitable catalysts to ensure that the product gas has high  $H_2$  content, low CO content and sufficient hydrogen yield. It is also necessary to release gas by using appropriate process conditions. In this respect, thermal reaction and endothermic reaction need thermal coupling to provide reasonable energy utilization. In addition, the catalyst used should have a certain degree of carbon resistance, and can appropriately increase the  $H_2O$  content to inhibit the occurrence of a carbon precipitation reaction.

### Factors influencing hydrogen production from autothermal reforming of diesel oil

The effects of catalyst bed inlet temperature, water-carbon ratio, oxygen-carbon ratio, and diesel liquid space velocity on the autothermal reforming reaction were studied by a single factor experiment. Based on the single factor experiment, the significance of each influencing factor was analyzed by an orthogonal experiment, and the suitable operating conditions for hydrogen production from the autothermal reforming of diesel were determined.

### Structure design of reactor

In this study, an adiabatic tubular reactor with a preheating section (Type A) and an adiabatic tubular reactor with a nozzle and preheating section (Type B) was designed and built in-house. In this type of reactor, the reaction materials first come to the preheating section of the reactor from the gasification chamber (superheated steam, diesel oil and oxygen), and then enter the diesel hydrogen reaction catalyst bed after preheating to the specified temperature. The catalyst bed is equipped with thermal insulation layer to prevent heat loss.

Type A and Type B reactors are 12 mm in diameter, and the ratio of the lengths of the preheating section and adiabatic section is 2:1. The PdCeCrFeCu/ $Al_2O_3$  catalyst with a particle size of 20–40 mesh is placed in the adiabatic section, and a porcelain ring is fixed at the bottom. Figure 1 and Figure 2 show the schematic diagrams of Type A and Type B reactors, respectively. The nozzle shown in Figure 2 is an air atomization nozzle.

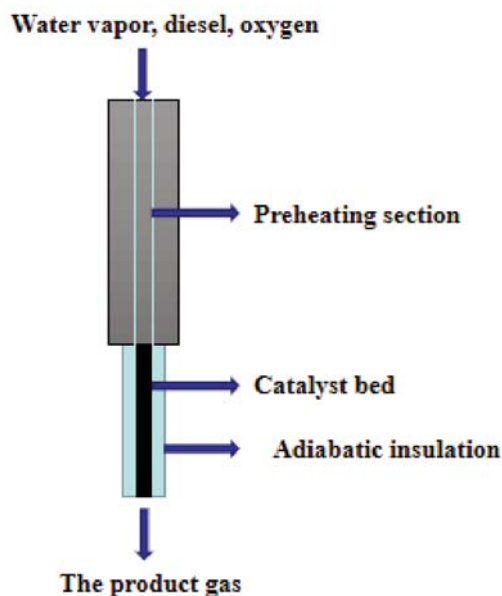


Figure 1. Schematic diagram of Type A reactor

As shown in Figure 1, the reaction raw materials (water vapor, diesel and oxygen) from the gasification chamber first enter the preheating section of the reactor and then enter the catalyst bed for hydrogen production from diesel oil. The exterior of the catalyst bed is coated with a thermal insulation layer to prevent high heat losses.

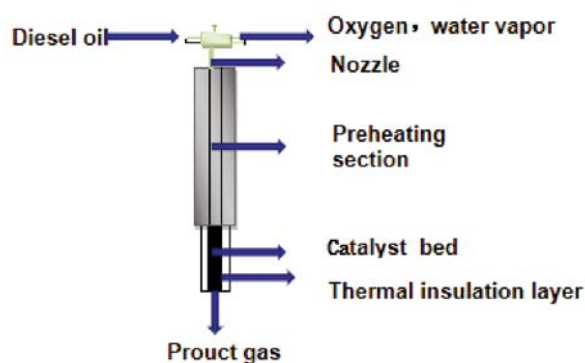
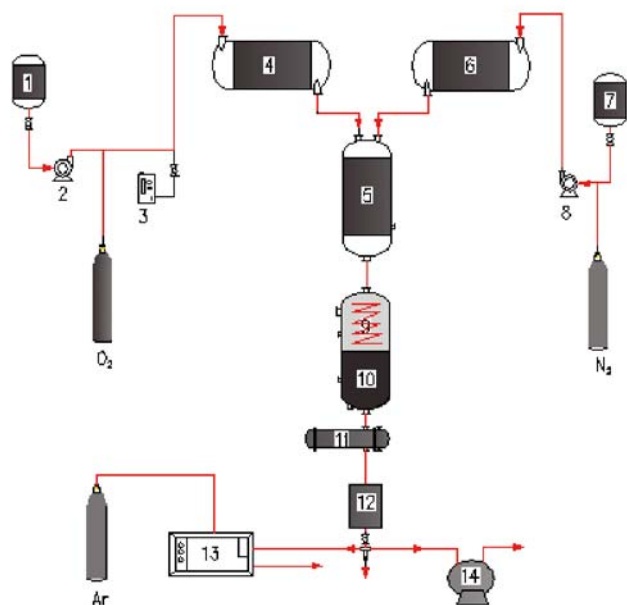


Figure 2. Schematic diagram of Type B

For the Type B reactor (Fig. 2), diesel oil directly enters through the left inlet of the nozzle without vaporizing in the vaporization chamber. Superheated steam from the water vaporization chamber is mixed with oxygen in the static mixer, which then enters the right inlet of the nozzle. Diesel oil, oxygen, and steam are ejected from the nozzle, following which they sequentially enter the preheating section and the reactor to complete the reforming and hydrogen production processes.

### Hydrogen production process and device diagram of diesel autothermal reforming (using type a reactor)

A certain proportion of diesel oil and water are metered by advection pump and delivered to diesel oil vaporization chamber and water vaporization chamber respectively, and oxygen enters diesel oil vaporization chamber. Gasified diesel oil, oxygen, water and nitrogen (entrained gas) enter a static mixer for mixing and then enter a catalyst bed filled with a catalyst for the reaction after preheating in a preheating section. The product gas enters a water cooler and a cold trap to condense and separate unreacted diesel oil and excessive water, or is vented after metering, or enters a gas chromatograph for on-line analysis, and the hydrogen yield is calculated according to the dry gas flow rate and composition of the product gas and diesel oil analysis (Scheme 1).



**Scheme 1.** Autothermal reforming of diesel to hydrogen flow chart: 1. diesel tanks, 2. oil pumps, 3. hydrogen generator, 4. diesel vaporization chamber, 5. static mixer, 6. water vaporization chamber, 7. water tanks, 8. water pump, 9. preheating, 10. catalyst bed, 11. condenser, 12. cold hydrazine, 13. gas chromatograph, 14. wet gas flowmeter

### Determination of suitable conditions for hydrogen production from autothermal reforming of diesel oil

Based on the single factor experiment, significance of each influencing factor was analyzed through an orthogonal experiment, and the most suitable operating conditions for hydrogen production by autothermal reforming of diesel oil over the PdCeCrFeCu/Al<sub>2</sub>O<sub>3</sub> catalyst were determined.

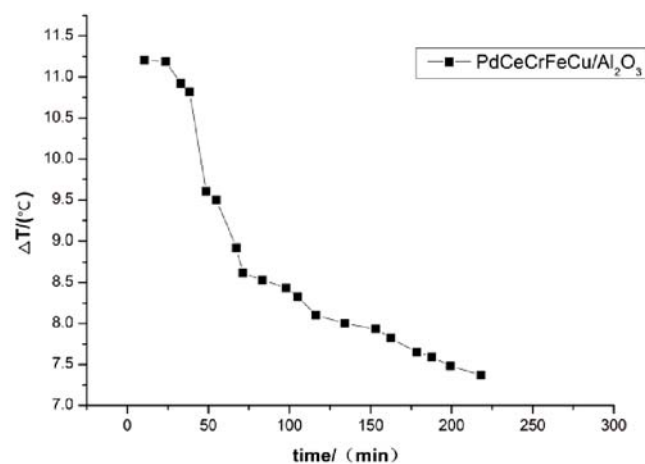
## RESULTS AND DISCUSSION

### Analysis of self-heating state

#### Bed temperature difference observation

Theoretically, if the reactor is well insulated, i.e., it does not undergo any heat loss, and the reaction system is in the self-heating state, there should be no difference between the inlet and outlet temperatures of the reactor. In this study, the temperature difference between the inlet

and outlet of the catalyst bed is recorded to determine whether the reaction system is in a self-heating state. For this experiment, space velocity of diesel oil is 0.16, water-carbon ratio is 10, oxygen-carbon ratio is 0.1, and the inlet temperature of the PdCeCrFeCu/Al<sub>2</sub>O<sub>3</sub> catalyst bed is 650°C. The relationship between the difference in the inlet and outlet temperatures of the catalyst bed and time is shown in Figure 3. Through experiment concluded that the catalyst bed inlet temperature is 700°C when the hydrogen content and hydrogen yield is the largest, but the temperature is too high will cause more energy consumption, unreasonable economic, various alkanes in diesel oil and high temperature is not stable, easy carbon deposit. And 700°C when non-noble metal Pt based catalyst active component is easy sintering, easy coking. So the appropriate to reduce temperature 650°C can effectively inhibit carbon analysis of active components, improve the stability of the catalyst. Therefore, we choose is slightly lower than the optimal temperature of 650°C for another test.



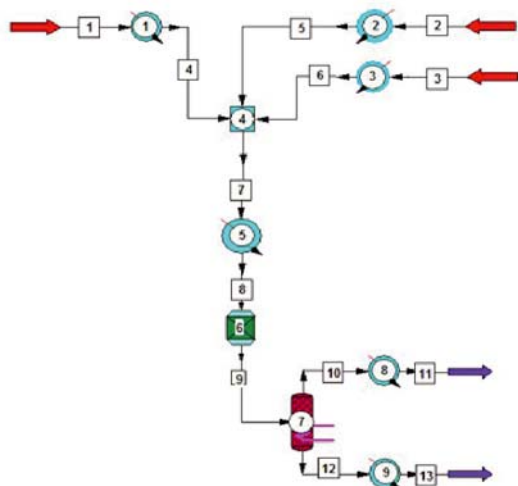
**Figure 3.** Change in temperature difference between the inlet and outlet of catalyst bed with time

It is evident from Figure 3 that the difference between the inlet and outlet temperatures of the catalyst bed gradually decreases, confirming hydrogen production under an overall exothermic condition, without any external heat supply. It also confirms that this diesel reforming reaction system is in a self-heating state. The temperature difference between the inlet and outlet of the catalyst bed did not drop to zero at the end owing to the difficulty in preventing the complete heat loss under laboratory conditions. Thus, the outlet temperature of the catalyst bed was slightly lower than the inlet temperature.

### Process simulation

(a) Simulation conditions were set as follows: oxygen-carbon ratio, 0.3 & water-carbon ratio, 10 & diesel liquid space velocity, 0.24 & catalyst bed inlet temperature, 710°C.

(b) Simulation flow chart (Fig. 4):



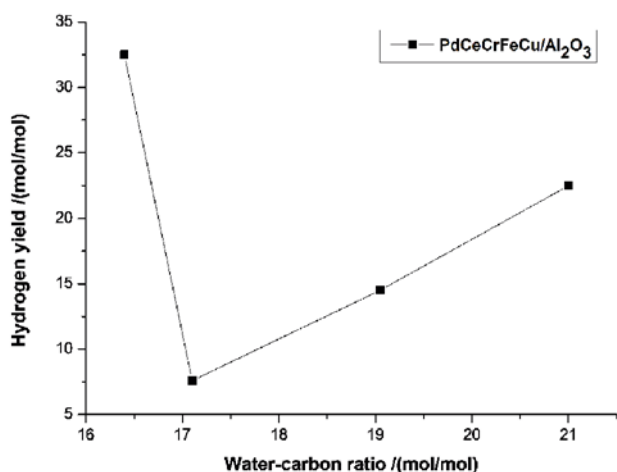
**Figure 4.** Simulation flowchart of hydrogen production by autothermal reforming of diesel oil. Logistics: 1 (water), 2 (oxygen), 3 (diesel oil), 7 and 8 (materials entering the reactor), 9 (wet reaction gas), 10 (dry reaction gas), 11 (condensate), and 13 (product gas). Description of equipment units: 1, 2, 3, 5, 8, and 9 are heat exchangers, 4 is a mixer, 6 is a reactor, and 7 is a separator.

(c) Simulation results: The yield of hydrogen is 28.3 mol/mol under the simulation conditions. Heat release from the reaction system to the environment is  $\sim 0.0033$  kJ/kmol, which is negligible. Therefore, it is confirmed that hydrogen is produced by the autothermal reforming of diesel oil under autothermal conditions<sup>32–35</sup>.

### Analysis of influencing factors

#### Influence of catalyst bed inlet temperature

Figure 5 shows the relationship between the hydrogen yield and the catalyst bed inlet temperature at an oxygen-carbon ratio of 0.6, space velocity of diesel oil solution of  $0.15 \text{ h}^{-1}$ , and water-carbon ratio of 20. It is evident that the hydrogen yield increases with increasing catalyst bed inlet temperature. The hydrogen yield is the lowest when the catalyst bed inlet temperature is  $550^\circ\text{C}$  and increases to 22.50 (mol/mol) at  $700^\circ\text{C}$ . The experimental results show that a high inlet temperature of the

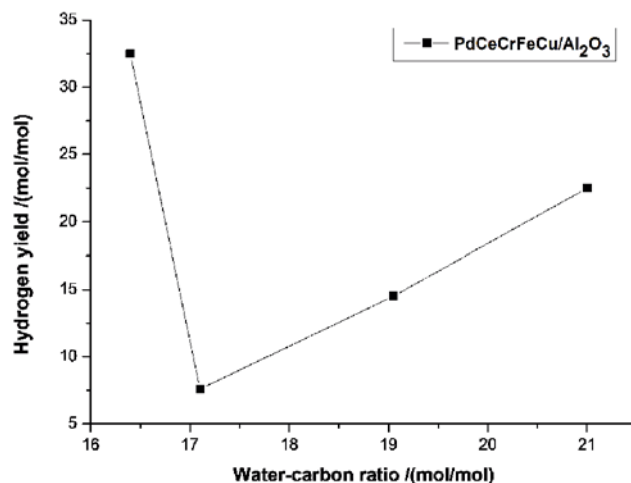


**Figure 5.** Effect of catalyst bed inlet temperature on  $\text{H}_2$  yield

catalyst bed is beneficial for the reaction, although high temperatures will lead to increased energy consumption, which is economically unreasonable. Moreover, various alkanes in diesel oil are unstable at high temperatures, and the higher the temperature, the easier is the precipitation of carbon, which shall ultimately damage the reactor material.

#### Influence of water-carbon ratio

Figure 6 shows the relationship between the hydrogen yield and water-carbon ratio when the diesel liquid space velocity is  $0.16 \text{ h}^{-1}$ , catalyst bed inlet temperature is  $650^\circ\text{C}$ , and oxygen-carbon ratio is 0.6.



**Figure 6.** Effect of  $\text{H}_2\text{O}/\text{C}$  feed ratio on  $\text{H}_2$  yield

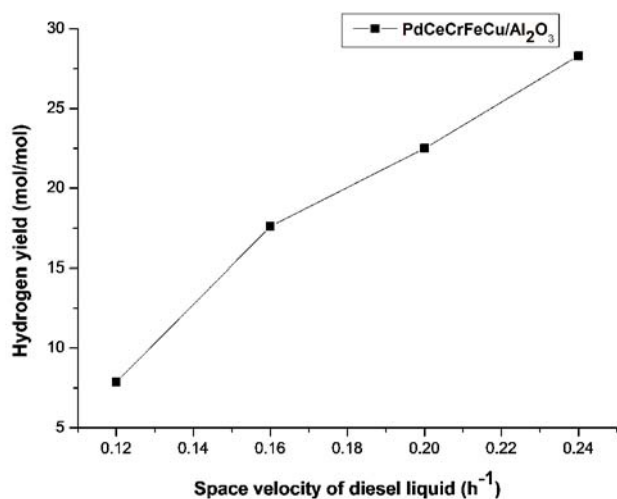
It is evident that the hydrogen yield first decreases and then increases with increasing water-carbon ratio. Perhaps, there was no carbon evolution at the beginning of the reaction, however, with the progress of the reaction, the low water-carbon ratio initiated carbon evolution, causing catalyst deactivation. Increasing the water-carbon ratio can eliminate carbon deposition, which is beneficial for the reaction. Theoretically, a high water-carbon ratio is beneficial for the water reforming reaction, and it can also prevent carbon evolution. However, a very high water-carbon ratio will not only increase steam consumption but also increase the load of recovering excess steam, which would be economically irrational.

Figure 6 shows that with the increase of water-carbon ratio, hydrogen content and hydrogen production first decrease and then increase, which may be attributed to the initial reaction. There is no carbon reaction during the reaction. With the progress of the reaction, the smaller the ratio of water to carbon is, the catalyst will be deactivated due to carbon precipitation, while the larger the ratio of water to carbon is, the carbon deposition will be eliminated and the reaction will be promoted. In theory, it is beneficial to increase the water-carbon ratio in water reforming reaction, but it is also necessary to prevent the occurrence of carbon precipitation reaction to a certain extent and thus inhibit carbon precipitation.

#### Influence of oxygen-carbon ratio

Figure 7 shows the relationship between the hydrogen yield and oxygen-carbon ratio when the diesel oil space





**Figure 7.** Effect of  $O_2/C$  feed ratios on  $H_2$  yield

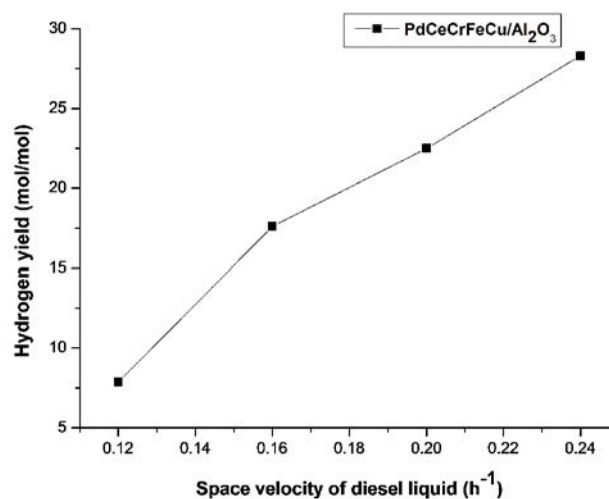
velocity is  $0.16 \text{ h}^{-1}$ , catalyst bed inlet temperature is  $650^\circ\text{C}$ , and water-carbon ratio is 20.

It is evident that the hydrogen yield first increases and then decreases with increasing oxygen-carbon ratio. The maximum hydrogen yield is 23.05 (mol/mol) when the oxygen-carbon ratio is 0.6. Analysis of the mechanism suggests that the oxygen-carbon ratio is an important factor for realizing hydrogen production by autothermal reforming of diesel oil. The heat required by water reforming is generated by oxygen reforming, following which the autothermal reaction is realized. In addition, with increasing oxygen-carbon ratio, a large amount of heat is released through combustion. This increases the temperature of the reacting system, which, in turn, increases the hydrogen yield. However, excess oxygen will react with hydrogen, thereby reducing the hydrogen yield.

#### Influence of diesel liquid space velocity

Figure 8 shows the relationship between the hydrogen yield and space velocity of diesel oil when the oxygen-carbon ratio is 0.6, catalyst bed inlet temperature is  $650^\circ\text{C}$ , and water-carbon ratio is 20.

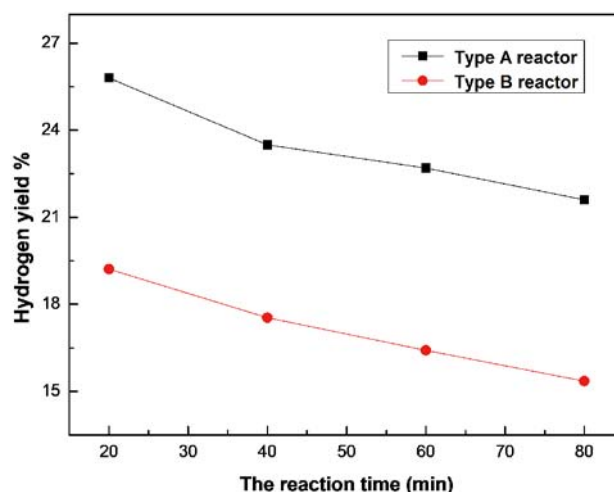
Liquid airspeed refers to the volume of diesel oil passing through a unit volume of catalyst per unit time. Both hydrogen yield and hydrogen content show a monotonic upward trend with the increase of liquid space velocity, but the upward trend slows down when the oxygen-carbon ratio reaches 0.18. This is because the flow rate of diesel oil itself is very small. Increasing the liquid space velocity of diesel oil under experimental conditions can make the flow rate in the vaporization chamber of diesel oil more uniform and stable, which is beneficial to the hydrogen production process. However, the residence time will be shortened if the liquid space velocity continues to increase, and the hydrogen yield will show a downward trend. It is evident from the figure that the hydrogen yield increases linearly with increasing liquid space velocity. Analysis suggests that as the flow rate of diesel oil is very low, increasing the space velocity of diesel oil can make the flow rate in the vaporization chamber of diesel oil more uniform and stable, which would be beneficial for hydrogen production.



**Figure 8.** Effect of diesel liquid space velocity on  $H_2$  yield

#### Comparison of hydrogen production effects

Figure 9 shows that under the conditions of diesel liquid airspeed  $0.24 \text{ h}^{-1}$ , oxygen/carbon ratio 0.4, water/carbon ratio 17, and catalyst inlet temperature  $700^\circ\text{C}$ , two types of reactors, Type A and Type B, are used to compare the effects of hydrogen production according to the corresponding processes.



**Figure 9.** Effect of hydrogen production on A- and B-type reactor and process

It can be seen from the experimental results that the hydrogen yield of type A reactor and process is more than 25, while the hydrogen yield of type B reactor and process is only about 19, but it is relatively stable. The analysis reasons are as follows:

Under experimental conditions, the flow rate of diesel oil is low. when b-type process is adopted, the expected atomization effect of diesel oil through MJN air atomization nozzle is not achieved, so that a large part of diesel oil can not be gasified instantaneously, but enters the catalyst bed in large droplets, which affects the reaction process.

According to the distillation range of straight-run diesel oil used in this paper, diesel oil can be completely gasified at  $310^\circ\text{C}$ . The gasifier temperature of type a process is  $450^\circ\text{C}$ , and the oil and gas exiting the gasifier is superheated oil steam. the experimental study shows that the superheated oil and gas at this time already

contains a part of cracked methane and a small amount of hydrogen, which can be considered as the pre-reaction. After preheating to the specified temperature in the preheating section, the steam conversion reaction and reforming can be directly carried out in the reactor, and the reaction is relatively complete, which is beneficial to the process of hydrogen production from diesel oil. In the B-type process, besides the incomplete gasification of diesel oil, there is also a lack of pre-reaction stage, which relatively increases the load in the reactor. Therefore, in the same residence time, the reaction is not complete enough, resulting in a decrease in hydrogen yield.

Under experimental conditions, the pre-reaction in the gasifier of type A process will increase the gas flow rate, form local gas resistance and cause certain fluctuation. In the B-type process, after passing through the static mixer and nozzle, the material flows are mixed evenly, and all reactions take place in the reactor, so the system is relatively stable.

It can be seen that both Type A and Type B reactors can be used for hydrogen production from diesel oil, but when Type B reactor is used, a preheater should be set in the process before entering the nozzle, and the length of preheating section of the reactor should be appropriately lengthened to ensure that the diesel oil is completely gasified and some pre-reaction of diesel oil cracking occurs before entering the catalyst bed.

#### Measurement of adsorption capacity

Figure 10 is an isotherm, which well reflects the relationship between the nitrogen adsorption capacity of PdCeCrFeCu/Al<sub>2</sub>O<sub>3</sub> catalyst and the relative pressure of nitrogen. With the increase of the relative pressure of nitrogen, the nitrogen adsorption capacity of the tested components also increases.

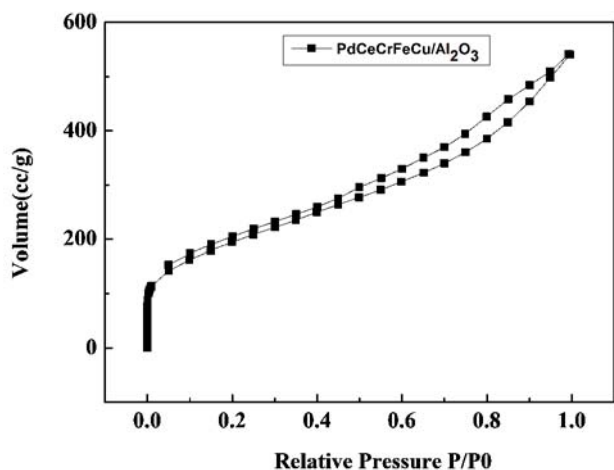


Figure 10. Relationship between nitrogen adsorption capacity and relative pressure of PdCeCrFeCu/Al<sub>2</sub>O<sub>3</sub> catalyst

It can be seen from SEM that the surface of this catalyst is smooth and has a loose and porous structure. It is supported by Al<sub>2</sub>O<sub>3</sub> and added with Ce, which shows that the carrier used in this experiment can make the added catalyst components distribute more evenly to a certain extent, while the addition of Ce can make the oxide of active components disperse more evenly and the particles become finer, which is more beneficial to the experiment itself.

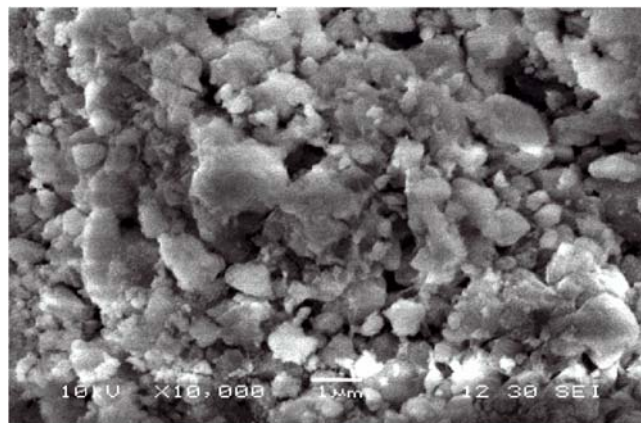


Figure 11. SEM diagram of catalyst PdCeCrFeCu/Al<sub>2</sub>O<sub>3</sub>

#### Suitable conditions for hydrogen production by autothermal reforming of diesel oil

To determine the suitable operating conditions for hydrogen production by autothermal reforming of diesel oil over PdCeCrFeCu/Al<sub>2</sub>O<sub>3</sub> catalyst, orthogonal experiments were performed according to L9(34) orthogonal table, with hydrogen yield as the experimental index. Table 1 and Table 2 represent the factor level and range analysis of the orthogonal experiment.

Table 1. Factor and Level

Factor	Entrance temperature catalyst bed (°C)	Water-carbon ratio	Oxygen-carbon ratio	Space velocity of diesel liquid (h <sup>-1</sup> )
Level	a	b	c	d
1	600	15	0.4	0.16
2	650	18	0.6	0.2
3	700	20	0.8	0.24

Table 2. Analysis of range

Mean value	a	b	c	d
I j/Kj	15.6452	15.5653	15.6384	13.9250
II j/Kj	15.9309	17.6536	18.61325	15.8618
III j/Kj	19.5338	17.8911	16.8583	21.3231
Rj	3.8885	2.3258	2.9749	7.3981

The range analysis in Table 3 suggests that the liquid space velocity of diesel oil has the maximum influence on hydrogen yield, followed by the catalyst bed inlet temperature, oxygen-carbon ratio, and water-carbon ratio. Thus, the suitable reaction conditions are as follows: catalyst bed inlet temperature, 700°C & water-carbon ratio, 20 oxygen-carbon ratios, 0.6 and diesel liquid space velocity, 0.24 h<sup>-1</sup>. Under these conditions, the hydrogen yield is 28.3 (mol/mol). Table 3 shows the specific surface areas of different catalysts before use, as well as the hydrogen yield and hydrogen content produced during hydrogen reforming. It can be seen from the test results of the specific surface area of the catalyst that when the carrier is Al<sub>2</sub>O<sub>3</sub>, the smaller the catalyst component is, the larger the specific surface area is. It can be seen from the data in the table that the activity of the precious metal catalysts is better than other catalysts, which also indicates that the specific surface area of the catalyst is not the only index to evaluate the activity of the catalyst.

**Table 3.** Compared with the parameters of other catalysts studied before

Catalyst	Hydrogen yield (mol/mol)	Total pore volume (m <sup>3</sup> /g)
LaCeCoCrFeNi/Al <sub>2</sub> O <sub>3</sub>	17	0.2865
LaCeCoFeNi/Al <sub>2</sub> O <sub>3</sub>	15	0.3156
LaCoFeNi/Al <sub>2</sub> O <sub>3</sub>	12	0.3436
LaFeNi/Al <sub>2</sub> O <sub>3</sub>	10	0.3554
LaNi/Al <sub>2</sub> O <sub>3</sub>	9	0.3658
Ni/Al <sub>2</sub> O <sub>3</sub>	8	0.3785
PdCeCrFeCu/Al <sub>2</sub> O <sub>3</sub>	28.3	0.4512

## CONCLUSIONS

(a) The noble metal catalyst PdCeCrFeCu/Al<sub>2</sub>O<sub>3</sub> shows good activity toward the autothermal reforming of diesel oil for hydrogen production.

(b) The influence of various factors on hydrogen production through autothermal reforming of diesel over the PdCeCrFeCu/Al<sub>2</sub>O<sub>3</sub> catalyst decreases in the following order: diesel liquid space velocity > catalyst bed inlet temperature > oxygen-carbon ratio > water-carbon ratio.

(c) The suitable operating conditions for hydrogen production by autothermal reforming of diesel oil over the PdCeCrFeCu/Al<sub>2</sub>O<sub>3</sub> catalyst are as follows: temperature, 700°C diesel liquid space velocity, 0.24 h<sup>-1</sup>, water-carbon ratio 20 and oxygen-carbon ratio 0.6. Under these conditions, the hydrogen yield is 28.3 (mol/mol).

(d) The adiabatic tubular reactor with a preheating section designed in this study is structurally simple and reasonable, thereby allowing diesel reforming reactions to be conducted under autothermal conditions.

## ACKNOWLEDGMENT

This work was supported financially by Specialized Research Fund for Introducing Talents of Hebei Agricultural University (No. YJ201908), 2019 Scientific Research Fund of Shenyang Medical College (20191023), Liaoning Science and Technology Project Management (2019-BS-192), Shenyang medical college of science and technology fund project (20186071), 2018 Provincial Key Research Program Guidance Plan (2018225021), Science Pounicatom Of China (21804093).

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