

REACTION OF ALCOHOLS WITH SUPERCRITICAL WATER

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The reaction of alcohols (methanol, ethanol, 1-propanol and 2-propanol) with supercritical water was studied in tubular reactors made of alloy 625. Almost complete conversion was observed at 600° C and 25 MPa. The composition of the product gas strongly depends on the reaction parameters, mainly on temperature, residence time and feed concentration. Main products are hydrogen, methane and carbon dioxide.

The study showed a strong influence of the reactor wall composition on the conversion and the product gas composition (catalysis by the metals of the reactor wall). Complete conversion could only be achieved if the reactor surface was pre-treated with dilute hydrogen peroxide solution at about 600 °C and 25 MPa. The conversion was considerably lower without this pre-treatment. Methanol reforming was stable for several hundreds of hours without any significant change in conversion and product gas composition. The conversion and the hydrogen yield decreased with increasing test time for the reaction of ethanol and propanol with supercritical water.

Small amounts of potassium carbonate (about 100 ppm of potassium) will be sufficient to slow down the aging of the catalytically active reactor wall. At the same time, the occurrence of larger amounts of carbon monoxide in the product gas is suppressed; the potassium salt obviously catalyzes the water gas shift reaction. However, the salts cause some corrosion. In a few tests, the thin-walled capillary inside the reactor used for monitoring the reaction temperature failed because of corrosion.

INTRODUCTION

There are two objectives for the work presented in this manuscript: the development of a process with small and compact reactors to produce hydrogen for fuel cells (PEMFC) by reforming of alcohols (preferential methanol) and the utilization of dilute organic matter for the hydrogen or methane generation in larger plants. This work is part of our R&D work on gasification of wet biomass in hot pressurized water.

In the last decade a lot of R&D work was done on the reforming of alcohols at low pressure, mainly methanol. The aim was the on-board generation of hydrogen for fuel cell powered vehicles. Methanol is easy to produce, to store and to transport using already existing techniques and can be distributed via the existing gasoline stations. Hydrogen can be produced on-board using a reforming reactor. Gasification of organic material in supercritical water was first investigated in the '70s in the USA [1,2]. Hydrothermal reforming of methanol provides hydrogen at high pressure for easy intermediate storage. The use of regenerative fuels like bio-ethanol for the reforming reaction is of general interest. Bio-ethanol is produced by fermentation of carbohydrates.

EXPERIMENTAL

The experimental setup and the analytical devices were described in [3,4]. The residence time values were calculated from the flow rate, the density of pure water under reaction conditions and the reaction volume. The pVT-data for the real multi-component system are not available,

the composition of the mixture will change during reaction as well. Calculating the residence time using the density of pure water will be a good approach at least for dilute solutions.

The reactor used for the reforming reaction of alcohols was made of alloy 625 or stainless steel SS316. To achieve the required short residence times, the volume of the reactor has been reduced by cylindrical rods made of alloy 625 or stainless steel SS316 ($d=8.0$ mm, $l=1000$ mm) resulting in an annular gap shaped reaction space (about 3 ml). The annular gap measured about 150 μm . Both types of reactors were pre-treated with hydrogen peroxide solution (3 wt.-%) at reaction conditions for about 50 hours [3,4]. A movable thermocouple placed inside a capillary tube (1/16 inch diameter) passed through a centric bore of this cylindrical displacer records the internal temperature profile of the reactor. The temperature gradient between centre of the displacer and fluid phase is assumed to be negligible. This capillary was made of alloy C276 or stainless steel SS316. The chemicals were p.a. grade by Merck.

RESULTS AND DISCUSSION

The experimental work started with a 5 wt. % methanol in water solution. The maximum experimental temperature was 600° C and the pressure 25 MPa. Total experimental time for the reforming of methanol was more than 1000 h. Several samples analyzed showed a stable operation concerning gas production, the results were reproducible. These results (the details are published in [3,4]) encouraged us to start a detailed research program.

The treatment with a solution of H_2O_2 in water (3 wt.-%) at 600° C and 25 MPa for about 50 hours turned out to be crucial for high conversion rates and high hydrogen yields. The conversion with a new reactor, which was not pre-treated with aqueous H_2O_2 -solution, was lower than with the 'oxidized' reactor. The analysis of the heavy metal concentration in the aqueous effluent during the H_2O_2 pretreatment showed that chromium and molybdenum are oxidized and preferably dissolved from the inner surface of the reactor. The speciation of chromium in the aqueous effluent showed only Cr(VI). Analysis of the catalytically active surface with the SEM/EDX method revealed that some of the nickel-oxides formed after treatment with H_2O_2 have been reduced during the gasification reaction to pure nickel. Nickel oxides and nickel are presumably the catalytically active compounds.

To compare the catalytic effect of the alloy 625 to that of SS316 (the most common materials for high pressure lab-scale reactors), some of the experiments were done in a reactor made of stainless steel SS316 with displacers made of SS316. The reactors made of stainless steel SS316 showed poor performance, the methanol conversion and as a consequence the hydrogen yield at 600° C are low [4].

The conversion products of the reaction of methanol with supercritical water in all cases were hydrogen, carbon dioxide, carbon monoxide and methane. The net effect of the variation of residence time on the gas yield (mol gas / mol methanol in the feed) at 600° C using an aqueous feed concentration of 26 wt.-% methanol is illustrated in figure 1. The conversion of methanol (determined by analyzing the TOC of the aqueous effluent) was higher than 98 %.

The maximum value of 2.4 for the hydrogen yield at about 5 s is caused by increased hydrogen amount due to the water gas shift reaction and the following decrease due to hydrogen consumption by methanation. Carbon monoxide yield at low residence times is up to 0.5. The concentration of carbon monoxide and carbon dioxide is mainly determined by the water gas shift reaction.

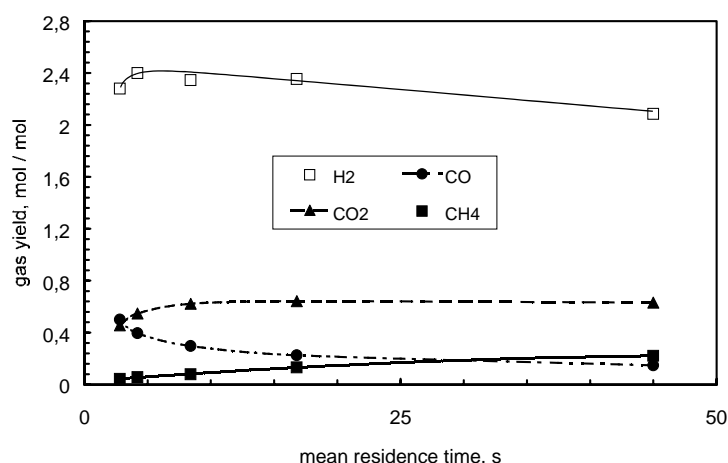


Figure 1: Gas yield (mol gas / mol methanol in the feed) as a function of mean residence time. Experimental conditions: $T=600^{\circ}\text{C}$, $p=25\text{ MPa}$, aqueous methanol concentration 26 wt.-%, reactor material alloy 625 with displacers made of SS316.

Experiments at lower temperatures showed lower conversion of methanol, temperatures of about 600°C are requested for complete conversion. In the experiments at 400°C , traces of methanol and formic acid could be detected in the effluent. These compounds are assumed to be intermediates in the formation and reforming of methanol.

Calculation of the gas yield in equilibrium at 600°C and 25 MPa results in the values given in table 1. The gas composition is not in equilibrium even for longer residence times. Using a reactor with pure nickel surface lead to a gas composition which was closer to the equilibrium state for longer residence times.

Table 1: Equilibrium gas yield for the reaction of methanol (26 wt.-%) with water at 600°C and 25 MPa, calculated with the Equitherm V. 5.06 code.

CO2	CH4	CO	H2
0,36	0,63	0,01	0,47

The material of the cylindrical displacers was changed to alloy 625 for studying the reforming of ethanol. The reactor was pre-treated with aqueous hydrogen peroxide solution as described before. After some ten hours the pressure drop in the reactor increased, the test had to be stopped because of clogging. Inspection of the tube and the displacers showed that the clogging was caused by soot deposition in the heating-up section of the reactor. The test was repeated several times. Figure 2 shows the time dependence of the gas composition and the TOC values for one of these tests. Carbon monoxide concentration increased with test time (up to about 6 vol. %), carbon dioxide concentration decreased. The conversion became lower with increasing test time, as can be seen by the rising TOC values. The time until clogging was about 45 hours for this test.

Soot formation could not be reduced by prior degassing the feed with ultrasound and sweeping with nitrogen to remove the main part of oxygen. Most of the soot was deposited at a distance of 22 to 32 cm from the reactor inlet, corresponding to a temperature of about 450 to 600°C . The deposit was analyzed by the SEM/EDX method, the components were carbon and small quantities of heavy metal oxides caused by reactor corrosion.

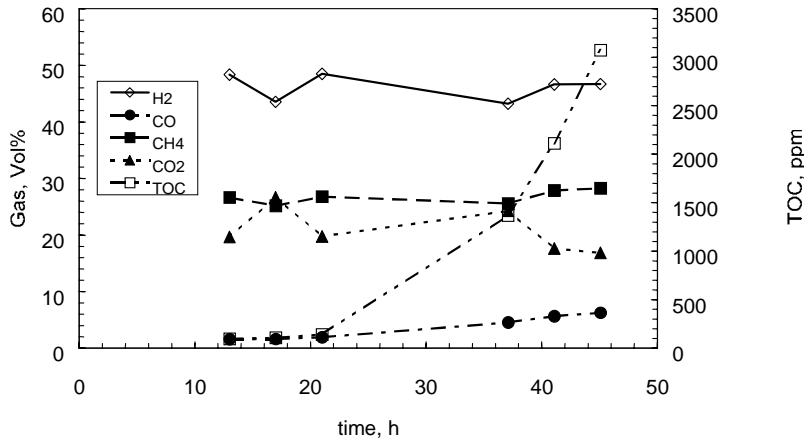


Figure 2: Gas composition and TOC as a function of test time. Experimental conditions: $T=600^{\circ}\text{C}$, $p=25\text{ MPa}$, aqueous ethanol concentration 14 wt.-%, reactor material alloy 625 with displacers made of alloy 625.

The reactor tube and the displacers were first cleaned mechanically with brushes, sandpaper, by an ultrasound cleaner and washed with methanol before re-assembling. The reactor was then pre-treated with aqueous hydrogen peroxide for about 50 hours. Experience showed that careful cleaning could extend the period of stable operation to about 50 hours without significant loss of conversion.

Table 2: Equilibrium gas yield for the reaction of ethanol (30 wt.-%) with water at 600°C and 25 MPa, calculated with the Equitherm V. 5.06 code.

CO ₂	CH ₄	CO	H ₂
0,63	1,35	0,02	0,57

Short-time experiments (some ten hours of operation) were performed with the freshly cleaned reactor. The results for the reaction of a 30 wt.-% ethanol solution are shown in figure 3. For residence times longer than 10 s, a constant gas yield is reached. The measured gas yields correspond to the calculated values (table 2). TOC of the effluent was below 100 ppm. Experiments with varied feed concentration showed an increase of methane yield and decrease of hydrogen yield for concentrated feed solutions.

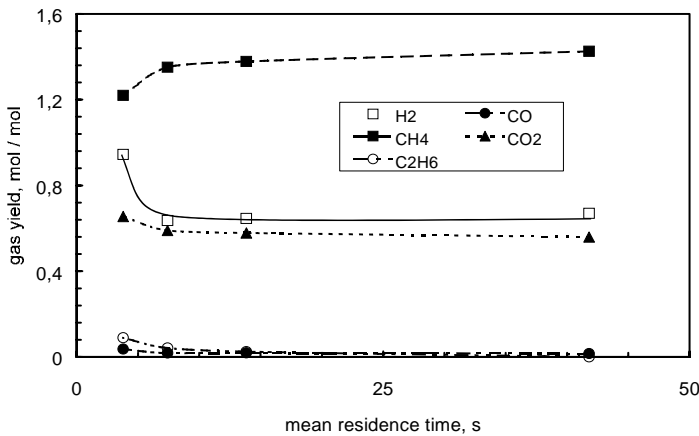


Figure 3: Gas yield as a function of mean residence time. Experimental conditions: $T=600^{\circ}\text{C}$, $p=25\text{ MPa}$, aqueous ethanol concentration 30 wt.-%, reactor material alloy 625 with displacers made of alloy 625.

At short residence times, considerable amounts of ethane are detected. In [5] the appearance of ethene and ethanal as intermediates are reported for the non-catalyzed ethanol reforming reaction in quartz tubes. Ethene could react by hydrogenation to form ethane. The period of

stable operation could be prolonged to a few hundred hours if small amounts of potassium carbonate (100 ppm K) were added to the aqueous feed. At the same time, the occurrence of larger amounts of carbon monoxide in the product gas is suppressed; the potassium salt obviously catalyzes the water gas shift reaction or boosts the catalytic activity of the reactor wall (figure 4). However, the salts have a slightly negative effect on the corrosion resistance. In a few tests, the thin-walled capillary inside the reactor used for monitoring the reaction temperature failed because of corrosion. This occurred for both capillary materials tested (alloy C276 and SS316). In other experiments, the test was stopped because of clogging, but the time of operation was several times the operation time without potassium additive. Conversion was high for the total operation time.

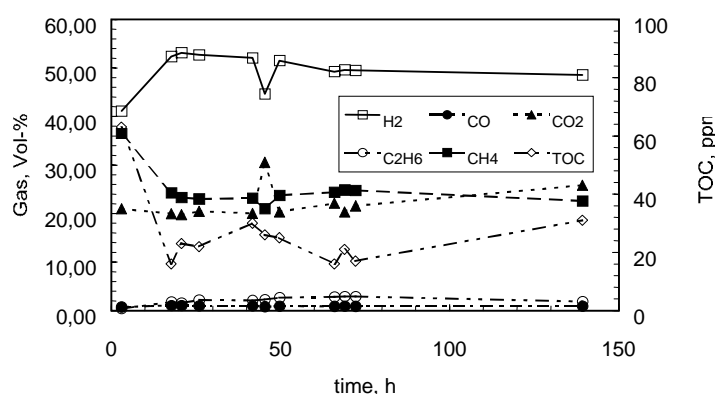


Figure 4: Gas concentration and TOC as a function of test time. Experimental conditions: T=600° C, p=25 MPa, aqueous ethanol concentration 14 wt.-% with 100 ppm K (K₂CO₃), reactor material alloy 625 with displacers made of alloy 625.

Short-time experiments for the reforming of both propanol isomers (1-propanol and 2-propanol) were conducted in a reactor made of alloy 625 without addition of potassium carbonate. Feed concentrations used were 5, 13 and 26 wt.-%. The results with 2-propanol were similar to that for ethanol, except that the methane yield is higher. The results for the reaction of 1-propanol are different for short residence times. Ethane concentrations up to 6 vol.-% are measured (figure 5). Ethane concentration rapidly decreases with rising residence time. At the same time, double the quantity of methane is formed according to equation (1).

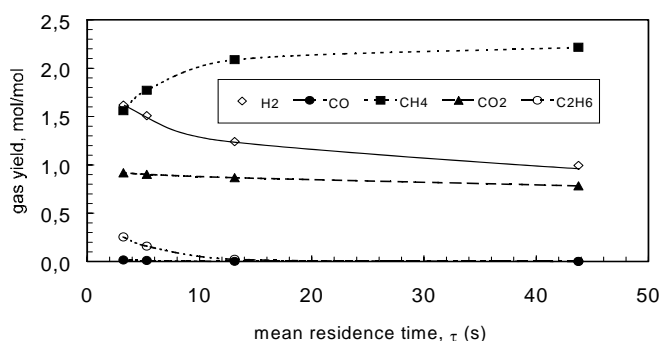
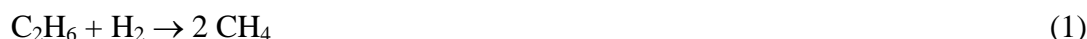


Figure 5: Gas yield as a function of mean residence time. Experimental conditions: T=600° C, p=30 MPa, aqueous 1-propanol concentration 13 wt.-%, reactor material alloy 625 with displacers made of alloy 625.

The gas composition and therefore the gas yield for residence times above 15 s is identical for both propanol isomers. The main component of the product gas is methane, as calculated by thermodynamical computation. The conversion for all residence times measured (computed using gas composition and gas flow) is 100% ± 10% reflecting the tolerances of the analytical, mass and gas flow measurements. The TOC values of the effluent were less than 100 ppm indicating a complete conversion of the alcohols to gas.

In the experiments with aqueous ethanol or propanol feed, the measured gas composition converges towards the equilibrium values for higher residence times. The gas composition in the presented experiments for the reforming of methanol differs from calculated equilibrium values even for higher residence times. One reason is the different material of the cylindrical displacers (SS316 in the case of methanol reforming, alloy 625 for the other experiments). This results in doubling the catalytically active area. The multiple oxidation/cleaning steps of the displacers could lead to a further enrichment of Ni at the surface (the tube was changed several times, the displacers were not). The displacers will be analyzed to verify this supposition. This is supported by the fact that experiments for the reforming of methanol in nickel-lined tubes with nickel displacers resulted in gas compositions much closer to the equilibrium composition.

CONCLUSION

Complete conversion to gas (hydrogen, methane, carbon dioxide and some ethane and carbon monoxide) was achieved at 600° C for aqueous methanol, ethanol and propanol solutions. Product gas composition and conversion is largely affected by the catalytic effects of the reactor wall. Thus tube material, history (cleaning, corrosion and deposits), geometry and factors like fluid dynamics and surface/volume ratio will influence the results. This makes it difficult to directly compare results for different plants.

Almost no soot formation appears for methanol feeds. The product gas composition was almost constant for several hundreds of hours. Reaction of higher alcohols results in some soot deposition mainly in the heating-up section; this poisons the catalytically active metals in the wall material. Soot formation can be reduced by adding small quantities of potassium carbonate to the aqueous feed.

The chemical structure of the alcohol affects the product gas composition at short residence times, when reaction kinetics controls the product distribution. Further experiments at lower temperatures may show intermediates explaining the varying behaviour of the different propanol isomers. At higher residence times, the rough product gas composition can be predicted by thermodynamic calculations.

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