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A novel test method for catalysts in the treatment of biomass pyrolysis oil

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Abstract

A novel microscale test method was developed for testing catalysts. A pyrolyser connected to a gas chromatograph was used for pyrolysing the biomass sample and for leading the pyrolysis vapours through the catalyst for instant analysis. The injection port of the gas chromatograph was used as a fixed-bed catalyst reactor. Detection of reaction products was carried out with an atomic emission detector to quantify the various elements or with a mass selective detector to identify the compounds.

The test method was applied to treating pyrolysis vapours of Scots pine sawdust with ZnO, MgO, dolomite and limestone. Mass balances for carbon and hydrogen were determined with and without the catalyst. The carbon yields in liquid fraction decreased with all the catalysts studied. The highest yields were obtained with ZnO. Product distribution in pyrolysis vapours was rather similar with ZnO or without any catalyst. With MgO, dolomite and limestone, the compounds of pyrolysis vapours comprised mainly gases, water and degradation products of polysaccharides as well as some aromatic hydrocarbons.

Keywords: Catalyst screening; Biomass; Pyrolysis; Pyrolysis vapours

1. Introduction

Solid biomasses can be converted into liquid form by means of rapid pyrolysis. The products, mechanism and kinetics of pyrolytic reactions have been discussed in [1]. These pyrolysis oils could be used, e.g., as fuels for energy production. However, the major limitation is their instability, i.e., quality changes during storage. Therefore, some upgrading, e.g., catalytic conversion with or without hydrogen [2] is required.

The only way to evaluate the applicability of various catalysts is to measure their activity. In the preliminary evaluation of catalytic performance it is important to use a method that is fast and reliable. Further, freshly produced oils should be used in catalyst testing for upgrading of pyrolysis oils because of their instability. For these reasons we developed a test method for the screening of the catalytic activities of various materials for the treatment of pyrolysis vapours without hydrogen. The product quality was estimated on the basis of the main compounds of pyrolysis vapours.

Zeolite cracking of pyrolysis oils has been widely studied [3–9]. The results of zeolite cracking with this novel method in a previous study by the authors [10] were comparable to those obtained with conventional test procedures [11–14]. Pyrolysis vapours were con-

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verted mainly into gases and aromatic hydrocarbons with zeolites. The zeolite catalysts were effective in the removal of oxygen but the liquid yields were low. Because of this drawback less acidic materials can be more beneficial in upgrading of pyrolysis oils in order to achieve better liquid yields. Therefore, in this study ZnO, MgO, dolomite and limestone were screened for their activity with this rapid method.

2. Experimental

2.1. *Catalysts*

The catalysts used were ZnO (Merck 8846, powder), MgO (Janssen 22.253.40, powder), Finnish dolomite (Kalkkimaa, SA $8\ m^2\ g^{-1}$) and dolomitic limestone (Parainen, SA $12\ m^2\ g^{-1}$). Dolomite and limestone were ground and sieved. The 100–250 μm fraction was collected for testing. The catalysts were activated in air at 600°C over night and stored in a desiccator.

2.2. *Methods*

A microscale pyrolysis and vapour-phase catalyst reactor was developed from commercially available instruments. The pyrolysis unit was a CDS Instruments Pyroprobe 1000 pyrolyser (Py) connected to an HP 5890 Series II gas chromatograph (GC). The injection port of the GC was used as a fixed-bed catalytic reactor. The catalyst was placed into the liner tube (7.8 cm×4 mm i.d.) of the GC's split/splitless injector. The placement of the catalyst bed (about 4 mm) was adjusted with glass wool [10]. In order to maintain a constant residence time of pyrolysis vapours (about 30 ms) in all tests without catalyst more glass wool was used. The maximum injection port temperature is normally 400°C. Some catalysts require higher temperatures. For this reason, the thermostat was modified to achieve a catalyst temperature of 500°C. A fixed resistor was added in parallel with the thermostat's platinum resistance-sensor. The correct temperature versus set point was calculated to achieve the catalyst temperature desired. Detection was carried out with an HP 5921A atomic emission detector (AED). The system was controlled by an HP D3968A ChemStation computer and software G2360AA.

The chromatographic separation was carried out using an HP Ultra 1 fused silica capillary column (50 m×0.32 mm i.d., film thickness 0.52 μm). The oven temperature program was 2 min at 30°C, $10°C\ min^{-1}$ to $300°C\ min^{-1}$, and 25 min at 300°C. Helium was used as carrier gas and the column pressure was 125 kPa.

In pyrolysis studies air-dried, bark-free sawdust of Scots pine (*Pinus sylvestris*) was used. The elemental composition of the pine sawdust (moisture and ash-free basis) was: 51.1 wt% carbon, 5.4 wt% hydrogen, 0.1 wt% nitrogen and 43.4 wt% oxygen (calculated by difference) [15]. The sawdust was ground and sieved on a round-holed screen (105–125 μm). The sample of 1–2 mg was pyrolysed in a quartz tube (2.5 cm×1.0 mm i.d.) at 600°C (heating rate $1000°C\ s^{-1}$ and heating time 20 s). The interface temperature of the pyrolyser was 300°C. Vapours from rapid pyrolysis were led through the liner tube with or without the catalyst for instant analysis with the GC.

For quantitative carbon and hydrogen determinations the AED's mass responses were calibrated by injecting benzene solution. The wavelengths used for hydrogen and carbon were 486.1 and 495.7 nm, respectively. In pyrolysis, the pine sawdust was converted into GC-eluated compounds, pyrolysis residue, coke and loss. The term 'loss' was used for high-molecular-mass compounds not eluated through the GC column but released from the raw material. In this study the GC-eluated compounds were classified into light volatile compounds (light fraction) and heavy volatile compounds (heavy fraction). The retention time (4 min) of *n*-pentane (b.p. 36°C) was the upper limit of the light fraction. The sample was weighed with a microbalance Mett-ler AT20 before the pyrolysis and the pyrolysis residue was weighed afterwards. The pyrolysis residue did not contain GC-eluated compounds and hence was assumed to be carbon. The total mass balances for carbon and hydrogen were calculated from the calibration results and the weighed masses. A mass selective detector (MSD) HP 5970 was used for identification of the main compounds. The peak identification based on automatic library search (NBS REV_F/HP 9000 series 310) and on literature data [16–18].

3. Results and discussion

3.1. Mass balances for carbon and hydrogen

The method developed was used for studying the conversion of pine sawdust pyrolysis products with ZnO, MgO, dolomite and limestone catalysts. Mass balances for carbon and hydrogen were determined with various catalysts at the temperature of 500°C by Py-GC/AED. The carbon and hydrogen yields (wt% of carbon or hydrogen in the raw material) are shown in Fig. 1. The first column presents the yields in the GC-eluated compounds (light and heavy fraction) and the second one the yields in the pyrolysis residue and in the coke and loss. The carbon yields in GC-eluated compounds (light and heavy fraction combined) of pine sawdust were without any catalyst 57 wt% and with ZnO 51 wt%, MgO 36 wt%, dolomite 26 wt% and limestone 32 wt%. The carbon yields of the heavy fraction decreased with all catalysts compared to results without a catalyst (43 wt%). The carbon yield in the heavy fraction was highest among the catalysts tested with ZnO (34 wt%) and low with MgO, dolomite and limestone (13–20 wt%). The hydrogen amounts of the heavy fraction decreased with the catalysts like the carbon amounts. The carbon yields in the light fraction were quite similar: no catalyst 14 wt%, ZnO 18 wt%, MgO 20 wt%, dolomite 13 wt%, limestone 12 wt%. The light fraction contained the maximum hydrogen. The carbon amounts of pyrolysis residue were about the same (27–31 wt%) in all experiments. The catalyst does not affect the pyrolysis residue but the changes are dependent on the standard tube of pyrolysis [19]. The variation in residue yields could be avoided by using a cut pyrolysis tube. During the treatment the activated white-coloured catalyst changed to grey. The coke content of the catalyst was too low to be quantified. For these reasons, the coke and loss were combined and calculated by difference. The carbon amounts of the coke and loss increased in the order: no catalyst <ZnO<MgO<limestone<dolomite.

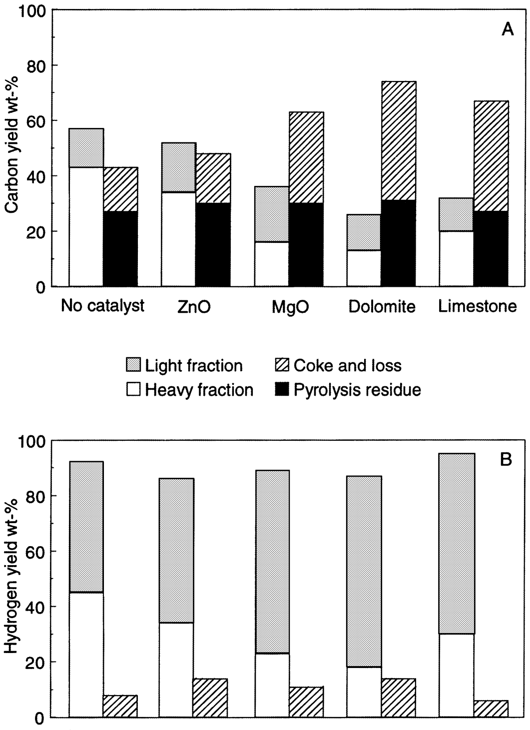

Fig. 1. The yields of (A) carbon and (B) hydrogen (wt% of carbon or hydrogen in the raw material).

Reproducibility of the method was studied with ZnO. The average of standard deviation was about 3 wt% in carbon yields and 10 wt% in hydrogen yields.

3.2. Identification and comparison of reaction products with or without catalyst

The rapid pyrolysis products of pine sawdust with or without a catalyst were identified by Py-GC/MSD. The main compounds in pyrolysis vapours without a catalyst and with MgO are shown in Fig. 2. Without a catalyst the pyrolysis products of pine sawdust consisted mainly of carbon monoxide, carbon dioxide, water, degradation products of polysaccharides like acetic acid and levoglucosan as well as degradation products of lignin like guaiacol and its derivatives. Compound distribution with MgO, dolomite and limestone was fairly similar consisting mainly of gases, water and other degradation products of polysaccharides like acetic acid and furaldehyde derivatives and also some aromatic hydrocarbon like benzene and toluene. The degradation products of lignin were decomposed by MgO, dolomite and limestone. The product distribution with ZnO was almost the same as without a catalyst. However, the ZnO decomposed the levoglucosan, as did the other catalysts.

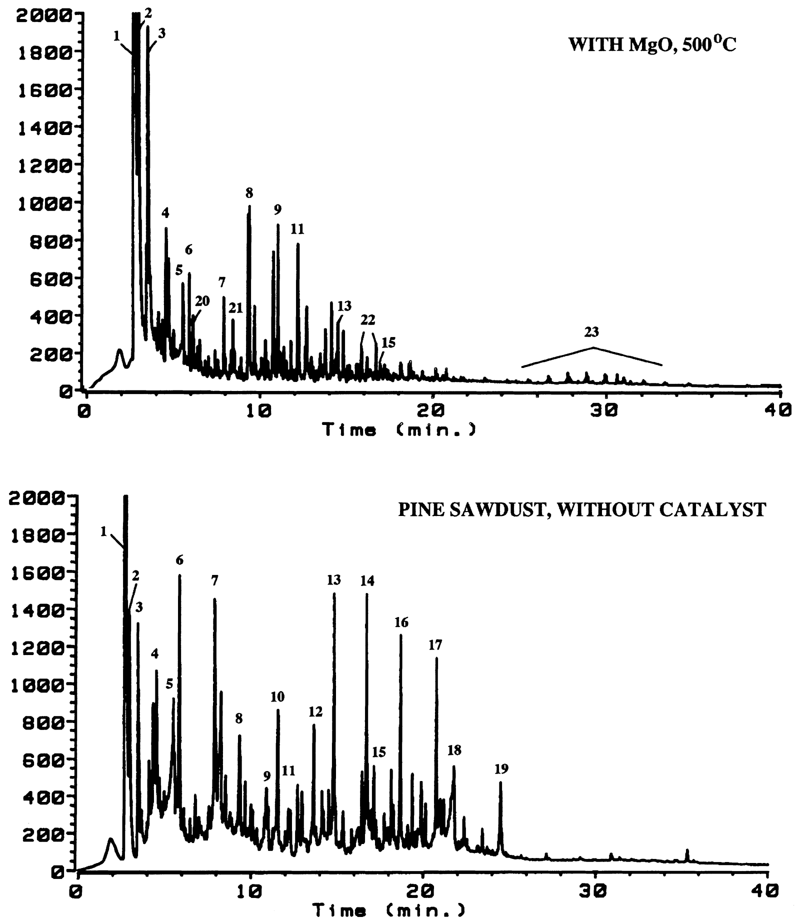

Fig. 2. The main compounds of pine sawdust pyrolysed at 600°C without a catalyst and with MgO catalyst at 500°C: **1** $CO/CO_2/H_2O$, **2** acetaldehyde, **3** 2-propanone, **4** methylfurans, **5** acetic acid, **6** 1-hydroxy-2-propanone, **7** 1-hydroxy-2-butanone, **8** 2-furaldehyde, **9** α-angelica lactone, **10** 1-acetyloxy-2-propanone, **11** 5-methyl-2-furaldehyde, **12** 2-hydroxy-3-methyl-2-cyclopenten-1-one, **13** guaiacol, **14** 4-methylguaiacol, **15** 5-(hydroxymethyl)-2-furaldehyde, **16** 4-vinylguaiacol, **17** isoeugenol, **18** levoglucosan, **19** coniferaldehyde, **20** benzene, **21** toluene, **22** dimethylphenols, **23** hydrocarbons.

3.3. Comparison of results with zeolites

The cracking activities of H-ZSM-5, commercial FCC catalyst and H-mordenite were screened with this method in the previous study [10]. Carbon yields of the heavy fraction for these were 21, 12 and 11 wt%, respectively. The carbon amounts were comparable with the results of MgO, dolomite and limestone, while the product composition was different. The zeolites produced mainly gases and aromatic hydrocarbons while the reaction products for MgO, dolomite and limestone comprised mainly degradation products of polysaccharides and lignin.

4. Conclusions

The microscale pyrolysis and vapour-phase catalyst reactor was suitable for testing the catalyst activity. The advantages of this method were high speed and the small amount of materials needed in the test. However, on the basis of these experiments it was not possible to draw conclusions about the stability of the catalytically treated oils. Therefore, in the future pyrolysis oil will be produced in a bench-scale reactor by using promising catalysts, and their stability will be determined.

The results of the mass balances and the quite similar compound distributions with ZnO and without the catalyst indicated that ZnO was a less active catalyst for pyrolysis vapours. The highest liquid yield was obtained with ZnO. MgO, dolomite and limestone had a fairly similar catalytic activity but the liquid yields were low.

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