Efficient production of synthetic natural gas from biomass by hydrothermal gasification

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Summary

Biomass can be effectively converted to synthetic natural gas (SNG) in a hydrothermal environment. Lower temperatures favor the production of methane rather than hydrogen. At around 420°C, catalysts are needed to ensure reasonable rates of reaction. They are tested in a new rig in terms of activity, selectivity and stability. Experiments were carried out using different feeds, such as ethanol and synthetic liquefied wood. A ruthenium doped Raney Ni catalyst exhibited an improved stability over an undoped one.

Introduction

Biomass may be converted to a variety of energy forms, including heat, electricity and fuels. Synthetic natural gas (SNG), a renewable energy carrier that produces few atmospheric pollutants and generates less carbon dioxide per unit mass than fossil fuels, is an attractive alternative.

"Hydrothermal" designates an aqueous system at elevated pressures and temperatures, especially near the critical point of water (374°C, 22.1 MPa) or above it. The hydrothermal route to convert wet biomass to SNG makes the energy intensive need to dry the feedstock before thermal conversion obsolete. Thermal process efficiencies for wood-to-methane as high as 70% can be expected (Vogel and Waldner 2005).

According to thermodynamics, methane is preferably formed at lower temperatures (below 600°C), whereas at higher temperatures hydrogen is the main product, besides CO_2 . The thermodynamic equilibrium concentration of methane at 400°C and 30 MPa depends on the feed concentration (see Figure 1). It reaches maximum values of 49% for feed concentrations exceeding 20 wt%, corresponding to a max. yield of 0.33 g CH₄/g wood (dry ash-free).



Fig. 1: Equilibrium gas concentration at 30 MPa (Peng-Robinson equation of state used) for different temperatures and wood concentrations.

At temperatures around 400°C, a catalyst is needed to increase gasification rates. The catalyst of choice must be active for methane formation over a long period, avoid side-products and especially be stable under hydrothermal conditions.

Pioneering work in the field of catalytic hydrothermal biomass gasification has been carried out at the Pacific Northwest National Laboratory and resulted in the TEES (Thermochemical Environmental Energy System) process (Elliott *et al.* 1993). Typical TEES conditions are in the subcritical region (350° C, 20 MPa). Several catalysts were examined and tested for long-term activity. Ruthenium, rhodium and nickel proved to be active metal catalysts. Hong and Spritzer (2002) used a continuously operated reactor made of stainless steel to study the partial oxidation of wood in supercritical water at a concentration of 9 wt%. Two modes of operation, autothermal (where ethanol and air were added in order to produce heat by partial oxidation) and allothermal, were tested. The allothermal mode yielded higher methane concentrations in the product gas, around 34 vol% at 650°C. Antal and coworkers studied the gasification of several types of biomass in a tubular flow reactor at 685°C catalyst bed temperature using a carbon catalyst (Antal *et al.* 2000). A gel-like mixture of sawdust (11 wt%) and cornstarch (4 wt%) yielded 17% CH₄, while 43% hydrogen was formed.

We report on preliminary results from a test rig specially designed for long-term catalyst testing under hydrothermal conditions. Instead of real biomass slurry, ethanol, glucose and other simple molecules have been used as model substances.

Experimental Method

The test rig was made of 316L stainless steel. All surfaces that were in contact with hot media were gold plated to avoid any reaction with steel. Two HPLC pumps were used to feed the biomass model substance and water (both degassed with N₂ to remove dissolved oxygen) at an adequate pressure (up to 40 MPa). The water was preheated in a heater and brought to the supercritical state before being mixed with the cold model substance stream prior to entering the tubular reactor (I.D.: 5.2 mm, L: 260 mm). Below and above the catalyst packing was a bed of α -Al₂O₃. During the gasification experiments, the product gas was analyzed with respect to its composition by gas chromatography (HP GC 6890) and its quantity was measured by a wet gas meter. The liquid phase was collected and its content in organics analyzed with a Dohrmann DC-190 TOC analyzer. In addition, HPLC analysis was carried out to identify possible side-products as well as to explore the ease at which specific components were gasified.



Fig. 2: Picture of the continuous hydrothermal catalyst test rig.

A picture of the continuous catalyst test rig is shown in Figure 2. The rig is not designed to pump slurries, only liquids can be used as feedstock. Ethanol was used in preliminary experiments. Later, glucose solutions were used before using synthetic liquefied wood. Its composition was determined according to an HPLC analysis of hydrothermally liquefied spruce wood, as follows. Bark-free spruce was liquefied in the presence of Raney[®] Nickel 2800 in a batch reactor (see Waldner and Vogel 2005) at 300°C. The wood liquefied into a brownish, viscous liquid that was analyzed by HPLC (ion exclusion chromatography). The residue of a wood gasification experiment with spruce was analyzed to determine which substances are easily gasified and which ones persist after the gasification reaction. Among the identified substances, the following model mixture was chosen for synthetic liquefied wood: formic acid (36.7 wt%), acetic acid (20.1 wt%), anisole (16.2 wt%), phenol (14.6 wt%), and ethanol (11.7 wt%). This mixture had the same C:H:O as the initial wood.

Results and Discussion

Gasification of Ethanol

Ethanol was gasified with 1%Ru/TiO₂ as catalyst. To test the catalyst for deactivation and to bracket good reaction parameters, a long term experiment was carried out for more than 70 hours with ethanol as feed. Three different gasification temperatures were used: 460°C, 415°C and 360°C. Figure 3 shows the accumulated gas volume over time. There was a problem with the gas/liquid separator at 460°C, which leads to a split in the graph. As expected, more gas is formed over time at higher temperatures. However, hydrogen is thermodynamically favored at higher temperatures (compare Figure 1), leading to an increase in the total number of moles of gas. An intermediate temperature should thus be chosen. During the reaction, samples of the residual liquid phase were collected and analyzed (Table 1). The time of sampling can be seen in Figure 3. Note that the mass flow was varied at 415°C from a weight hourly space velocity (WHSV) of 36 h⁻¹ to 18 h⁻¹.



Fig. 3: Volume of gas produced over some 70 hours using ethanol as feed. P = 30 MPa. Ethanol feed concentration was 30 wt%. The indicated temperature is the reactor oven setpoint.

Sample no.	TOC g/L	Х _{тос} %	Sample no.	TOC g/L	Х _{тос} %
1	3.5	97.8	5	125.9	19.3
2	15.5	90.1	6	75.0	51.9
3	15.4	90.1	7	89.7	42.5
4	123.7	20.7	8	86.7	44.4

Table 1: Carbon content in the residual liquid. X_{TOC} is the organic carbon conversion.

Gasification of Synthetic Liquefied Wood (Raney Ni 2800)

The synthetic liquefied wood was gasified with Raney[®] Ni 2800 in a 50 hours experiment. The evolution of the gas production is depicted in Figure 4.



Fig. 4: Total volume of gas produced during a 50 hours run with synthetic liquefied wood as feed. The indicated temperature is the reactor oven setpoint.

The gas production rate was independent of temperature, in contrast to the ethanol experiment. The catalyst probably deactivated gradually, indicated by an increase of the hydrogen content and a decrease of the methane content in the product gas (see Fig. 5). The temperature profile along the reactor revealed information about the location of endothermic and exothermic reactions (Fig. 6). The catalytic bed was located between 3 and 18 cm from the reactor inlet with α -alumina before and after it.

A cold spot of ca. 8 K at the beginning of the catalytic bed (oven setpoint 402°C) indicates the predominance of endothermic reforming reactions with CO_2 and H_2 as main products. The temperature profile after 16 h on stream does not differ significantly from the initial profile. At the higher oven setpoints of 427°C and 452°C no distinct cold spot at the beginning of the catalyst bed can be observed. This could indicate that the reforming reactions are slowed down by catalyst deactivation. Interestingly, the temperature profiles after 20 h, 25 h and 41 h on stream with the same oven setpoint are almost identical.



Fig. 5: Dry gas composition versus time on stream for the gasification of a synthetic liquefied wood mixture with Raney Ni 2800.



Fig. 6: Temperature profile along the reactor. The catalyst was located between 3 and 18 cm. Fluid flow is from left to right.

Gasification of Synthetic Liquefied Wood (Raney Ni/Ru)

The decrease in methane concentration from 50% to below 30% in the previous experiment with concurrent increase of the hydrogen concentration indicated a reduction of the catalyst's

methanation activity. As a remedy we performed another experiment with a Raney Nickel catalyst that was doped with a small amount of ruthenium. This doping had been reported to enhance catalyst stability by suppressing the sintering of the nickel phase (Elliott and Hart 2000).

The gas analysis was improved to produce less scatter. Over a period of 3 months synthetic liquefied wood was gasified with a total time on stream of ca. 100 h. The process parameters were: WHSV = 2 $g_{HC}/g_{cat}/h$, p = 30 MPa, feed concentration = 20 wt%, catalyst bed temperature = 420°C. Several problems forced us to stop and restart the rig twice. Figure 7 depicts the dry gas composition for the whole time on stream. Up to a few hours on stream total conversion of the model mixture, together with equilibrium gas compositions, was observed. Then, a rapid decrease of the methane concentration, accompanied by a significant reduction of the conversion, took place. After ca. 14 h a steady-state of the methane concentration was reached.

After restarting the plant with a two months interruption, equilibrium gas composition was attained, again followed by a decrease of the methane concentration. The slope looks a bit less steep, however, no steady state was reached. Restarting the rig after a week-end shutdown did not restore the initial high gas yields.

In order to check whether the catalyst still had any methanation activity at that point, we increased the water flow rate by a factor of 2.25 after ca. 90 h on stream. By doing so the feed concentration and the residence time were halved, while keeping the WHSV constant.



Fig. 7: Dry gas composition versus time on stream for the gasification of a synthetic liquefied wood mixture with Ru-doped Raney Ni.

The methane concentration dropped and the hydrogen concentration increased sharply. This was a proof that the catalyst still exhibited a significant methanation activity. It makes also clear that the space velocity (WHSV) alone is not sufficient to compare catalysts. Note that the CO concentration did not increase to more than 1-2 vol% in these experiments. The watergas shift reaction seems to proceed fast even on a partially deactivated Raney Ni catalyst.

Conclusions

1%Ru/TiO₂ is a suitable catalyst for the hydrothermal gasification of ethanol to SNG. A strong dependence of the conversion on the temperature was found. The 1%Ru/TiO₂ catalyst remained active during the 70 h test and its activity could be increased by higher Ru loadings. Raney[®] Ni 2800 proved to be an active catalyst for the hydrothermal gasification of synthetic liquefied wood, but was not stable at supercritical conditions. A ruthenium doped Raney[®] Ni catalyst exhibited a better stability with the 20 wt% synthetic wood mixture. Detailed analyses of the fresh and spent catalysts are underway and will help understand the deactivation mechanism. Experiments with the current test rig will continue and serve as long-life tests for various catalysts.

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