Studies on the Microwave Induced Pyrolysis of Lignocellulosic Biomasses and Sewage Sludge

A. Facchini[1], A. Zeffiro[2], P. Arcioni[1], A. Buttafava[2], D. Dondi[2]

[1]Dipartimento di Ingegneria Industriale e dell'Informazione, University of Pavia, Pavia, Italy
[2]Dipartimento di Chimica, University of Pavia, Pavia, Italy

This work reports the first results of a project aimed at producing second-generation biofuels from non-food biomasses by using microwave assisted pyrolysis. We present a measurement setup to obtain the dielectric permittivity of lignocellulosic biomasses and sewage sludge vs. temperature. A TM_{010} cylindrical resonant cavity with heating system working at 2.45 GHz has been designed to obtain complex permittivity in a temperature range of 25-200 °C. We also discuss the design of a microwave heater, intended to treat these materials in a pyrolysis process. This structure was built from a waveguide modified to allow the heating of biomasses in controlled conditions of pressure and temperature, as well as of absorbed microwave power. The possibility to treat not only small amounts of biomass, but also a continuous flow of material, was also foreseen. To conclude, some preliminary results are reported.

Introduction

In the latest years the interest in reducing greenhouse gas emission and the need to disengage from the rise in the price of oil and natural gas led us to consider renewable and locally available energy sources. Second-generation biofuels from non-food biomasses seem to be a good way to achieve these aims. Recent studies have shown that the effect of microwave heating to pretreat lignocellulosic materials gives a rapid and selective heating for the production of bioethanol in a pyrolysis process[1-2], improving the destruction of structures that hinder the digestion process. Similarly, microwave-assisted pyrolysis leads to the formation of combustible liquids. Cheapness and easy availability of commercial generators (magnetron) operating at 2.45 GHz, allow to think about applicators which take advantage of microwave heating to pretreat these materials. Dielectric characterization (ε_r and $\tan\delta$) of these materials is necessary in order to design applicators which maximize the interactions between microwaves and biomasses and in order to understand their absorption capacity. Moreover, the characterization of materials is of crucial importance to understand the pyrolysis dynamics.

For this reason an experimental setup has been assembled, where a sample is placed into a cylindrical cavity (TM_{010} mode) and perturbation expressions are used to derive dielectric constant [3-5]. The cavity design allows for heating of the sample, to provide data at different temperatures. Connecting the cavity to a network analyzer HP 8510 through small loops and coaxial cables, the complex permittivity is obtained by elaborating the frequency dependent *S*-parameters around the resonating frequency of the cavity with and without sample, whereas the temperature of materials is observed with a thermocouple. Once ε_r and $\tan\delta$ values are obtained, we design a special applicator able to heat biomasses efficiently.

Technique

Fig. 1 shows the TM_{010} cavity used in the measurement setup. The cavity has a diameter of 94 mm and a height of 30 mm. The sample is placed in a quartz pipe (i.d. = 4 mm; o.d. = 5 mm),

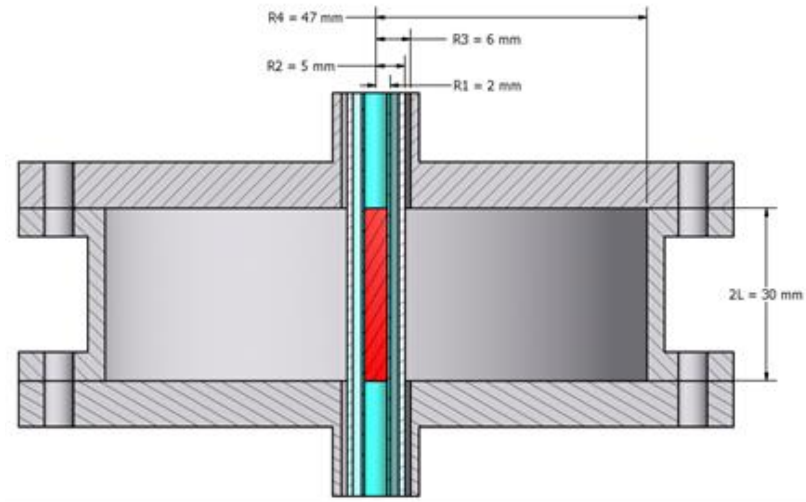


Figure 1. The TM_{010} cylindrical cavity used in the measurement setup.

which is inserted into another quartz pipe (i.d. = 11 mm; o.d. = 12 mm), used to confine the heating flow. The quartz pipes are held in position along the axis of the cavity by two metal pipes (diameter 12 mm and length 20 mm). These dimensions have been chosen to reduce the leakage of the EM field from the cavity to a value that is so small that it doesn't affect the measurement.

According to perturbation formulas [3-6], ε_r and $\tan\delta$ are obtained from the following expressions:

$$\varepsilon_r = 1 + \frac{1}{a}\frac{f_0 - f_1}{f_1}\left(\frac{D}{d}\right)^2, \quad \tan\delta = \frac{1}{2a\varepsilon_r}\left(\frac{D}{d}\right)^2\left(\frac{1}{Q_{u1}} - \frac{1}{Q_{u0}}\right)$$

where the constant *a* has a value of 1.855 for the mode TM_{010}, *D* is the cavity diameter, *d* is the sample diameter, and f_1, Q_{u1}, f_0, Q_{u0} are the resonant frequency and the unloaded quality factor measured for the cavity with and without sample, respectively. To speed up the measurement procedure, *S*-parameters are recorded by a simple *LabView* package, which also performs all the computation and stores the measured values in a file. Fig. 2 shows a typical set of values of S_{21} vs. frequency recorded by the package.

Complex permittivity of typical samples of lignin, starch, cellulose and sewage sludge at room temperature are reported in Table I. These values are in good agreement with those reported in the literature for cellulose and starch [8, 9].

Fig. 3 shows the complex permittivity vs. temperature in the case of lignin, fibrous cellulose and sewage sludge. Values initially decrease with increasing temperature, due to water loss (this effect is more evident in the lignin sample, which had a higher water content at room temperature). At higher temperature, both relative permittivity and loss tangent increase with temperature, a fact that may cause thermal runaway during treatment [7].

On the basis of the measured permittivity of biomasses, a microwave reactor has been designed, to treat either small quantities of material (~50 cc) inserted in a dielectric vessel, or a continuous flow of biomass running through it. The applicator has to be connected to a commercial microwave generator working at 2.45 GHz with adjustable power output. The material is exposed to the EM field inside a short circuited rectangular waveguide (WR340). An inductive iris and an adjustable tuning screw are used to minimize the reflection coefficient when

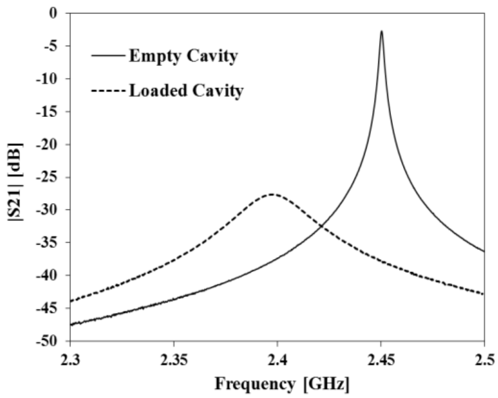


Figure 2. Frequency response of the cavity with and without sample.

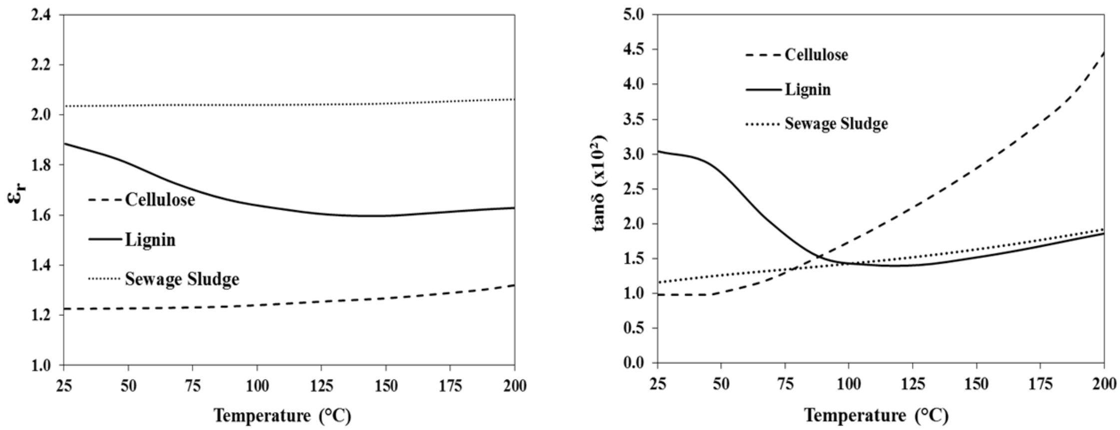
Table I. Relative Permittivity and the Loss Tangent of Some Biomasses

Material	ε_r	$\tan\delta$ (x 10^2)
Lignin	1.885	3.04
Microcrystalline Cellulose	1.577	4.97
Starch	2.668	11.15
Sewage Sludge	5.407	16.69
Alpha-Alpha	1.407	3.75

different biomasses are inserted into the vessel. Fig. 4 shows the designed applicator in both configurations (the lateral wall of the waveguide is transparent to show the inside of the structure). The vessel is included in a shielding structure to prevent leakage of EM field. To allow for monitoring of pressure and temperature of the biomass, two dielectric probes can be inserted into the vessel through small metal pipes, designed as waveguide well below cutoff at the operating frequency.

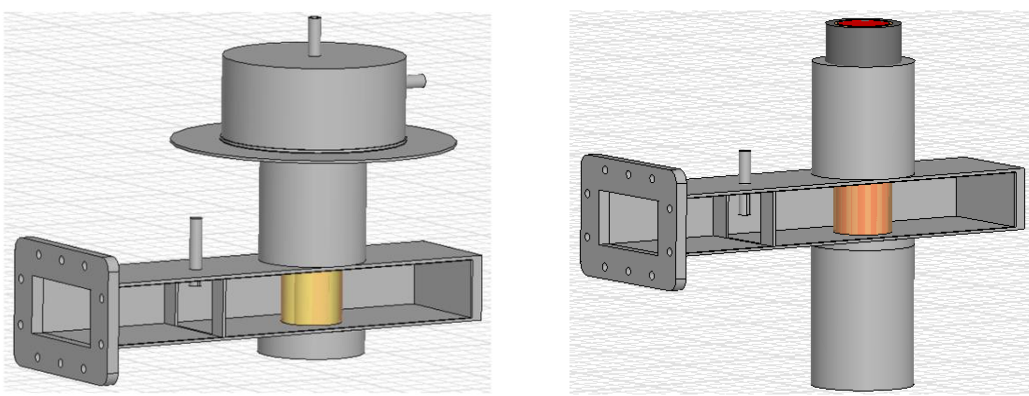
Results

At present, first experiments have been performed both on sewage sludge and alpha-alpha, trying to get the best heating rate and product yields (solid, liquid and gas). In the case of sewage sludge, we are interested in how much bio-oil can be extracted and which are the best conditions to obtain it, whereas for lignocellulosic materials like alpha-alpha, what is most interesting is how microwave pre-heating, combined with the addition of solvents, eases the enzymatic digestion for sugar extraction. Fig. 5a shows the percentage of bio-oil extracted from sewage sludge at different pyrolysis temperatures. According to literature [10], the best pyrolysis temperature to get oil is near 400 °C, while the percentage of oil obtained does not reach the optimum value achievable [11] because the sewage sludge used was not pristine, but came from an anaerobic digestion process. Figure 5b shows how many sugars have been obtained by alpha-alpha in different solutions, compared with the one achievable from pristine alpha-alpha. In all cases shown (except for pristine alpha-alpha), different solutions have been prepared and then heated with microwaves up to a temperature of 180 °C. The main advantages in using microwaves are the possibility of speeding up the process, obtaining better heating rates and



(a) (b)

Figure 3. Relative permittivity (a) and the loss tangent (b) vs. temperature of lignin, cellulose and sewage sludge.



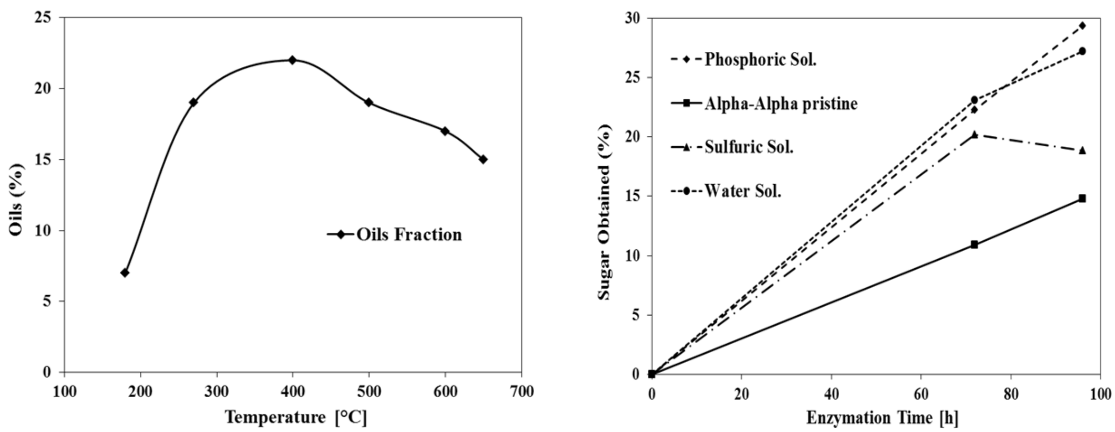
(a) (b)

Figure 4. Microwave heater in batch (a) and continuous flow (b) operating mode.

consumption compared to a conventional heating. Later, for all these samples, an enzymatic digestion has been carried on for 4 days. Comparison results are shown in Fig. 5.

Conclusion

In this paper, the perturbation method has been used to measure complex permittivity of lignocellulosic materials and sewage sludge at room temperature. Temperature dependency of complex permittivity of lignin, cellulose and sewage sludge has also been shown. The design of a microwave heater has been discussed and some preliminary results on sewage sludge pyrolysis and alpha-alpha enzymation have been presented. For the sewage sludge, we have pointed out that the best pyrolysis temperature is around 400 °C. The obtained quantity of oil is not optimal, but this is mainly due to the pre-treating of the samples. The enzymatic digestion of alpha-alpha has been studied for different solutions heated up to a temperature of 180°C. It was found that a microwave-aided preliminary treatment improves the sugar quantity that can be extracted, and the best results can be achieved with a phosphoric solution.



(a) (b)

Fig. 5. Oil fraction obtained by sewage sludge pyrolysis at different temperatures (a); sugars (%) obtained by alpha-alpha enzymation in different solutions (b).

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