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Additional Information

Analytical procedure.

The non-condensable gases analysis is performed online using a Refinery Gas Analyzer (Global Analyser Solution). This device is equipped with three different detectors, two thermal conductivities detector (TCD) and a flame ionization detector (FID). Table A1 summarizes the settings of the RGA.

Table A1. RGA parameters used to analyze the non-condensable gases.

Detectors	FID, 523 K, range of 10 % Aux. left TCD, positive polarity, 383 K Aux. right TCD, negative polarity, 383 K
Injection	Online injection
FID First column	Rtx-1 5 m x 0.53 mm I.D. x 0.3 µm df
FID Second column	Al_2O_3/KCl 25 m x 0.53 mm I.D.
Oven temperature	333 K hold 120 seconds, then→ 573 K at 0.5 K/seconds
Carrier gas	FID He, constant flow ($5.83 \cdot 10^{-7}$ m^3/s). Aux. left TCD He, constant flow ($5.83 \cdot 10^{-7}$ m^3/s). Aux. right TCD N_2, constant flow ($6.66 \cdot 10^{-7}$ m^3/s).

The bio-oil analysis is performed using two ThermoScientific TRACE GC×GCs (Rtx-1 PONA x BPX-50, Interscience). Both devices are equipped with a dual-stage cryogenic CO_2 modulator. Two different detectors, a flame fonization detector (FID) and a time-of-flight mass spectrometer

(TOF-MS), mounted on different GC×GCs are used. A pProgrammed temperature vaporization (PTV) injector is used for the FID analysis, in order to avoid component discrimination during the injection. For the TOF-MS analysis, a split/splitless (SSL) injector is used because the component discrimination is not so important as in the FID analysis. Table A2 summarizes the settings of the GCxGCs (similar settings are used for the TOF-MS).

Table A2: GCxGC parameters used to analyze the bio-oil.

Detector	FID, 573 K, range of 10 %
Injection	Autosampler + PTV, 0.5 µl and $5 \cdot 10^{-7}$ m^3/s split flow
First column	Rtx-1 PONA 50 m x 0.25 mm I.D. x 0.5 µm df
Second column	BPX-50 2 m x 0.15 mm I.D. x 0.15 µm df
Oven temperature	233 K→ 573 K at $5 \cdot 10^{-2}$ K/s
Modulation period	7 seconds, delay of 1080 seconds
Carrier gas	He, constant flow ($3.5 \cdot 10^{-7}$ m^3/s)

Data acquisition and processing are carried out using Thermo Scientific's Chrom-Card data system for the FID and Thermo Scientific's XCalibur software for the TOF-MS. The raw GC × GC-FID data files are exported as computable document format (CDF) files and imported into GC Image software (Zoex Corporation). With the aid of the GC Image software, the contour plotting, retention time measurement, peak fitting and blob integration are performed. The combined information from the pattern in the chromatogram obtained by the orthogonal separation of GC × GC-FID and the National Institute of Standards and Technology (NIST) library MS confirmation are used for the tentative identification of the peaks. The mass fraction $wt.\%_i$ of each compound is calculated using the mass fraction of the internal standard $wt.\%_{st}$, peak volumes obtained and the response factor relative to CH_4 as indicated in Equation A1.

$$wt.\%_i = \frac{f_i \cdot V_i}{f_{st} \cdot V_{st}} wt.\%_{st} \quad \text{(A1)}$$

where f_i is the relative response factor for compound i, V_i is the peak volume of compound i, f_{st} is the relative response factor for the internal standard, and V_{st} is the peak volume of the internal standard. The response factor of each compound is calculated by means of Equation A2 which is based on the effective carbon number approach [1, 2]

$$f_i = \frac{M_i}{M_{CH_4} \cdot C_{i,eff}} \quad \text{(A2)}$$

where M_i is the molar mass of compound i, M_{CH_4} is the molar mass of CH_4 (the chosen reference compound), and $C_{i,eff}$ is the effective carbon number of compound i. In the case of hydrocarbons, $C_{i,eff}$ is approximately equal to the carbon number of the compound. For oxygen containing compounds, $C_{i,eff}$ is calculated as a function of both the carbon number of the compound and the type of oxygen containing functional groups as indicated in Equation A3 [3].

$$C_{i,eff} = C_i - nc \quad \text{(A3)}$$

where C_i is the carbon number of compound i and nc is the correction value for functional groups. The agreement between the calculated and the experimental effective carbon number for oxygen containing compounds has been experimentally validated for well-known bio-oil compounds [4]

References.

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