

Gasification of diesel oil in supercritical water for fuel cells

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Abstract

Experiments have demonstrated the reforming of hydrocarbons in supercritical water. The hydrocarbons were reformed in a continuously operated tubular V4A reactor. The influences of four different commercial steam reforming catalysts were analysed. The experimental results showed that *n*-decane can be converted to a hydrogen-rich gas. Furthermore, experiments with diesel oil showed the possibility of fuel conversion at low temperature with commercial steam reforming catalysts. Low temperatures and the use of catalysts lead to inhibition of coke formation during the process. The supercritical reforming offers the possibility of a new low temperature hydrocarbon conversion process to hydrogen for fuel cell applications.

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1. Introduction

Until now, there have been controversial discussions about possible fuel for the use in low temperature fuel cells. The most prominent candidates are hydrogen, methanol and beside these, petrol and heavy oils. Although the availability of hydrogen is low compared to petrol and heavy oils, hydrogen is favoured because of its possible direct use. On the other hand, the storage and the infrastructure of hydrogen are more complicated. Therefore the industry conducts activities into the use of methanol as fuel. Today a direct methanol fuel cell for all applications is not available. The methanol has to be converted to hydrogen by reforming processes. The advantage of the reforming process is that besides methanol, heavy oils and, in view of sustainability, biomass seem to be alternative fuels. The major draw back is that the reforming process, especially of heavy oils, needs high temperatures and therefore the effectiveness of the overall system will be lowered. To overcome these problems reforming methods, other than the conventional, should be taken into account, such as those working at lower temperatures.

Supercritical water is an environmentally friendly medium and is well known in industry and science. Thermo physical properties of supercritical water such as density, viscosity, relative permittivity and hydrogen bonding are quite different from those of steam or liquid water [1]. In contrast to the

liquid state, the mixing of supercritical water with non-polar gases and organic compounds containing large, non-polar groups is generally possible [2]. Gasification of hydrocarbons in supercritical water is based on the characteristics that supercritical water acts not only as a solvent but also as a reagent [3]. Table 1 gives a compared overview for density ρ , dynamical viscosity η and static dielectricity ϵ of the liquid, gaseous and supercritical aggregate state.

The purpose of the reforming process is the fuel conversion into a hydrogen-rich product gas using supercritical water and a catalyst at low temperatures like normal reforming processes.

2. Experimental

Experiments have been carried out in a continuous flow reactor. Fig. 1 shows a schematic view of our laboratory scale apparatus. This supercritical water flow reactor system consists of two separate reactors. Water is transferred in the supercritical state in the first reactor. The hydrocarbons are then added to this supercritical water and the reforming process takes place in the second flow reactor. This procedure prevents the formation of coke or slag, because the solubility of hydrocarbons is complete in supercritical water. The second reactor offers the possibility for a simple replacement of tested catalysts. The reaction conditions, like reaction time and mixture ratio were controlled by high pressure pumps.

For process simulation *n*-decane (>99%, ACROS) was used as a diesel model compound. The *n*-decane reforming

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Table 1
Density, dynamical viscosity and static dielectricity of water in different aggregate states

	Liquid (25 °C, 0.1 MPa)	Supercritical (400 °C, 25 MPa)	Gaseous (400 °C, 0.1 MPa)
ρ (g cm ⁻³)	1	0.17	0.0003
η (mPa s)	0.89	0.03	0.02
ϵ	78	5.9	1

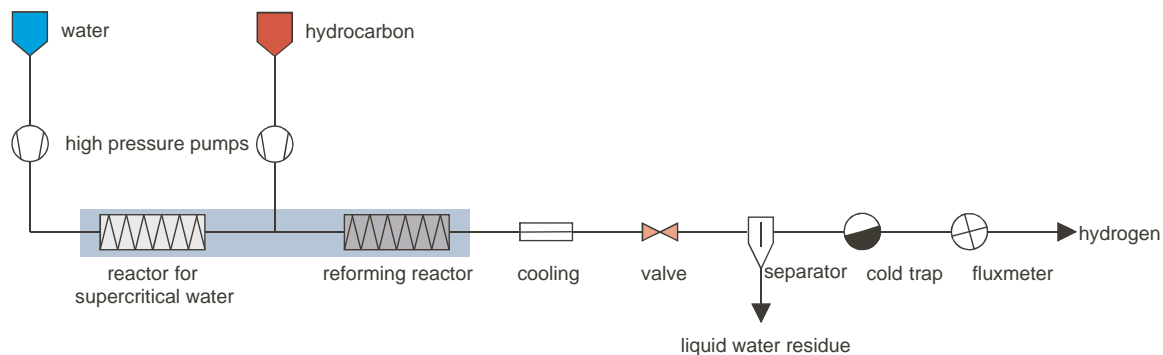


Fig. 1. Schematic of supercritical water reactor.

Table 2
Comparison of the catalysts used

	Probe A	Probe B	Probe C	Probe D
Typical feed	Naphtha, natural gas, LPG	Natural gas	Naphtha	Methanation
Weight fraction (wt.%)				
NiO–nickel oxide	45.2	>1	20	32.4
MgO–magnesium oxide	12	–	12–16	–
K ₂ O–potassium oxide		–	8.5	–
CaO–calcium oxide			8–10	4
SiO ₂ –silicon oxide	10		14–16	
Al ₂ O ₃ –aluminium oxide	10		30–40	Variable
Carrier		CaAl ₁₂ O ₁₉ –calcium-aluminate	Calcium-aluminate	
Shape	Tablets	Ring	Ring multi-hole	Spheres
Catalyst-volume (ml)	0.072			0.047
Catalyst-surface (mm ²)	95			64
Bulk density (kg l ⁻¹)	0.95–1.0	0.9	1.0	1.0
Mass of catalyst in the reactor (g)	15.0	15.9	14.8	13.4

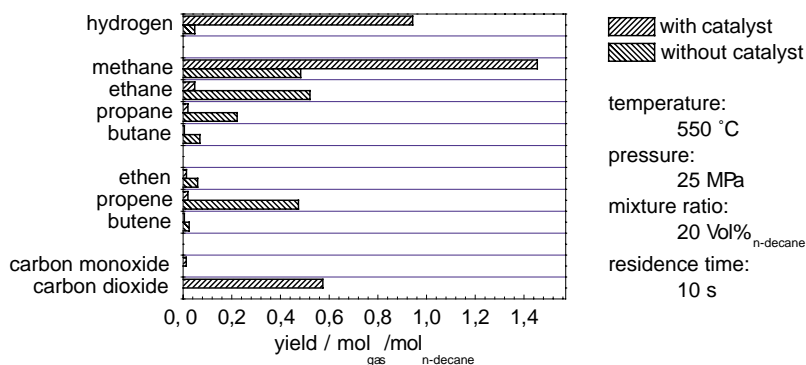


Fig. 2. Gas yield as function of mols of *n*-decane used and dependence on catalyst.

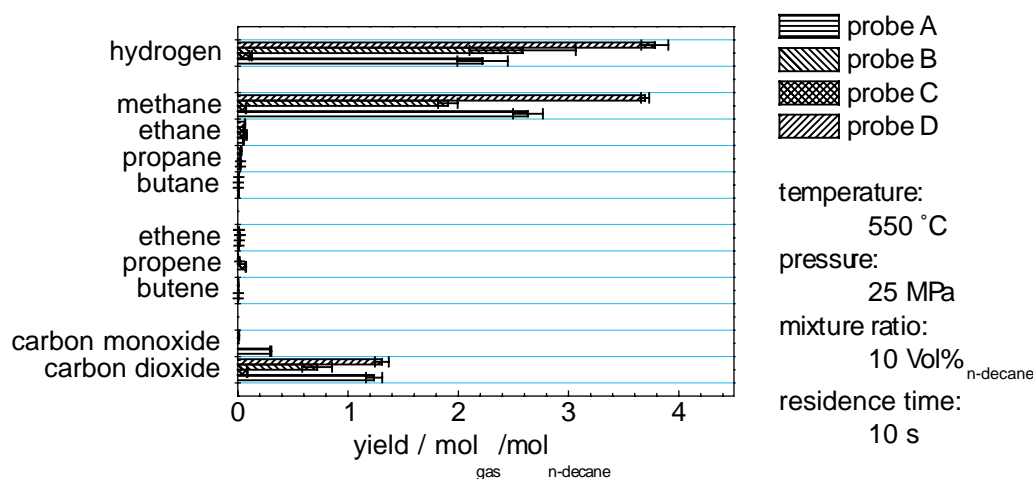


Fig. 3. Gas yields from different commercial catalysts.

process was investigated by different commercial catalysts to find the optimal substances for the reforming process. The catalyst used for the diesel fuel gasification process was (Greenergy Conti Deutschland GmbH).

To determine the influence of a catalyst on the process, four different commercial catalysts, well known from steam reforming process, were selected. These catalysts differ mainly in their typical feed and the weight fraction of nickel oxide (Table 2). These materials were used without a previous conditioning. Furthermore influences of these catalysts were investigated by constant reaction conditions. The process temperature (550 °C) and pressure (25 MPa) were constant during the experiments. The volume fraction of *n*-decane was constant at 10 vol%. This was in agreement with a steam to carbon ratio of 9.6.

The product gas samples were immediately analysed using high-pressure gas chromatography and the liquid samples by high-pressure liquid chromatography.

3. Results and discussion

Our first experiments without any catalysts were carried out to investigate the oxidizing behaviour of supercritical water. The results show that hydrocarbons on their own can be cracked with supercritical water.

Fig. 2 clearly shows that the use of a catalyst increases the hydrogen yield compared to a process without catalyst. Furthermore it is possible to convert hydrocarbons to a hydrogen rich gas without any oxidizing agent like air. This prevents the formation of NO_x which can inhibit the catalyst activity.

In a number of experiments the process parameters were optimised for the reforming of *n*-decane. Comparing the hydrogen yields, one can see that the yield increases in relation to the catalyst composition (Fig. 3). However, the tested catalysts are not optimised for supercritical reforming. A maxi-

mum hydrogen yield was observed with catalyst D, followed by B and D and by C.

Additionally, the comparison of conversion shows that probe D has the best performance in supercritical *n*-decane reforming. More than 80% of *n*-decane was converted to hydrogen and methane. Fig. 4 shows the reaction conversion as a function of catalyst materials.

The comparison of the composition of the two best catalysts (probe A and D) come to the conclusion that the potassium oxide (probe D) leads to a higher hydrogen yield. This positive influence of alkaline or alkaline earth metals probably does not occur by a partial oxidation process alone [4] but also by supercritical reforming. Furthermore experimental results show that carbon monoxide formation is almost suppressed because of the high steam to carbon ratio.

This investigation of the extensive influence on the carbon monoxide concentration is confirmed by the work of Taylor et al. [5].

These experimental conditions were now used for diesel fuel reforming. First experiments showed that the residence time has to be higher than for *n*-decane reforming. Highest yields were obtained with a residence time of 40 s instead of 10 s for *n*-decane. Fig. 5 shows a comparison of the different product yields depending on the use of catalyst. These

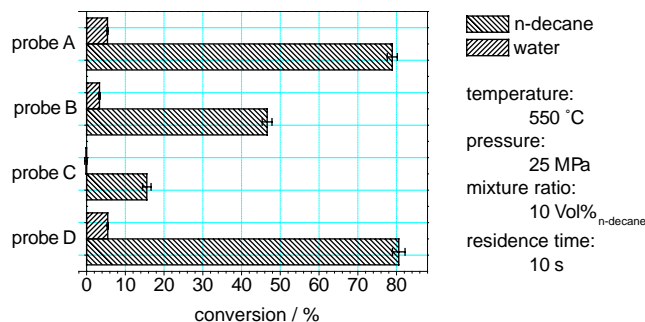


Fig. 4. Conversion dependence on different commercial catalysts.

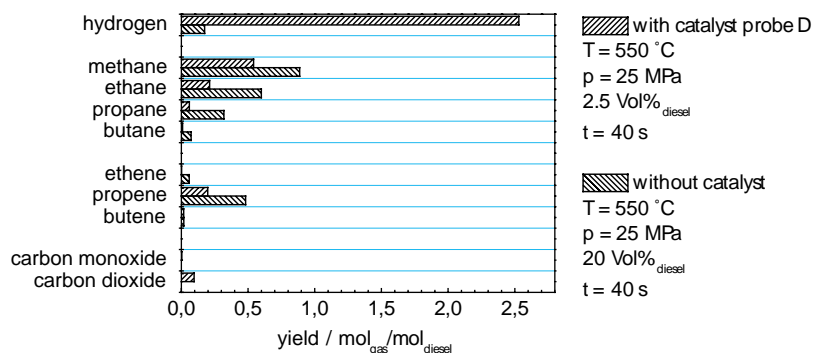


Fig. 5. Comparison of yield as a function of catalysts and mixture ratio.

experimental results show that diesel can be converted to a hydrogen rich gas.

The reforming processes of *n*-decane and diesel take place without an external feed of oxidizing agent. Besides, the coke formation (which is a pervasive problem in steam reforming process) was inhibited. These experimental results confirmed the work of Rostrup-Nielsen, that formation of coke can be depressed by contacting steam and fuel with a reforming catalyst at relatively low temperatures [6,7]. Furthermore the rate of char-forming polymerization reactions is also inhibited.

4. Conclusion

Supercritical reforming of hydrocarbons offers a possible way to convert hydrocarbons at lower temperatures than in conventional industrial reforming processes. The experimental results show that the hydrogen yield increases by using commercial catalysts even if they are not yet optimised for these conditions. On the basis of these experiments we strongly support, that diesel, heavy oils or biomass could be

reformed with satisfying H₂-yields using supercritical conditions.

Acknowledgements

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