Disposal of Acid Components from Biomass Produced Syngas

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Abstract-
This article deals with the possibility of purifying syngas in a pilot-scale continuous slipstream dolomite fixed-bed, which serves to reduce tar and dust contained in the gas during the gasification of the biomass by high-temperature adsorption method. Listed in the methods here are the basic filter parameters of sorbents, test apparatus, basic operating conditions, and analytical methods used and the results obtained. Although the development of this device was not yet and, in particular, the operating conditions are still being optimized, very low tar content values have been reached behind the filter and dust in gas. These results already allow the target to be met -the possibility of introducing treated gas into the internal combustion engine.

Key words: High temperature adsorption, tar, dust, dolomite, fixed-bed

1. Introduction
In general, biomass means any recovering substance of organic origin, i.e. plants, animals and their wastes. Biomass is a huge source of renewable raw materials and energy that can be used for many purposes in special industrial, technical and energy sectors. The current energy trends are leading to wider use of renewable energy sources. Renewable energy is one of the effective ways of meeting the global energy demands in the nearest future as the fossil fuel reserve depletes continuously [1-3]. Biomass is currently considered one of the most promising renewable resources in Europe. There is a wide range of procedures for converting biomass to more valuable fuels. One of these technologies of greater energy use of biomass will be gasification and subsequent processing of energy-gas in cogeneration units in the future. The syngas produced from gasification can be used directly or stored after subsequent treatment; it is expected to be a future energy carrier. However, many factors influence the gas composition. The produced gas contains oxides of carbon, water, sulphur content and some undesirable components. Accompanying components of gas are trace amounts of higher hydrocarbons (ethane and ethene, etc.), small particles of charcoal and ash, tars and other substances [4].

For use in high-temperature fuel cells, the concentration/threshold of acidic components, in particular, sulphate, hydrofluoric and hydrochloric acid, are strictly limited. Therefore, it is necessary to remove the above compounds from the product gas. The concentration of tar is a function of the gasification temperature, type of reactor used and processing conditions. Tests have shown that the production of syngas during the gasification of wood is much greater than in coal or peat and that these syngas tend to be heavier, more stable aromatic substances [5].
2. Materials and Method

2.1 Materials

Figure 1 shows the experimental test rig used to test the properties of the sorbents used. The considerable variety of physicochemical properties of the components to be removed and their different chemical reactivity at the same temperature requires careful selection of the individual processes used to remove them and place particular demands on compatibility. The presented system consists of four basic technological steps.

![Figure 1: Schematic diagram of the experimental test rig.](image)

1. The reactor is designed to produce gas from biomass sources. Due to the choice of the fluidized bed and the presence of calcium materials (dolomite, magnesite), the tar content can be reduced, coarse desulphurization and dehalogenation can be performed directly in the reactor. Due to the intense abrasion of the fluidized bed material, the CaO reaction surface is continually being renewed, leading to an increase in the rate of ongoing reactions. The CaS, CaCl₂ formed are removed from the reactor and collected on a hot filter.

2. The hot filter is a continuously operating device allowing filtration on the material layer. The maximum filtration temperature (650 °C) is limited by the acceptable vapor phase vapor pressure of alkaline chlorides. The lower temperature (450 °C min.) is limited by the adsorption activity of the filter material used and the desired residual HCl and H₂S value in the gas. Adsorbent materials actively retaining residual amounts of HCl and H₂S can be used as the filter material.

3. The removal of the residual tars and unsaturated hydrocarbons takes place on an active nickel catalyst operating at 450 - 550 °C. The smooth operation of the catalyst is ensured by the correct choice of temperature and H₂O/CₘHₙ ratio. At the same time, the gas past the catalyst acting as an extra low H₂S trap (>0.5 ppm) contains only CO, CO₂, H₂, CH₄, H₂O. The gas composition is controlled by chemical equilibrium, stabilizing at the catalyst temperature of 9.10.
2.2 Method
Sorbet weight (2 g) was poured onto the reactor bed. The desired temperature was set and the furnace turned on. After warming up to the specified temperature was started by dosing the aqueous HCl solution and the HF with a linear pump and the gas mixture feed was opened from a cylinder. The desired H2O, HCl, and HF inlet concentration were generated by evaporating the solution into the stream gaseous mixtures. For separation of analytical branches for sulfate and acid, the condensation diagram was used. Determination of the concentration of trapped components at the exit of the reactor after passing the gas mixture through the layer of the tested sorbent was carried out by several analytical methods.

The fuel cell is briefly characterized as an electrochemical device that converts chemical energy contained directly in the fuel. Unlike other methods of obtaining energy, this method achieves higher electrical efficiency - over 60 %. There are a wide variety of fuel cells - they differ as used electrolyte and the temperature at which they can be operated. Usage is assumed for our research High-Temperature Solid Oxide Fuel Cell (HTSOFC) high-temperature fuel cell utilizing a high-temperature fuel cell electrolyte solid metal oxide working in the temperature window 650 - 1000 °C.

2.3 Tested Sorbents
A range of sorbents was prepared for testing. The preparation was mainly based on metal nitrates. Between for example: Zn(NO3)2·6H2O, Fe(NO3)3·9H2O, Cu(NO3)3·3H2O and Mn(NO3)·4H2O. As carriers e.g. γ-Al2O3, α-Al2O3, SiO2, graphite and activated carbon have proven themselves. The dolomites with varying degrees of treatment (annealing, scrubbing) were tested for natural substances. Also, commercial catalysts based on magnesium, copper and zinc were tested on various carriers.

2.4 Methods for Preparing Tested Sorbents
The tested sorbents were prepared by the following three methods: co-precipitation, homogeneous precipitation and impregnation.

The co-precipitation procedure uses nitrates of desired metals Zn(NO3)2, Fe(NO3)3 and ammonia water for treatment. The pH of the solution is 10. The sorbitol is either γ alumina or silica. The mixture is filtered, dried under vacuum 70 °C and calcined at 500 °C The product is a ZnFe2O4-based sorbent deposited with the selected carrier.

The homogeneous precipitation process is based on Zn(NO3)2·6H2O, to which urea is added. After filtering and drying under vacuum to obtain Zn(NO3)2, which is calcined at temperatures from 400 to 500 °C.

The impregnation process uses a solution of Zn(NO3)2 and Fe(NO3)3 and the carrier γ-Al2O3 / SiO2. After drying and calcination it is obtained zinc-iron mixed sorbent.

2.5 High Temperature Adsorption Principle
Metal oxides are used for the high-temperature adsorption of undesirable components of the generator gas. These oxides (MO; M = metal) directly react with the entrapped substance according to the following reactions:

For halide adsorption: 2MO + 2HCl / 2HF → H2O + MCl2 / MF2

For hydrogen sulfide adsorption: MO + H2S → H2O + MS

Three different gas mixtures were used for laboratory measurements with the following composition of the main components (in percentage volume): CO 16, H2 14, CO2 14, H2O 13.
Gas mixtures differed in methane and ethane concentrations; these two components could influence the balance of adsorption on the metal oxides used in terms of thermodynamics. Input concentration of undesirable substances in ppm volume: \( H_2S \) 100\( \pm \)200, \( COS \) 15, \( HCl \) 75\( \pm \)150, \( HF \) 10\( \pm \)20. Desired concentration of undesirable substances in ppm volume: \( H_2S \) 1, \( COS \) 1, \( HCl \) below 10, \( HF \) below 10.

The temperature window of the experiments was 500 - 900 °C and all measurements were made at normal pressure 101.325 kPa.

### 3. Result and discussions

The characteristics of the generated gas, as well as the fuel cell requirements, are summarized in Table 1. Obviously, it is necessary to remove sulfur compounds such as sulfate and carbonyl sulfide. These substances are very aggressive (strongly corrosive, catalytic poisons), so their concentration is strictly limited to less than 1 ppm.

It is also necessary to capture mineral acids, such as hydrochloric acid and hydrofluoric respectively. Their concentration must not exceed 10 ppm by volume. Commercial zinc and copper catalysts on alumina have proven to be the most effective for sulphate sorption. However, they cannot be used for acid capture. For the above-mentioned commercial catalysts, the desired sulphate concentration below 1 ppm can be achieved.

Table 1: Generator gas composition and HTSOFC requirements

| Sample         | Quantity       | Input          | Output                   |
|----------------|----------------|----------------|--------------------------|
| CO             | Volume %       | 16             | Fuel                     |
| \( H_2 \)      | Volume %       | 14             | Fuel                     |
| \( CO_2 \)     | Volume %       | 14             | Safely                   |
| \( H_2O \)     | Volume %       | 13             | Safely                   |
| \( CH_4 \)     | Volume %       | 4              | Safely                   |
| \( N_2 \)      | Volume %       | 36             | Safely                   |
| \( C_2H_4 \)   | Volume %       | 16             | C-deposition             |
| \( C_2H_6 \)   | Volume %       | 14             | C-deposition             |
| Benzene        | Volume %       | 0.4            | C-deposition             |
| Toluene        | Volume %       | 0.1            | C-deposition             |
| \( H_2S \)     | Vppm           | 100 - 200      | 1 ppm                    |
| COS            | Vppm           | 15             | 1 ppm                    |
| \( NH_3 \)     | Vppm           | 2000 – 3000    | Fuel                     |
| HCl            | Vppm           | 75 – 150       | 10 ppm                   |
| HF             | Vppm           | 10 – 20        | 10 ppm                   |
| Tar            | mg/mn³         | 7000           | -                        |
| Fly Ash        | g/mn³          | 6              | -                        |

As for naturally sourced dolomites (from Ikpeshi, Edo State, Nigeria), they showed good results in capturing mineral acids, but they were not applicable in the case of sulphate adsorption. In the future, there will be tests of other natural substances, mainly limestone, with varying degrees of treatment. The research will also focus on the laboratory preparation of other sorbets.
Figure 2, where the simultaneous condensation of both acids is utilized (ideally at 53 °C), while the sulfate continues to be a gaseous phase.

Moreover, the commercial catalysts used are also interesting for price reasons. These catalysts adsorb with less mineral acid activity. On the other hand, natural carbonate adsorbents (chemically modified dolomite) have not been proven to be too strong for sulphate capture. The literature describes the sorption of sulphide at the high concentration limiting agent (about 1000 ppm), but the limits set for fuel cells cannot be reached by our experience. The results obtained for the German commercial BASF catalyst indicate the following graph in Figure 3.
Analytical Methods for Determining Followed Components

The output concentration of the individual components of the gas mixture was determined by the following analytical methods:

H$_2$S was determined chromatographically using a sulfide electrode for the continuous determination of sulfate. Liquid chromatography is used to determine HCl and HF. A sample for chromatographic determination of these the condensate formed by cooling the gas exiting the reactor of Figure 4.

![Figure 4: Chromatograms of dry and wet gas after passing through an inert dolomite bed at 500 °C.](image)

The content of sulfane and carbonyl sulfide in the gas was determined at minute intervals on a gas chromatograph with a flame photometric detector (FPD) as shown in Figure 4. According to the areas under the peaks, the figure shows that in dry gas (left part of the picture) the COS concentration is comparable to the concentration of sulphane, in wet gas (the right side of the picture) there is COS below the detection limit of the method.

![Figure 5: Panel filter during filtration and regeneration, pressure loss on the filter depending on the porosity.](image)
The natural dolomite material used as packing in the bed does not have drawbacks and therefore are able to operate over a wide temperature range. The principle of filtration is firstly to capture small micron particles in the gaps of the filter bed, where an intense change in the direction of gas flow occurs and as a result of the collision, dust is collected on the surface of the bed material particles. After a short initial time, a filter cake is formed on the surface of the filter material and filtration takes place on its surface where all particles are trapped. This stage of filtration is the most effective. Unfortunately, with the increase in the filter cake, the pressure loss is directly proportional to its thickness, flow velocity and characteristic filter and cake resistance. After a period of time, it is necessary to remove the filter cake and regenerate the bed. The continuous operation of the filter bed has a good comparison with those found in the work of Risner [6].

4. Conclusion

On the basis of the experimental assessment of the processes required for high temperature removal of acid components (unwanted substances) from the gas generated through gasification of biomass, a purification method has been proposed for solid flue gas gases producing gas free of dust, tar, sulfur compounds, and chlorine.

5. Recommendation

Although the sub-processes of the current removal of acid components, dust and tar have been successfully tested, the whole process so far tested has not been and cannot be without further detailed research and experiment under real world conditions to confirm the applicability in practice. However, from a theoretical point of view, there are no theoretical obstacles to its implementation, and in the case of proper functioning of individual processes, the goal can be achieved.

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