

Study on the Online Reforming of Low Concentration Alcohol as Vehicle Fuel

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Abstract: This research studied catalytic reforming mechanism of low concentration alcohol, analyzed the producing conditions and influencing factors of a mixture of combustible gas, took an analysis towards the composition of the mixture produced by reforming, and studied the respective effects of temperature, traffic, alcohol concentration and catalyst on the components of mixed gas. It is found that, under different working conditions of the engine, the external condition of the reforming reaction changes, and the composition of the reforming gas will differ as well. As a result, the optimum air-fuel ratio of the engine must at the same time adapt to different working conditions.

Keywords: Vehicle; low concentration alcohol; online reforming; catalyst

1 Background

With the intensification of the energy crisis and the deterioration of the environmental pollution, energy conservation and environmental protection has received escalating attention from the society [1]. As a non-renewable energy source, oil consumption speed is accelerating with the rapid increase of the total number of cars in the world. Therefore, the search for a renewable, alternative, clean and environmental friendly new automotive fuel has become an important means to solve the environmental problem [2]. Traditional ethanol-gasoline is a mixture of high-concentration ethanol and regular gasoline in a certain proportion. As a new type of automobile fuel, ethanol-gasoline has many advantages, such as sufficient combustion, good anti-knock performance and improved engine emission performance [3]. However, due to the strong water absorption of ethanol, the ethanol gasoline is prone to water absorption stratification, resulting in the declination of engine combustion stability. The latent heat of ethanol vaporization is large, which makes it difficult for the engine to cold-start [4]. Ethanol gasoline contains a small amount of organic acid, which will cause corrosion to the important parts of the engine and reduce the life of the machine. Additionally, ethanol-based gasoline requires the use of dehydrated ethanol with an alcohol concentration of at least 99.5% [5], which makes the production cost of ethanol concentrate much higher than the production cost of gasoline. These potential weaknesses restrict the popularization and application of ethanol-gasoline and limit the application and spread of ethanol-gasoline in other power plants.

In order to overcome the shortcomings of ethanol gasoline, we use the low-concentration alcohol reforming to generate a flammable mixed gas solution to achieve the direct application of



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low-concentration alcohol on the engine. The application and promotion of low-concentration alcohol fuel can also promote the development of agriculture and fuel ethanol industry, and promote the optimization and upgrading of the agricultural industry structure. At present, the reformation of low-concentration alcohol is currently used in the chemical industry, and there is still little research on alternative fuels for vehicles. The entire process of low-concentration alcohol reforming is affected by factors such as reforming temperature, alcohol concentration, alcohol flow rate, and catalyst. In this paper, the exhaust heat from the engine exhaust is used to provide heat for reforming. Due to changes in engine operating conditions, the situation is more complicated.

2 Reforming Mechanism of Low Concentration Alcohol

Low concentration alcohol is catalyzed by heavy metal reforming under high temperature, which is widely used in chemical industry. The purpose of reforming is to obtain industrial hydrogen, which is widely used in the production of hydrogen fuel for fuel cell. At present, there are not many studies on the application of using the gas mixture of low concentration alcohol after reforming as a substitute of automobile fuel and directly put it into engine to combust, but the process and mechanism of reforming are basically similar to that of chemical industry. Therefore, the research on low concentration ethanol reforming as an alternative fuel for automobiles can also refer to the existing research results in the field of chemical engineering.

2.1 Process of Reforming

Because of the low boiling point of alcohol, which is lower than the boiling point of water, about 78°C , it is easy to gasify, which makes it suitable for catalytic reforming by gas phase reforming, in order to make the mixture of combustible gas rich in hydrogen. Compared with automotive engines, when the engine is in normal operation state, the temperature of exhaust gas emission is generally above 200°C [6], which is suitable for using the residual heat from the exhaust gas as the energy to gasify the low concentration alcohol and realize the recycling and reuse of the engine's residual heat. Install supplementary heat system before the start of engine to preheat the engine before the process of reforming. The flow chart of reforming reaction using waste heat of engine exhaust is shown in Fig. 1.

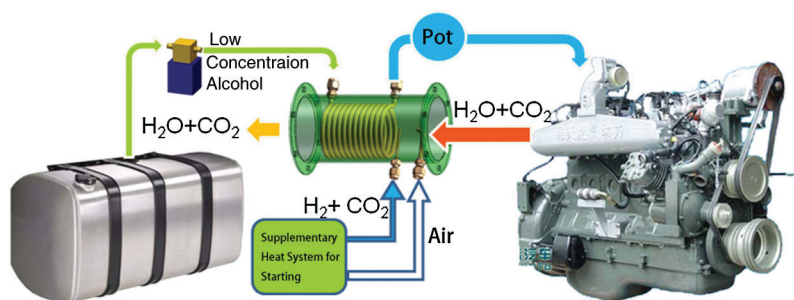
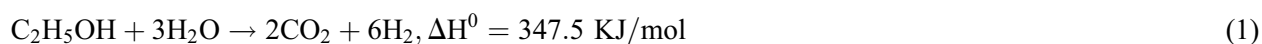


Figure 1: Flow chart of reforming reaction

The process of alcohol gas phase reforming includes steam reforming, some parts of oxidation and self-heating reforming [7].

Steam reforming requires the boiling point of reactants to be low. The number of carbon atoms in the chemical formula is generally less than three, and in the actual steam reforming process, the steam to carbon molar ratio that is commonly used falls between 3.5 and 4.5. So long as the process is endothermic, the outside world needs to provide heat for the reaction process, which is also a means of heat recycling [8].

The ideal chemical reaction Eq. (1) for steam reforming of low concentration alcohol is:



Some oxidation is usually carried out in a specific reactor at high temperature and atmospheric pressure. Under the condition of catalyst, such as Pt/Al₂O₃, Rh/CeO₂, Pt/CeO₂, the reaction can be carried out at a temperature of 300°C. Some parts of oxidation can also be carried out in the absence of catalyst, but the temperature needs to reach over 1000°C.

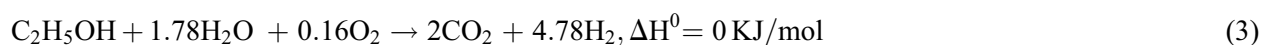
The ideal chemical reaction Eq. (2) for some oxidation of low concentration alcohol is:



In the actual reaction, there will be a lot of side reactions, so the products always include water, methane, carbon deposition, cracking of small molecules and so on. The H₂/CO value of outlet can be improved by using a better catalyst. Using nitrogen and air as the gasification agent, the molar ratio of C₂H₅OH/O₂ was 2, the mass/volume flow of catalyst (W/Q) was 0.16 gs/cm³, the temperature of which reached over 400°C, and the alcohol was completely converted. When the temperature reaches 800°C, the proportion of different type of gas output from the outlet was: 11% of H₂, 6.5% of CO₂, 5% of CO, 11% of water vapor, 65% of N₂. When Pt/V – CeO₂ is added to the outlet of the conversion device as catalyst of the reforming reaction, and the percentage of CO drops to less than 2% at a temperature of 300°C.

Natural reforming is generally carried out under the conditions of 400°C–1200°C [9], atmospheric pressure and catalysis. Common catalysts include Ni radical, Cu radical, Lr, Pt-Rh, etc., and common carriers include ZrO_x, Al₂O₃, CeO₂. Ce has a certain function of storage and release for oxygen and can effectively prevent carbon accumulation. Cu catalyst has high activity to water gas conversion. The natural reforming process can be carried out rapidly and continuously at the temperature of engine exhaust. Furthermore, the coupling of steam reforming and part of the oxidation can improve the temperature control of the reactor, effectively reducing the formation of hot spots, and avoiding the decrease of catalyst activity caused by carbon deposition and sintering.

The ideal chemical reaction Eq. (3) for natural reforming of low concentration alcohol is:



Fierro tested different Ni-based catalysts with alcohol in which H₂O/C₂H₅OH was 1.6 and O₂/C₂H₅OH was 0.68. The catalytic contact time was 0.2 min kg/mol and the temperature was 627–750°C. The results showed that the hydrogen production amount of different catalysts carrier was also different [10]. At 697°C, the catalytic activity sequence was Ni-Zn>Ni-Fe>Ni-Cr>Ni>Ni-Cu. He found that the catalyst with the largest yield of hydrogen was Al₂O₃, supported by Ni-based catalyst with 5% of Rh.

2.2 Reaction Mechanism of Reforming

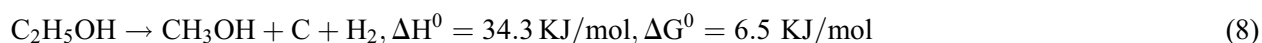
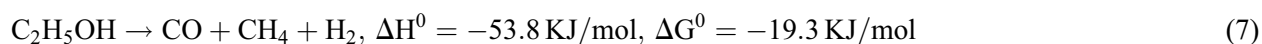
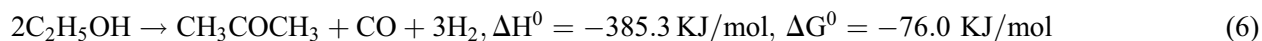
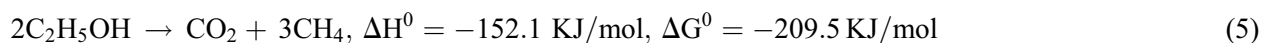
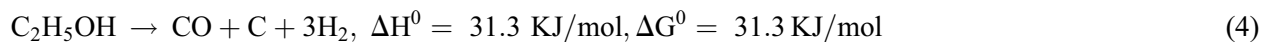
The process of catalytic reforming with low concentration alcohol is very complex and produces many chemical reactions. Moreover, with the change of external conditions, such as reforming temperature, reforming flow rate, alcohol concentration and different type of catalyst, the chemical reaction path and process are different. In the complex process of reforming, we summarize the whole reaction mechanism into the following two types:

1. Ethanol firstly dehydrogenates to form hydrogen and acetaldehyde. Part of acetaldehyde continues to interact with oxygen to form the acetate form, which then decomposes into CO₂ and CH₄. Part of acetaldehyde will crack and form CH₄ and CO. CO reacts with water gas to form CO₂ and H₂, and CH₄ undergoes renormalization to form CO₂, CO and H₂.

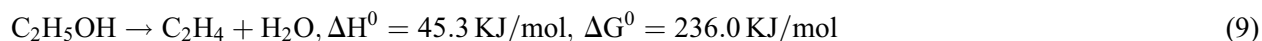
2. Ethanol firstly dehydrates to produce hydrogen and ethylene, and some ethylene undergo reforming reaction to produce H_2 and CO_2 ; And the other part is just going to come off of the product. CO reacts with water gas to form CO_2 and H_2 . Among the reactions above, the active sites of the reactions are mostly metal atoms, and different carriers sometimes provide different adsorption sites.

The chemical reactions in catalytic reforming are as follows:

Cracking reaction:



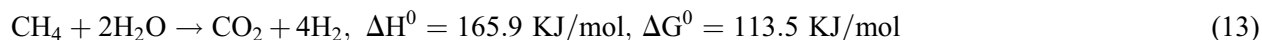
Dehydration and dehydrogenation reaction:



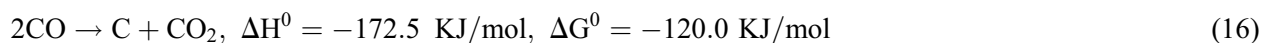
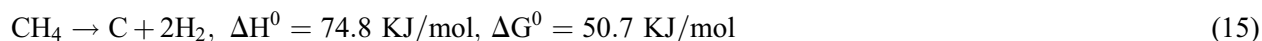
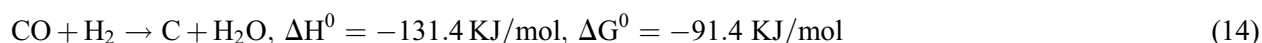
Water gas conversion reaction:



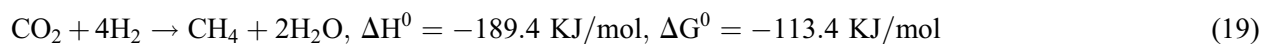
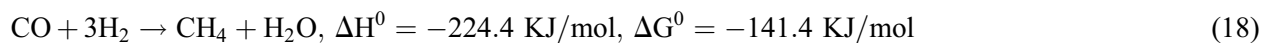
Methane steam reforming reaction:



Carbon deposition reaction:



Other reactions (reactions between reaction products):



From the reaction path and possible chemical reaction equation of catalytic reforming of low concentration alcohol, we can see that the resulting mixture of combustible gas contains the following components: H_2 , CO, CO_2 , CH_4 , H_2O , CH_3CHO , C_2H_4 , CH_3OH , C and so on, totally a dozen of products.

3 Influencing Factors of Alcohol Reforming at Low Concentration

The whole chemical reaction process is changed with the variation of alcohol concentration, reforming traffic, reforming temperature and catalyst selection. Therefore, the reforming rate of low concentration alcohol can also be affected by the factors above. The proportion of combustible mixture will directly affect the air consumption of fuel engine with low concentration alcohol, and the air fuel ratio will also be affected.

Reforming rate have multiple concepts, such as mass reforming rate, mass component reforming rate, calorific value reforming rate, etc. In order to simplify the test operation, the mass reforming rate is adopted.

$$\text{mass reforming rate} = \frac{\text{input alcohol with water} - \text{residual unreformed alcohol}}{\text{input alcohol with water}} \times 100\% \quad (20)$$

3.1 Influence of Reforming Temperature

Engine exhaust waste heat is used to provide reforming heat for low concentration alcohol, and the temperature is generally less than 500°C. Based on the consideration of energy density of fuel, the low-concentration alcohol with the volume concentration of water to alcohol molar ratio of 1 (volume concentration of about 75%) was selected, the traffic was selected as 8 g/min, and the Ni-based catalyst was used for the test at the temperature of 200°C–500°C. The mass reforming rate after catalytic reforming was analyzed, and the analysis results were shown in Fig. 2.

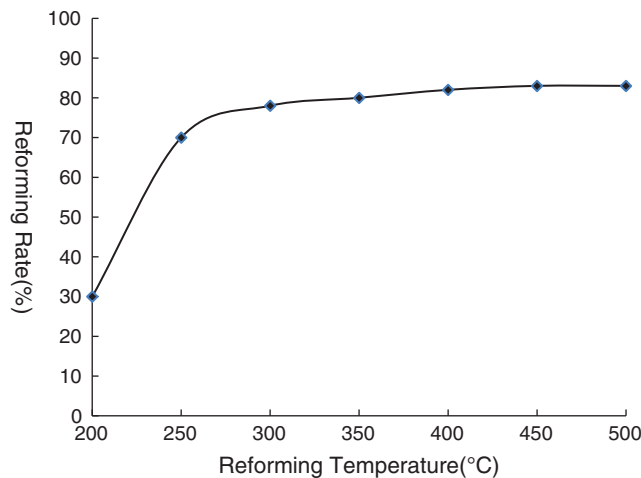


Figure 2: Influence of different temperatures on alcohol reforming rate

As can be seen from the figure above, under the condition of stable flow and alcohol concentration, the reforming rate of alcohol gradually increases with the increase of temperature, and the most rapid increase occurs between 200°C and 250°C. At 300°C, the reforming rate reached 80%. After more than 300°C, the improvement of reforming rate tends to be gentle.

3.2 Influence of Alcohol Concentration

According to 3.1, when the reforming temperature is higher than 300°C, the reforming rate concentration reaches over 80%, and the space for further increase is limited. Therefore, when studying the influence of alcohol concentration on the reforming rate, Ni-based catalyst is used, the reforming temperature of 250°C is selected, and the traffic of 8 g/min is chosen, to analyze the mass reforming rate after catalytic reforming. The analysis results are shown in Fig. 3.

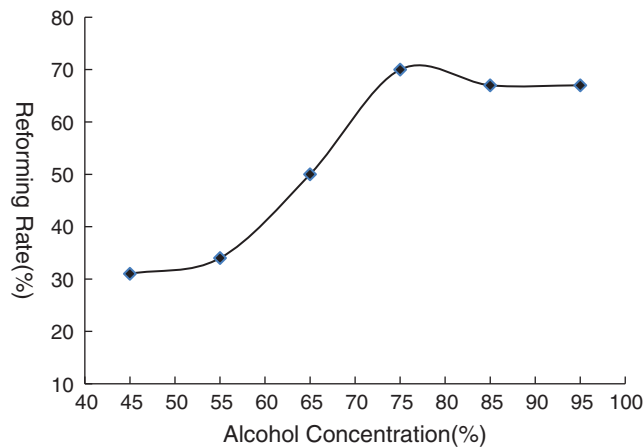


Figure 3: Effects of different alcohol concentrations on alcohol reforming rate

When the alcohol volume concentration is lower than 50% and the reforming rate is lower than 20%, the reforming rate is too low. After the alcohol volume concentration reaches over 50%, the reforming rate increases rapidly. When the alcohol volume concentration reaches 75%, the reforming rate is the highest, reaching about 80%. With the further increase of alcohol concentration, the reforming rate decreases. The 75% volume concentration of alcohol is still included in the category of low alcohol concentration, thus the most reasonable choice is to select the 75% volume concentration of alcohol.

3.3 Influence of Reforming Flow

The low-concentration alcohol with the volume concentration of water to alcohol molar ratio of 1 (volume concentration of about 75%) was selected, and the Ni-based catalyst was used at the temperature of 250°C, to analyze the influence of reforming traffic on reforming rate. The analysis results are shown in Fig. 4.

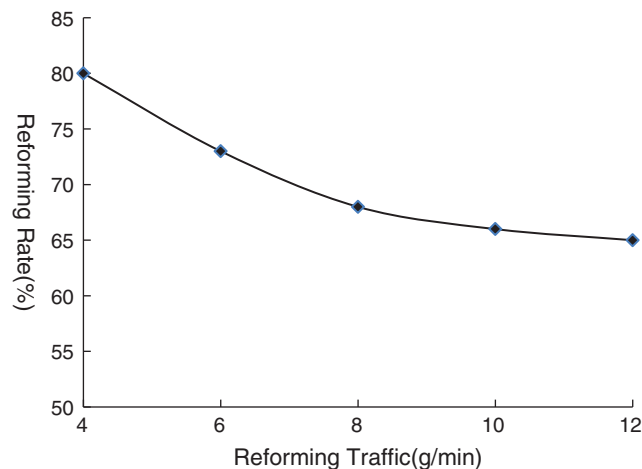


Figure 4: Influence of different reforming traffic on alcohol reforming rate

The result shows that the less the reforming traffic is, the higher the reforming rate will be. But too low a reforming traffic will make it difficult to meet the fuel supply requirement when the engine is running. The selection of optimum reforming traffic should not only consider the rate of reforming level, but should also

pay attention to the size of the reforming gas quantity, so that the alcohol reforming has a proper mass reforming rate, and can minimize the reaction area of the reformer to achieve the optimization of low concentration alcohol. Reforming traffic of 8 g/min was selected under the condition of vehicle exhaust heat reforming.

3.4 Influence of Catalyst

The low-concentration alcohol with the volume concentration of water to alcohol molar ratio of 1 (volume concentration of about 75%) was selected, the traffic was selected as 8 g/min, a temperature of 250°C is chosen, and considering the cost, Ni radical, Cu radical, 2/3Ni + 1/3Cu radical, 1/3Ni + 2/3Cu radical, NiMnFe radical were separately selected, to analyze the mass reforming rate after reforming. The analysis results are shown in Fig. 5.

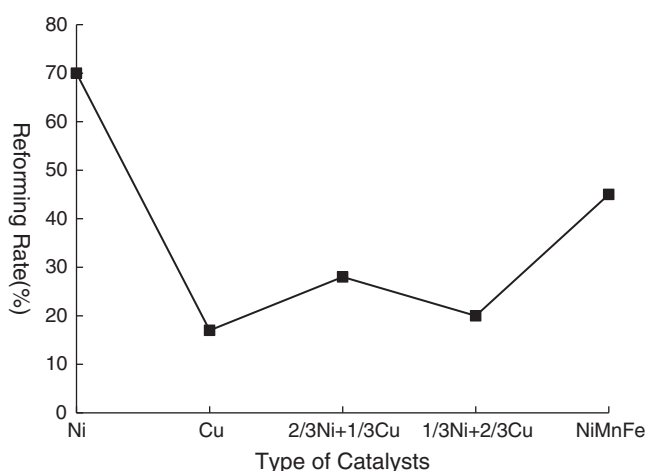


Figure 5: Effects of different catalysts on alcohol reforming rate

Under the same reforming temperature, traffic and alcohol concentration, different catalysts' influence on the mass reforming rate of alcohol is obviously distinctive. The catalytic effect of Ni-based catalyst is much better, and the catalytic reforming rate is 70% at 250°C. The choice of catalyst not only affects the alcohol reforming rate, but also affects the formation of other components.

4 Conclusion

This paper studied the mechanism and reaction conditions of low concentration alcohol reforming, and the effects of these conditions on reforming reaction, reforming rate and reforming gas composition. It is found that under the different working conditions of the engine, the external conditions of the reforming reaction will change, the composition of the reforming gas vary as well, thus the optimum air-fuel ratio of the engine must alter to suit different working conditions.

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Conflicts of Interest: We declare that we have no financial and personal relationships with other people or organizations that can inappropriately influence our work, there is no professional or other personal interest of any nature or kind in any product, service and/or company that could be construed as influencing the

position presented in the review of the manuscript entitled “Study on the Online Reforming of Low Concentration Alcohol as Vehicle Fuel”.

References

1. Xu, J. (2014). *Design and research of air-fuel ratio control system of low-concentration alcohol reforming fuel engine*. Hangzhou: Zhejiang University.
2. Chen., H. (2013). Comprehensive evaluation and development strategy of automotive alternative energy. *China Energy*, 35(1), 31–36+43.
3. Wang, Y. J. (2007). Development and exploration of alternative fuel for engine. *Journal of Taiyuan University*, 8 (2), 125–127.
4. Li, Y. P. (2007). Alternative fuel and its application in engine. *Energy and Environment*, 2007(06), 48–50.
5. Li, L., Tang, D. W., Song, Y. C., Jiang, B., Zhang, Q. (2018). Hydrogen production from ethanol steam reforming on Ni-Ce/MMT catalysts. *Energy*, 149, 937–943. DOI 10.1016/j.energy.2018.02.116.
6. He, S. F., Mei, Z. Q., Liu, N. S., Zhang, L., Lu, J. C. et al. (2017). The Ni/SBA-15 catalysts for hydrogen production by ethanol steam reforming: effect of nickel precursor. *International Journal of Hydrogen Energy*, 42(21), 14429–14438. DOI 10.1016/j.ijhydene.2017.02.115.
7. You, F. B. (2008). *Research on water-alcohol fuel reforming engine*. Wuhan: Wuhan University of Technology.
8. Maher Abdul-Resul Sadiq, A. B. (2002). A study on the hydrogen-ethyl alcohol dual fuel spark ignition engine. *Energy Conversion and Management*, 43(2), 199–204. DOI 10.1016/S0196-8904(01)00020-6.
9. Compagnoni, M., Tripodi, A., Rossettim, I. (2017). Parametric study and kinetic testing for ethanol steam reforming. *Applied Catalysis B: Environmental*, 203.
10. Li, D., Zeng, L., Li, X. Y., Wang, X., Ma, H. Y. et al. (2015). Ceria-promoted Ni/SBA-15 catalysts for ethanol steam reforming with enhanced activity and resistance to deactivation. *Applied Catalysis B: Environmental*, 176–177.