

Biomass pyrolysis reactions and products as studied by simultaneous thermal analysis techniques

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INTRODUCTION

From heterogeneous biomass, pyrolysis allows producing more homogeneous tar (oils) or char (carbonaceous solids) that are then easily stored and transported. The process conditions are known to affect the tar / char ratio and compositions [1,2]. A key step is the release of volatiles during the biopolymers early decomposition.

Among the thermal analysis techniques, Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA) are the best suited to simulate at the lab scale the pyrolysis processes. In the present study, influences of heating rate, sample mass, and grain size on the slow pyrolysis of cellulose, lignin, xylan and resinous wood samples were studied.

ENERGETICS OF BIOMASS PYROLYSIS

Tested materials: Cellulose, xylan, lignin, commercial pellets from resinous source (ground and sieved, resulting 0.125-0.250mm size fraction was used for the test).

Samples were heated in a SETARAM DSC131 Evo using an alumina pan between 25°C and 700°C at 10°C/min under nitrogen.

At low temperature, endothermic effects are observed due to free water evaporation. Resinous pellets exhibit an endotherm starting at 350.2°C and corresponding to cellulose depolymerization. It is followed by an exothermic effect attributed to presence of lignin.

As xylan represents only 10% of the hemicellulose [3] content of resinous wood, its thermal effect is not observed.

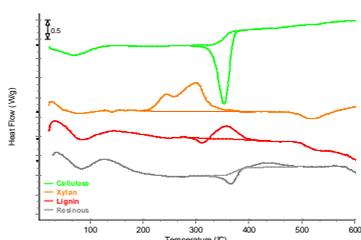


Figure 1 – superimposition of the HeatFlow = f(Temperature) data

| Sample | Heat of pyrolysis (J/g) | Temperature at peak maximum (°C) |
|-----------|-------------------------|----------------------------------|
| Cellulose | 260.7 | 353.9 |
| Xylan | -321.1 | 300.0 |
| Lignin | -72.2 (14.4 -86.6) | 310.9 / 360.3 |
| Resinous | 2.5 (41.5 -39.0) | 432.4 / 368.0 |

Table 1 – results of integration and characteristic temperatures

PARAMETERS AFFECTING THE CHARCOAL YIELD

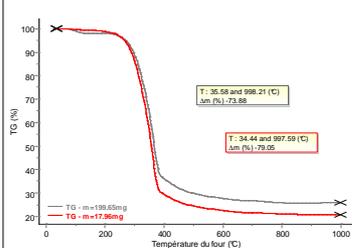


Figure 2 – Weight loss curves (%) for the comparison of different initial masses

Thermogravimetry allows acquiring data on pyrolysis steps involving mass losses [4].

Commercial pellets from resinous source were ground and sieved. The resulting 125-250µm and >500µm grain size fractions were used for the test. Samples were heated in a SETARAM SETSYS Evolution TGA using a platinum holder between 25°C and 1000°C at varying heating rates under 50mL/min helium flow.

The mass of remaining charcoal at 1000°C vs. initial sample mass ratio is determined for each test. It allows stating that the main parameters affecting charcoal yield are a high heating rate, a low sample mass and a low grain size.

| Sample mass (mg) | Heating Rate (°C/min) | Grain size (µm) | Mass residue at 1000°C (%) |
|------------------|-----------------------|-----------------|----------------------------|
| 17.96 | 10 | 125-250 | 20.95 |
| 199.65 | 10 | 125-250 | 26.12 |
| 17.73 | 1 | 125-250 | 22.29 |
| 18.04 | 50 | 125-250 | 20.49 |
| 20.37 | 10 | >500 | 21.77 |

Table 2 – residual masses

ANALYSIS OF THE EVOLVED GASES

Modern thermogravimetric systems allow evolved gases to be transferred to gas analyzers for identification.

Cellulose, xylan, lignin, and 125-250µm resinous samples were heated in a platinum holder between 25°C and 1000°C at 10°C/m in under 50mL/min helium flow. The released gases were continuously sent to a Thermo Nicolet 380 on-line FTIR equipped with a gas flow cell. The transfer line was heated to 200°C. Each spectrum was obtained with a resolution of 4 cm⁻¹.

In the case of cellulose, the maximum rate of decomposition was detected at 356°C. Figure 3 exhibits the FTIR spectra obtained at that temperature, showing the presence of water, carbon dioxide and formaldehyde in the flue gas. The other main gases are furfural and carbon monoxide. The temperatures T_{max} at which the intensity of their characteristic vibration bands was the highest are listed in Table 3.

The production of CO₂ is mainly caused by the cracking and reforming of carbonyl C=O and carboxyl COOH functional groups [5]. Depending on its chemical structure, each biopolymer thus goes through its own CO₂ production mechanism, as showed by Figure 4.

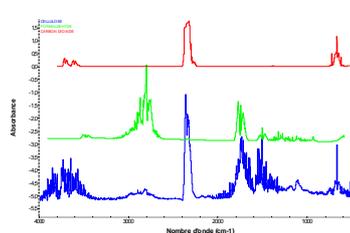


Figure 3 – Experimental FTIR spectrum obtained at 356°C (blue), compared to library spectra of CO₂ (red) and formaldehyde (green)

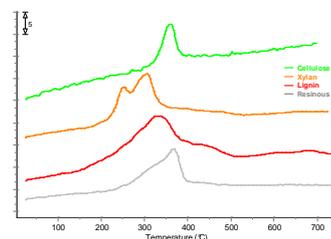


Figure 4 – Intensity variations of the stretching vibration band of CO₂ as a function of temperature for the 4 tested samples

| Wavenumber (cm ⁻¹) | Assignment (Bond) | Vibration | Compound | T _{max} (°C) |
|--------------------------------|-------------------|------------------|------------------|-----------------------|
| 2143-2223 | C-O | Stretching | CO | 364 |
| 2020-2138 | C-O | Stretching | | |
| 2237-2397 | C=O | Stretching | CO ₂ | 360 |
| 671 | C=O | Bending | | |
| 3425-3991 | O-H | Stretching | H ₂ O | 364 |
| 1282-2010 | O-H | In-plane rocking | | |
| 1712 | C=O | Stretching | Furfural | 350 |
| 754 | C-H | Bending | | |
| 1651-1834 | C=O | Stretching | Formaldehyde | 360 |
| 2590-3132 | C-H | Bending | | |

Table 3 – characteristic vibration bands of some of the detected chemicals in the flue gas during cellulose pyrolysis

CONCLUSION

Adapted analytic tools are necessary to achieve the challenges faced while improving biomass pyrolysis processes. While calorimetry allows acquiring key thermodynamic data such as heat of pyrolysis and heat capacity of biomass materials, thermogravimetry allows understanding the chemistry and kinetics of the involved decompositions. By coupling these techniques with gas analysis, the data offered allow selecting the best suited pyrolysis process conditions.

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[2] H. Luik, L. Luik, L. Tiikma and N. Vink, J. Anal. Appl. Pyrolysis, 79 (2007) 205.

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[4] M.V. Gil et al., Bioresource Technology 101 (2010) 8859–8867.

[5] H. Yang and al, Fuel, Vol.86, pp. 1781-1788, 2007.

Monitoring of biodiesel synthesis reactions by isothermal microcalorimetry

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INTRODUCTION

Biodiesels are synthesized from a transesterification reaction of triglycerides by low molecular weight alcohols leading to the formation of fatty acid alkyl esters. This reaction requires the use of a liquid catalyst (KOH, NaOH, H₂SO₄...) or of a solid catalyst (zinc aluminates, zeolithes, silica mesostructured materials or immobilized enzymes [1-3]).

The base-catalyzed ethanolysis of colza oil was studied by isothermal microcalorimetry, which is an analytical technique in which the heat released or absorbed by a reacting sample is monitored against time and temperature. In the specific case of isothermal calorimetry, temperature remains constant and reaction kinetics drive the heat release of the sample.

EXPERIMENTAL SET-UP

A C80 microcalorimeter was used under isothermal conditions at 30°C, 40°C and 50°C with membrane mixing vessels as shown on figure 1. They allow in-situ mixing and stirring.

Tested materials: commercial colza oil (~1.3g / test) mixed with 3.4w% NaOH in EtOH (~0.45g / test), with 10.72w% K₂CO₃ in EtOH, or with solid NaOH.

Samples were mixed at experimental temperatures and stirred during 20 minutes at a rate of 10 rpm.

The sample surrounding calorimetric sensor (thermopile) allowed measuring quantitatively the heat released by the reaction during its occurrence.

A reference vessel filled with ethanol and colza oil was used to compensate the phenomena of heat accumulation, heat of stirring and heat losses through the stirrer.

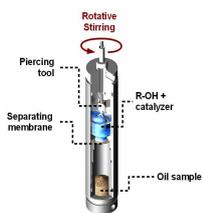


Figure 1 – Hastelloy made reaction vessel

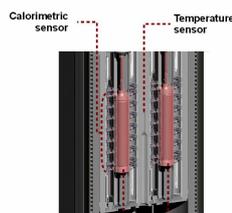


Figure 2 – Inside the C80 calorimeter

INFLUENCE OF TEMPERATURE

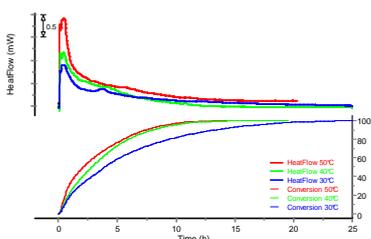


Figure 3 – Comparison of isothermal tests at 30°C, 40°C, and 50°C

Heat release data (figure 3) during the transesterifications are integrated in order to reach the reaction enthalpy. It is equal to -10.9 ± 0.6 J/g of ethanolate (NaOH + EtOH solution).

Thermal conversion α is obtained from partial integration:

$$\alpha = \frac{1}{\Delta H_R} \cdot \int_{t_{start}}^t \frac{dH_R}{dt} \cdot dt$$

Both maximum heat release rate and conversion data confirm the acceleration of the reaction with increasing temperature. The thermal conversion reaches 98% after 10.8h at 50°C, 11.7h at 40°C and 20.0h at 30°C.

| Reaction Temp (°C) | Enthalpy (J/g EtONa) | Conversion after 2 hours (%) | Max heat release rate (mW/g) |
|--------------------|----------------------|------------------------------|------------------------------|
| 30 | -10.3 | 31.8 | 0.69 |
| 40 | -10.9 | 39.0 | 0.89 |
| 50 | -11.5 | 48.6 | 1.37 |

Table 1 – Integration of exothermic peaks

INFLUENCE OF THE CATALYST

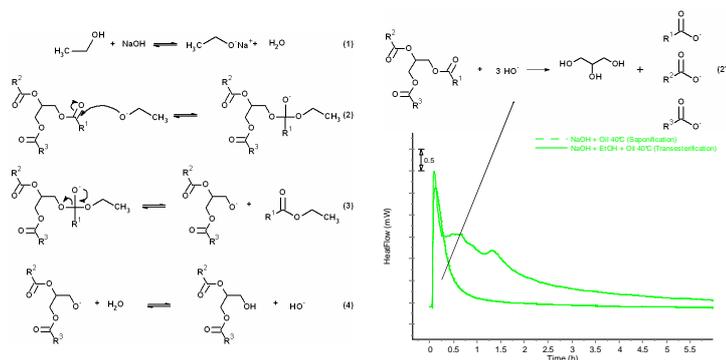


Figure 4 – Typical base-catalyzed transesterification of a triglyceride by ethanol

Figure 5 – Direct saponification tests at 40°C

The reaction goes through a first step of alcoholate formation (Figure 4), leading to the formation of water. It gives rise to the hydrolysis of some of the produced ester, with subsequent soap formation, reducing the ester yields [4]. Moreover, the presence of unreacted NaOH in the ethanolate solution leads to direct saponification of the triglyceride (step 2').

This fast exothermic reaction is clearly showed on figure 5. The green solid line was obtained by placing fresh NaOH and EtOH in the mixing vessel instead of using previously prepared EtONa solution. Unlike the other tests showed on Figure 3, an intense, sharp peak appears at the beginning of the reaction. The green dashed line corresponds to a solid NaOH (8.44mg) + colza oil mixing leading only to direct saponification and perfectly fitting the first half hour of the solid line.

This was confirmed by the run of the same transesterification reaction using K₂CO₃ as a catalyst (Figure 7) which does not lead to saponification, and thus to initial high exotherm. The reaction is also faster and less energetic (-0.55 J/g EtOK).

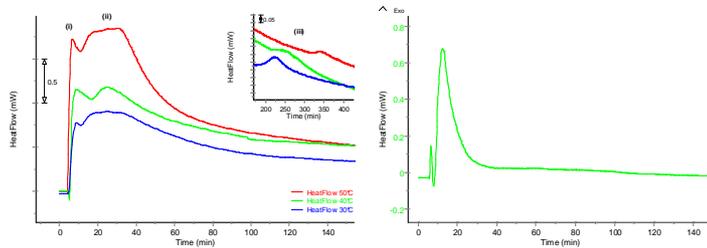


Figure 6 – Thermal steps of NaOH catalyzed reaction

Figure 7 – K₂CO₃ catalyzed transesterification at 40°C

CONCLUSION

Transesterification reaction of colza oil by ethanol using sodium hydroxide as a catalyst could be followed up by calorimetry. The high sensitivity and stability of the instrument allowed to get accurate data even with long term experiments.

Three main thermal steps could be noticed: (i) fast direct saponification, (ii) ethanolate diffusion rate-limited step, (iii) Heat production acceleration that may be linked with the hydrolysis of some of the produced ester (could be confirmed by simultaneous spectroscopic methods).

[1] D. Ballerini, Les biocarburants: état des lieux, perspectives et enjeux du développement, IFP Publications, (Technip Ed, Paris, 2006).
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