Hydrothermal reforming of alcohols, pyroligneous acid and pyrolysis oil

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Hydrothermal reforming is a promising method to generate a product gas rich in hydrogen and methane. Feeds with a high water content and thus low calorific value can be used without any pre-drying or upgrading step. At hydrothermal conditions the organic compounds react with water to form a fuel gas. Depending on the educts, conversions at a hydrocarbon/water molar ratio up to 1:1 (for methanol, corresponding to a solution of 64 wt.-%) are possible; the residence times are in the range of a few seconds.

Reforming reactions were studied in laboratory scale in tubular flow reactors, the tube length was 1000 mm. The high pressure tubes were made of the nickel base alloy 625 or the stainless steel SS316. Experiments were performed at pressures of 25 up to 45 MPa and temperatures in the range of 400 to 700° C.

Bio-ethanol, pyroligneous acid and the water-soluble pyrolysis oil (often called 'bio crude oil') fraction are starting materials from renewable primary products. Bio-ethanol is generated by fermentation, pyroligneous acid and bio crude oil by thermo-chemical treatment of biomass.

Pyroligneous acid is a by-product from the production of charcoal and consists of about 75 % water, in which 12 % acetic acid and homologues, 2 % methanol, 1 % acetone and methyl acetate and about 10 % wood tar are dissolved. The production of bio crude oil delivers a water-miscible fraction with a lower calorific value whose use for conventional gasification procedures is not cost-effective, however is well suitable for hydrothermal reforming.

The product gas consists mainly of hydrogen and smaller amounts of methane, carbon dioxide and carbon monoxide. Decomposition, methanation and watergas-shift reaction are strongly influenced by the choice of the material of the inner reactor wall, the surface to volume ratio and addition of catalysts like potassium salts.

Introduction

The objective for this work is the development of a process with compact reactors to produce hydrogen for fuel cells (PEMFC) and methane by reforming of alcohols and dilute organic matter like pyroligneous acid. In the last decade a lot of R&D work was done on the reforming of alcohols, mainly methanol. The aim was the generation of hydrogen for fuel cell powered cars. One possibility for the storage of hydrogen on-board is the chemical storage as methanol. Methanol is easy to produce, to store and to transport using already existing techniques. Hydrogen can be produced on-board using a reforming reactor. Hydrothermal reforming of methanol provides hydrogen at high pressure. This technique enables the use of regenerative fuels like bio-ethanol for the reforming reaction. Bio-ethanol is produced by fermentation of carbohydrates.

Pyroligneous acid is a by-product of the charcoal production. The main component of pyroligneous acid is water (about 75 wt.-%). In industrial charcoal production, pieces of wood are carbonized in large-volume retorts (Römpp 1999, Winnacker-Küchler 1995). A series of complex decomposition reactions take place if wood is heated in the absence of oxygen above 100 °C. Up to 270 °C, the primary reactions are hydrolysis and isomerizations. At higher temperatures, secondary reactions predominate: the larger molecules are broken down and recombine by condensation and polymerization. Reaction water, methanol, acetic acid and pyrolysis oil are formed. The gaseous carbonization products are mainly hydrogen, methane and ethylene.

The highest charcoal yields are obtained by slow carbonization with a final temperature of about 400 °C. Short residence times (about 1 s) and temperatures between 450 and 500° C favour the formation of volatile products (flash pyrolysis). Flash pyrolysis of dry wood will result in about 65-70 wt-% of bio crude oil, 15-20 wt-% gas and 10-15wt-% of charcoal. The bio crude oil contains about 25 wt-% of water (Marquevich et al., 2003, Meier, 2003, Wang et al., 1997, Wang et al., 1998). Larger amounts of water decrease the suitability for storage of the bio crude oil. Water-rich fractions can be separated by fractional condensation in the pyrolysis plant. This leads to a bio crude oil with lower water content and thus higher calorific value. The water-rich fraction (water content > 50 wt-%), which has a composition similar to pyroligneous acid, is suitable for hydrothermal gasification.

Experimental

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) for the reforming of alcohols. The annular gap measured about 150 μm. For the experiments with pyroligneous acid, these cylindrical rods were placed only in the heating-up and cooling-down section of the reactor. The reaction volume amounts to 30 ml for this tubular reactor. Both types of reactors were pre-treated with hydrogen peroxide solution (3 wt.-%) at reaction conditions for about 50 hours (Boukis et al., 2003). 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.

A HPLC - pump (Bischoff Model 3010) compressed the aqueous feed solution with a flow rate of a few ml/min. Experimental pressure was up to 30 MPa. After reaction, the product mixture is expanded to atmospheric pressure by a backpressure regulator (Tescom) and the liquid and the gaseous phase are separated in a phase separator. Gas analysis was carried out by HP 5880 and HP 6890 gas chromatographs. In the liquid effluent, the residual total organic carbon (TOC) content was measured (Rosemount Dohrmann DC- 190 instrument).

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 is a good approach at least for dilute solutions.

Results and discussion

The experimental work started with an aqueous methanol solution. The maximum experimental temperature was 600° C and the maximum pressure 45 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.

The conversion products of the reaction of methanol with supercritical water in all cases were hydrogen, carbon dioxide, carbon monoxide and methane (Boukis et al., 2002, Diem et al., 2003). 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 better than 98 %.

The maximum value of 2.4 for the hydrogen yield at about 5 s is caused by the reverse effects of enhanced decomposition of methanol and water gas shift reaction, which will raise the hydrogen amount with increasing residence time, and the 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.
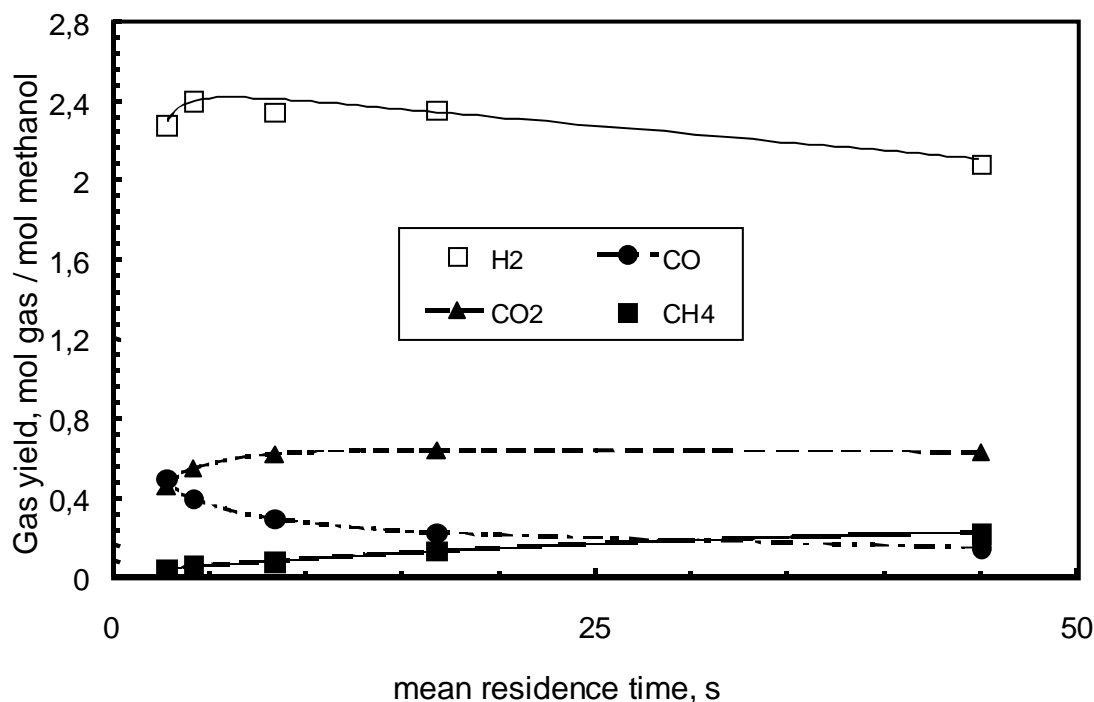

Figure 1: Gas yield (mol gas / mol methanol in the feed) as a function of mean residence time. Experimental conditions: T=600° C, p=25 MPa, aqueous methanol concentration 26 wt.-%, reactor material alloy 625 with displacers made of SS316.

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 methanal and formic acid could be detected in the effluent. These compounds are assumed to be intermediates in the reforming of methanol.

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 carbon 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.
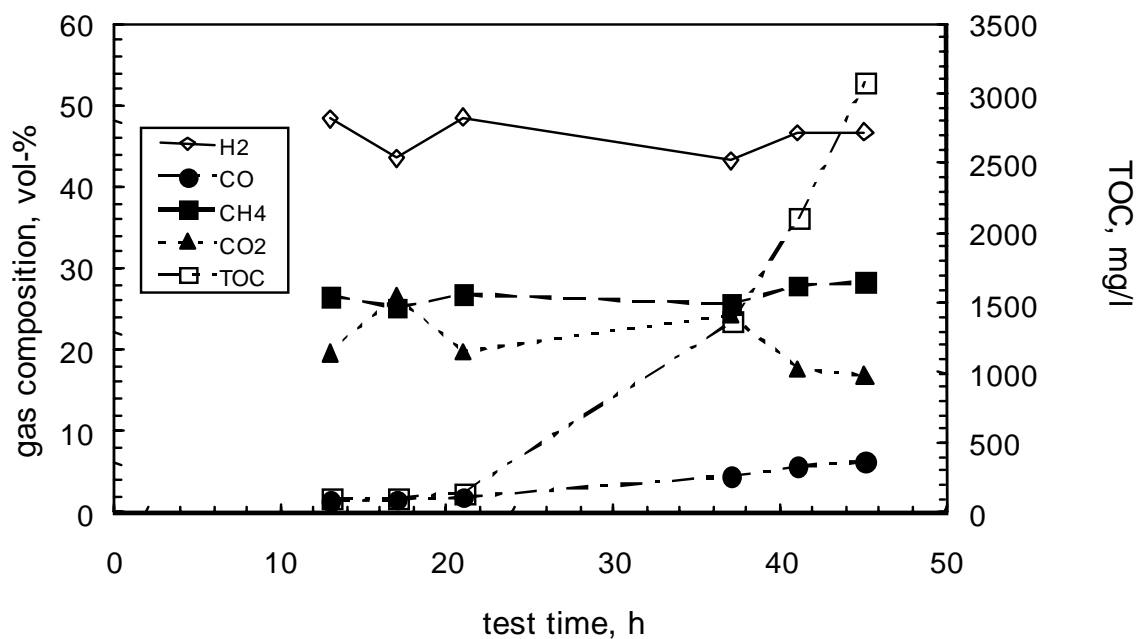
Figure 2: Gas composition and TOC as a function of test time. Experimental conditions: T=600° C, p=25 MPa, aqueous ethanol concentration 14 wt.-%, reactor material alloy 625.

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 composition is reached. The measured concentrations of the gaseous compounds correspond to the calculated equilibrium values (see figure 5). The TOC-value of the effluent was below 100 mg/l.

At short residence times, considerable amounts of ethane are detected. In Arita et al. (2003) 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.

Experiments with varied feed concentration showed an increase of methane yield and decrease of hydrogen yield for concentrated feed solutions. This was expected by thermodynamic calculations (see figure 5).

Figure 4 shows the gas composition for the reaction of ethanol (30 wt.-%) with water at 695° C. Higher temperatures favour the formation of hydrogen. For the short residence times the hydrogen amount is in the order of the methane amount. The drop in hydrogen concentration with increasing residence time is less pronounced than for the experiments at 600° C.
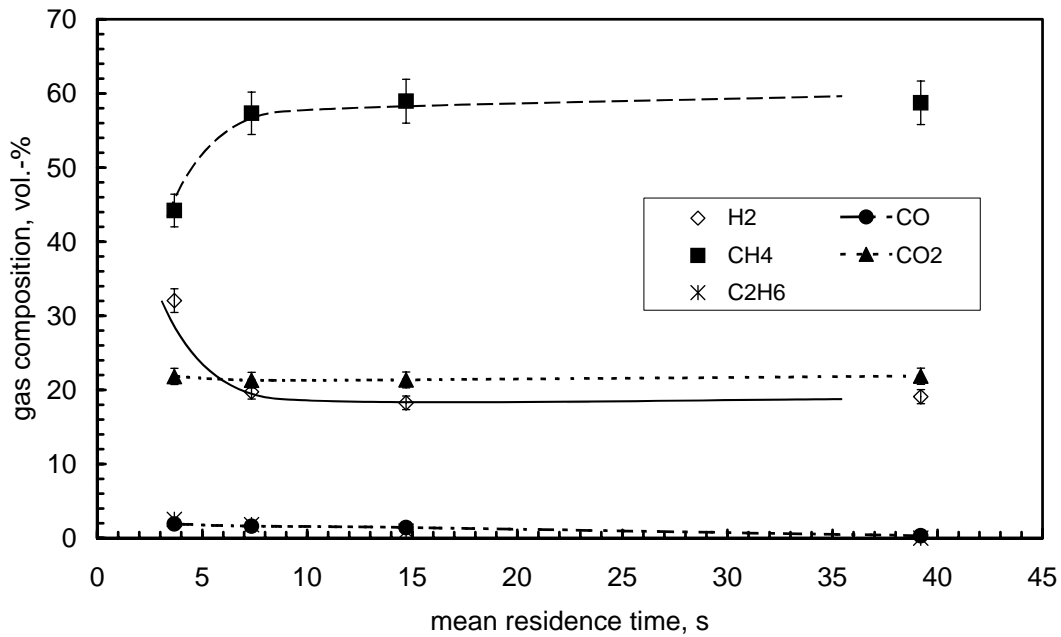
Figure 3: Gas yield as a function of mean residence time. Experimental conditions: T=600°C, p=25 MPa, aqueous ethanol concentration 30 wt.-%, reactor material alloy 625.

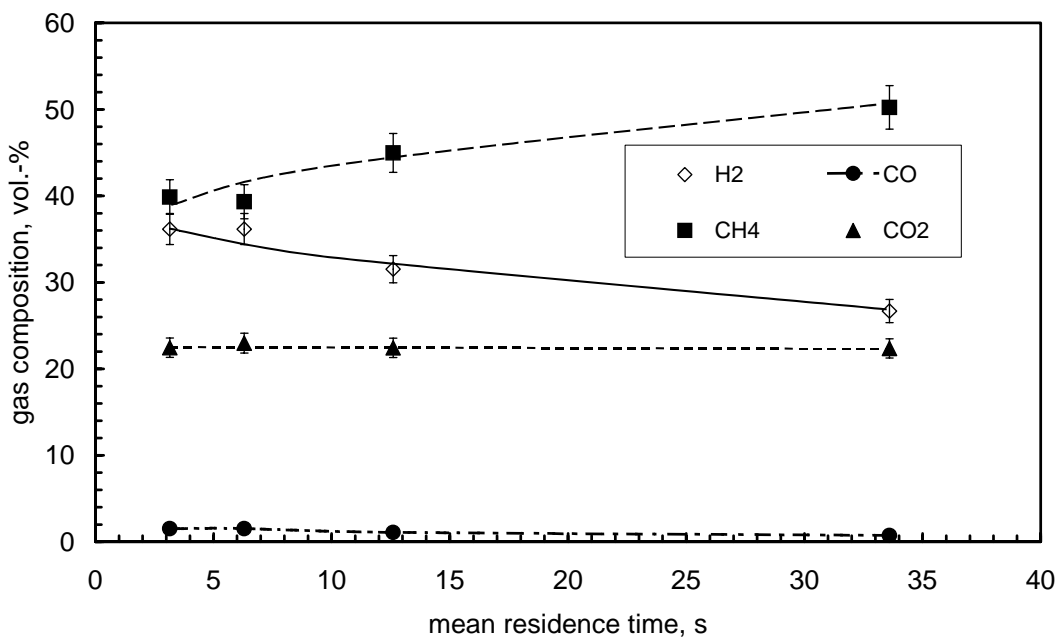Figure 4: Gas composition as a function of mean residence time. Experimental conditions: T=695 °C, p=25 MPa, aqueous ethanol concentration 30 wt.-%, reactor material alloy 625.

The period of stable operation could be prolonged to a few hundred hours if small amounts of potassium carbonate (100 mg/l K) were added to the aqueous feed. At the same time, the occurrence of larger amounts of carbon monoxide in the product gas for higher test times is suppressed; the potassium salt obviously catalyzes the water gas shift reaction and

conserves the catalytic activity of the reactor wall (figure 6). 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.
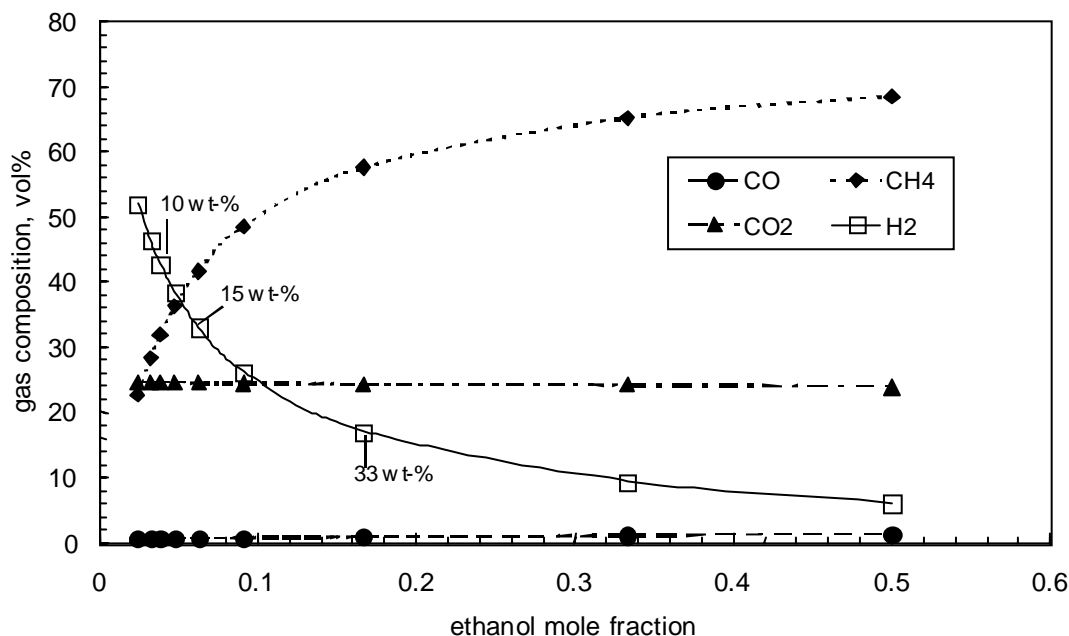

Figure 5: Equilibrium gas composition for the reaction of ethanol with water at 600° C and 25 MPa, calculated with ASPEN using the Peng-Robinson EOS.

The experiments on the gasification of pyroligneous acid showed that all organic compounds except some phenols are completely degraded at temperatures of 650° C and above (see table 1). Hydrogen concentrations in the product gas up to 50 volume-% can be realized (at 700° C). Carbon monoxide and ethane are in the range of 1 to 2 volume percent, carbon dioxide amounts to about 20 %, the balance up to 100 % is mainly methane.

Table 1: Reforming of dilute pyroligneous acid at 650° C and 25 MPa (addition of K_2CO_3 with 100 mg/l K).

	Dilute pyroligneous acid	Product aqueous phase
TOC	31445 mg/l	151 mg/l
Formic acid	2,27 g/l	48 mg/l
Acetic acid	31,9 g/l	6 mg/l
Formaldehyde	871 mg/l	0 mg/l
Phenols	1070 mg/l	160 mg/l

The addition of some potassium carbonate is strongly recommended for the reforming reaction of pyroligneous acid. Without this additive the conversion decreases sharply with reaction time. The aqueous TOC concentration increases, after about 10 h a small amount of an additional oil phase separates from the aqueous effluent. The hydrogen yield drops at the same time (see figure 7).
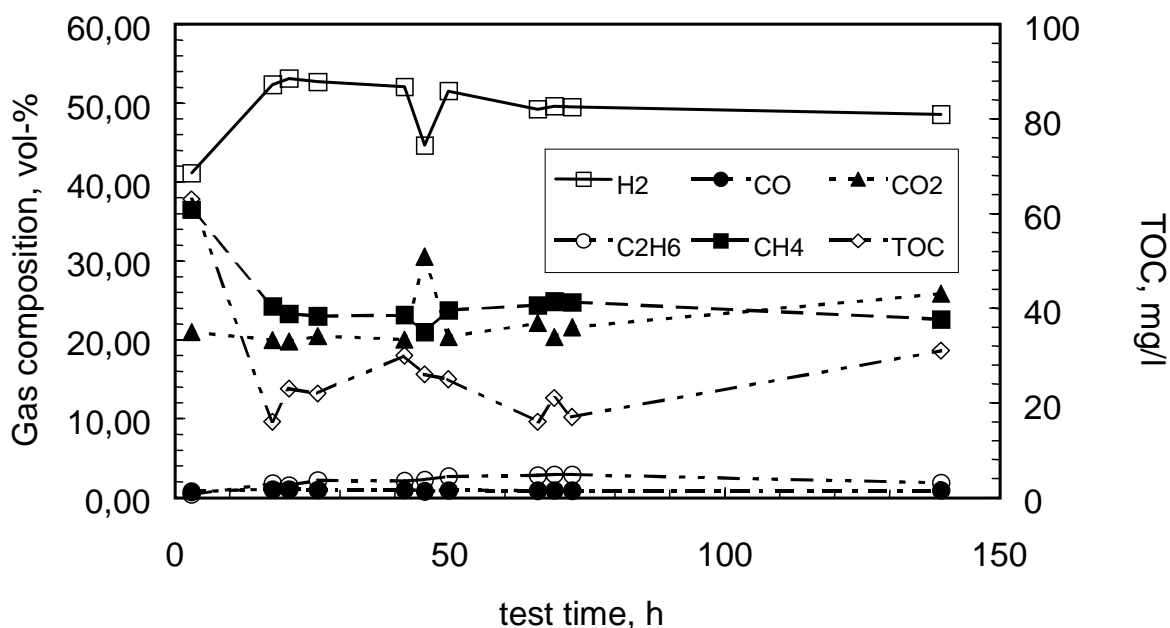
Figure 6: Gas composition and TOC as a function of test time. Experimental conditions: T=600° C, p=25 MPa, aqueous ethanol concentration 14 wt.-% with 100 mg/l K (K_2CO_3), reactor material alloy 625 with displacers made of alloy 625.

Conclusion

The hydrothermal reforming is suitable for the hydrogen and methane production of educts with high water content. The most part of the organic compounds of the feed is converted to gas, there is only low residual TOC in the aqueous effluent. A high water surplus favours the water-gas shift reaction and lowers the methane amount in the product. Complete conversion to gas (hydrogen, methane, carbon dioxide and some ethane and carbon monoxide) was achieved at 600° C for aqueous methanol and ethanol 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. 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 carbon deposition mainly in the heating-up section. Carbon formation can be reduced by adding small quantities of potassium carbonate to the aqueous feed.

Temperatures of 650° C and addition of some potassium carbonate is needed for the reforming reaction of pyroligneous acid to get almost complete conversion to gas. About 50 volume-% of hydrogen can be achieved at 700° C.
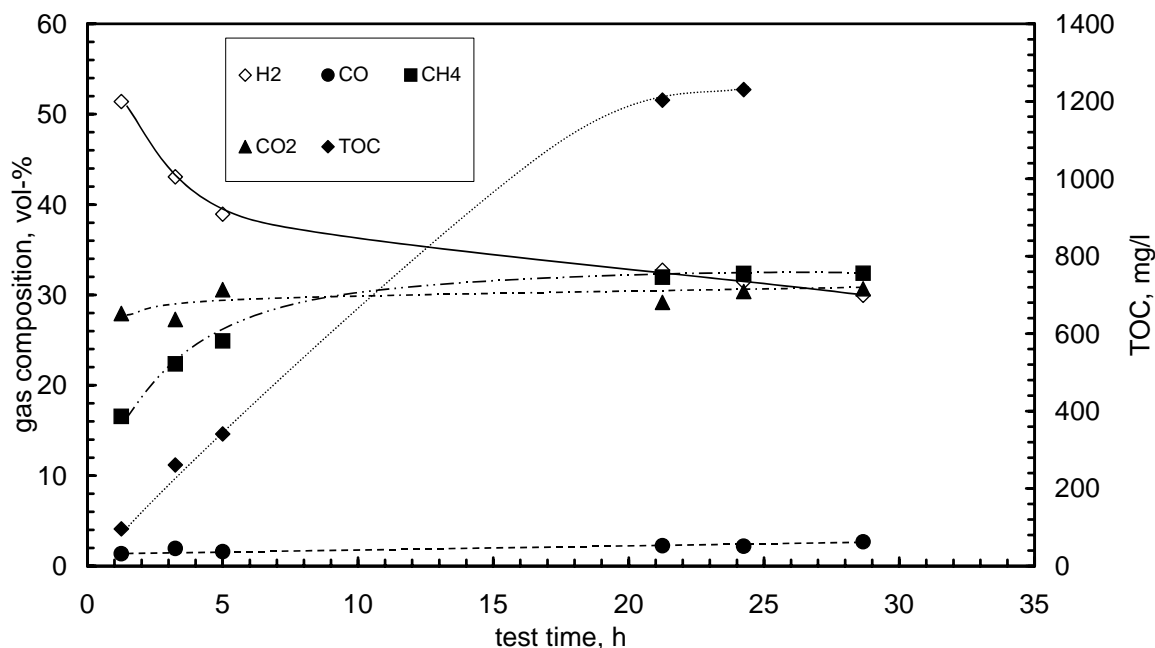

Acknowledgement

Figure 7: Gas composition and TOC for the reforming of pyroligneous acid as a function of test time. Experimental conditions: T=650° C, p=25 MPa, feed dilute pyroligneous acid (TOC 28470 mg/l) without addition of K_2CO_3, reactor material alloy 625.

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