

Hydrogen generation from biogenic and fossil fuels by autothermal reforming

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Abstract

Hydrogen generation for fuel cell systems by reforming technologies from various fuels is one of the main fields of investigation of the Fraunhofer ISE. Suitable fuels are, on the one hand, gaseous hydrocarbons like methane, propane but also, on the other hand, liquid hydrocarbons like gasoline and alcohols, e.g., ethanol as biogenic fuel. The goal is to develop compact systems for generation of hydrogen from fuel being suitable for small-scale membrane fuel cells. The most recent work is related to reforming according to the autothermal principle — fuel, air and steam is supplied to the reactor. Possible applications of such small-scale autothermal reformers are mobile systems and also miniature fuel cell as co-generation plant for decentralised electricity and heat generation. For small stand-alone systems without a connection to the natural gas grid liquid gas, a mixture of propane and butane is an appropriate fuel. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Autothermal reforming; Propane reformer; Compact system; Decentralised power generation

1. Introduction

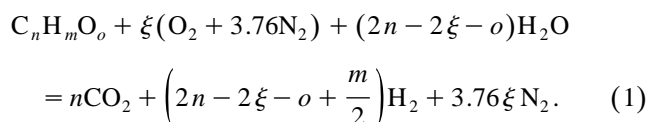
A small-scale autothermal reformer for propane has been designed, constructed and characterised under various operation conditions [1]. In this reactor, two reactions occur adjacently on one catalyst system which is a metal honeycomb structure being coated with platinum. Thirty to 40% of the fuel is oxidised by injecting air, releasing heat. This heat is required to convert the remaining fuel with steam to hydrogen carbon monoxide and carbon dioxide in the endothermal steam reforming reaction. This direct coupling of the two reactions enables a dynamic response to changing loads: the reformer quickly adapts to new operation conditions. In the starting phase, the reactor is operated solely as catalytic heater until the operating temperature is reached. Additional external burners with the accompanying power supplies are not required, which makes the system simpler and less expensive.

Experimental results about the different operation modes like reforming with or without air preheating, air ratio (equivalence ratio) and steam-to-carbon ratio (s/c ratio) are presented. The efficiency of the propane reforming process and the hydrogen production rate are discussed.

2. Experimental results and discussion

Fig. 1 schematically illustrates the propane reformer. It includes the heat exchanger for the internal preheating of the ducts. Usually, the two components of the reforming process air and water are mixed before they are fed to the reactor in counterflow to the product gas outside of the reactor wall, where the water is vaporised and the steam and air are heated up. Then, these two components are mixed with the propane at the bottom of the reactor where the ducts stream into the metal honeycomb catalyst. Due to the different reaction rates of the combustion and the reforming reaction, the catalyst structure may be divided into two zones: in the first zone, the oxidation of propane is dominant; the second zone is mainly required for complete reforming. Thus, the catalyst at the inlet of the reactor is mainly heated by direct heat transfer of the combustion reaction, the second zone by the heat content of the generated product gases.

The autothermal reforming process is generally defined by the following (Eq. (1)):



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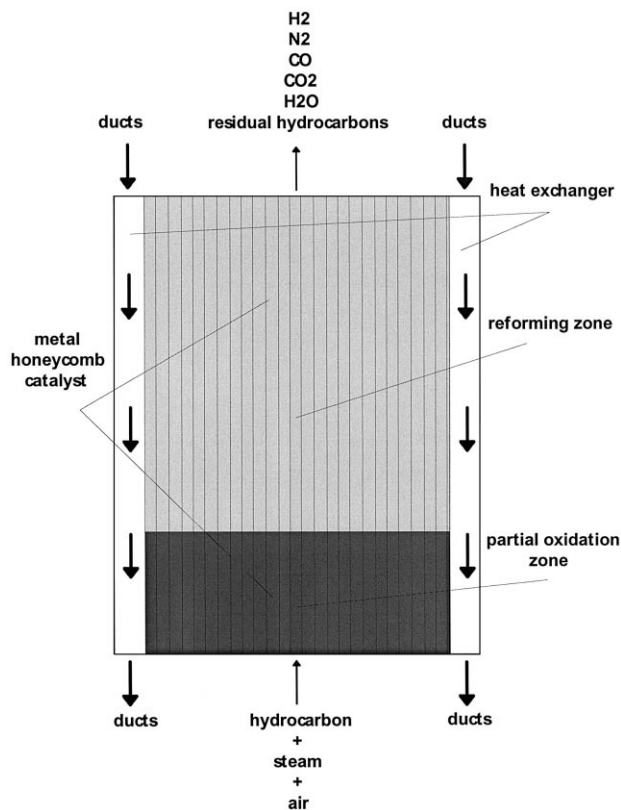


Fig. 1. Schematic design of the autothermal propane reformer.

The reformer is designed for a thermal power of 1 kW. The basis for the performance calculation is the lower heating value (LHV) of hydrogen. Typical hydrogen and carbon monoxide concentrations in the product gas can be given from thermodynamic calculation of the equilibrium values at a reforming temperature of 700°C. For a partial oxidation of propane with an air ratio of $\lambda = 0.4$ and a steam/carbon ratio of $s/c = 1.0$, the reforming process of propane is described by the relationship (Eq. (2)):

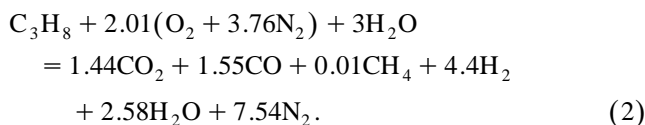


Table 1 presents the designed parameters of the propane reformer. The performance of 1 kW corresponds to the

Table 1
Parameters of the propane reformer

Performance	1	kW
s/c ratio	1.0	mol C/mol H_2O
Air ratio	0.4	mol air _{reaction} /mol air _{stoichiometric}
Propane mole stream	2.5	mol/h
Air mole stream	26.1	mol/h
Water mole stream	7.5	mol/h
Space velocity	2895	$l_{\text{ducts}}/(l_{\text{catalyst}}h)$
Honeycomb volume	286.7	cm^3

Table 2
Parameters of the propane reforming process

s/c ratio
Air ratio
Propane inlet performance
With or without air preheating

lower heating value of the generated hydrogen stream. The propane mole stream, air mole stream and water mole stream represent the inlet mole stream of the ducts.

The space velocity (SV) is defined as the proportion between the standard volumetric flow of the ducts and the volume of the catalyst material:

$$\text{SV} = \frac{V_{\text{ducts}}}{V_{\text{catalyst}}}. \quad (3)$$

The advantages of the platinum-coated honeycomb structure compared with a fixed bed catalyst is the lower pressure loss, the lower thermal mass and the higher thermal conductivity coefficient. The latter guarantees a good heat conduction, as well from the POX zone at the inlet of the reactor into the reforming zone as in the radial extension of the reactor.

In Table 2, the parameters, which have been used during the investigations of propane reforming, are listed. The inlet performance characterises the heat value of the propane stream into the reformer.

Fig. 2 represents the experimentally determined composition of the dry product gas as a function of in dependence on the air ratio in an air-preheated operation mode and an s/c ratio of 1.0. The CO-, CO₂- and CH₄ mole content are measured with an IR spectrometer. The hydrogen, nitrogen and propane contents are determined by calculating the mole balance. The percentages of these gas components are based upon the assumption that no other hydrocarbons are present in the product gas.

The highest value of the hydrogen mole content is reached at an air ratio of 0.4. Simultaneously, the methane

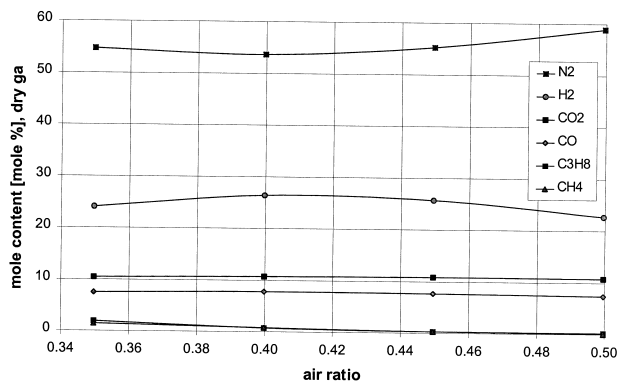


Fig. 2. Gas composition of the dry reforming product gas in dependence on the air ratio with an $s/c = 1.0$, with air preheating [1].

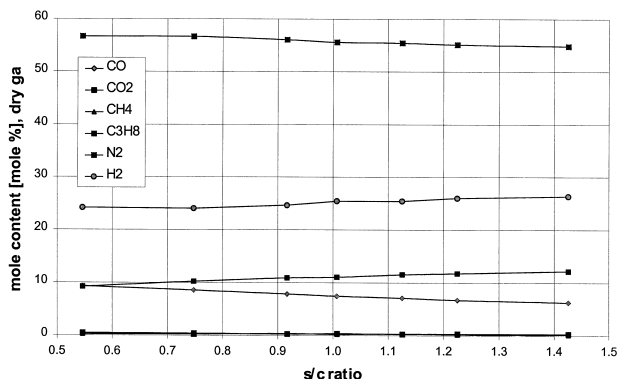


Fig. 3. Gas composition of the dry reforming product gas in dependence on the s/c ratio at an air ratio $\lambda = 0.45$, with air preheating [1].

mole content decreases continuously with rising air ratio. This is in accordance with the thermodynamic calculations: the methane content decreases with rising reaction temperature and higher air ratio leads to higher reaction temperatures. If the air ratio exceeds the value 0.4, the hydrogen content decreases due to the higher nitrogen content in the product gas.

Assuming a complete conversion of the CO by the water gas shift reaction in subsequent reactors, it is possible to reach a hydrogen content of 34.2%. The CO- and CO₂ contents are nearly constant about the range of the air ratio. In this experiment, the optimum air ratio is 0.4. The thermodynamic equilibrium calculation of the propane reforming process at a temperature of 700°C, an s/c ratio of 1.0 and an air ratio of 0.4 releases 29.5% of hydrogen content in the dry gas flow. The higher mole content of hydrogen (34.2%), which is reached during the experimental reforming investigations, shows that the water gas shift reaction takes place at the end of the reforming zone. The cause of the CO conversion is the reduced temperature at the outlet of the honeycomb. The temperature is less than 700°C.

The dry product gas composition dependent on the s/c ratio is illustrated in the Fig. 3. The increasing s/c ratio

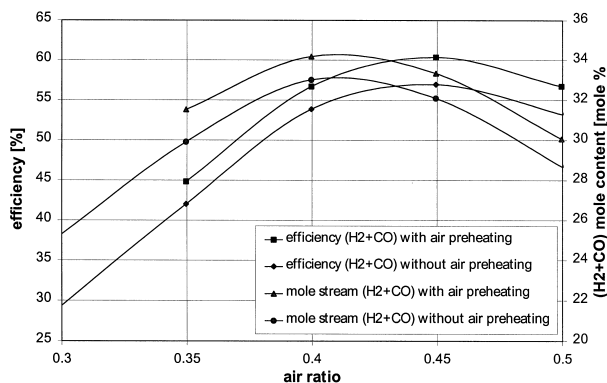


Fig. 4. Comparison of the efficiency (LHV of H₂) and the (H₂ + CO) mole content of the reformer product gas in dependence on the air ratio and with/without air preheating at an $s/c = 1.0$ [1].

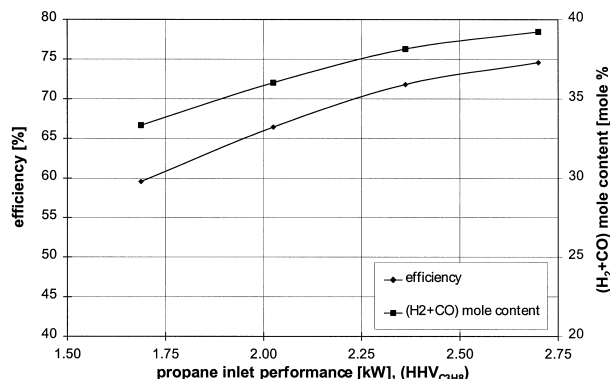


Fig. 5. (H₂ + CO) efficiency (HHV of H₂) and (H₂ + CO) mole content of the reforming product gas in dependence on the propane inlet performance with an s/c ratio = 1.0 and an air ratio $\lambda = 0.40$, with air preheating [1].

has a positive influence on the hydrogen production during the reforming process, the hydrogen content increases from 24.1% to 26.3%. Simultaneously, the CO content decreases with rising s/c ratio and the CO₂ content grows. This effect is due to the water gas shift reaction occurring in the reforming reactor. The methane content is constant about the s/c ratio range.

The two different operation modes with or without air preheating are characterised by the efficiency and (H₂ + CO) mole content curves in Fig. 4. Preheated air operation mode means that the air flow is mixed with the water and flow together over the vaporiser to the reformer. In the other case, the air directly streams into the reformer. Eq. (4) shows the definition of the efficiency, which is represented in the Fig. 5:

$$\eta_{(H_2+CO)}(\text{LHV}) = \frac{(n_{H_2} + n_{CO}) \text{LHV}(H_2)}{n_{C_3H_8} \text{LHV}(C_3H_8)} \quad (4)$$

The parameter of this measurement is the air ratio which varied in a range from 0.3 to 0.5. The s/c ratio is constant at a value of 1.0. The shape of the curves is very similar in both cases, the maximum efficiency lies at about an air ratio of 0.45. In the case of air preheating, the

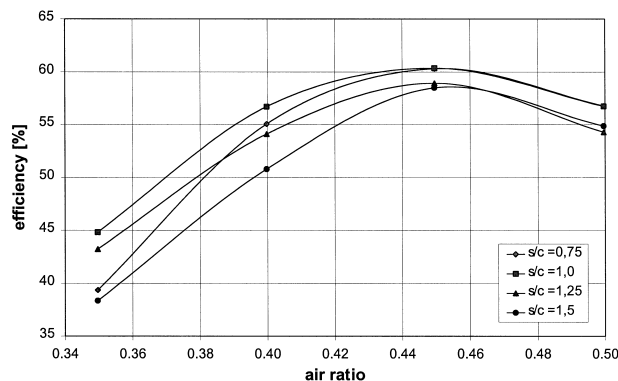


Fig. 6. (H₂ + CO) efficiency (LHV of H₂) of the reforming process in dependence on the s/c ratio and the air ratio, with air preheating [1].

(H₂ + CO) mole content in the dry product gas is about 1.3% higher than without air preheating. This difference is independent of the air ratio that is chosen. Due to the fact that the (H₂ + CO) efficiency is directly proportional to the (H₂ + CO) mole content, the same behaviour is noticed for the efficiency. The efficiency value in the preheating mode is about 4% higher than in the nonpreheating mode. Consequently, a heat exchanger to heat up the water and specially the air should be integrated.

The efficiency of the propane reforming process and the H₂ and CO mole content in the product gas in dependence on the power are illustrated in Fig. 5. The efficiency is calculated with the H₂ + CO mole stream in the product gas, in this case, the efficiency value base on the higher heat value (HHV) of hydrogen.

Eq. (5) defines the efficiency as calculated for the data in the Fig. 5:

$$\eta_{(H_2+CO)}(\text{HHV}) = \frac{n_{H_2} + n_{CO} \text{ HHV}(H_2)}{n_{C_3H_8} \text{ HHV}(C_3H_8)} \quad (5)$$

The efficiency increases from 59.6% to 74.6% if the propane inlet performance rises from 1.69 to 2.70 kW. Simultaneously, the H₂ and CO mole content grows from 33.3% to 39.2% in the dry product gas. The maximum efficiency has not been reached in this measurement, but a higher propane inlet flow was not realisable with the experimental equipment. The gradient of the both curves decreases but it seems to be possible to achieve higher

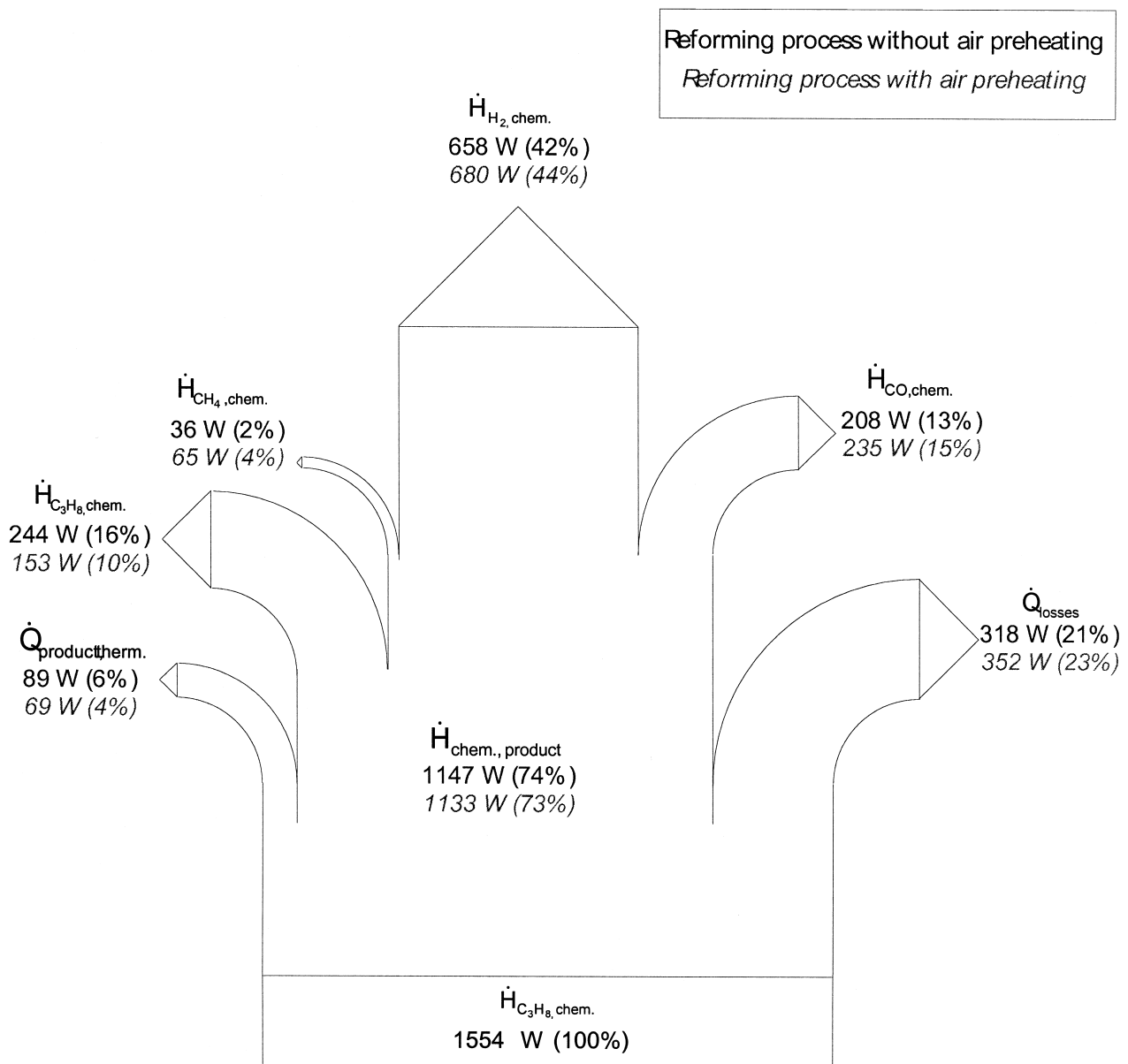


Fig. 7. Energy balance of the autothermal propane reformer with and without air preheating [1].

values at a power exceeding 2.7 kW. One limiting factor of this process is the temperature of the honeycomb catalyst in the POX zone due to the stability of the catalyst material. If the reformer is operated with an inlet performance above 2.7 kW, the temperature of the catalysts rises up to 900°C.

At 2.7 kW, the space velocity reaches a value of $4611 l_{\text{ducts}}/(l_{\text{catalyst}}h)$. This value is about 60% higher than the space velocity in the design point. The hydrogen output of the reformer reaches about 1.70 kW.

The ($H_2 + CO$) efficiency, which is presented in the Fig. 6, relates to the lower heating value of H_2 . The air ratio is varied in a range from 0.35 to 0.49 and the s/c ratio in a range from 0.75 to 1.5 during the measurements. For all curves, a common point at an air ratio of 0.45 is observed.

This value seems to be independent of the duct temperature because the same result is noticed if the reforming process works without air preheating. The best results are reached at an air ratio of 0.45 and an s/c ratio of 1.0. There, the efficiency value is 60.3%, whereas in the designed point, the efficiency reaches only a value of 56.7%.

The energy balance is represented in the Fig. 7. The lower numbers (in italics) show the energy values of the reformer in operation mode with air preheating, the upper numbers represent the reforming process without air preheating. The inlet performance of the propane flow is calculated with the lower heating value. It should be mentioned that the propane conversion increases from 84% to 90% if the air stream is preheated. The higher air stream temperature results in a higher temperature of the metal honeycomb catalyst and thereby improved kinetics of the reforming reaction. These results are confirmed by the content of the hydrogen and carbon monoxide in the product gas, corresponding to a higher equilibrium temperature.

Table 3 shows the temperature of the honeycomb catalyst and the temperature of the ducts at the inlet area of the reformer.

Moreover, the Sankey diagram illustrates that the efficiency shall be improved if the isolation of the reformer will be optimised reducing heat losses. The reforming process in the air-preheated mode has about 10% higher heat losses compared with the nonpreheated process.

The efficiency of the chemical conversion of propane during the reforming process is determined by the ratio of chemical energy of the propane and the chemical energy of the product gas. The efficiency of the nonpreheated process reaches 74% and is absolute 1% higher than the preheated process. The energy content of the hydrogen and the carbon monoxide, which both shall be used (as hydrogen) in the fuel cell system, reaches 59% in the case of the preheated system which is 4% more than the nonpreheated operation.

3. Conclusion

During the construction phase of the propane reformer, the compact design has been one main target. Therefore, the vaporiser, the heating system for the duct stream and the CO shift steps are integrated in the reformer. The hydrogen output of the reformer reaches about 1.70 kW with a metal catalyst honeycomb volume of 287 cm³. The complete system with the reformer, the CO shift steps and the heat exchanger has a diameter of 100 mm and a height of 600 mm.

The influence of different parameters on the propane reforming process has been investigated. At first, the operation mode with or without air preheating has been tested. In the case of preheating operation mode, the air flow is mixed with the water and this stream flows together over the vaporiser to the reformer; in the other case, the air directly streams into the reformer. The preheated operation mode is favoured because the H_2 - and CO mole content in the reformer product gas raises up to about 34%, which is 1.3% as in the nonpreheated mode. Therefore, the efficiency is also around 4% higher. The higher inlet air temperature leads to a higher temperature level in the reaction zone, which improves the kinetics of the reforming reaction.

Furthermore, the influence of the air ratio has been investigated. The measurements show that the variation of the air ratio has a great effect on the operation results of the propane reforming process. The best results are noticed at an air ratio of $\lambda = 0.45$. In this operation point, the reformer reaches the maximum of propane conversion, the highest outlet performance, the maximum of the H_2 - and CO volume stream in the reformer product gas and the highest efficiency.

During the s/c ratio variation, it was not possible to recognise a great influence on the characteristic performance data. The best results are reached with an s/c ratio of 1.0.

The efficiency of the propane reformer is about 75% (based on the HHV of hydrogen) in the investigated power range. By improvement of the isolation of the reformer and operation at higher power, an increase in efficiency will be possible.

Table 3
Temperature distribution in the propane reformer

	With air preheating [°C]	Without air preheating [°C]
Duct temperature	255	108
Honeycomb inlet temperature	836	820
Honeycomb outlet temperature	638	631

4. Nomenclature

SV	space velocity [$l_{\text{ducts}}(l_{\text{catalyst}} h)$]
LHV	lower heat value [J/mol]
HHV	higher heat value [J/mol]
P	performance [W]
p	pressure [bar]
s/c ratio	steam to carbon [$\text{mol}_{\text{steam}}/\text{mol}_{\text{carbon}}$]
POX	partial oxidation

$\eta_{(\text{H}_2\text{O}+\text{CO})}(\text{LHV})$	efficiency based on the LHV of hydrogen and propane
$\eta_{(\text{H}_2\text{O}+\text{CO})}(\text{HHV})$	efficiency based on the HHV of hydrogen and propane

References

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